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Preparation of 4,7-Bis[cyano(ethoxycarbonyl)methylene]-4,7-dihydrobenzofuran, 4,7-Bis[cyano(ethoxycarbonyl)methylene]-4,7-dihydrobenzothiophene, and 11,12-Bis(ethoxycarbonyl)-11,12-dicyano-1,4-naphthoquinodimethane and Their Polymerization Behavior

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ABSTRACT: As stable quinonoid compounds of benzofuran, benzothiophene, and naphthalene, 4,7-bis[cyano(ethoxycarbonyl)methylene]-4,7-dihydrobenzofuran (BF), 4,7-bis[cyano(ethoxycarbonyl)methylene]-4,7-dihydrobenzothiophene (BT), and 11,12-bis(ethoxycarbonyl)-11,12-dicyano-1,4-naphthoquinodimethane (NQ) were prepared. First reduction potential values of BF, BT, and NQ were determined by cyclic voltammetry to be -0.14, -0.23, and -0.29 V, respectively. When BF, BT, or NQ was dissolved in aprotic polar solvents such as acetonitrile, acetone, tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO), BF was found to polymerize sponteneously in all the solvents except for THF, BT oligomerized in DMF and DMSO but did not react in the other solvents, and NQ did not react in the solvents. Butyllithium is able to initiate anionic polymerization of BF, BT, and NQ, the first of which takes place in THF at -78 °C and is a living type. BF is homopolymerizable with a radical initiator, but BT and NQ are not. Polymerization of BF was found to be an equilibrium type, as well as that of 7,8-bis(alkoxycarbonyl)- and 7,8-diacyl-7,8-dicyanoquinodimethanes, and its equilibrium monomer concentration, enthalpy, and entropy of polymerization were determined. At BF concentrations higher than the equilibrium monomer concentration, copolymerization of BF with styrene (St) takes place in a random fashion to give r_1(BF) = 0.18 ± 0.05 and r_2(St) = 0.065 ± 0.025 at 50 °C, whereas at BF concentrations not higher than the equilibrium one, it changes to an alternating fashion. Copolymerizations of BT and NQ with St occur in an alternating fashion. These copolymerization fashions were explained in terms of equilibrium polymerization behavior of BF, BT, and NQ.

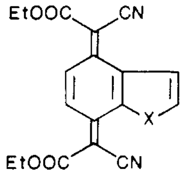
Introduction

As a new class of quinodimethane monomers that are homopolymerizable and capable of being prepared as crystalline compounds, we recently found 7,8-bis(alkoxycarbonyl)-7,8-dicyanoquinodimethanes,[1,2] 7,8-diacyl-7,8-dicyanoquinodimethanes,[3] and 7,8-bis(alkylthio)-7,8-dicyanoquinodimethanes,[4] all of which characteristically carry different substituents at the 7- and 8-positions. In the detailed kinetic study[5] of the former two compounds, it was found that these polymerizations behave as typical equilibrium polymerizations with appreciable influence of depolymerization and that entropy changes of polymerization for these compounds are one-third as large as those of conventional vinyl monomers, and also enthalpy changes of polymerization are much smaller than the corresponding ones for vinyl compounds. In addition, their copolymerizations with styrene were found to be in a random fashion despite their highly electron-accepting character, suggesting that the mode of their copolymerizations must be determined by their homopolymerizability in addition to their electron-accepting character. These new polymerization behaviors should be helpful in the improvement of polymer chemistry. However, other compounds with such characteristics have not been found.

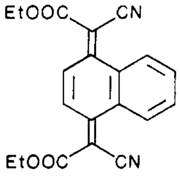
In this paper are described preparations and polymerizations of 4,7-bis[cyano(ethoxycarbonyl)methylene]-4,7-dihydrobenzofuran (BF), 4,7-bis[cyano(ethoxycarbonyl)methylene]-4,7-dihydro-benzothiophene (BT), and 11,12-bis(ethoxycarbonyl)-11,12-dicyano-1,4-naphthoquinodimethane (NQ) as quinonoid compounds of benzofuran, benzothiophene, and naphthalene.

Experimental Section

BF, BT, and NQ were successfully prepared according to the respective procedure shown in Schemes I and II.



BF, X = O
BT, X = S



NQ

4,7-Bis(bromomethyl)benzofuran (2a). 4,7-Dimethylbenzofuran[6] (1a) (26.0 g, 0.18 mol), 77.6 g (0.44 mol) of *N*-bromosuccinimide (NBS), and 0.24 g (1 mmol) of benzoyl peroxide (BPO) were dissolved in 530 mL of carbon tetrachloride and the solution was refluxed with stirring for 3 days. In the meantime, five 0.24-g portions of BPO were added into the solution every 12 h. Then the reaction mixture was placed under reduced pressure to remove solvents. The remaining dark brown residue was suspended in 500 mL of water and the resulting suspension was extracted with three 200-mL portions of chloroform. The combined extract was washed with two 200-mL portions of water, dried over anhydrous magnesium sulfate, and placed under reduced pressure to remove solvents to afford 41.1 g of brown solid, which was recrystallized from chloroform to give 36.1 g (in 66.7% yield) of white needles of **2a**: mp 154-154.5 °C; IR (KBr) ν (C-O-C) 1120, σ (C-Br) 680 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.71 (s, 2 H), 4.77 (s, 2 H), 6.97 (d, *J* = 2 Hz, 1 H), 7.26 (s, 2 H), 7.77 (d, *J* = 2 Hz, 1 H). Anal. Calcd for $C_{10}H_8OBr_2$: C, 39.51, H, 2.66; Br, 52.57; O, 5.26. Found: C, 39.70; H, 2.71; Br, 52.51.

4,7-Bis(bromomethyl)benzothiophene (2b). 4,7-Dimethylbenzothiophene,[7] (**1b**) instead of **1a**, was brominated in a process similar to that for **2a** to give white needles of **2b** in 41.9% yield: mp (CHCl$_3$) 168-169 °C; IR (KBr) ν (C-S-C) 1200, σ (C-Br) 710 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.73 (s, 2 H), 4.80 (s, 2 H), 7.35 (s, 2 H), 7.62 (s, 2 H). Anal. Calcd for $C_{10}H_8SBr_2$: C, 37.52; H, 2.52; Br, 49.93; S, 10.02. Found: C, 37.55, H, 2.48; Br, 50.02.

4,7-Bis(cyanomethyl)benzofuran (3a). Sodium cyanide (5.8 g, 0.12 mol) was dissolved in a mixture of 16.5 mL of water, 33 mL of ethanol, and 33 mL of *p*-dioxane. Into the solution was added 8.3 g (0.027 mol) of **2a**, and the mixture was stirred at room temperature for 24 h. Then the mixture was poured into 1 L of water to deposit 5.3 g of pale yellow solid, which was recrystallized from a mixture of dichloromethane and hexane (1:2 by volume)

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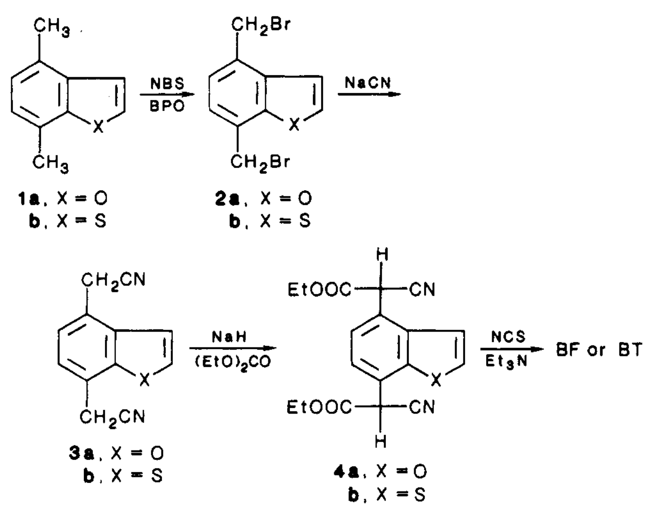
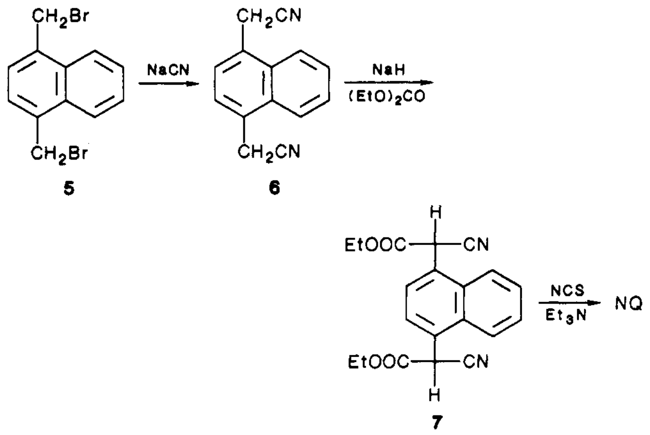
Scheme I



Scheme II



to give 5.2 g (in 95.1% yield) of pale yellow needles of **3a**: mp 103.5–104.5 °C; IR (KBr) ν (CN) 2230, ν (C-O-C) 1130 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.95 (s, 2 H), 4.02 (s, 2 H), 6.92 (d, J = 2 Hz, 1 H), 7.32 (s, 2 H), 7.75 (d, J = 2 Hz, 1 H). Anal. Calcd for $C_{12}H_8N_2O$: C, 73.46; H, 4.11; N, 14.28; O, 8.15. Found: C, 73.73; H, 4.10; N, 14.12.

4,7-Bis(cyanomethyl)benzothiophene (3b). The compound **2b** was reacted with sodium cyanide in a process similar to that for **3a** to obtain pale yellow needles of **3b** in 93.8% yield: mp (CH$_2$Cl$_2$/hexane) 113.5–114 °C; IR (KBr) ν (CN) 2250, ν (C–S–C) 1240 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.97 (s, 2 H), 4.04 (s, 2 H), 7.46 (s, 2 H), 7.50 (d, J = 5.4 Hz 1 H), 7.66 (d, J = 5.4 Hz, 1 H). Anal. Calcd for $C_{12}H_8N_2S$: C, 67.90; H, 3.80; N, 13.20; S, 15.10. Found: C, 68.04; H, 3.52; N, 13.11.

4,7-Bis[cyano(ethoxycarbonyl)methyl]benzofuran (4a). A solution of **3a** (5.9 g, 0.03 mol) in 40 mL of tetrahydrofuran (THF) was added dropwise to the suspension of 1.9 g (0.08 mol) of sodium hydride in 60 mL of THF with stirring under nitrogen and the mixture was refluxed for 30 min. Into it was added dropwise 8.2 g (0.07 mol) of diethyl carbonate under refluxing and, additionally, the resulting mixture was refluxed for 12 h. The reaction mixture was placed under reduced pressure to remove volatile materials. The remaining dark brown residue was dissolved in 200 mL of water and, after acidified by adding 100 mL of acetic acid, the resulting aqueous solution was extracted with three 100-mL portions of chloroform. The combined extract was washed with two 200-mL portions of water, dried over anhydrous magnesium sulfate, and placed under reduced pressure to obtain 10.1 g of yellow solid, which was recrystallized from methanol to give 9.6 g (in 93.2% yield) of white needles of **4a**: mp 101–102 °C; IR (KBr) ν (CN) 2255, ν (C=O) 1755, ν (C—O—C) 1225 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.26 (t, J = 7.2 Hz, 3 H), 1.28 (t, J = 7.2 Hz, 3 H), 4.25 (q, J = 7.2 Hz, 2 H), 4.30 (q, J = 7.2 Hz, 2 H), 4.98 (s, 1 H), 5.26 (s, 1 H), 7.08 (d, J = 2 Hz, 1 H), 7.46 (s, 2 H), 7.78 (d, J = 2 Hz, 1 H). Anal. Calcd for $C_{18}H_{16}N_2O_5$: C, 63.53; H, 4.74; N, 8.23; O, 23.50. Found: C, 63.40; H, 4.62; N, 8.26.

4,7-Bis[cyano(ethoxycarbonyl)methyl]benzothiophene (4b). The compound **3b** was reacted with diethyl carbonate in a process similar to that for **4a** to obtain **4b** in 52.5% yield: mp (EtOH) 79.5–81 °C; IR (KBr) ν (CN) 2250, ν (C=O) 1760, ν (C—O—C) 1100 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.27 (t, J = 7.2 Hz, 3 H), 1.30 (t, J = 7.2 Hz, 3 H), 4.26 (q, J = 7.2 Hz, 2 H), 4.29 (q, J = 7.2 Hz, 2 H), 5.04 (s, 1 H), 5.14 (s, 1 H), 7.62 (s, 2 H), 7.65 (s, 2 H). Anal. Calcd for $C_{18}H_{16}N_2O_4S$: C, 60.66; H, 4.53; N, 7.86; O, 17.96; S, 9.00. Found: C, 60.56; H, 4.61; N, 7.78; S, 8.87.

4,7-Bis[cyano(ethoxycarbonyl)methylene]-4,7-dihydrobenzofuran (BF). The compound **4a** (0.84 g, 2.5 mmol) was dissolved in 25 mL of acetonitrile under nitrogen. To the solution kept at 0 °C was added 0.7 g (5.1 mmol) of *N*-chlorosuccinimide (NCS). The mixture was stirred for 5 min and 0.35 mL (2.5 mmol) of triethylamine was added to change the color of the mixture from pale yellow to red and at the same time to precipitate red crystals which were filtered off. The crystals obtained were recrystallized from toluene to give 0.8 g (in 94.5% yield) of red needles of BF: mp 196.5–197 °C; IR (KBr) ν (CN) 2220, ν (C=O) 1759, ν (C=C) 1560, ν (C—O—C) 1255 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.43 (t, J = 7.2 Hz, 6 H), 4.42 (q, J = 7.2 Hz, 4 H), 7.87 (s, 2 H), 8.35 (s, 2 H); UV (CHCl$_3$) 440 (shoulder, $\epsilon = 1.21 \times 10^4$), 390 ($\epsilon = 4.08 \times 10^4$), 261 nm ($\epsilon = 5.73 \times 10^3$). Anal. Calcd for $C_{18}H_{14}N_2O_5$: C, 63.90; H, 4.18; N, 8.28; O, 23.64. Found: C, 63.40; H, 4.10; N, 8.15.

4,7-Bis[cyano(ethoxycarbonyl)methylene]-4,7-dihydrobenzothiophene (BT). The compound **4b** was treated in a process similar to that for BF to obtain BT in 63.2% yield: mp (toluene) 184.5–185 °C; IR (KBr) ν (CN) 2220, ν (C=O) 1730, ν (C=C) 1540, ν (C—O—C) 1140 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.41 (t, J = 7.2 Hz, 6 H), 4.41 (q, J = 7.2 Hz, 4 H), 7.80 (d, J = 5.4 Hz, 1 H), 8.41 (s, 2 H), 8.68 (d, J = 5.4 Hz, 1 H); UV (CHCl$_3$) 460 (shoulder, $\epsilon = 1.15 \times 10^4$), 400 ($\epsilon = 3.08 \times 10^4$), 265 nm ($\epsilon = 4.96 \times 10^3$). Anal. Calcd for $C_{18}H_{14}N_2O_4S$: C, 61.00; H, 3.99; N, 7.90; O, 18.06; S, 7.76. Found: C, 60.86; H, 4.06; N, 7.61; S, 7.71.

1,4-Bis(cyanomethyl)naphthalene (6). Sodium cyanide (6.8 g, 0.14 mol) was dissolved in a mixture of 10 mL of water, 17 mL of ethanol, and 20 mL of *p*-dioxane. Into the solution was added 10 g (32 mol) of 1,4-bis(bromomethyl)naphthalene[8] (**5**), and the mixture was stirred at room temperature for 24 h. Then it was poured into 500 mL of water to obtain 5.7 g of pale yellow solid, which was recrystallized from acetone to give 5.3 g (in 81.4% yield) of pale yellow fine crystals of **6**: mp 147.5–149 °C; IR (KBr) ν (CN) 2250, ν (C=C) 1600 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.16 (s, 4 H), 7.61 (s, 2 H), 7.70 (m, 2 H), 7.94 (m, 2 H). Anal. Calcd for $C_{14}H_{10}N_2$: C, 81.53; H, 4.90; N, 13.57. Found: C, 81.41; 4.92; N, 13.67.

1,4-Bis[cyano(ethoxycarbonyl)methyl]naphthalene (7). The compound **6** (2.5 g, 0.012 mol) and 3.0 g (0.025 mol) of diethyl carbonate were dissolved in 30 mL of monoglyme. The resulting solution was added dropwise to the suspension of 0.5 g (0.025 mol) of sodium hydride suspended in 30 mL of monoglyme with stirring under nitrogen, and the resulting mixture was refluxed for 3 h. The reaction mixture was placed under reduced pressure to remove volatile materials. The dark brown residue obtained was dissolved in 100 mL of water. After it was acidified by adding 100 mL of acetic acid, the resulting aqueous solution was extracted with three 50-mL portions of dichloromethane. The combined extract was washed with two 50-mL portions of water, dried over anhydrous magnesium sulfate, and placed under reduced pressure to leave 3.1 g of brown viscous material, which was recrystallized from isopropyl ether to give 2.2 g (in 53.9% yield) of pale yellow fine crystals of **7**: mp 112–113.5 °C; IR (KBr) ν (CN) 2260, ν (C=O) 1740, ν (C—O—C) 1260 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.25 (t, J = 7.2 Hz, 6 H), 4.27 (q, J = 7.2 Hz, 4 H), 5.38 (s, 2 H), 7.80 (s, 2 H), 7.75 (m, 2 H), 8.10 (m, 2 H). Anal. Calcd for $C_{20}H_{18}N_2O_4$: C, 68.55; H, 5.19; N, 8.00; O, 18.26. Found: C, 68.17; H, 5.04; N, 8.07.

11,12-Bis(ethoxycarbonyl)-11,12-dicyano-1,4-naphthoquinodimethane (NQ). The compound **7** (0.4 g, 1.14 mmol) was dissolved in 7 mL of acetonitrile under nitrogen. To the solution kept at 0 °C, 0.3 g (2.3 mmol) of NCS was added. After the mixture was stirred for 3 min, 0.3 mL of triethylamine was added to change its color from pale yellow to yellow. The reaction mixture was poured into 500 mL of water to deposit a yellow solid which was extracted with two 100-mL portions of dichloromethane. The combined extract was washed with 100 mL of water, dried over anhydrous magnesium sulfate, and placed under reduced pressure to remove solvents. The remaining yellow viscous residue was dissolved in 2 mL of benzene, and the resulting solution was passed through a column of 1.5-cm diameter and 20-cm length packed with silica gel with benzene as eluent. The yellow portion collected was placed under reduced pressure to leave 0.3 g of yellow solid, which was recrystallized from isopropyl ether to give 0.22 g (in 54.9% yield) of yellow needles of NQ: mp 111–112 °C; IR (KBr) ν (CN) 2210, ν (C=O) 1720, ν (C=C) 1550, ν (C—O—C) 1120 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.41 (t, J = 7.2 Hz, 6 H), 4.40 (q, J = 7.2 Hz, 4 H), 7.66 (m, 2 H), 8.34 (s, 2 H), 8.55 (m, 2 H); UV (CH_2Cl_2) 371 nm ($\epsilon = 4.21 \times 10^4$). Anal. Calcd for $C_{20}H_{16}N_2O_4$: C, 68.94, H, 4.64; N, 8.04; O, 18.38. Found: C, 68.71; H, 4.62; N, 7.92.

Other Materials. 2,2′-Azobis(isobutyronitrile) (AIBN) and benzoyl peroxide (BPO) were recrystallized from methanol and chloroform, respectively. Boron triluoride etherate was distilled under reduced pressure in an atmosphere of nitrogen. Commercial butyllithium (Aldrich Co.) was used without further purification. *N,N*-Dimethylaniline (DMA), toluene, and triethylamine were refluxed over metal sodium for 12 h and then distilled under nitrogen. Styrene (St) was washed with 2% sodium hydroxide solution and water and dried over barium oxide for a day. Its supernatant was dried again over calcium hydride with stirring at room temperature for 3 h and distilled under reduced pressure. Chloroform, acetonitrile, and acetone were refluxed over phosphorous pentoxide for 12 h and then distilled. *N,N*-Dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were dried over molecular sieves for a day and then distilled under reduced pressure. Dichloromethane was refluxed over calcium hydride for 12 h and then distilled. Tetrahydrofuran (THF) was refluxed over lithium aluminium hydride for 12 h and its distillate was distilled again over benzophenone and metal sodium. Tetrabutylammonium perchlorate was dried under reduced pressure at 150 °C for 16 h.

Measurement of Electron-Accepting Property. Voltammetric measurement was carried out in dichloromethane containing tetrabutylammonium perchlorate (0.1 mol/L) at room temperature to measure the first reduction potential of the compound by Yanako new cyclic voltammetric analyzer Model VMA-010. A Ag/AgCl, glassy carbon, and a platinum wire were used as reference, working, and third electrodes, respectively.

Polymerization in Aprotic Polar Solvents. BF, BT, or NQ (about 3 mg) was dissolved in 1 mL of an aprotic polar solvent such as acetonitrile, acetone, THF, DMF, and DMSO at room temperature. After standing for a given time, an aliquot of the solution was taken out by syringe and diluted with excess THF. The resulting THF solution was subjected to gel permeation chromatography (GPC) to determine the molecular weight of the reaction product by using standard polystyrene as reference and THF as eluent. GPC was performed on a Toyo Soda Model 803D instrument with a series of four columns, Toyo Soda G 2000H, G 2500H, G 3000H, and G 4000H.

Anionic Polymerization Procedure. The polymerization was carried out with the apparatus reported previously.[2]

A given amount of BF, BT, or NQ as monomer was placed in the apparatus, which was filled with argon. Into it was introduced a given amount of THF by syringe. After it was completely degassed by the freeze–thaw method (repeated twice), the apparatus was filled with argon and sealed. Then it was set in a bath thermostated at the temperature of 0 or −78 °C and a fixed amount of butyllithium or triethylamine as an initiator was injected into it by syringe. After a given time of polymerization, 0.5 mL of acetic acid was added to interrupt the polymerization. The reaction mixture was poured into excess methanol to deposit a polymeric product. In the case of polymerization with large amount of solvent at −78 °C, the reaction mixture was first placed under reduced pressure to remove solvent until its volume amounted to 30 mL and then poured into excess methanol. The precipitated polymeric product was dissolved again in a small amount of chloroform and the resulting solution was poured into methanol for purification. When no polymeric product was deposited in this process, the methanol solution was placed under reduced pressure to remove volatile materials. The remaining residue was dissolved in a small amount of solvent such as chloroform or benzene and the resulting solution was passed through a column packed with silica gel to separate it in two portions: the colored band as unreacted monomer and the colorless band as 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 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. The polymerizations with various molar ratios of butyllithium to BF monomer were carried out as follows: 30.5 mg of BF was dissolved in 150 mL of THF under argon and the 0.6 mmol/L solution was cooled to −78 °C. Into the cooled solution was injected 0.1 mL of a respective butyllithium solution in hexane with five concentrations of 13–87 mmol/L by syringe under argon. After a given time of the reaction, 0.5 mL of acetic acid was added to interrupt the polymerization. The rest of the procedure was carried out similarly to the above-mentioned one.

In the determination of initiator efficiency, a probable volume change in a monomer solution due to addition of the initiator solution was neglected because its volume change (0.1 mL) was regarded as very small compared to 150 mL of the BF monomer solution.

The successive monomer addition polymerization was carried out as follows: To 15 mL of red 10.7 mmol/L BF solution in THF kept at 0 °C was added 0.68 mL of 17 mmol/L butyllithium solution in hexane. After the red color due to BF monomer had disappeared, an aliquot of the polymerization mixture was taken out of the apparatus by syringe to determine the molecular weight of the polymer by GPC. Into the remaining portion of the colorless polymerization mixture was added an additional 15-mL portion of 10 mmol/L BF solution in THF by syringe. After the red color disappeared again, the same procedure was carried out. As a whole, additional monomer additions were carried out three times.

Cationic Polymerization Procedure. The polymerization was carried out under argon and dry conditions by using the same apparatus as for the above-mentioned anionic polymerization. Given amounts of BF, BT, or NQ as monomer and dichloromethane as solvent were placed into the apparatus, which was degassed by the freeze–thaw method. The apparatus was set in a bath thermostated at 0 °C, and a fixed amount of boron trifluoride etherate solution in dichloromethane was injected into it by syringe. After a given time of the reaction, an aliquot of the reaction mixture was taken out of the apparatus and diluted with excess THF. The resulting THF solution was subjected to GPC to determine the molecular weight of the reaction product.

Radical Polymerization Procedure. In the case of conventional radical polymerization, given amounts of BF, BT, or NQ as monomer, chloroform or toluene as solvent, and AIBN or BPO–DMA redox system as radical initiator were placed into an ampule, which was degassed by the freeze–thaw method (repeated three times) and sealed. The ampule was set in a bath thermostated at the temperature of 0 or 60 °C for the time of polymerization.

In the case of photoinitiated polymerization, given amounts of BF, BT, or NQ as monomer, chloroform or toluene as solvent, and AIBN as photoinitiator were placed in a quartz ampule, which was degassed by the freeze–thaw method (repeated three times), filled with nitrogen, and then capped with a Rubber Septa (Aldrich Co.) stopper. It was set in an ice–water bath, irradiated with a high pressure mercury lamp at a distance of 5 cm for a given time, and then opened.

The reaction mixture was poured into excess methanol to deposit the polymeric product, which was dissolved in a small amount of chloroform, and the resulting solution was poured again into excess methanol for purification. The deposited polymeric product was dried under reduced pressure. When a polymeric product was not deposited in excess methanol, the methanol solution was placed under reduced pressure to remove volatile materials. The rest of the procedure was carried out similarly to the above-mentioned anionic polymerization.

In the case of copolymerization, given amounts of BF, BT, or NQ as monomer, St as comonomer, chloroform or toluene as solvent, and AIBN as initiator were placed into an ampule, which was degassed by the freeze–thaw method (repeated three times)

Table I
First Reduction Potential[a] of BF, BT, NQ, BCQ, and TCNQ

monomer	E_1, V	monomer	E_1, V
TCNQ	+0.19	BT	−0.23
BCQ	−0.10	NQ	−0.29
BF	−0.14		

[a] Solvent, CH_2Cl_2 containing $(Bu_4N)ClO_4$ (0.1 mol/L); reference electrode, Ag/AgCl; relative error, ±0.01 V.

and sealed. The ampule was set in a bath thermostated at the temperature of 50, 60, or 70 °C for the time of polymerization. The rest of the procedure was carried out similarly to the above-mentioned polymerizations.

Polymerization Kinetics of BF. Given amounts of BF as monomer, chloroform as solvent, and AIBN as initiator were placed in an ampule, which was degassed completely by the freeze–thaw method (repeated three times) and sealed. The ampule was set in a bath thermostated at the temperature of 50, 60, or 70 °C for the time of polymerization and then opened. The concentration of BF was measured spectrophotometrically with an absorption band of 390 nm ($\epsilon = 4.08 \times 10^4$) characteristic of BF. The polymerization rate, Rp, was calculated on the basis of the monomer consumption for a given time of polymerization.

Results and Discussion

Electron-Accepting Character of BF, BT, and NQ. The values of first reduction potential, E_1, for BF, BT, and NQ are summarized in Table I, together with those of TCNQ and 7,8-bis(butoxycarbonyl)-7,8-dicyanoquinodimethane (BCQ) for comparison. It is obvious that BF, BT, and NQ are much weaker in electron-accepting character than TCNQ and also weaker than BCQ. The electron-accepting character of BF, BT, and NQ is in the following order: BF > BT > NQ. Although the values of the ionization potential,[9] Ip, of benzofuran, benzothiophene, and naphthalene were reported to be 8.29, 8.17, and 8.13 eV, respectively, their values of electron affinity,[9] EA, have not been reported except for that of naphthalene, −0.19 eV. It was pointed out in the π-electron linear combination atomic orbital molecular orbital method[10] that many aromatic hydrocarbons exhibit a complementarity between Ip and EA. Then, it is presumable that the EA values are in the following order: benzofuran > benzothiophene > naphthalene, being in agreement with the above order observed in first reduction potential.

Polymerization of BF, BT, and NQ in Aprotic Polar Solvents. The results of the polymerizations of BF, BT, and NQ in five kinds of aprotic polar solvents such as acetonitrile, acetone, THF, DMF, and DMSO are summarized in Table II, together with the corresponding ones of BCQ.[2] When BF was dissolved in those solvents except for THF, BF solutions changed gradually from red to pale yellow. The red color of the BF solution in THF remained almost unchanged for a long time. When BF and BCQ were dissolved in acetone, the former solution changed slowly from red to colorless in 6 h, while the latter rapidly lost its yellow color to colorless in only 1 min. The fading rate in the BF solution was found to be one three hundred sixtieth as fast as that in the BCQ solution. It was found therefore that BF is polymerizable even though with slow rate in aprotic polar solvent such as acetonitrile, acetone, DMF, and DMSO, and it is not polymerizable in THF. When BT was dissolved in these aprotic polar solvents, the red color of its solutions remained almost unchanged for a week. After standing for a week, its solutions were subjected to GPC to determine the molecular weight of the reaction products. Its acetonitrile, acetone, and THF solutions were found to exhibit the only monomer peaks. On the other hand, its DMF and DMSO solutions showed both monomer and oligomer peaks, the latter of which was produced in 1–2% yield and had a molecular weight of 600–1500 and degree of polymerization, $\overline{DP}$, of about 2–5, suggesting that BT is reluctantly polymerizable in DMF and DMSO. When NQ was dissolved in these five aprotic polar solvents, the yellow color of its solutions remained unchanged for 10 days and the solutions showed only a monomer peak in their GPC charts, indicating that NQ is not polymerizable in these solvents. In comparison of the color fading rates in the aprotic polar solvents among BF, BT, NQ, and BCQ, it can be pointed out that the higher electron-accepting monomer exhibits the faster fading rate, suggesting that the polymerizations with aprotic polar solvent would take place via an anionic mechanism.

Table II
Spontaneous Polymerizations[a] of BF, BT, NQ, and BCQ in Various Aprotic Polar Solvents

solvent	ν(OD) shift[b] of MeOD	$\bar{M}_n/10^4$ molec wt of polym obtained BF	BT	NQ	BCQ
acetonitrile	49	3			410
acetone	64	8.5			455
tetrahydrofuran	93				86
N,N-dimethylformamide	107	2.4	0.09		340
dimethyl sulfoxide	141	0.5	0.12		360

[a] At room temperature; monomer, 3 mg; solvent, 1 mL; time of polymerization, 6 h for BF, 168 h for BT, 216 h for NQ, and 0.5 h for BCQ. [b] As solvent basicity, ν(OD) stretching frequency shift of methanol-*d* due to hydrogen bond formation with the solvent was determined.

Anionic Polymerization of BF, BT, and NQ. The polymerizations of BF, BT, and NQ were attempted with butyllithium and triethylamine as summarized in Table III. It was found that butyllithium, a strong anionic initiator, is capable of initiating the polymerizations of BF, BT, and NQ, but triethylamine, a weak anionic initiator, is not.

When 1 mL of 4.7×10^{-3} mol/L butyllithium solution in hexane was added to 31.61 mg (0.093 mmol) of BF in THF at −78 °C, the red color of the solution due to BF monomer faded gradually and disappeared completely in 5 h. The polymerization of BF gave a polymer with a molecular weight of 7000 and $\overline{DP}$ of about 20, in 100% yield.

The polymerization of BF was carried out with various molar ratios of butyllithium to BF in feed as summarized in Table IV. In runs 1–4, the reactions were performed until the red color of the BF monomer solution disappeared, corresponding to complete consumption of the monomer. In run 5, the reaction was interrupted after 16 h when the red color still remained, and the reaction mixture was poured into excess methanol to give 18 mg of the polymer, corresponding to 59% conversion. The molecular weight of the polymers obtained increased linearly with the molar ratio of butyllithium to BF in the monomer feed as shown in Figure 1, and the initiator efficiency of the polymerization was found in comparison between the ratios in the monomer feed and the molecular weight of the polymers to be close to unity. In addition, the ratios $\bar{M}_w/\bar{M}_n$ of the polymers obtained were found to be in the region 1.1–1.3, indicating a narrow molecular weight distribution of the polymers.

The results of the successive monomer addition polymerization of BF are summarized in Table V, and the GPC charts of the polymers obtained in each step are shown in Figure 2. It was found that molecular weights of the polymers obtained at each step are in agreement with ones

Table III
Homopolymerizations of BF, BT, and NQ with Various Initiators

run	monomer, mg	initiator, I	[monomer]/[I]	solvent, mL	temp, °C	time, h	conv, %	$\bar{M}_n{}^a$
				Monomer, BF				
1	50.11	$BF_3{\cdot}Et_2O$	30	CH_2Cl_2, 10	0	2	0	
2	52.80	BuLi	19.5	THF, 15	0	1	87	15000
3	31.61	BuLi	20	THF, 150	−78	5	100	7000
4	30.46	Et_3N	18	$CHCl_3$, 10	0	5	0	
5	53.71	AIBN	4	$CHCl_3$, 1	60	26.5	9.2	9000
6	44.15	AIBN	4	$CHCl_3$, 5	60	19	0	
7	61.95	AIBN, $h\nu$	11	$CHCl_3$, 5	0	17	8.1	8800
8	49.05	BPO/DMA	50	$CHCl_3$, 10	0	64	5.7	2100
				Monomer, BT				
9	30.15	$BF_3{\cdot}Et_2O$	23	CH_2Cl_2, 10	0	24	0	
10	29.78	BuLi	29	THF, 10	0	18.5	35.4	4500
11	29.84	BuLi	10	THF, 130	−78	23	8.6	700–2000
12	30.40	Et_3N	20.6	$CHCl_3$, 10	0	23	0	
13	50.07	AIBN	19	$CHCl_3$, 1	60	24	0	
14	50.05	BPO/DMA	50	$CHCl_3$, 10	0	21	0	
				Monomer, NQ				
15	50.13	$BF_3{\cdot}Et_2O$	30	CH_2Cl_2, 5	0	10	0	
16	50.20	BuLi	20.5	THF, 2	0	4	0	
17	50.19	BuLi	20.5	THF, 5	−78	17	3.0	700–2000
18	30.07	Et_3N	10	THF, 2	0	43	0	
19	50.48	AIBN	24	toluene, 5	60	23	0	
20	50.10	AIBN, $h\nu$	24.5	toluene, 2	0	23	0	
21	50.06	BPO/DMA	23	toluene, 2	0	50	0	

[a] Molecular weight of polymers determined by GPC. THF as eluent.

Table IV
Anionic Polymerization[a] of BF with BuLi at −78 °C

				polymer			
				$\bar{M}_n$			
run	[BF]/[BuLi]	time of polym, h	conv, %	obsd	calcd	$\bar{M}_w/\bar{M}_n$	initiator[b] effic
1	10	2	100	2 400	3 400	1.31	
2	20	5	100	7 000	6 800	1.20	0.97
3	33	6.75	100	13 000	11 000	1.12	0.85
4	46	12.5	100	17 000	16 000	1.08	0.94
5	69	16	59	14 000	13 800	1.09	0.98

[a] 30.5 mg of BF was dissolved in 150 mL of THF, [BF] = 0.60 mmol/L; 0.1 mL of 13–87 mmol/L BuLi solution in hexane was added to the BF solution in THF. [b] Initiation efficiency was calculated from dividing $\bar{M}_{n\,\mathrm{calcd}}$ by $\bar{M}_{n\,\mathrm{obsd}}$.

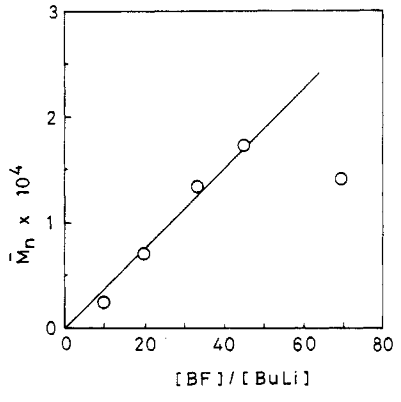


Figure 1. Relationships of the molecular weight of the polymer versus the ratio of the concentration of monomer to initiator in the polymerization of BF with butyllithium: temperature of polymerization, −78 °C; solvent, THF, 150 mL; monomer concentration, 0.60 mmol/L.

calculated from the molar ratio, [BF]/[I], of monomer to initiator, indicating that, after the BF monomer has completely polymerized, the anionic growing species retains enough reactivity to be capable of propagating again when additional monomer is supplied. Moreover, the ratios $\bar{M}_w/\bar{M}_n$ for all the polymers obtained were found to be about 1.2, regarded as almost unity. It may be concluded therefore that the anionic polymerization of BF with butyllithium is a living type, similar to that of BCQ.[2]

Table V
Polymerization[a] of BF in THF at 0 °C by the Successive Monomer Addition Method

				polymer		
step	no. of monomer additn	[BF]/[I]	time of polymn, min	$\bar{M}_{n\,\mathrm{calcd}}{}^b$	$\bar{M}_{n\,\mathrm{obsd}}{}^c$	$\bar{M}_w/\bar{M}_n$
1	0	13.9	12	4 700	5 600	1.22
2	1	28.5	15	9 600	11 000	1.20
3	2	43.7	20	15 000	17 000	1.20
4	3	59.3	25	20 100	24 000	1.20

[a] Initial step: 15 mL of 10.7 mmol/L BF solution in THF with 0.68 mL of 17 mmol/L BuLi solution in THF as initiator. Successive steps: addition of 15 mL of 10 mmol/L BF solution in THF. [b] $\bar{M}_{n\,\mathrm{calcd}}$ was calculated accoding to the equation $\bar{M}_{n\,\mathrm{calcd}}$ = 338.3[BF]/[I]. [c] Determined by GPC. THF as eluent.

BT (29.78 mg, 0.084 mmol) was polymerized with butyllithium (2.9×10^{-3} mmol) in THF at 0 °C for 18.5 h. Although it remained red, the reaction mixture was chromatographed over silica gel with chloroform as eluent to separate 18.5 mg of unreacted monomer and 10.8 mg (in 35.4% conversion) of reaction product, the latter of which was found by GPC measurement to be an oligomer with molecular weight of 4500, $\overline{DP}$ of 13. The polymerization of BT with butyllithium at −78 °C for 23 h gave 2.6 mg (in 8.6% conversion) of the reaction product, which was an oligomer with molecular weidght of 700–2000, $\overline{DP}$ of 2–6. From these results it can be said that BT is polym-

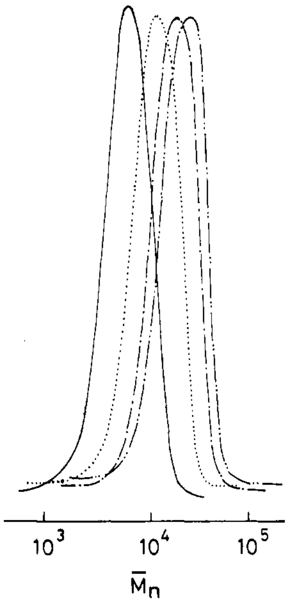


Figure 2. GPC charts of poly-BF in each step of the successive monomer addition method: initiator, butyllithium; temperature of polymerization, 0 °C; solvent, THF; concentration of the monomer solution, 10 mmol/L; volume of the monomer solution at each addition, 15 mL. (—) The initial step; (···) the second step after first monomer addition; (-·-) the third step; (-··-) the fourth step.

erizable with butyllithium even though much more reluctantly than BF.

The polymerization of NQ (50.19 mg, 0.144 mmol) was attempted with butyllithium (7×10^{-3} mmol) in THF at −78 °C. Although it remained yellow, the reaction mixture was charomatographed over silica gel with benzene as eluent to separate 47 mg of unreacted monomer and 1.5 mg (in 3% conversion) of reaction product, the latter of which was an oligomer with a molecular weight of 700–2000, $\overline{DP}$ of 2–6. Accordingly it is obvious that NQ is polymerizable with much more difficulty than BF and BT. In comparison with the anionic polymerizations among BF, BT, and NQ, it can be pointed out that their polymerizability is associated well with their electron-accepting character.

The polymerizations of BF, BT, and NQ with boron trifluoride etherate as cationic initiators were tried but they were unsuccessful to recover unreacted monomers in quantitative amount as shown in Table III.

Radical Polymerizations of BF, BT, and NQ. The results of the radical polymerizations of BF, BT, and NQ are summarized in Table III. When the monomer concentration was as low as 0.026 mol/L (run 6), the polymerization of BF at 60 °C with AIBN failed to obtain polymeric product. Unreacted monomer of BF was recovered in a quantitative amount. On the other hand, when the concentration was as high as 0.16 mol/L (run 5), BF was able to polymerize to give 4.9 mg (in 9.2% conversion) of the polymer with molecular weight of 9000, $\overline{DP}$ of 27. In the case of the low monomer concentration of 0.037 mol/L, photoinitiated polymerization with AIBN was carried out at 0 °C for 17 h (run 7) to obtain 5.0 mg (in 8.1% conversion) of the polymer with molecular weight of 8800, $\overline{DP}$ of 26. Redox-initiated polymerization with BPO/DMA system was performed at 0 °C for 64 h to give 3.0 mg (in 5.7% conversion) of the polymer with molecular weight of 2100, $\overline{DP}$ of 6. Polymerization of BF with high monomer concentration at low temperature was found to take place even more slowly. It is concluded therefore that BF is polymerizable with radical initiator and its polymerization probably shows an equilibrium behavior similar to that of 7,8-dibenzoyl-7,8-dicyanoquinodimethane (BzCQ),[5] 7,8-diacetytl-7,8-dicyanoquinodimethane (AcCQ),[5] and BCQ.[5] In order to study the equilibrium behavior, the polymerization of BF with various monomer concentrations was carried out at temperatures of 50, 60, and 70 °C. The results are summarized in Table VI. Rates, Rp, of polymerization at 50, 60, and 70 °C are plotted against monomer concentration, [BF], in Figure 3 where the extrapolation of the linear relationship to the rate of zero allows one to estimate an equilibrium monomer concentration, $[BF]_e$, at a respective polymerization temperature, as summarized in Table VII, together with the corresponding ones[5] for the polymerization of BzCQ, AcCQ, and BCQ for comparison. BF exhibits a higher equilibrium monomer concentration at a respective temperature compared to the corresponding ones of BzCQ, AcCQ, and BCQ. The relationship of log values of $[BF]_e$ versus the reciprocal of the absolute polymerization tem-

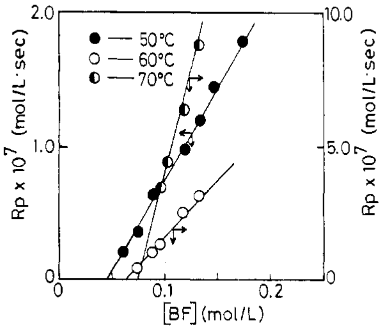


Figure 3. Plots of Rp versus [BF] for the polymerization of BF in chloroform at various temperatures: 50 (●), 60 (○), and 70 (◐) °C. [AIBN] = 1.83×10^{-2} mol/L.

Table VI
Rate, Rp, of Polymerization[a] of BF in Chloroform with Various Monomer Concentrations at 50, 60, and 70 °C

10^1[BF], mol/L	polymeriztn time, h	convn, %	10^7Rp, mol/L·s
	50 °C		
0.59	43.5	5.55	0.21_5
0.75	42.5	7.37	0.36_3
0.89	23.0	5.96	0.64_9
1.19	26.0	7.72	0.98_1
1.34	22.5	7.32	1.21
1.47	23.0	8.16	1.45
1.74	18.7	6.90	1.79
	60 °C		
0.74	21.0	9.16	0.89
0.89	19.4	8.21	1.04
0.97	16.5	8.38	1.36
1.18	20.0	15.63	2.56
1.33	15.0	12.94	3.19
	70 °C		
0.96	7.5	9.77	3.48
1.03	7.0	10.88	4.46
1.18	5.8	11.40	6.43
1.32	5.0	12.06	8.83

[a] [AIBN] = 1.83×10^{-2} mol/L; solvent, $CHCl_3$.

Table VII
Equilibrium Monomer Concentration, $[M]_e$, of BF, BzCQ, AcCQ, and BCQ

	$10^3[M]_e$, mol/L			
temp, °C	BF	BZCQ	AcCQ	BCQ
50	45.9	29.5	6.51	4.46
60	58.3	36.6	9.17	6.50
70	73.4	47.9	11.2	7.91

Table VIII
Enthalpy Change, ΔH, and Entropy Change, ΔS, for the Polymerization of BF, BzCQ, AcCQ, and BCQ

monomer	$-\Delta H$, kJ/mol	$-\Delta S$, J/K·mol
BF	21.6	41.4
BZCQ	21.6	37.5
AcCQ	25.4	36.9
BCQ	26.4	36.8

perature, $1/T$, gave a good straight line, the slope and the intercept of which gave the values of enthalpy change, ΔH, and entropy change, ΔS, for the polymerization of BF, as summarized in Table VIII, together with the corresponding values[5] for BzCQ, AcCQ, and BCQ for comparison. It is obvious that BF as well as BzCQ, AcCQ, and BCQ exhibits a fixed range of entropy change of polymerization which is about one-third as large as the corresponding values (−105 to −130 J/K·mol)[11] for vinyl monomers. As shown in Table VIII, the enthalpy change of polymerization for BF is as small as −21.6 kJ/mol and its free energy change of polymerization at a given polymerization temperature is smaller than those for BCQ and BzCQ, indicating that the polymerization of BF is more seriously subject to depolymerization than those of BCQ and BzCQ. BT and NQ could not have their thermodynamic parameters of polymerization obtained directly from their equilibrium polymerization behavior because they are not polymerizable with radical initiators. However, since they were found to be barely polymerizable with anionic initiators, it is presumable that they should carry a negative change in free energy of polymerization even if the change would be much smaller than the corresponding one of BF.

BT (runs 13 and 14) and NQ (runs 19–21) did not polymerize under the experimental conditions as shown in Table III.

Radical Copolymerizations of BF, BT, and NQ with St. The results of the copolymerizations of BF, BT, and NQ with St are summarized in Table IX. The copolymerization composition diagram of BF with St is shown in Figure 4 and those of the latter two copolymerizations are shown in Figure 5.

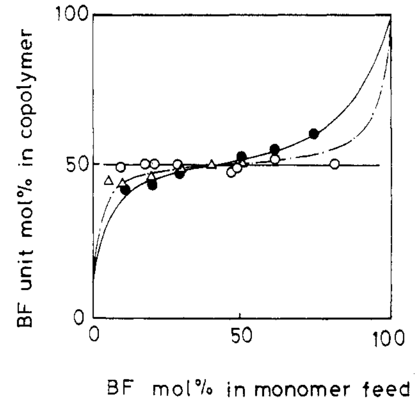


Figure 4. Copolymerization composition diagrams of BF with St: (○) [BF] = 0.015–0.053 mol/L at 60 °C; (●) [BF] = 0.133 mol/L at 50 °C; (△) [BF] = 0.133 mol/L at 70 °C.

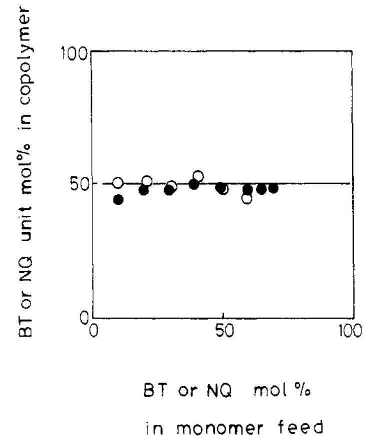


Figure 5. Copolymerization composition diagrams of BT (○) and NQ (●) with St at 60 °C.

In the copolymerization of BF with St, experiments of runs 1–8 in Table IX, were carried out in a monomer feed of the low BF concentration range 0.015–0.053 mol/L at

Table IX
Copolymerization[a] of BF with St in Chloroform

	monomer feed						copolymer compn				
	mg		mol %	solvent,		convn,	anal. %			mol %	
run	BF	St	BF	mL	time, h	%	H	C	N	BF	$\bar{M}_n/10^{4\,b}$
				[BF] = 0.015–0.053 mol/L at 60 °C							
1	52.3	152.0	9.6	10	6.1	18.6	4.98	70.88	6.28	49.2	2.7
2	87.3	125.8	17.6	10	5.3	5.0	4.92	70.51	6.35	50.3	2.0
3	93.9	111.6	20.6	10	5.5	11.5	5.07	70.30	6.34	50.2	2.0
4	119.7	91.6	28.7	10	5.1	7.7	5.09	70.43	6.34	50.2	2.0
5	166.0	58.8	46.5	10	9.6	11.3	5.67	70.17	6.16	47.2	1.2
6	179.5	58.5	48.6	10	9.0	11.9	5.45	70.84	6.25	48.7	1.0
7	288.9	45.1	61.0	20	11.1	3.8	4.92	69.92	6.46	52.2	1.6
8	538.3	38.5	81.1	40	15.5	2.0	5.19	70.51	6.35	50.3	0.8
				[BF] = 0.133 mol/L at 50 °C							
9	45.5	124.1	10.1	1	5	13.0	4.90	71.88	5.84	42.4	11.0
10	90.0	109.7	20.2	2	5	8.5	4.82	71.66	5.90	43.3	6.5
11	89.5	65.1	29.7	2	7	9.6	4.86	70.84	6.17	47.4	3.2
12	134.2	41.3	50.0	3	12	10.5	4.72	70.14	6.40	51.2	2.4
13	133.6	27.2	60.2	3	14	9.2	4.64	67.49	6.62	55.1	1.8
14	180.2	19.6	73.9	4	16.25	5.7	4.62	67.91	6.90	60.6	1.4
				[BF] = 0.133 mol/L 70 °C							
15	45.6	265.6	5.0	1	0.5	8.6	4.88	71.03	5.99	44.6	13.0
16	45.5	124.9	10.1	1	1.0	11.7	4.91	71.51	5.92	43.6	7.2
17	89.5	113.7	19.5	2	1.2	13.5	4.85	71.27	6.06	45.7	3.6
18	89.9	64.9	29.9	2	1.7	12.5	4.82	70.88	6.22	48.2	2.4
19	135.5	62.2	40.2	3	2.5	8.6	4.76	70.33	6.36	50.5	1.9
20	135.5	41.5	50.1	3	2.25	5.6	4.74	69.77	6.40	51.2	1.5

[a] Initiator, AIBN 2 mg. [b] Determined by GPC. THF as eluent.

Table X
Copolymerization[a] of BT and NQ with St in Chloroform

	monomer feed					copolymer compn				
	mg		mol %			anal. %			mol %	
run	acceptor	St	acceptor	time, h	convn, %	H	C	N	acceptor	$\bar{M}_n/10^4$ [b]
				[BT] = 0.014–0.042 mol/L at 60 °C						
1	49.3	134.5	9.7	5	12.5	4.67	68.23	6.11	50.0	2.5
2	70.4	77.4	21.1	6	10.3	5.66	68.97	6.15	50.8	1.4
3	90.5	60.4	30.6	7	7.4	5.43	69.17	6.08	49.5	1.1
4	109.8	47.0	40.7	8	5.8	5.12	69.19	6.31	53.8	0.94
5	129.2	38.1	49.9	9	3.8	4.21	65.19	5.84	47.4	0.87
6	148.9	30.3	59.1	10	2.2	5.04	65.58	5.76	44.2	0.84
				[NQ] = 0.035–0.336 mol/L at 60 °C						
7	60.1	159.0	10.0	50	15.8	5.67	74.70	5.84	44.2	0.86
8	100.3	120.4	20.0	50	19.5	5.85	74.63	6.05	47.6	0.82
9	150.8	106.2	29.7	48.5	17.1	5.81	74.31	6.05	47.6	1.78
10	200.3	90.1	39.6	18.5	5.1	5.09	74.14	6.15	49.5	1.15
11	250.2	77.4	49.3	48.5	13.0	5.53	74.12	6.09	48.2	1.90
12	200.6	41.8	59.2	44	5.9	5.83	74.14	6.06	47.6	0.67
13	400.3	66.1	64.2	40	4.7	5.74	74.27	6.05	47.6	0.84
14	585.6	76.7	69.4	29	3.3	5.74	74.74	6.10	48.3	1.90

[a] Solvent, 10 mL of chloroform and 5 mL of toluene for the BT–St and NQ–St systems, respectively. Initiator, 2 mg of AIBN and 1 mg of AIBN for the BT–St and NQ–St systems, respectively. [b] Determined by GPC. THF as eluent.

60 °C, those of run 9–14 were done in the high BF concentration 0.133 mol/L at 50 °C, and those of runs 15–20 were done with the same high BF concentration at 70 °C. The copolymerizations of BF with the low BF concentration at 60 °C took place in an alternating fashion. On the other hand, the copolymerizations with the high BF concentration at 50 and 70 °C took place in a random fashion. The results of these random copolymerizations with the high monomer concentration were calculated according to the Kelen–Tüdös[12] and the intersection[13] methods to obtain the monomer reactivity ratios; r_1 (BF) = 0.18 ± 0.055, r_2 (St) = 0.065 ± 0.025 at 50 °C and r_1 (BF) = 0.055 ± 0.023, r_2 (St) = 0.027 ± 0.010 at 70 °C. Since the high BF concentrations in these copolymerizations are much higher than the equilibrium monomer concentration, 0.0459 mol/L, at 50 °C, the copolymerization of BF with St at 50 °C can be regarded to take place without influence of the depolymerization. Then monomer reactivity ratios at 50 °C allowed one to estimate Alfrey-Price's *Q*–*e* value for BF to be $Q = 2.8$ and $e = +1.31$, indicating that BF is highly conjugative as well as highly electron accepting.

The fashion of the copolymerization of BF with St was found to change from random to alternating, when the BF concentration of 0.133 mol/L in monomer feed was reduced to 0.045–0.053 mol/L. Moreover, the r_1 ratios of the copolymerizations, where M_1 refers to BF, were found to decrease when the polymerization temperature was changed from 50 to 70 °C. Therefore, it can be pointed out that the copolymerization of BF with St is seriously influenced by the depolymerization of BF similarly to the copolymerization of BzCQ with St,[5] strongly supporting the new mechanism of an alternating copolymerization as proposed in the previous paper.[5] Copolymerizations of BT and NQ with St were found to take place in an alternating fashion as shown in Figure 5, being attributable to the lack of radical polymerizability of BT and NQ due to the serious influence of depolymerization.

In conclusion, it was found that the annelated compounds of 7,8-bis(ethoxycarbonyl)-7,8-dicyanoquinodimethane (ACS) with furan, thiophene, and benzene nuclei, such as BF, BT, and NQ, respectively, remarkably decrease in homopolymerizability compared to the parent compound, ACS. The order in homopolymerizability was found to be BF ≫ BT > NQ, corresponding well to the reverse order in aromaticity of annelating nuclei, benzene > thiophene > furan,[14] in addition to the order in their electron-accepting character, BF > BT > NQ. It is certain that the annelation significantly influences the reactivity (stability) of the compounds, in the other words the free energy of polymerization, in relation to the aromaticity of the annelated nucleus. BF is polymerizable with anionic and radical initiators similarly to ACS even though its reactivity is much lower and also its radical polymerization exhibits a typical equilibrium polymerization.

In the copolymerizations with St it also was found that when the monomers lack homopolymerizability due to depolymerization, their copolymerizations become more alternating.

Registry No. **1a**, 28715-26-6; **1b**, 30566-10-0; **2a**, 117626-13-8; **2b**, 117626-14-9; **3a**, 117626-15-0; **3b**, 117626-16-1; **4a**, 117652-14-9; **4b**, 117626-17-2; **5**, 58791-49-4; **6**, 38153-21-8; **7**, 117626-20-7; BF, 117626-18-3; BF (homopolymer), 117626-22-9; (BF)(St) (copolymer), 117626-25-2; BT, 117626-19-4; BT (homopolymer), 117626-23-0; (BT)(St) (alternating copolymer), 117626-26-3; NQ, 117626-21-8; NQ (homopolymer), 117626-24-1; (NQ)(St) (alternating copolymer), 117626-27-4; St, 100-42-5; NaCN, 143-33-9; $(EtO)_2CO$, 105-58-8.

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