Macromolecules

Volume 27, Number 18 August 29, 1994

Synthesis of 7,7,8-Tris(alkoxycarbonyl)-8-cyanoquinodimethanes and Their Amphoteric Polymerization Behavior in Alternating Copolymerization

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Received March 7, 1994; Revised Manuscript Received May 26, 1994[⊛]

ABSTRACT: 7,7,8-Tris(alkoxycarbonyl)-8-cyanoquinodimethanes (1) with ethoxy (**1a**), methoxy (**1b**), isopropoxy (**1c**), butoxy (**1d**), and *tert*-butoxy (**1e**) alkoxy groups were successfully prepared as pure, isolable yellow crystals. Compounds **1a** and **1e** formed charge-transfer complexes not only with styrene (St) but also with 7,7,8,8-tetracyanoquinodimethane (TCNQ), indicating that **1a** and **1e** exhibited an amphoteric polar character in the charge-transfer complex formation. When **1a–e** were dissolved in basic polar aprotic solvents such as acetone, acetonitrile, tetrahydrofuran, *N,N*-dimethylformamide, and dimethyl sulfoxide, **1a–d**, but not **1e**, spontaneously polymerized to give polymers. Compounds **1a–e** were homopolymerizable with 2,2′-azobis(isobutyronitrile) (AIBN) and butyllithium but not with boron trifluoride etherate. Compound **1e** had a very poor polymerizability compared with **1a–d**, probably due to the steric hindrance of the *tert*-butyl group. Homopolymerizable compound **1a** copolymerized with St in the presence of AIBN to obtain the monomer reactivity ratios $r_{1a} = 1.62 \pm 0.28$ and $r_{St} = 0.005 \pm 0.01$ at 60 °C and Q and e values of $Q = 30.5$ and $e = +1.40$, indicating that **1a** is highly conjugative (highly reactive) and electron-accepting and copolymerized with acceptor monomer TCNQ in a perfectly alternating fashion. Poorly homopolymerizable compound **1e** also copolymerized not only with donor monomer St but also with acceptor monomer TCNQ in a perfectly alternating fashion, indicative of the amphoteric polymerization behavior of **1e**. Compounds **1a** and **1e** were found to be isolable 1,4-quinodimethane monomers which exhibited amphoteric behavior in the charge-transfer complex formation as well as in the alternating copolymerization.

Introduction

Unsubstituted 1,4-quinodimethane (QM) is so reactive that it gives polymeric materials immediately at room temperature.[1] Introduction of electron-withdrawing substituents such as cyano and ester groups on its exocyclic carbon makes QM less reactive, and crystalline materials may be obtained at room temperature: e.g., 7,7,8,8-tetracyanoquinodimethane (TCNQ),[2] 7,7,8,8-tetrakis(methoxycarbonyl)quinodimethane (TMCQ),[2] 7,7,8,8-tetrakis(ethoxycarbonyl)quinodimethane (TECQ),[3] 7,8-bis(alkoxycarbonyl)-7,8-dicyanoquinodimethanes (ACQ),[4,5] and so on. These isolable, electron-accepting quinodimethanes show different polymerization behaviors depending on the nature and number of the electron-withdrawing substituents. TCNQ carrying four cyano groups at the 7 and 8 positions is not homopolymerizable with any initiator but is copolymerizable as an acceptor monomer with a donor monomer such as styrene (St) in an alternating fashion.[6] TMCQ carrying four ester groups is homopolymerizable, but TECQ is not homopolymerizable.[3,4] Their polymerizability depends on the nature of the alkoxy groups. Moreover, both TMCQ and TECQ copolymerized alternatingly in an amphoteric fashion;[4,7] that is, they can copolymerize not only as acceptor monomers toward the donor monomer St but also as donor monomers toward the powerful electron-accepting monomer TCNQ. ACQ carrying two different electron-withdrawing substituents such as cyano and ester groups is homopolymerizable with radical and anionic initiators and copolymerizable with St in a random fashion.[5,8] As the polymerization behavior of the electron-accepting 1,4-quinodimethanes greatly depends on their substitution mode, we are interested in the polymerization behavior of a new type of isolable 1,4-quinodimethanes with substitution mode different from the 1,4-quinodimethanes mentioned above.

In this work are described the syntheses and polymerizations of 7,7,8-tris(alkoxycarbonyl)-8-cyanoquinodimethanes (**1a–e**) with ethoxy, methoxy, isopropoxy, butoxy, and *tert*-butoxy alkoxy groups, respectively, as a

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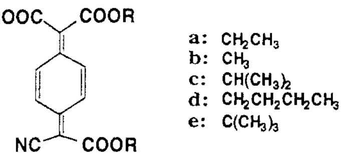
[⊛] Abstract published in *Advance ACS Abstracts,* July 15, 1994.

0024-9297/94/2227-4859$04.50/0 © 1994 American Chemical Society

new type of isolable, electron-accepting 1,4-quinodimethanes.



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Experimental Section

Preparation of 7,7,8-Tris(alkoxycarbonyl)-8-cyanoquinodimethane (1). The preparations of 8-[cyano(ethoxycarbonyl)methylene]-1,4-dioxaspiro[4.5]decane (**3a**), 8-[cyano(methoxycarbonyl)methylene]-1,4-dioxaspiro[4.5]decane (**3b**), 8-[cyano(isopropoxycarbonyl)methylene]-1,4-dioxaspiro[4.5]decane (**3c**), 8-[cyano(butoxycarbonyl)methylene]-1,4-dioxaspiro[4.5]decane (**3d**), 4-[cyano(ethoxycarbonyl)methylene]cyclohexanone (**4a**), 4-[cyano(methoxycarbonyl)methylene]cyclohexanone (**4b**), 4-[cyano(isopropoxycarbonyl)methylene]cyclohexanone (**4c**), and 4-[cyano(butoxycarbonyl)methylene]cyclohexanone (**4d**) were described in a related paper.[9]

8-[Cyano(*tert*-butoxycarbonyl)methylene]-1,4-dioxaspiro[4.5]decane (3e). 1,4-Cyclohexanedione monoethylene ketal (**2**) (10.0 g, 64.0 mmol) and 9.05 g (64.1 mmol) of *tert*-butyl cyanoacetate were refluxed in the presence of 1.0 g of ammonium acetate and 3.0 g of acetic acid in 20 mL of benzene using a Dean–Stark water separator to isolate water formed for 1 h. The reaction mixture was washed with 20 mL of saturated sodium chloride aqueous solution and 20 mL of saturated sodium bicarbonate aqueous solution and dried over anhydrous magnesium sulfate. It was placed under reduced pressure to remove solvent to obtain a white solid, which was recrystallized from hexane to give 13.0 g (74% yield) of **3e** as white plates: mp 75.0–76.0 °C; IR (KBr) ν_{CH} 2940, ν_{CN} 2204, $\nu_{C=O}$ 1685, $\nu_{C=C}$ 1571, ν_{C-O} 1239, 1076 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.99 (s, 4H), 3.13 (t, J = 7.0 Hz, 2H), 2.82 (t, J = 7.0 Hz, 2H), 1.87 (t, J = 7.0 Hz, 2H), 1.82 (t, J = 7.0 Hz, 2H), 1.53 (s, 9H). Anal. Calcd for $C_{15}H_{17}NO_4$: C, 65.44; H, 6.22; N, 5.09. Found: C, 65.21; H, 6.31; N, 4.91.

4-[Cyano(*tert*-butoxycarbonyl)methylene]cyclohexanone (4e). Ketal **3e** (13.0 g, 47.1 mmol) was added to 270 mL of tetrahydrofuran containing 30 mL of 20% hydrochloric acid and then stirred at room temperature for 40 h. The reaction mixture was placed under reduced pressure to remove tetrahydrofuran and then extracted with 200 mL of ethyl acetate. The extract was washed with 100 mL of saturated sodium chloride aqueous solution and 100 mL of saturated sodium bicarbonate aqueous solution, dried over anhydrous magnesium sulfate, and then placed under reduced pressure to remove solvent to give a white solid, which was recrystallized from hexane to obtain 10.41 g (96% yield) of **4e** as white plates: mp 78.0–80 °C; IR (KBr) ν_{CH} 2940, ν_{CN} 2208, $\nu_{C=O}$ 1683, $\nu_{C=C}$ 1573, ν_{C-O} 1243, 1079 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.37 (t, J = 6.9 Hz, 2H), 3.10 (t, J = 6.9 Hz, 2H), 2.56 (t, J = 6.9 Hz, 2H), 2.54 (t, J = 6.9 Hz, 2H), 1.55 (s, 9H). Anal. Calcd for $C_{13}H_{13}NO_3$: C, 67.52; H, 5.67; N, 6.06. Found: C, 67.41; H, 5.31; N, 5.89.

1-[Cyano(ethoxycarbonyl)methylene]-4-[bis(ethoxycarbonyl)methylene]cyclohexane (5a). Titanium tetrachloride (8 mL, 72.8 mmol) in 16 mL of carbon tetrachloride was added to 100 mL of tetrahydrofuran at 0 °C, and then into the yellow suspension was added 5.80 g (31.0 mmol) of 4-[cyano(ethoxycarbonyl)methylene]cyclohexanone (**4a**) and 4.96 g (31.0 mmol) of diethyl malonate. To the resulting brown suspension was added 12 mL (149 mmol) of pyridine in 13 mL of tetrahydrofuran over a period of about 30 min, and the mixture was stirred at room temperature for 3 days. The reaction mixture was poured into 200 mL of water and then extracted three times with 50 mL of ethyl acetate. The extracts were combined, successively washed with 50 mL of saturated sodium chloride aqueous solution, 50 mL of saturated sodium bicarbonate aqueous solution, and 50 mL of saturated sodium chloride aqueous solution, dried over anhydrous magnesium sulfate, and placed under reduced pressure to remove solvent to give a pale brown viscous oil, which was dissolved in a small amount of isopropyl ether. The resulting solution was passed through a silica gel column using isopropyl ether as an eluent. The second elution band was collected and placed under reduced pressure to remove solvent to leave a white solid, which was recrystallized twice from hexane to give 7.36 g (68% yield) of **5a** as white needles: mp 63.5–64.5 °C; IR (KBr) ν_{CH} 2944, ν_{CN} 2202, $\nu_{C=O}$ 1670, $\nu_{C=C}$ 1570, ν_{C-O} 1224, 1093 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.26 (m, 6H), 3.17 (t, J = 6.2 Hz, 2H), 2.87 (s, 4H), 2.76 (t, J = 6.2 Hz, 2H), 1.31 (m, 9H). Anal. Calcd for $C_{18}H_{23}NO_6$: C, 61.88; H, 6.64; N, 4.01. Found: C, 61.83; H, 6.42; N, 3.91.

1-[Cyano(methoxycarbonyl)methylene]-4-[bis(methoxycarbonyl)methylene]cyclohexane (5b). Compound **5b** was obtained as white needles in 60% yield from the reaction of 4-[cyano(methoxycarbonyl)methylene]cyclohexanone (**4b**) with dimethyl malonate in a process similar to that for **5a**: mp 103.7–104.3 °C; IR (KBr) ν_{CH} 2920, ν_{CN} 2202, $\nu_{C=O}$ 1684, $\nu_{C=C}$ 1568, ν_{C-O} 1229, 1092 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.81 (s, 3H), 3.77 (s, 6H), 3.18 (t, J = 6.3 Hz, 2H), 2.87 (s, 4H), 2.74 (t, J = 6.3 Hz, 2H). Anal. Calcd for $C_{15}H_{17}NO_6$: C, 58.63; H, 5.58; N, 4.56. Found: C, 58.39; H, 5.71; N, 4.61.

1-[Cyano(isopropoxycarbonyl)methylene]-4-[bis(isopropoxycarbonyl)methylene]cyclohexane (5c). Compound **5c** was obtained as white needles in 65% yield from the reaction of 4-[cyano(isopropoxycarbonyl)methylene]cyclohexanone (**4c**) with diisopropyl malonate in a process similar to that for **5a**: mp 52.0–52.5 °C; IR (KBr) ν_{CH} 2944, ν_{CN} 2202, $\nu_{C=O}$ 1671, $\nu_{C=C}$ 1570, ν_{C-O} 1230, 1091 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.15 (m, 3H), 3.18 (t, J = 6.6 Hz, 2H), 2.86 (s, 4H), 2.75 (t, J = 6.6 Hz, 2H), 1.34 (d, J = 6.3 Hz, 6H), 1.28 (d, J = 6.3 Hz, 12H). Anal. Calcd for $C_{21}H_{29}NO_6$: C, 64.43; H, 7.47; N, 3.58. Found: C, 64.51; H, 7.18; N, 3.69.

1-[Cyano(butoxycarbonyl)methylene]-4-[bis(butoxycarbonyl)methylene]cyclohexane (5d). Compound 5d was obtained as white needles in 66% yield from the reaction of 4-[cyano(butoxycarbonyl)methylene]cyclohexanone (**4d**) with dibutyl malonate in a process similar to that for **5a**: mp 41.0–42.0 °C; IR (KBr) ν_{CH} 2920, ν_{CN} 2202, $\nu_{C=O}$ 1688, $\nu_{C=C}$ 1571, ν_{C-O} 1223, 1094 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.20 (m, 6H), 3.18 (t, J = 6.2 Hz, 2H), 2.87 (s, 4H), 2.76 (t, J = 6.6 Hz, 2H), 1.64 (m, 6H), 1.38 (m, 6H), 0.93 (m, 9H). Anal. Calcd for $C_{24}H_{35}NO_6$: C, 66.49; H, 8.14; N, 3.23. Found: C, 66.51; H, 8.18; N, 3.41.

1-[Cyano(*tert*-butoxycarbonyl)methylene]-4-[bis(*tert*-butoxycarbonyl)methylene]cyclohexane (5e). Compound **5e** was obtained as white needles in 63% yield from the reaction of 4-[cyano(*tert*-butoxycarbonyl)methylene]cyclohexanone (**4e**) with di-*tert*-butyl malonate in a process similar to that for **5a**: mp 112–113 °C: IR (KBr) ν_{CH} 2942, ν_{CN} 2202, $\nu_{C=O}$ 1684, $\nu_{C=O}$ 1571, ν_{C-O} 1236, 1091 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.14 (t, J = 6.3 Hz, 2H), 2.83 (s, 4H), 2.72 (t, J = 6.3 Hz, 2H), 1.52 (s, 9H), 1.50 (s, 18H). Anal. Calcd for $C_{24}H_{35}NO_6$: C, 66.49; H, 8.14; N, 3.23. Found: C, 66.71; H, 8.23; N, 3.10.

7,7,8-Tris(ethoxycarbonyl)-8-cyanoquinodimethane (1a). Compound **5a** (2.0 g, 5.7 mmol) was dissolved in 1000 mL of benzene, and then into the resulting solution were added 16 g (186 mmol) of activated manganese dioxide and 10 g of 3A molecular sieves. The mixture was stirred at room temperature for 4 h and then filtered. The yellow filtrate was placed under reduced pressure to remove solvent to give a yellow solid which was dissolved in a small amount of dichloromethane. The resulting solution was passed through a silica gel column using dichloromethane as an eluent. The yellow elution band was collected and placed under reduced pressure to remove solvent to obtain a yellow solid, which was recrystallized from hexane to give 0.52 g (26% yield) of **1a** as yellow needles: mp 120 °C (dec); IR (KBr) ν_{CH} 2946, ν_{CN} 2192, $\nu_{C=O}$ 1684, $\nu_{C=C}$ 1533, ν_{C-O} 1226, 1088 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.33 (dd, J = 2.0, 10.2 Hz, 1H), 7.67 (dd, J = 2.0, 9.9 Hz, 1H), 7.57 (dd, J = 2.0, 10.2 Hz, 1H), 7.36 (dd, J = 2.0, 9.9 Hz, 1H), 4.35 (q, J = 7.2 Hz, 4H), 4.34 (q, J = 7.2 Hz, 2H), 1.39 (t, J = 7.2 Hz, 6H), 1.35 (t, J = 7.2 Hz, 3H); UV($CHCl_3$) λ 383 nm ($\epsilon = 4.16 \times 10^4$). Anal. Calcd for $C_{18}H_{19}NO_6$: C, 62.60; H, 5.55; N, 4.06. Found: C, 62.47; H, 5.29; N, 3.83.

7,7,8-Tris(methoxycarbonyl)-8-cyanoquinodimethane (1b). Compound **1b** was obtained as yellow needles in 31% yield from **5b** in a process similar to that for **1a**: mp 140 °C (dec); IR (KBr)

ν_{CH} 2918, ν_{CN} 2200, $\nu_{C=O}$ 1681, $\nu_{C=C}$ 1540, ν_{C-O} 1221, 1092 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.34 (dd, J = 2.0, 10.1 Hz, 1H), 7.66 (dd, J = 2.0, 10.0 Hz, 1H), 7.56 (dd, J = 2.0, 10.1 Hz, 1H), 7.37 (dd, J = 2.0, 10.0 Hz, 1H), 3.91 (s, 3H), 3.90 (s, 6H); UV (CHCl$_3$) λ 383 nm (ϵ = 4.24 × 10^4). Anal. Calcd for $C_{15}H_{13}NO_6$: C, 59.41; H, 4.32; N, 4.02. Found: C, 59.21; H, 4.35; N, 3.88.

7,7,8-Tris(isopropoxycarbonyl)-8-cyanoquinodimethane (1c). Compound **1c** was obtained as yellow needles in 24% yield from **5c** in a process similar to that for **1a**: mp 77.5–78.0 °C; IR (KBr) ν_{CH} 2942, ν_{CN} 2188, $\nu_{C=O}$ 1681, $\nu_{C=C}$ 1538, ν_{C-O} 1213, 1090 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.32 (dd, J = 2.0, 10.2 Hz, 1H), 7.66 (dd, J = 2.0, 9.9 Hz, 1H), 7.56 (dd, J = 2.0, 10.2 Hz, 1H), 7.34 (dd, J = 2.0, 9.9 Hz, 1H), 5.20 (m, 3H), 1.36 (d, J = 6.3 Hz, 6H), 1.33 (d, J = 6.3 Hz, 12H); UV(CHCl$_3$) λ 384 nm (ϵ = 3.95 × 10^4). Anal. Calcd for $C_{21}H_{25}NO_6$: C, 65.10; H, 6.50; N, 3.62. Found: C, 65.31; H, 6.62; N, 3.81.

7,7,8-Tris(butoxycarbonyl)-8-cyanoquinodimethane (1d). Compound **1d** was obtained as yellow needles in 29% yield from **5d** in a process similar to that for **1a**: mp 72.5–73.0 °C; IR (KBr) ν_{CH} 2920, ν_{CN} 2183, $\nu_{C=O}$ 1714, $\nu_{C=C}$ 1537, ν_{C-O} 1224, 1094 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.33 (dd, J = 2.0, 10.1 Hz, 1H), 7.66 (dd, J = 2.0, 9.9 Hz, 1H), 7.56 (dd, J = 2.0, 10.1 Hz, 1H), 7.36 (dd, J = 2.0, 9.9 Hz, 1H), 4.30 (t, J = 6.6 Hz, 4H), 4.29 (t, J = 6.6 Hz, 2H), 1.74 (m, 2H), 1.46 (m, 4H), 1.41 (m, 4H), 0.96 (t, J = 7.2 Hz, 2H), 0.95 (t, J = 7.3 Hz, 6H); UV (CHCl$_3$) λ 384 nm (ϵ = 4.08 × 10^4). Anal. Calcd for $C_{24}H_{31}NO_6$: C, 67.11; H, 7.28; N, 3.26. Found: C, 66.97; H, 7.12; N, 2.98.

7,7,8-Tris(*tert*-butoxycarbonyl)-8-cyanoquinodimethane (1e). Compound **1e** was obtained as yellow needles in 26% yield from **5e** in a process similar to that for **1a**: mp 101–102 °C; IR (KBr) ν_{CH} 2940, ν_{CN} 2180, $\nu_{C=O}$ 1678, $\nu_{C=C}$ 1535, ν_{C-O} 1227, 1090 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.26 (dd, J = 2.0, 9.8 Hz, 1H), 7.62 (dd, J = 2.0, 10.2 Hz, 1H), 7.51 (dd, J = 2.0, 9.8 Hz, 1H), 7.30 (dd, J = 2.0, 10.2 Hz, 1H), 1.56 (s, 18H), 1.55 (s, 9H); UV (CHCl$_3$) λ 384 nm (ϵ = 4.36 × 10^4). Anal. Calcd for $C_{24}H_{31}NO_6$: C, 67.11; H, 7.28; N, 3.26. Found: C, 67.28; H, 7.30; N, 3.24.

UV–Vis Measurement for the 1a–St, 1a–TCNQ, 1e–St, and 1e–TCNQ Systems. Absorption spectra of the charge-transfer transition for four systems were taken in chloroform at room temperature. The concentrations of the solutions employed were as follows: [**1a**] = 4.93 × 10^{-3} mol/L and [St] = 0.37 mol/L for the **1a**–St system, [**1a**] = 5.55 × 10^{-2} mol/L and [TCNQ] = 1.02 × 10^{-3} mol/L for the **1a**–TCNQ system, [**1e**] = 6.73 × 10^{-3} mol/L and [St] = 0.60 mol/L for the **1e**–St system, and [**1e**] = 4.22 × 10^{-2} mol/L and [TCNQ] = 9.84 × 10^{-4} mol/L for the **1e**–TCNQ system.

Cyclic Voltammetry Measurement. Voltammetric measurement was carried out at room temperature at a scanning rate of 100 mV/s using dichloromethane as the solvent containing tetrabutylammonium perchlorate (0.1 mol/L) as the supporting electrolyte, and Ag/AgCl, glassy carbon, and platinum wire were used as the reference electrode, working electrode, and counter electrode, respectively.

Spontaneous Polymerizations of 1a–e in Some Solvents. Compounds **1a–e** (about 1 mg) were dissolved in 1 mL of a solvent such as benzene, toluene, chloroform, acetone, acetonitrile, tetrahydrofuran, *N,N*-dimethylformamide, and dimethyl sulfoxide. After standing for 2 h at room temperature, an aliquot of the solution was taken out by a syringe and was subjected to gel permeation chromatography (GPC) to determine the molecular weight of the reaction product.

Polymerization Procedure. Radical Polymerization. Given amounts of **1a**, **1b**, **1c**, **1d**, or **1e**, St or TCNQ as a comonomer if necessary, benzene or dichloromethane as a solvent, and 2,2′-azobis(isobutyronitrile) (AIBN) as a radical initiator were placed in a glass ampule, which was degassed by the freeze–thaw method (repeatedly three times) and sealed. The ampule was placed in a bath thermostated at 60 °C for the time of polymerization and then opened. The reaction mixture was poured into an excess of hexane to precipitate the product, which was purified in three or more redissolution–reprecipitation cycles. Dichloromethane and hexane were used as solvent and precipitant, respectively. When TCNQ was used as a comonomer, acetonitrile and methanol were used as solvent and precipitant, respectively. The product obtained was dried under reduced pressure at room temperature until a constant weight was reached.

Ionic Polymerization. The polymerization was carried out with the apparatus reported previously.[5] A given amount of **1a**, **1b**, **1c**, **1d**, or **1e** as a monomer was placed in the apparatus, which was filled with nitrogen. Into it was introduced a given amount of solvent by a syringe. After the resulting solution was degassed by the freeze–thaw method (repeated twice), the apparatus was filled with nitrogen and sealed. Then it was set in a bath thermostated at 0 °C, and a fixed amount of butyllithium, triethylamine, pyrrolidine, or boron trifluoride etherate was injected into it by a syringe. After a given time of the reaction, the reaction mixture was poured into excess hexane to deposit a polymeric product. The precipitated polymeric product was dissolved again in a small amount of dichloromethane, and the resulting solution was poured into hexane for purification. When no polymeric product was deposited in this process, the hexane solution was placed under reduced pressure to remove volatile materials. An aliquot of the residue was dissolved in a small amount of benzene, and the resulting benzene solution was subjected to GPC to determine the molecular weight of the reaction product.

Other Materials. TECQ[3] and 7,8-bis(ethoxycarbonyl)-7,8-dicyanoquinodimethane (ECQ)[4] were prepared according to the methods reported previously. TCNQ was prepared according to the method reported by Acker et al.[2] and recrystallized twice from acetonitrile. Styrene [bp 52 °C (30 mmHg)] was washed with 2% aqueous sodium hydroxide solution and water, dried over anhydrous magnesium sulfate, stirred over calcium hydride, and then distilled under reduced pressure. Chloroform (bp 61 °C), acetonitrile (bp 82 °C), dichloromethane (bp 40 °C), and acetone (bp 56 °C) were refluxed over calcium hydride for 12 h and then distilled. Tetrahydrofuran (bp 66 °C) was refluxed over lithium aluminum hydride for 12 h and then distilled. Dimethyl sulfoxide [bp 68 °C (10 mmHg)] and *N,N*-dimethylformamide [bp 70 °C (10 mmHg)] were dried over 3A molecular sieves for a day and then distilled under reduced pressure. AIBN was recrystallized from ethanol. Boron trifluoride etherate [bp 50 °C (50 mmHg)] was distilled under reduced pressure under nitrogen. Triethylamine (bp 89 °C) and pyrrolidine (bp 87 °C) were distilled over potassium hydroxide. Commercial tetrabutylammonium perchlorate, butyllithium, dimethyl malonate, diethyl malonate, dibutyl malonate, methyl cyanoacetate, ethyl cyanoacetate, isopropyl cyanoacetate, and butyl cyanoacetate were used without further purification. Di-*tert*-butyl malonate and diisopropyl malonate were prepared from the reactions of malonyl dichloride with *tert*-butyl alcohol and with isopropyl alcohol, respectively.[10] *tert*-Butyl cyanoacetate was prepared according to the method reported by Ireland.[11]

Characterization. Copolymer composition was established by elemental analysis. Number-average molecular weights, M_n, of the homopolymers of **1a–e** and the copolymers of **1a** or **1e** with St and of **1e** and TCNQ were determined by GPC using standard polystyrenes as reference and tetrahydrofuran as an eluent without correction. Solution viscosity was determined at 30 °C in concentrated sulfuric acid for the copolymers of **1a** with TCNQ. ^{1}H NMR measurement was carried out in chloroform-*d* with tetramethylsilane as an internal standard. The glass transition temperatures, T_gs, of the polymers were determined by differential scanning calorimetry (DSC) at a scanning rate of +10 °C/min under nitrogen.

Instrumentation. A Büchi capillary melting point apparatus was used for melting point measurement, a JEOL JNM-EX270 FT NMR spectrometer for ^{1}H NMR spectroscopy, Jasco IR-700 and UVIDEC-430B spectrometers for infrared and UV–vis spectroscopy, respectively, a Yanaco CHN Corder MT-3 for elemental analysis, a GPC Tosoh HPLC-803D with a series of two columns (Tosoh G4000H and G3000H) for measuring number-average molecular weight (M_n), and a Perkin-Elmer differential scanning calorimeter DSC-2C for thermogravimetry (TG), differential thermal analysis (DTA), and differential scanning calorimetry (DSC), respectively.

Results and Discussion

Preparation. 7,7,8-Tris(alkoxycarbonyl)-8-cyanoquinodimethanes (**1a–e**) with ethoxy, methoxy, isopropoxy,

Scheme 1

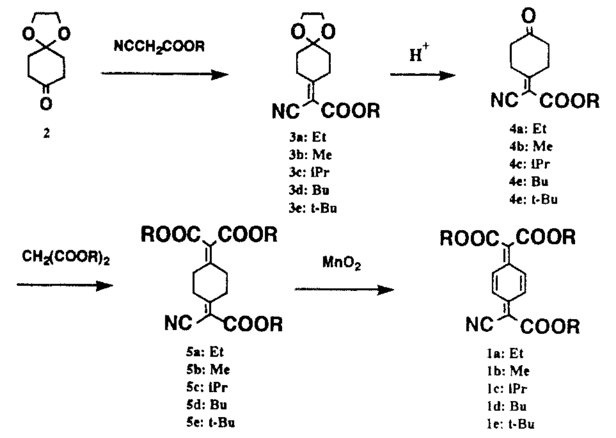


Table 1. First Reduction Potentials of 1,4-Quinodimethanes

1,4-quinodimethane	first reduction potential (V)[a]
TCNQ	+0.16
ECQ	−0.12
1b (Me)	−0.27
1a (Et)	−0.32
1d (Bu)	−0.39
1c (iPr)	−0.40
1e (tBu)	−0.50
TECQ	−0.86

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

butoxy, and *tert*-butoxy alkoxy groups were successfully prepared according to Scheme 1.

8-[Cyano(alkoxycarbonyl)methylene]-1,4-dioxaspiro[4.5]decanes (**3a–e**) were prepared in good yield by the Knoevenagel reaction of 1,4-cyclohexanedione monoethylene ketal (**2**) with alkyl cyanoacetates in the presence of ammonium acetate and acetic acid in benzene for **3e** and in the presence of β-alanine in water for **3a–d**. Ketal **3e** was readily hydrolyzed with 20% hydrochloric acid in tetrahydrofuran at room temperature and ketals **3a–d** with 2% sulfuric acid aqueous solution to give 4-[cyano(alkoxycarbonyl)methylene]cyclohexanones (**4a–e**) in quantitative yields. 4-[Cyano(alkoxycarbonyl)methylene]cyclohexanones (**4a–e**) were subjected to the Knoevenagel reaction with alkyl malonates using titanium tetrachloride and pyridine as the dehydrating system to give 1-[cyano(alkoxycarbonyl)methylene]-4-[bis(alkoxycarbonyl)methylene]cyclohexanones (**5a–e**) in moderate yields, which were readily oxidized with activated manganese dioxide in the presence of 3A molecular sieves in benzene to give 7,7,8-tris(alkoxycarbonyl)-8-cyanoquinodimethanes (**1a–e**) as yellow needles. Their IR and ^{1}H NMR spectra and elemental analyses strongly supported the chemical structures of 7,7,8,8-tetrasubstituted 1,4-quinodimethanes. The total yield in four steps was 10–15%.

Electron-Accepting Character. The electron-accepting character of **1a–e** was estimated as the value of the first reduction potential, E_1, by cyclic voltammetry. The values for **1a–e** are summarized in Table 1, together with those of TCNQ, ECQ, and TECQ for comparison. It is obvious that **1a–e** are weaker in electron-accepting character than TCNQ and ECQ and stronger in electron-accepting character than TECQ as expected from the difference in the electron-accepting character between the cyano and ester groups and the number of them. Moreover, the electron-accepting character of **1a–e** can be explained fairly well in terms of Taft's polar substituent constant values,[12] σ_p*, of the methyl (0.0), ethyl (−0.100), isopropyl (−0.190), butyl (−0.130), and *tert*-butyl (−0.300) groups.

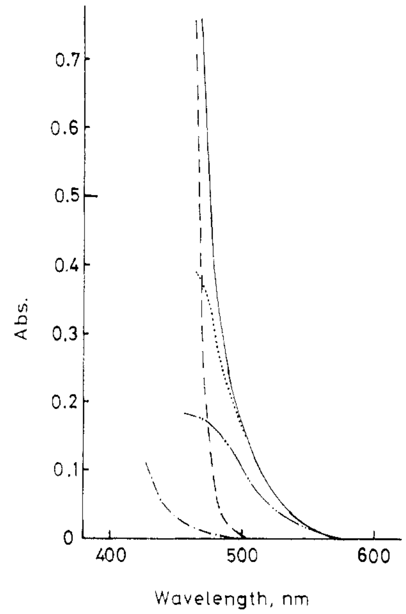


Figure 1. UV–vis spectra of a mixture of **1e** with St in chloroform: (—) spectrum of a mixture of **1e** with St; (- -) spectrum of **1e**; (···) difference spectrum between the above two spectra, corresponding to that of the complex. (—··) Difference spectrum between **1a** and a mixture of **1a** and St. (—-—) Difference spectrum between TECQ and a mixture of TECQ with St. Concentrations of solutions employed are [**1a**] = 4.94 × 10^{-3} mol/L and [St] = 0.37 mol/L for the **1a**–St system, [**1e**] = 6.73 × 10^{-3} mol/L and [St] = 0.6 mol/L for the **1e**–St system, and [TECQ] = 1.02 × 10^{-2} mol/L and [St] = 0.94 mol/L for the TECQ–St system.

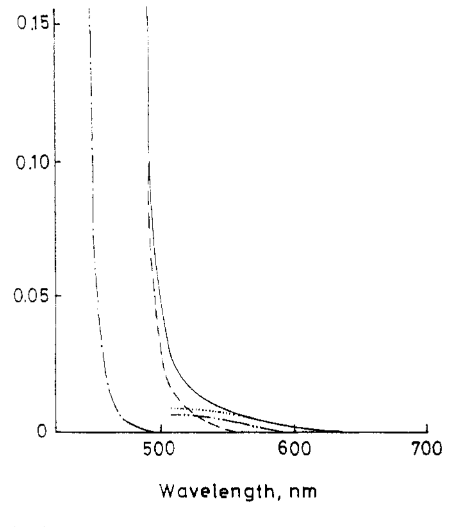


Figure 2. UV–vis spectra of a mixture of **1e** with TCNQ in chloroform: (—) spectrum of a mixture of **1e** with TCNQ; (- -) spectrum of **1e**; (—-—) spectrum of TCNQ; (···) difference spectrum, corresponding to that of the complex. (—··) Difference spectrum between **1a** and a mixture of **1a** and TCNQ. Concentrations of solutions employed are [**1a**] = 5.55 × 10^{-2} mol/L and [TCNQ] = 1.02 × 10^{-3} mol/L for the **1a**–TCNQ system and [**1e**] = 4.22 × 10^{-2} mol/L and [TCNQ] = 9.84 × 10^{-4} mol/L for the **1e**–St system.

Charge-Transfer Absorption Band. Addition of St to **1e** in benzene caused the yellow color of the **1e** solution to deepen as shown in Figure 1, where the difference spectrum between the mixture and **1e** shows a broad absorption band in the wavelength range 460–580 nm, corresponding to the charge-transfer transition between **1e** and St. St does not absorb any light at wavelengths

Table 2. Spontaneous Polymerizations of 1a–e in Various Aprotic Polar Solvents

solvent		mol wt of polymer obtained, $M_n/10^4$				
	ν(OD) shift of MeOD^a	1a	1b	1c	1d	1e
acetonitrile	49	15	3	4.5	3.5	—
acetone	62	20	3.5	4.5	3	—
tetrahydrofuran	93	0.75	1.8	4	2	—
N,N-dimethylformamide	107	20	2	5	4	—
dimethyl sulfoxide	141	100	4.5	5	4	—

[a] As solvent basicity, the ν(OD) stretching frequency shift of methanol-*d* due to hydrogen bond formation with the solvent was determined.

longer than 400 nm. The corresponding absorption band between TECQ and St exists in the wavelength range 440–500 nm as shown in Figure 1. From comparison of both absorption bands, it may be said that **1e** is a stronger electron acceptor than TECQ, corresponding well with the results obtained by cyclic voltammetry: **1e** ($E_1 = -0.50$ V) and TECQ ($E_1 = -0.86$ V). The charge-transfer transition spectrum between **1e** and TCNQ is shown in Figure 2, where the difference spectrum between the mixture and the components reveals a broad absorption band in the wavelength range 520–580 nm though the absorbance is weak. It seems that **1e** interacts as a donor compound with TCNQ, indicating that there exists a sufficient difference in electron density for the charge-transfer complexation between **1e** and TCNQ. When **1a** was used instead of **1e**, the charge-transfer transition spectra between **1a** and St and between **1a** and TCNQ exhibit broad absorption bands in the wavelength ranges 460–580 nm in Figure 1 and 500–590 nm in Figure 2, respectively. Consequently, it can be pointed out that **1a** and **1e** exhibit amphoteric polar character in their charge-transfer complex formation as well as TMCQ[7] and TECQ.[3]

Homopolymerizations. The polymerization behavior of **1a–e** dissolved in various solvents was examined. In so-called nonpolar common solvents such as toluene, benzene, chloroform, and dichloromethane, all compounds remained yellow for 24 h, and their GPC chromatograms showed only peaks as the monomer state. In so-called basic aprotic polar solvents such as dimethyl sulfoxide, *N,N*-dimethylformamide, tetrahydrofuran, acetone, and acetonitrile, **1a–d**, but not **1e**, changed in a few minutes from yellow to colorless in dimethyl sulfoxide, *N,N*-dimethylformamide, acetone, and acetonitrile and changed slowly in 24 h from yellow to pale yellow in tetrahydrofuran. After standing for 2 h, compounds **1a–d** in such basic aprotic polar solvents were subjected to GPC, the chromatograms of which exhibited two peaks, one for **1a–d** themselves and the other for polymers of **1a–d** with molecular weights of 0.75×10^3 to 1.0×10^6 as shown in Table 2. However, **1e** in such basic aprotic solvents remained yellow for 24 h, and its chromatograms showed only a peak for **1e** itself, indicating that **1e** is not homopolymerizable in those solvents. It was found that **1a–d**, but not **1e**, are spontaneously polymerizable with basic aprotic polar solvents as well as ECQ,[4] 7,8-bis(butoxycarbonyl)-7,8-dicyanoquinodimethane (BCQ),[5] 7,8-diacyl-7,8-dicyanoquinodimethane (AcCQ),[13] and 7,8-dibenzoyl-7,8-dicyanoquinodimethane (BzCQ).[13]

Homopolymerizations of **1a–e** were carried out with the radical initiator AIBN, the anionic initiator butyllithium, and the cationic initiator boron trifluoride etherate. Homopolymerizations of **1a** were also carried out with the weak bases triethylamine and pyrrolidine. The polymerization results are summarized in Table 3. Polymers were obtained as white powders, which were soluble in chloroform, dichloromethane, tetrahydrofuran, acetone, and ethyl acetate and insoluble in hexane and methanol. It can be pointed out from Table 3 that **1a–e** are homopolymerizable with the radical and anionic initiators but not with the cationic initiator. For the polymerizations of **1a–e** under the conditions with monomer concentration of 0.16 mol/L in the presence of AIBN at 60 °C for 24 h, the polymer yield for **1e** is much lower than those for **1a–d**, indicating that the polymerizability of **1e** is much less than those of **1a–d**. Previously, it was pointed out that the polymerizability of 7,8-diacyl-7,8-dicyanoquinodimethanes greatly depends on the steric effect of the acyl groups.[14] Taft's steric substituent constants,[12] E_s, of the methyl, ethyl, isopropyl, butyl, and *tert*-butyl groups as

Table 3. Homopolymerizations of 1a–e

run no.	**1a–e** (mg)	initiator	[**1a–e**]/[initiator]	solvent	[**1a–e**] (mol/L)	temp (°C)	time (h)	conv (%)	$M_n/10^4$ ^a
				1a (R = Et)					
1	56.4	AIBN	60	benzene	0.16	60	24	86.3	5.9
2	52.1	$BF_3 \cdot Et_2O$	10	$CHCl_3$	0.03	0	6	0	
3	55.5	BuLi	10	toluene	0.03	0	6	19.6	2.0
4	54.7	Et_3N	10	toluene	0.03	0	6	48.1	10.0
5	66.8	Et_3N	0.1	toluene	0.03	0	0.25	100	4.0
6	65.6	pyrrolidine	10	toluene	0.03	0	6	15.0	0.23
7	54.0	pyrrolidine	0.1	toluene	0.03	0	0.5	93.0	—
				1b (R = Me)					
8	54.9	AIBN	60	benzene	0.16	60	24	92.0	0.4
9	50.8	$BF_3 \cdot Et_2O$	10	$CHCl_3$	0.03	0	6	0	
10	51.3	BuLi	10	toluene	0.03	0	6	12.4	1.8
				1c (R = iPr)					
11	50.6	AIBN	60	benzene	0.16	60	24	81.5	9.0
12	52.3	$BF_3 \cdot Et_2O$	10	$CHCl_3$	0.03	0	6	0	
13	49.0	BuLi	10	toluene	0.03	0	6	10.5	2.5
				1d (R = Bu)					
14	50.9	AIBN	60	benzene	0.16	60	24	91.0	9.5
15	54.3	$BF_3 \cdot Et_2O$	10	$CHCl_3$	0.03	0	6	0	
16	55.6	BuLi	10	toluene	0.03	0	6	8.0	1.3
				1e (R = tBu)					
17	62.0	AIBN	60	benzene	0.16	60	24	3.2	2.5
18	54.9	$BF_3 \cdot Et_2O$	10	$CHCl_3$	0.03	0	6	0	
19	58.2	BuLi	10	toluene	0.03	0	6	5.4	0.2

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

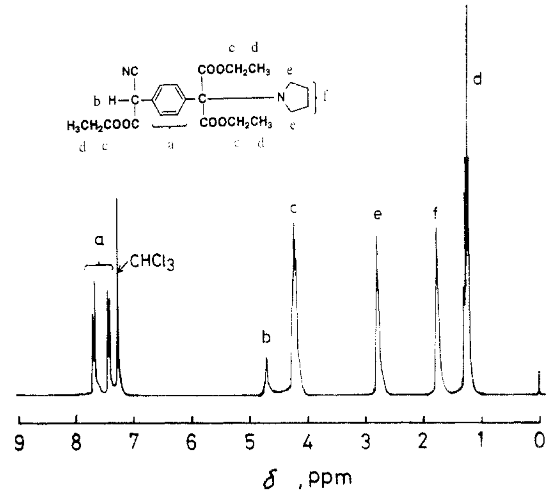


Figure 3. ^{1}H NMR spectrum of the reaction product of **1e** with pyrrolidine obtained under the condition of [**1e**]/[pyrrolidine] = 0.1.

alkyl groups on the alkoxycarbonyl of **1** are reported to be 0.0, –0.07, –0.47, –0.39, and –1.54, respectively, indicating that the E_s value of *tert*-butyl group is much larger than those of the other groups. Therefore, it is considered that the poor polymerizability of **1e** is probably attributable to the bulkiness of the *tert*-butyl group. Here, as the ethyl group is larger in steric hindrance than the methyl group, **1a** is expected to be less reactive on polymerization than **1b**. However, it was found from Table 3 that **1a** is more reactive on polymerization than **1b**. Therefore, it is likely that factors other than steric hindrance also affect the polymerizability, though the factors are not clear at present.

The polymerization of **1a** with weak bases such as triethylamine and pyrrolidine under the condition of [**1a**]/[base] = 10 gave polymers with molecular weights of 1×10^5 and of 2.3×10^3, respectively. Under the condition of [**1a**]/[base] = 0.1, the polymerization of **1a** with triethylamine gave a polymer with a molecular weight of 4×10^4, but that with pyrrolidine gave no polymer, though the system changed from yellow to colorless instantaneously. So, the reaction mixture with pyrrolidine was placed under reduced pressure to remove solvent, and the residue was treated with chromatography using a silica gel column and chloroform as an eluent to give 61 mg (93% yield based on **1a**) of a colorless viscous oil. Its IR spectrum showed absorption bands at 2232 cm^{-1} due to the cyano group and at 1694 and 1226 cm^{-1} due to the ester group. Its ^{1}H NMR spectrum in chloroform-*d* is shown in Figure 3, where individual peaks are assignable to the respective individual protons of the chemical structure illustrated therein. The elemental analysis values (C, 63.51; H, 6.71; N, 6.48) for the viscous oil were in good agreement with the calculated ones (C, 63.45; H, 6.78; N, 6.73) of the chemical structure illustrated in the figure. It is obvious that the product is the 1:1 adduct. Therefore, it is conceivable that an electron transfer reaction occurs between **1a** and pyrrolidine to give a zwitterion with pyrrolidinium ion and α-cyano-α-(ethoxycarbonyl)benzyl anion as terminals, as shown in Scheme 2, the anionic end of which is considered to be able to add a **1a** monomer. When excess pyrrolidine is present, it is conceivable that a number of the zwitterions will be formed and an intermolecular proton transfer from a pyrrolidinium moiety to the anionic moiety will give the 1:1 adduct before reaction with another **1a** monomer. In the case of triethylamine, a similar reaction was considered to take place to form a zwitterion with triethylammonium ion and α-cyano-α-(ethoxycarbonyl)benzyl anion. However, since the quaternary ammonium ion has no hydrogen for the proton transfer reaction, it was thought that the zwitterion would be able to add a **1a** monomer in preference to the termination reaction to give a polymer with a molecular weight of 4×10^4.

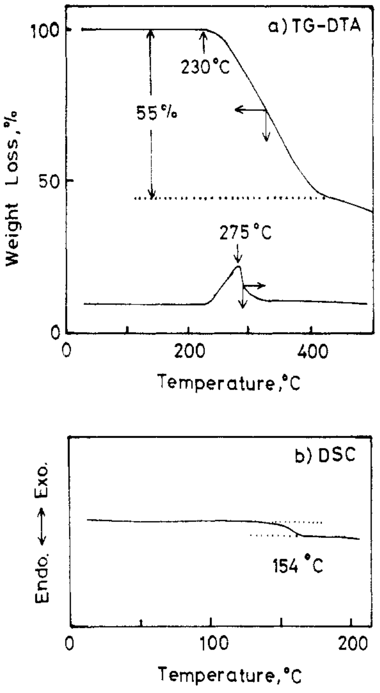
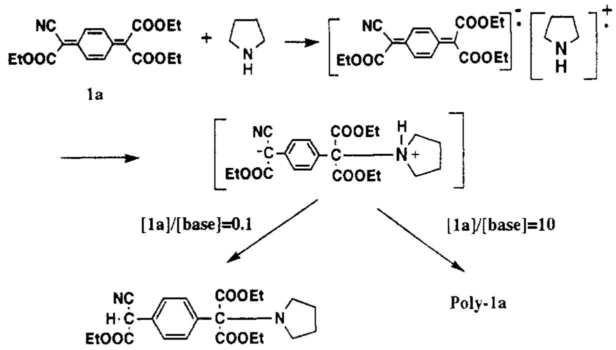


Figure 4. Thermal analysis of the polymer of **1a** at an elevating rate of temperature of 10 °C under nitrogen: (a) TG–DTA curves; (b) DSC curve.

Scheme 2



The polymer of **1a** (run no. 1) is capable of being cast from chloroform solution to give a brittle film. The results of TG–DTA and DSC measurements for the polymer of **1a** (run no. 1) are shown in parts a and b of Figure 4, respectively. Weight loss began at about 230 °C and the weight loss from 230 to 420 °C amounted to 55%, which approximately corresponds to the weight percent of the ethoxycarbonyl group to the **1a** unit. The glass transition temperature, T_g, of the polymer of **1a** was 154 °C as shown in Figure 4b.

Copolymerizations. The copolymerizations of St with **1a** and with **1e** in the presence of AIBN were carried out in benzene at 60 °C with monomer concentrations of **1a** of 0.15 mol/L and **1e** of 0.12 mol/L. All copolymers were obtained as white powders, which were soluble in chloroform, dichloromethane, tetrahydrofuran, acetone, and ethyl acetate but insoluble in hexane and methanol. The results of the copolymerizations are summarized in Table

Table 4. Copolymerizations[a] of St with 1a and with 1e in Benzene at 60 °C

run no.	monomer feed: 1a or 1e (mg)	monomer feed: St (mg)	1a or 1e (mol %)	solv (mL)	time (min)	conv (%)	anal.: % C	anal.: % N	copolym compn 1a or 1e (mol %)	$M_n/10^4$ [b]
				1a (R = Et)						
1	50.0	589.1	2.5	1	17	9.0	69.51	3.11	49.8	55
2	50.0	303.9	4.7	1	17	8.5	68.41	3.26	55.3	20
3	50.0	201.3	7.0	1	17	9.8	68.55	3.24	54.6	40
4	99.9	196.0	13.3	2	17	8.4	67.41	3.40	60.9	28
5	199.8	113.5	34.7	4	15	9.8	66.89	3.47	64.1	11
6	249.8	54.7	57.9	5	15	6.8	65.25	3.70	75.5	9
7	299.7	50.7	64.1	6	15	5.3	64.95	3.73	77.8	7
8	399.7	39.9	75.2	8	15	6.6	64.02	3.86	85.7	4
				1e (R = tBu)						
9	99.5	426.3	10.0	2	30	7.4	71.97	2.63	50.3	11
10	100.1	49.9	32.7	2	30	8.9	72.30	2.59	48.3	15
11	200.5	58.0	45.6	4	30	9.1	71.55	2.69	53.1	9
12	300.8	60.2	54.6	6	30	5.4	72.10	2.61	49.5	9
13	451.2	49.1	72.3	9	30	6.9	71.80	2.65	51.3	4
14	800.4	40.8	82.6	16	25	5.2	71.49	2.69	53.5	9

[a] [1a] = 0.15 mol/L, [1e] = 0.12 mol/L, and [AIBN] = 1.2 × 10^{-3} mol/L. [b] Determined by GPC using tetrahydrofuran as an eluent and standard polystyrenes as reference.

Table 5. Copolymerizations[a] of TCNQ with 1a and with 1e in Dichloromethane at 60 °C

run no.	monomer feed: 1a or 1e (mg)	monomer feed: St (mg)	1a or 1e (mol %)	solv (mL)	time (min)	conv (%)	anal.: % C	anal.: % N	copolym compn 1a or 1e (mol %)	$M_n/10^4$ [b]	η_{sp} (dL/g)[c]
					1a (R = Et)						
1	60.4	349.5	9.3	3	10	4.2	65.49	12.51	51.1		0.76
2	80.3	111.2	29.8	4	10	5.8	65.56	12.72	50.1		1.23
3	120.8	35.3	66.9	6	10	7.1	65.64	12.95	49.1		0.67
4	401.6	25.2	90.4	20	10	8.2	65.31	12.31	52.0		0.57
					1e (R = tBu)						
5	60.1	264.0	7.8	3	60	9.8	68.20	10.84	51.0	10	
6	80.5	133.3	22.3	4	60	9.7	68.25	11.14	49.6	7	
7	140.2	68.3	49.3	7	60	9.6	68.21	10.87	50.9	12	
8	180.0	32.4	72.5	9	60	8.9	68.23	11.04	50.0	12	
9	320.3	15.8	90.6	16	60	6.4	68.17	10.61	52.1	7	

[a] [1a] = 0.058 mol/L, [1e] = 0.047 mol/L, and [AIBN] = 1.2 × 10^{-3} mol/L. [b] Determined by GPC using tetrahydrofuran as an eluent and standard polystyrenes as reference. [c] Solvent, concentrated sulfuric acid; temperature, 30 °C; concentration, c = 0.04–0.1 g/dL.

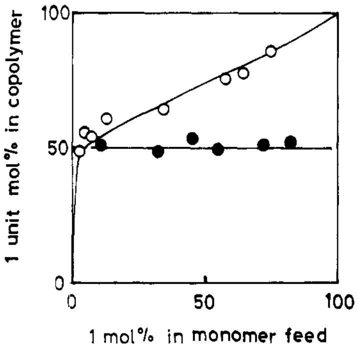


Figure 5. Copolymerization composition curves for the copolymerization of St with 1a (○) and with 1e (●) in benzene at 60 °C.

4, and the copolymerization composition curves are shown in Figure 5. The results for the 1a–St system were rationally analyzed according to the intersection[15] and Kelen–Tüdös[16] methods to obtain monomer reactivity ratios r_{1a} = 1.62 ± 0.28 and r_{St} = 0.005 ± 0.01 at 60 °C. The Alfrey–Price *Q* and *e* values of 1a were calculated on the basis of the monomer reactivity ratios to be 30.5 and +1.40, respectively, indicating that 1a is highly conjugative (highly reactive) and electron-accepting similar to BCQ,[5] AcCQ,[13] and BzCQ.[13] The copolymers for the 1e–St system were always composed of about 50% of the 1e unit regardless of the monomer feed ratios, indicating that 1e is copolymerizable with St in a perfectly alternating fashion. It is obvious that 1a and 1e react as acceptor monomers toward St. The difference in the copolymerization fashions between 1a and 1e probably corresponds to the difference in homopolymerizability of homopolymerizable compound 1a and poorly homopolymerizable compound 1e, and it can be explained in terms of our mechanism of alternating copolymerization in connection with equilibrium polymerization behavior.[17]

The copolymerizations of TCNQ with 1a and with 1e in the presence of AIBN were carried out in dichloromethane at 60 °C with monomer concentrations of 1a of 0.058 mol/L and 1e of 0.047 mol/L. All copolymers were obtained as white powders. The copolymers for the 1a–TCNQ system are only soluble in hot concentrated sulfuric acid and insoluble in common organic solvents, and those for the 1e–TCNQ system are soluble in chloroform, dichloromethane, tetrahydrofuran, acetone, and ethyl acetate and insoluble in hexane and methanol. The results of both copolymerizations are summarized in Table 5, and the copolymerization composition curves are shown in Figure 6. The copolymerizations of TCNQ with 1a and with 1e were found to take place in a perfectly alternating fashion, indicating that both 1a and 1e react as donor monomers toward TCNQ. It is concluded, therefore, that when compounds 1 are poorly homopolymerizable or nonhomopolymerizable as is 1e, compounds 1 can amphoterically copolymerize as can TMCQ[7] and TECQ.[3]

In summary, 7,7,8-tris(alkoxycarbonyl)-8-cyanoquinodimethanes (1a–e) with methoxy, ethoxy, isopropoxy, butoxy, and *tert*-butoxy alkoxy groups were successfully prepared as pure, isolable yellow crystals. Compounds 1a and 1e exhibited an amphoteric polar character in charge-

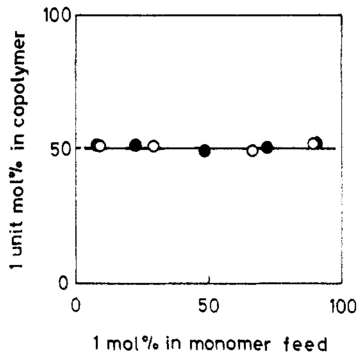


Figure 6. Copolymerization composition curves for the copolymerization of TCNQ with **1a** (○) and with **1e** (●) in dichloromethane at 60 °C.

transfer complex formation. When **1a–e** were dissolved in basic polar aprotic solvents such as acetone, acetonitrile, tetrahydrofuran, *N*,*N*-dimethylformamide, and dimethyl sulfoxide, **1a–d**, but not **1e**, spontaneously polymerized to give polymers. Compounds **1a–e** were homopolymerizable with radical and anionic initiators but not with a cationic initiator. It was found that **1e** is less reactive on polymerization than **1a–d**, probably due to the bulkiness of the *tert*-butyl group. Compound **1a** was copolymerizable in the presence of AIBN to obtain the monomer reactivity ratios $r_{1a} = 1.62 \pm 0.28$ and $r_{St} = 0.005 \pm 0.01$ at 60 °C and Q and e values of $Q = 30.5$ and $e = +1.40$, indicating that **1a** was highly conjugative (highly reactive) and electron-accepting and copolymerized with acceptor monomer TCNQ in a perfectly alternating fashion. Poorly homopolymerizable compound **1e** copolymerized not only with St but also with TCNQ in a perfectly alternating fashion. Compounds **1a** and **1e** exhibited amphoteric polymerization behavior in their alternating copolymerizations. It was found that **1a** and **1e** are another type of isolable 1,4-quinodimethane monomer showing amphoteric behavior in charge-transfer complex formation as well as in the alternating copolymerization, though they are stronger in electron-accepting character than both TMCQ and TECQ.

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