Synthesis and Polymerization of 7-(Alkoxycarbonyl)-7-cyano-1,4-benzoquinone Methides

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ABSTRACT: 7-(Alkoxycarbonyl)-7-cyano-1,4-benzoquinone methides 4 with four kinds of alkoxy groups, methyl, ethyl, isopropyl, and butyl, were successfully prepared as pure, isolable crystals. Acid-catalyzed 1,6-addition reactions of 7-cyano-7-(ethoxycarbonyl)-1,4-benzoquinone methide (**4a**) with phenol and *N,N*-dimethylaniline each gave 1:1 adducts in quantitative yield. Compound **4a** reacted with hydrogen chloride to give a 1,6-addition product in situ in quantitative yield, but it did not react with acetic acid. When dissolved in basic aprotic polar solvents such as acetone, acetonitrile, tetrahydrofuran, *N,N*-dimethylformamide, and dimethyl sulfoxide, **4a** spontaneously polymerized to give an oligomer with a molecular weight of 400–6000. Compounds 4 were homopolymerizable with 2,2′-azobis(isobutyronitrile) (AIBN), pyridine, and even boron trifluoride etherate. Pyridine afforded poly-**4a** with a high molecular weight of 1.1×10^5. Both anionic and radical poly-**4a** consisted of 1,6 or head-to-tail monomer unit placement. Compound **4a** was copolymerizable with styrene in a random fashion in the presence of AIBN to obtain the monomer reactivity ratios: $r_{4a} = 3.4 \pm 0.2$ and $r_{St} = 0.01 \pm 0.08$ at 60 °C to allow Q and e values for **4a** to be 23 and 1.04, respectively, indicating that it is highly conjugative (highly reactive) and electron-accepting.

Introduction

Unsubstituted 1,4-benzoquinone methide (**1**) is so reactive that, when prepared, it spontaneously reacts to form a carbon–carbon bond at the 7 position to give the dimeric compound 1,2-bis(4′-hydroxyphenyl)ethane.[1] Introduction of electron-accepting groups on the 7-carbon allows it to be less reactive but more easily obtainable as a pure compound. For instance, 7,7-bis(trifluoromethyl)-1,4-benzoquinone methide (**2**) is obtainable as a pure compound only at liquid-nitrogen temperature, and when warmed at room temperature, it spontaneously reacts to give its polymer instead of the dimeric compound.[2] 7,7-Dicyano-1,4-benzoquinone methide (**3**) is obtainable as a pure crystal even at room temperature,[3] and it becomes much less reactive so that it is not homopolymerizable with any kind of initiators but copolymerizable with styrene in an alternating fashion.[4] The fact that the substituted 1,4-benzoquinone methides become polymerizable in a 1,6 or head-to-tail monomer unit placement instead of carbon–carbon coupling at the 7 position at the same time when they are less reactive and obtainable as pure compounds attracted our attention. It was already reported[5–7] that 1,4-quinodimethanes with two different substituents at each of the 7 and 8 positions exhibit homopolymerizability while ones with the same substituents do not. Therefore, 1,4-benzoquinone methide compounds with two different electron-accepting substituents were expected to exhibit a similar behavior in the polymerization.

In this work, four kinds of 7-(alkoxycarbonyl)-7-cyano-1,4-benzoquinone methides (**4a–d**) were successfully prepared as crystals, though 7-(ethoxycarbonyl)-7-cyano-1,4-benzoquinone methide was already reported to be prepared as a yellow syrup,[3] and some of their physical and chemical properties and polymerizations were studied.

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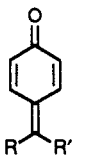

1: R = R′ = H
2: R = R′ = CF_3
3: R = R′ = CN
4a: R = CN, R′ = $COOCH_2CH_3$
4b: R = CN, R′ = $COOCH_3$
4c: R = CN, R′ = $COOCH(CH_3)_2$
4d: R = CN, R′ = $COOCH_2CH_2CH_2CH_3$

Experimental Section

Preparation of 7-(Alkoxycarbonyl)-7-cyano-1,4-benzoquinone Methides. 8-[1′-Cyano-1′-(ethoxycarbonyl)methylene]-1,4-dioxaspiro[4.5]decane (6a). 1,4-Cyclohexanedione monoethylene ketal (**5**; 7.4 g, 47.4 mmol) and 6.6 g (58.3 mmol) of ethyl cyanoacetate were refluxed in the presence of 0.2 g of β-alanine in 20 mL of water for 1 h. The reaction mixture was placed under reduced pressure to remove water to obtain a viscous oil which was dissolved in 15 mL of hot ethanol. The resulting solution was kept at 0 °C overnight to precipitate a crystalline product which was recrystallized from ethanol to obtain 8.2 g (69% yield) of **6a** as white needles: mp 79.0–80.0 °C; IR (KBr): $\nu_{C\equiv N}$ 2220, $\nu_{C=O}$ 1736, $\nu_{C=C}$ 1604, ν_{C-O} 1235, 1078 cm^{-1}; ^1H NMR ($CDCl_3$): δ 4.28 (q, J = 7.2 Hz, 2 H), 4.00 (s, 4 H), 3.15 (t, J = 6.6 Hz, 2 H), 2.85 (t, J = 6.6 Hz, 2 H), 1.89 (t, J = 6.6 Hz, 2 H), 1.82 (t, J = 6.6 Hz, 2 H), 1.35 (t, J = 7.2 Hz, 3 H). Anal. Calcd for $C_{13}H_{17}NO_4$: C, 62.14; H, 6.82; N, 5.57; O, 25.47. Found: C, 62.11; H, 6.84; N, 5.58.

8-[1′-Cyano-1′-(methoxycarbonyl)methylene]-1,4-dioxaspiro[4.5]decane (6b). 1,4-Cyclohexanedione monoethylene ketal (**5**; 3.20 g, 2.05 mmol) and 2.18 g (22.0 mmol) of methyl cyanoacetate were refluxed in the presence of 0.2 g of β-alanine in 10 mL of water for 100 min. The reaction mixture was placed under reduced pressure to remove water to obtain a viscous oil which was dissolved in a small amount of chloroform. The resulting solution was passed through a silica gel column using chloroform as an eluent. The second elution band was collected and placed under reduced pressure to remove solvent to obtain

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4.15 g (85% yield) of compound **6b** as a pale yellow viscous oil: IR (NaCl) $\nu_{C\equiv N}$ 2204, $\nu_{C=O}$ 1577, ν_{C-O} 1230, 1091 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.84 (s, 7 H), 3.28 (t, J = 6.2 Hz, 4 H), 2.95 (t, J = 6.2 Hz, 4 H). Anal. Calcd for $C_{12}H_{15}NO_4$: C, 60.75; H, 6.37; N, 5.90; O, 26.98. Found: C, 60.78; H, 6.34; N, 5.88.

8-[1′-Cyano-1′-(isopropoxycarbonyl)methylene]-1,4-dioxaspiro[4.5]decane (6c). Compound **6c** was obtained as white needles in 82% yield from the reaction of **5** with isopropyl cyanoacetate in a process similar to that for **6a** except for using a mixture of dichloromethane and hexane as the recrystallization solvent: mp 47.0–48.5 °C; IR (NaCl) $\nu_{C\equiv N}$ 2206, $\nu_{C=O}$ 1690, $\nu_{C=C}$ 1577, ν_{C-O} 1237, 1074 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.10 (m, 1 H), 4.00 (s, 4 H), 3.17 (t, J = 6.6 Hz, 2 H), 2.84 (t, J = 6.6 Hz, 2 H), 1.85 (t, J = 6.6 Hz, 4 H), 1.33 (d, J = 6.6 Hz, 6 H). Anal. Calcd for $C_{14}H_{19}NO_4$: C, 63.38; H, 7.22; N, 5.28; O, 24.12. Found: C, 63.33; H, 7.27; N, 5.28.

8-[1′-Cyano-1′-(butoxycarbonyl)methylene]-1,4-dioxaspiro[4.5]decane (6d). Compound **6d** was obtained as wax in 89% yield from the reaction of **5** with butyl cyanoacetate in a process similar to that for **6b**: mp ca. 35 °C; IR (NaCl) $\nu_{C\equiv N}$ 2206, $\nu_{C=O}$ 1693, $\nu_{C=C}$ 1577, ν_{C-O} 1234, 1075 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.22 (t, J = 6.6 Hz, 2 H), 4.00 (s, 4 H), 3.18 (t, J = 6.6 Hz, 2 H), 2.86 (t, J = 6.6 Hz, 2 H), 1.85 (q, J = 6.6 Hz, 4 H), 1.69 (q, J = 6.6 Hz, 2 H), 1.44 (q, J = 7.3 Hz, 2 H), 0.95 (t, J = 7.3 Hz, 3 H). Anal. Calcd for $C_{15}H_{21}NO_2$: C, 64.49; H, 7.58; N, 5.01; O, 22.91. Found: C, 63.22; H, 7.59; N, 5.24.

4-[1′-Cyano-1′-(ethoxycarbonyl)methylene]cyclohexanone (7a). Ketal **6a** (7.0 g, 27.9 mmol) was added to 400 mL of a 2% aqueous sulfuric acid solution, and the resulting suspension was refluxed for 20 min and then, after cooling, extracted with 800 mL of chloroform. The extract was dried over anhydrous magnesium sulfate and then placed under reduced pressure to remove solvent to give a white solid, which was recrystallized from ethanol to obtain 5.0 g (85% yield) of **7a** as white plates: mp 75.5–76.5 °C (lit.[3] mp 72–73 °C); IR (KBr) $\nu_{C\equiv N}$ 2222, $\nu_{C=O}$ 1725, $\nu_{C=C}$ 1596, ν_{C-O} 1235, 1088 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.29 (q, J = 7.2 Hz, 2 H), 3.29 (t, J = 6.6 Hz, 2 H), 3.15 (t, J = 6.6 Hz, 2H), 2.53 (t, J = 6.6 Hz, 4 H), 1.36 (t, J = 7.2 Hz, 3 H). Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.75; H, 6.32; N, 6.76; O, 23.16. Found: C, 63.90; H, 6.58; N, 6.67.

4-[1′-Cyano-1′-(methoxycarbonyl)methylene]cyclohexanone (7b). Compound **7b** was obtained as white needles in 43% yield in a process similar to that for **7a**: mp 66.5–67.8 °C; IR (KBr) $\nu_{C\equiv N}$ 2206, $\nu_{C=O}$ 1692, $\nu_{C=C}$ 1572, ν_{C-O} 1231, 1088 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.86 (s, 3 H), 3.42 (t, J = 6.9 Hz, 2 H), 3.14 (t, J = 6.9 Hz, 2 H), 2.57 (t, J = 6.9 Hz, 4 H). Anal. Calcd for $C_{10}H_{11}NO_3$: C, 62.16; H, 5.74; N, 7.25; O, 24.84. Found: C, 61.85; H, 5.73; N, 7.32.

4-[1′-Cyano-1′-(isopropoxycarbonyl)methylene]cyclohexanone (7c). Compound **7c** was obtained as white needles in 81% yield in a process similar to that for **7a**: mp 54.0–55.0 °C; IR (KBr) $\nu_{C\equiv N}$ 2204, $\nu_{C=O}$ 1686, $\nu_{C=C}$ 1571, ν_{C-O} 1235, 1085 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.12 (m, J = 6.3 Hz, 1 H), 3.41 (t, J = 6.9 Hz, 2 H), 3.13 (t, J = 6.9 Hz, 2 H), 2.56 (t, J = 6.9 Hz, 4 H), 1.34 (d, J = 6.3 Hz, 6 H). Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83; N, 6.33; O, 21.69. Found: C, 65.14; H, 6.91; N, 6.32.

4-[1′-Cyano-1′-(butoxycarbonyl)methylene]cyclohexanone (7d). Compound **7d** was obtained as white needles in 62% yield in a process similar to that for **7a**: mp 65.5–66.0 °C; IR (KBr) $\nu_{C\equiv N}$ 2202, $\nu_{C=O}$ 1687, $\nu_{C=C}$ 1565, ν_{C-O} 1233, 1085 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.24 (t, J = 6.6 Hz, 2 H), 3.41 (t, J = 6.6 Hz, 2 H), 3.13 (t, J = 6.6 Hz, 2 H), 2.55 (t, J = 6.6 Hz, 4 H), 1.69 (p, J = 6.6 Hz, 2 H), 1.44 (q, J = 7.3 Hz, 2 H), 0.96 (t, J = 7.3 Hz, 3 H). Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.29; N, 5.95; O, 20.40. Found: C, 66.21; H, 7.37; N, 5.99.

7-Cyano-7-(ethoxycarbonyl)-1,4-benzoquinone Methide (4a). Compound **7a** (0.8 g, 4.1 mmol) was dissolved in 400 mL of chloroform, and then into the resulting solution were added 6.4 g (73.6 mmol) of activated manganese oxide and 6.4 g of 3A molecular sieves. The mixture was refluxed with stirring for 40 min, cooled, and then filtered. The yellow-orange filtrate was placed under reduced pressure to remove solvent to give an orange solid which was dissolved in a small amount of chloroform. The resulting solution was passed through a silica gel column by using chloroform as an eluent. The pale-orange elution band was collected and placed under reduced pressure to remove solvent to obtain an orange solid which was recrystallized from hexane to give 0.30 g (39% yield) of **4a** as orange needles: mp 56.5–57.0 °C; IR (KBr) $\nu_{C\equiv N}$ 2202, $\nu_{C=O}$ 1697, $\nu_{C=C}$ 1611, 1587, ν_{C-O} 1222, 1071 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.57 (d, J = 10.2 Hz, 1 H), 7.70 (d, J = 9.9 Hz, 1 H), 6.62 (d, J = 9.9 Hz, 1 H), 6.52 (d, J = 10.2 Hz, 1 H), 4.41 (q, J = 7.2 Hz, 2 H), 1.42 (t, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 186.06, 160.90, 148.39, 136.15, 133.35, 132.76, 132.33, 114.41, 111.38, 63.38, 13.89; UV ($CHCl_3$) λ 320 nm (ϵ = 3.08 × 10^4). Anal. Calcd for $C_{11}H_9NO_3$: C, 65.02; H, 4.46; N, 6.89; O, 23.62. Found: C, 64.81; H, 4.43; N, 6.95.

7-Cyano-7-(methoxycarbonyl)-1,4-benzoquinone Methide (4b). Compound **4b** was obtained as orange needles in 23% yield from **7b** in a process similar to that for **4a**: mp 108.0–109.0 °C; IR (KBr) $\nu_{C\equiv N}$ 2202, $\nu_{C=O}$ 1687, $\nu_{C=C}$ 1607, 1588, ν_{C-O} 1222, 1069 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.58 (d, J = 10.2 Hz, 1 H), 7.72 (d, J = 10.2 Hz, 1 H), 6.63 (d, J = 10.2 Hz, 1 H), 6.55 (d, J = 10.2 Hz, 1 H), 3.97 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 186.09, 160.93, 148.75, 136.12, 133.51, 132.74, 132.51, 114.45, 111.20, 53.84; UV ($CHCl_3$) λ 320 nm (ϵ = 3.18 × 10^4). Anal. Calcd for $C_{10}H_7NO_3$: C, 63.49; H, 3.73; N, 7.40; O, 25.37. Found: C, 62.38; H, 3.56; N, 7.73.

7-Cyano-7-(isopropoxycarbonyl)-1,4-benzoquinone Methide (4c). Compound **4c** was obtained as orange needles in 29% yield from **7c** in a process similar to that for **4a**: mp 91.5–92.0 °C; IR (KBr) $\nu_{C\equiv N}$ 2192, $\nu_{C=O}$ 1686, $\nu_{C=C}$ 1610, 1588, ν_{C-O} 1235, 1088 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.57 (d, J = 10.2 Hz, 1 H), 7.71 (d, J = 10.2 Hz, 1 H), 6.61 (d, J = 10.2 Hz, 1 H), 6.53 (d, J = 10.2 Hz, 1 H), 5.22 (m, J = 6.3 Hz, 1 H), 1.40 (d, J = 6.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 186.14, 159.98, 148.19, 136.28, 133.37, 132.90, 132.33, 114.48, 111.9, 71.93, 21.57; UV ($CHCl_3$) λ 321 nm (ϵ = 3.18 × 10^4). Anal. Calcd for $C_{12}H_{11}NO_3$: C, 66.35; H, 5.10; N, 6.45; O, 21.70. Found: C, 66.35; H, 5.01; N, 6.47.

7-Cyano-7-(butoxycarbonyl)-1,4-benzoquinone Methide (4d). Compound **4d** was obtained as orange plates in 31.4% yield from **7d** in a process similar to that for **4b**: mp 61.0–62.0 °C; IR (KBr) $\nu_{C\equiv N}$ 2202, $\nu_{C=O}$ 1682, $\nu_{C=C}$ 1611, 1590, ν_{C-O} 1235, 1071 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.58 (d, J = 10.2 Hz, 1 H), 7.72 (d, J = 10.2 Hz, 1 H), 6.61 (d, J = 10.2 Hz, 1 H), 6.54 (d, J = 10.2 Hz, 1 H), 4.35 (t, J = 6.6 Hz, 2 H), 1.75 (t, J = 6.6 Hz, 1 H), 1.47 (q, J = 7.3 Hz, 2 H), 0.98 (t, J = 7.3 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 186.30, 160.60, 148.45, 136.21, 133.42, 132.81, 132.42, 114.48, 111.70, 67.21, 30.28, 18.98, 13.58; UV ($CHCl_3$) λ 320 nm (ϵ = 3.26 × 10^4). Anal. Calcd for $C_{13}H_{13}NO_3$: C, 67.52; H, 5.67; N, 6.06; O, 21.40. Found: C, 67.40; H, 5.61; N, 6.10.

Preparation of Model Compounds. Diethyl 2,3-Dicyano-2,3-diphenylsuccinate (8). Compound **8** was prepared according to the method of De Jongh et al.[8] To 2 mL of benzene was added 0.19 g (1.0 mmol) of ethyl 2-cyano-2-phenylacetate and 0.23 g (1.0 mmol) of silver oxide, and the mixture was stirred at room temperature for 30 min and then filtered out. The filtrate was concentrated under reduced pressure to leave a solid product which was recrystallized from a mixture of ethyl acetate and hexane to give 0.083 g of **8** in 43% yield (lit.[8] yield 60%) as white needles: mp 116.0–116.5 °C (lit.[8] mp 117–123 °C); IR (KBr) $\nu_{C\equiv N}$ 2228, $\nu_{C=O}$ 1715, ν_{C-O} 1220, 1081 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.30–7.42 (m, 10 H), 4.30 (q, J = 6.6 Hz, 4 H), 1.24 (t, J = 6.6 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 164.24, 130.03, 129.34, 128.97, 128.23, 116.01, 64.12, 60.38, 13.57. Anal. Calcd for $C_{22}H_{20}N_2O_4$: C, 70.20; H, 5.36; N, 7.44; O, 17.01. Found: C, 70.23; H, 5.26; N, 7.46.

Ethyl 2-Cyano-2-(4′-hydroxyphenyl)-2-(4′-methylphenoxy)acetate (9). *p*-Cresol (1.0 g, 9.3 mmol) and 0.2 g of triethylamine were dissolved in 20 mL of chloroform at room temperature, and then into the resulting solution was added 50 mg (0.27 mmol) of **4a** in 10 mL of chloroform. The resulting reaction mixture was stirred at room temperature for 2 h and then placed under reduced pressure to remove solvent to give a viscous oil which was dissolved in a small amount of a mixture of ethyl acetate and hexane. The resulting solution was passed though a silica gel column by using a mixture of ethyl acetate and hexane as an eluent. The second elution band was collected and placed under reduced pressure to remove solvent to obtain 30 mg (about 30% yield) of **9** as a colorless viscous oil: IR (NaCl) ν_{OH} 3358, $\nu_{C\equiv N}$ 2222, $\nu_{C=O}$ 1710, ν_{C-O} 1213 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.3–6.7 (m, 8 H), 4.28 (q, J = 7.2 Hz, 2 H), 2.33 (s, 3 H), 1.70 (br s, 1 H), 1.26 (t, J = 7.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 164.2, 156.05, 153.01, 133.60, 130.58, 129.10, 115.99, 110.84, 109.99, 77.20, 62.93, 21.08, 13.86.

Adduct Formation of 7-Cyano-7-(ethoxycarbonyl)-1,4-benzoquinone Methide (4a). (1) With Phenol. Compound **4a** (0.1 g, 0.5 mmol) and 0.11 g (1.17 mmol) of phenol were dissolved in 10 mL of tetrahydrofuran, and then 3 drops of concentrated hydrochloric acid was added. The orange color faded in several minutes. After standing at room temperature for 0.5 h, the reaction mixture was placed under reduced pressure to remove solvent to give a viscous oil which was dissolved in a small amount of a mixture of ethyl acetate and dichloromethane (1:3 by volume). The resulting solution was passed through a silica gel column by using a mixture of ethyl acetate and dichloromethane as an eluent. The second elution band was collected and placed under reduced pressure to remove solvent to obtain 0.143 g (98% yield) of ethyl 2-cyano-2,2-di(4'-hydroxyphenyl)acetate (**10**) as a colorless viscous oil: IR (NaCl) ν_{OH} 3200–3600, $\nu_{C\equiv N}$ 2232, $\nu_{C=O}$ 1700, ν_{C-O} 1210, 1101 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.56 (br s, 2 H), 7.21 (d, J = 8.6 Hz, 4 H), 6.88 (d, J = 8.6 Hz, 4 H), 4.32 (q, J = 6.9 Hz, 2 H), 1.30 (t, J = 6.9 Hz, 3 H). Anal. Calcd for $C_{17}H_{15}NO_4$: C, 68.68; H, 5.09; N, 4.71; O, 21.53. Found: C, 67.49; H, 5.40; N, 4.87.

(2) With *N,N*-Dimethylaniline. Compound **4a** (20.5 mg, 0.1 mmol) and 24 mg (0.4 mmol) of acetic acid were dissolved in 10 mL of tetrahydrofuran; into it was dropwise added 50 mg (0.4 mmol) of *N,N*-dimethylaniline in 5 mL of tetrahydrofuran and, then, the mixture was stirred at room temperature for 2 h. The reaction mixture was poured into 50 mL of water and then extracted twice with 20 mL of chloroform. The extract was dried over anhydrous magnesium sulfate and placed under reduced pressure to remove solvent to give a viscous oil which was dissolved in a small amount of dichloromethane. The resulting solution was passed through a silica gel column by using dichloromethane as an eluent. The second elution band was collected and placed under reduced pressure to remove solvent to obtain 30 mg (92% yield) of ethyl 2-cyano-2-(4'-hydroxyphenyl)-2-[4'-(*N,N*-dimethylamino)phenyl]acetate (**11**) as a colorless viscous oil: IR (NaCl) ν_{OH} 3200–3600, $\nu_{C\equiv N}$ 2230, $\nu_{C=O}$ 1708, ν_{C-O} 1210, 1047 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.23 (d, J = 8.9 Hz, 2 H), 7.22 (d, J = 8.9 Hz, 2 H), 6.79 (d, J = 8.9 Hz, 2 H), 6.69 (d, J = 8.9 Hz, 2 H), 5.58 (br s, 1 H), 4.32 (q, J = 6.9 Hz, 2 H), 2.97 (s, 6 H), 1.31 (t, J = 6.9 Hz, 3 H). Anal. Calcd for $C_{19}H_{20}N_2O_3$: C, 70.35; H, 6.22; N, 8.64; O, 14.81. Found: C, 70.47; H, 6.25; N, 8.58.

(3) With Hydrogen Chloride. Compound **4a** (50 mg, 0.25 mmol) was dissolved in 10 mL of dichloromethane, and then dry hydrogen chloride was bubbled through the resulting solution for 15 min. The orange color of the solution faded gradually with bubbling. The colorless solution was concentrated to about a 1-mL volume and passed through a silica gel column by using dichloromethane as an eluent. The first colorless elution band was collected and placed under reduced pressure to remove solvent to obtain 55 mg (93% yield) of a pale orange viscous oil: ^{1}H NMR ($CDCl_3$) δ 8.58 (d, J = 10.2 Hz), 7.71 (d, J = 9.9 Hz), 7.59 (d, J = 9 Hz), 6.92 (d, J = 9 Hz), 6.62 (d, J = 9.9 Hz), 6.52 (d, J = 10.2 Hz), 5.60 (br), 4.42 (q, J = 7.2 Hz), 4.34 (m), 1.42 (t, J = 7.2 Hz), 1.32 (t, J = 7 Hz); IR (NaCl) ν_{OH} 3378, $\nu_{C\equiv N}$ 2206, 2192, $\nu_{C=O}$ 1729, 1694, 1610, $\nu_{C=C}$ 1583, 1542, ν_{C-O} 1219 cm^{-1}.

Compound **4a** (10 mg, 0.05 mmol) was dissolved in 0.5 mL of chloroform-*d* at room temperature and was placed in a NMR tube. After dry hydrogen chloride was bubbled through the orange solution which immediately became colorless, a ^{1}H NMR spectrum was in situ taken which exhibited the following peaks: δ 7.59 (d, J = 9 Hz, 2 H), 6.92 (d, J = 9 Hz, 2 H), 4.34 (m, 2 H), 3.60 (br s, 1 H), 1.32 (t, J = 7 Hz, 3 H).

(4) With Acetic Acid. Compound **4a** (30.5 mg) was dissolved in 10 mL of chloroform or tetrahydrofuran as solvent, and then 30 mg of acetic acid was added. The solution was stirred at room temperature for 12 h. The solution remained an orange color of **4a** for long time, and also **4a** was recovered quantitatively.

Compound **4a** (11 mg, 0.06 mmol) in 0.5 mL of chloroform-*d* was placed in a NMR tube, and 5 mg (0.08 mmol) of acetic acid was added. Then the tube was sealed and placed in a bath thermostated at 60 °C for 33 h, and the ^{1}H NMR spectrum was taken which showed only peaks assignable to either **4a** or acetic acid.

Polymerization Procedure. Radical Homopolymerization and Copolymerization. Given amounts of 1,4-benzoquinone methide monomer, styrene as a comonomer and toluene as a solvent if necessary, and 2,2'-azobis(isobutyronitrile) (AIBN) as a radical initiator were placed in a polyethylene ampule and sealed after bubbling nitrogen for 5 min. Then the ampule was set in an oil bath thermostated at 60 °C for the time of polymerization. When no solvent was used, a small amount of dichloromethane was added to dissolve the reaction mixture. The resulting solution was poured into an excess of hexane to precipitate the product which was filtered out and then redissolved in dichloromethane and reprecipitated by pouring it into an excess of hexane. When solvent was used, the reaction mixture was directly poured into an excess of hexane to precipitate the product which was purified in three or more cycles of a redissolution–reprecipitation method. The product obtained was dried under reduced pressure at room temperature until a constant weight was reached.

Ionic Homopolymerization. Given amounts of 1,4-benzoquinone methide monomer, solvent, and initiator were placed in a glass ampule and sealed at liquid-nitrogen temperature in vacuum. The ampule was set in an oil bath thermostated at 60 °C for the time of polymerization. The rest procedure was similar to that for the radical homopolymerization.

Polymerization of 4a in Some Solvents. Compound **4a** (about 2 mg) was dissolved in 1 mL of a solvent such as benzene, toluene, chloroform, dichloromethane, acetone, acetonitrile, tetrahydrofuran, *N,N*-dimethylformamide, and dimethyl sulfoxide. After standing for 4 h, an aliquot of the solution was taken out by syringe and was subject to gel permeation chromatography (GPC) to determine the molecular weight of the reaction product.

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 reference electrode, working electrode, and counterelectrode, respectively.

Other Materials. Styrene [St; 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. Toluene (bp 111 °C) and benzene (bp 80 °C) were washed with concentrated sulfuric acid, water, 5% aqueous sodium hydroxide solution, and again water, dried over anhydrous magnesium sulfate, refluxed over metal sodium for 24 h, and then distilled. 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 8 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 1 day and then distilled under reduced pressure. Acetic acid (bp 118 °C) was distilled under nitrogen. 2,2'-Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol. Boron trifluoride etherate [bp 50 °C (50 mmHg)], *N,N*-dimethylaniline [bp 82 °C (20 mmHg)], phenol [bp 60 °C (20 mmHg)], and *p*-cresol [bp 50 °C (5 mmHg)] were distilled under reduced pressure under nitrogen. Pyridine (bp 115 °C) and triethylamine (bp 89 °C) were distilled over potassium hydroxide. Methyl cyanoacetate, ethyl cyanoacetate, isopropyl cyanoacetate, butyl cyanoacetate, and tetrabutylammonium perchlorate were used without further purification.

Characterization. Copolymer composition was established by elemental analysis. Number-average molecular weights, $\bar{M}_n$, of homopolymers and copolymers were determined by gel permeation chromatography (GPC) using standard polystyrenes as reference and tetrahydrofuran as an eluent without correction. ^{1}H NMR and ^{13}C NMR measurements were carried out in chloroform-*d* with tetramethylsilane as an internal standard. Glass transition temperatures (T_g) for polymers were determined by differential scanning calorimetry (DSC) at an elevating rate of temperature of 10 °C/min under nitrogen (30 mL/min).

Instrumentation. A Büch capillary melting point apparatus was used for melting point measurement, a JEOL JNM-EX270 FT NMR spectrometer for ^{1}H NMR and ^{13}C NMR spectroscopy, Jasco IR-700 and Jasco UVIDEC-430B spectrometers for infrared and UV–vis spectroscopy, respectively, a Yanaco CHN corder MT-3 for elemental analysis, gel permeation chromatography

Scheme I

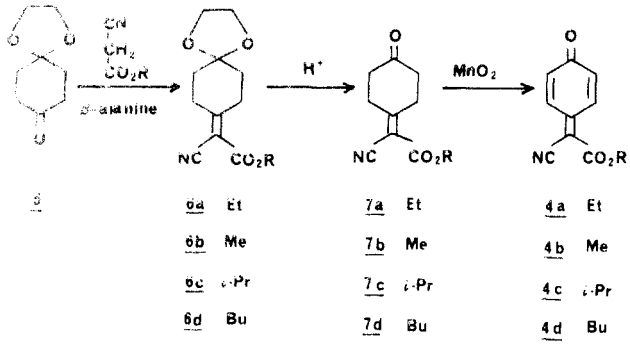


Table I
First Reduction Potential (E_1), the Wavelength of Maximum Absorption (λ_{max}), and the Molar Extinction Coefficient ($\epsilon_{\lambda_{max}}$) of 7-(Alkoxycarbonyl)-7-cyano-1,4-benzoquinone Methides (4a–d)

benzoquinone methide	R	λ_{max}/nm[a]	$\epsilon_{\lambda_{max}} \times 10^{-4}$	E_1/V[b]
4a	CH_3CH_2	320	3.08	−0.28
4b	CH_3	320	3.18	−0.27
4c	$(CH_3)_2CH$	321	3.18	−0.27
4d	$CH_3(CH_2)_3$	320	3.26	−0.28

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

TOSOH HLC-803D with a series of two columns, Tosoh G4000H and G3000H, or with a series of two columns, Tosoh G2500H and G2000H, for measuring number-average molecular weight ($\bar{M}_n$), and a Perkin-Elmer differential scanning calorimeter DSC-2C for thermogravimetry (TG), differential thermal analysis (DTA), and differential scanning calorimetry (DSC), respectively.

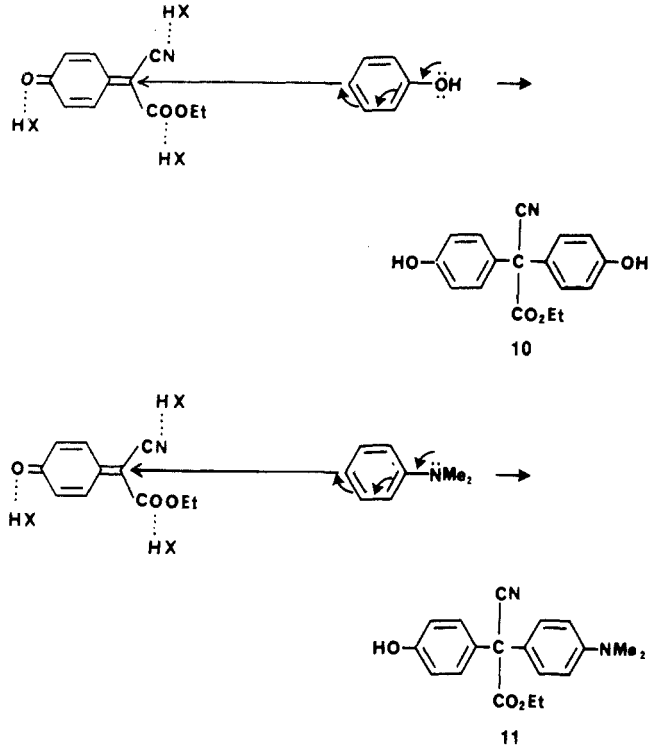
Results and Discussion

Preparation and Properties of 7-(Alkoxycarbonyl)-7-cyano-1,4-benzoquinone Methides. 7-(Alkoxycarbonyl)-7-cyano-1,4-benzoquinone methides (4) with four kinds of alkoxy groups, methyl, ethyl, isopropyl, and butyl, were successfully prepared according to Scheme I.

1,4-Cyclohexanedione monoethylene ketal (5) was subjected to Knoevenagel reaction with alkyl cyanoacetates in the presence of β-alanine to give 8-[1′-(alkoxycarbonyl)-1′-cyanomethylene]-1,4-dioxaspiro[4.5]decanes (6) in good yield. Compounds 6 were heated in a 2% aqueous sulfuric acid solution to undergo hydrolysis of ketal to afford 4-[1′-(alkoxycarbonyl)-1′-cyanomethylene]cyclohexanones (7), which were readily oxidized with activated manganese oxide in chloroform to give 4 as orange needles for **4a**, **4b**, and **4c** and as orange plates for **4d**. Their IR, ^{1}H-NMR, and ^{13}C-NMR spectra strongly suggested the chemical structure of 7-substituted 1,4-benzoquinone methides. Compounds 4 are obtainable at room temperature as stable crystals, probably because two strong electron-withdrawing groups, alkoxycarbonyl and cyano, at the 7 position allow 1,4-benzoquinone methide to be less reactive in a way similar to that of 7,7-dicyano-1,4-benzoquinone methide (3),[3] 2,6-dimethyl-7,7-bis(trifluoromethyl)-1,4-benzoquinone methide,[9] and 2,6-di-*tert*-butyl-7,7-bis(trifluoromethyl)-1,4-benzoquinone methide.[9]

The values of the first reduction potential (E_1), the wavelength of maximum absorption (λ_{max}), and the molar extinction coefficient ($\epsilon_{\lambda_{max}}$) for compounds **4a–d** are summarized in Table I. All of compounds **4a–d** exhibited approximately similar values for E_1, λ_{max}, and $\epsilon_{\lambda_{max}}$, respectively, independent of 7-alkoxycarbonyl groups, suggesting that alkoxycarbonyl groups may not make a difference in the polymerization among **4a–d** either.

Scheme II



Hereafter, **4a** was chosen as a representative of compounds 4 for studying chemical reactions and polymerizations.

When compound **4a** was stored in a Pyrex glass container with a tightly fitting stopper for a long time (about 1 month) in a refrigerator, the color of the neighborhood of the glass surface was found to change from orange to white, but the color of the middle of the container remained orange. The white part was not soluble in hexane and, when measured in GPC, was the polymer of **4a** with a molecular weight of 1.3×10^5. On the other hand, when stored in a polyethylene container, **4a** remained orange for a long time, indicating that a Pyrex glass surface is somewhat capable of inducing the polymerization of **4a** but a polyethylene surface is not. Therefore, it was considered that a polyethylene ampule was more appropriate than a Pyrex glass ampule in the cases of spontaneous and radical polymerizations in order to avoid the effect as much as possible.

Addition Reactions of 4a. Acid-catalyzed 1,6-addition reactions of **4a** with phenol and *N*,*N*-dimethylaniline gave the 1:1 adducts, **10** and **11**, respectively, in quantitative yield. Their possible reaction mechanism was proposed as shown in Scheme II, similar to that for corresponding reactions of 7,7-dicyano-1,4-benzoquinone methide (3)[3] and 2,6-dimethyl-7,7-dicyano-1,4-benzoquinone methide[10] as homologues of **4a**.

2,6-Dimethyl-7,7-bis(trifluoromethyl)-1,4-benzoquinone methide[9] reacted with hydrogen chloride to give 2,6-dimethyl-4-[1′-chloro-1′,1′-bis(trifluoromethyl)methyl]-phenol as white crystals in quantitative yield. Compound **4a** also reacted with hydrogen chloride to give a reaction product, but its product was a pale-orange viscous oil and its color deepened with time. The product was examined in ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of **4a** alone is shown in Figure 1a, where each peak is assignable to each proton of the chemical structure illustrated herein. The ^{1}H NMR spectrum of the oil reaction product of **4a** with hydrogen chloride was taken immediately after preparation as shown in Figure 1b, where new peaks appear at 1.3, 4.3, 5.6, 6.9, and 7.6 ppm in addition to peaks for

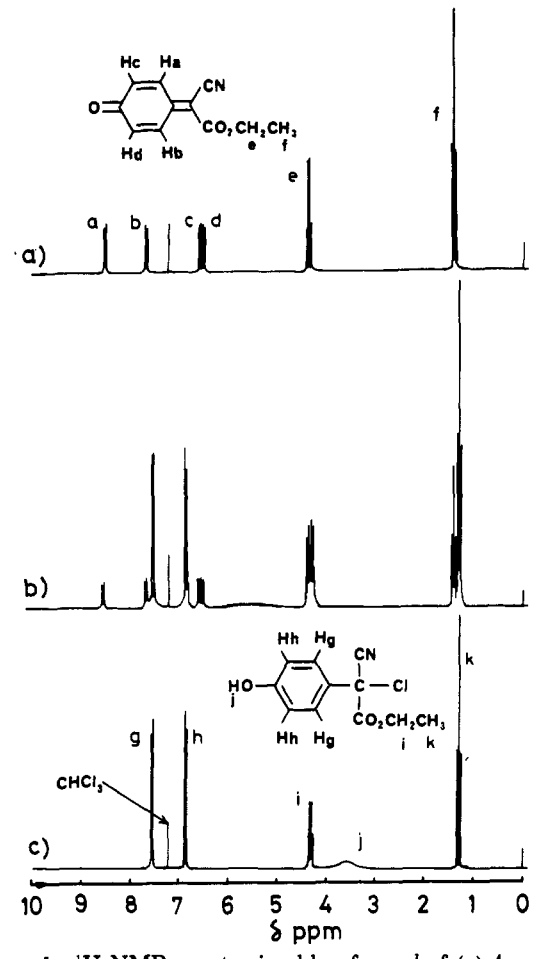


Figure 1. ^{1}H NMR spectra in chloroform-*d* of (a) **4a**, (b) an isolated reaction product of **4a** with hydrogen chloride, and (c) an in situ reaction product of **4a** with hydrogen chloride.

4a. An excess of hydrogen chloride was bubbled through **4a** in chloroform-*d* in a NMR tube and immediately the ^{1}H NMR spectrum was taken in situ as shown in Figure 1c, where double doublet peaks appeared at 6.9 and 7.6 ppm assigned to the phenylene group and a broad peak at 3.6 ppm assigned to the hydroxy group of phenol in place of the peaks for **4a**. In comparison with parts a–c of Figure 1, it can be pointed out that the 1,6-addition product (adduct 12) of **4a** with hydrogen chloride is in situ formed in a pure state, but it is not so stable that, when isolated as an oil product, it gradually decomposes to **4a** and hydrogen chloride. Compound **4a** is capable of reacting with hydrogen chloride to form an unstable adduct, whereas 2,6-dimethyl-7,7-bis(trifluoromethyl)-1,4-benzoquinone methide gives an isolable, stable adduct, indicating that **4a** is less reactive than 2,6-dimethyl-7,7-bis(trifluoromethyl)-1,4-benzoquinone methide.

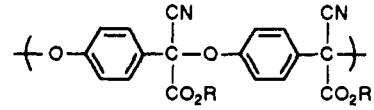
No addition reaction of **4a** with acetic acid took place anymore.

Homopolymerization. When dissolved in various solvents, **4a** was examined in polymerization behavior. In the so-called nonpolar common solvents such as benzene, toluene, chloroform, and dichloromethane, **4a** remained orange color for 24 h, and its GPC chromatogram showed only a peak as the monomer state. Besides, in the so-called basic aprotic polar solvents[7,11] such as acetonitrile, acetone, tetrahydrofuran, *N,N*-dimethylformamide, and dimethyl sulfoxide, **4a** spontaneously changed from orange to yellow, except for tetrahydrofuran in which the change of **4a** was so slow that it remained orange color for 6 h but finally changed to yellow after 24 h. After standing for 4 h, **4a** in such basic aprotic polar solvents was subject to GPC, the chromatograms of which exhibited two peaks, one for **4a** itself and the other for the oligomer of **4a** with a molecular weight of 400–6000, indicating that basic aprotic polar solvents are capable of inducing oligomerization of **4a**. 7,8-Bis(butoxycarbonyl)-7,8-dicyano-1,4-quinodimethane (BCQ), 7,8-diacetyl-7,8-dicyano-1,4-quinodimethane (AcCQ), and 7,8-dibenzoyl-7,8-dicyano-1,4-quinodimethane (BzCQ) as members of a family of **4** are spontaneously polymerizable with these basic aprotic polar solvents, and they afforded polymers with high molecular weight at that.[7,11] The difference between the oligomer for **4a** and high polymers for those quinodimethane compounds could be attributed to the difference in their electron-accepting character; i.e., E_1 = −0.28 V for **4a**, −0.10 V[7] for BCQ, +0.03 V[7] for AcCQ, and −0.02 V[7] for BzCQ.

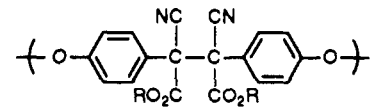
Homopolymerizations of **4a–d** were carried out with AIBN as a radical initiator, with pyridine as an anionic initiator at 60 °C, and with BF_3·Et_2O as a cationic initiator at room temperature. Besides, **4a** was polymerized in bulk without initiator. A polyethylene ampule was used for polymerizations with AIBN and without initiator. The polymerization results are summarized in Table II. It can be pointed out from Table II that compounds **4** are homopolymerizable with all of the initiators to give polymers; especially, pyridine affords high polymers with molecular weights of 10–6 × 10^4. When heated in bulk at 60 °C, **4a** was spontaneously homopolymerizable to give a polymer with a molecular weight equivalent to that for the polymer with AIBN, but the polymer yield at a given time was much less, suggesting that the spontaneous polymerization would take place via a radical mechanism but the amount of radical species generated would be much less.

BF_3·Et_2O gave only oligomers with low molecular weight. It would be difficult to understand a mechanism that **4** could react with acid because of the electron-accepting character of **4**. It is likely to be proposed in analogy with acid-catalyzed addition reactions of **4a** with phenol and *N,N*-dimethylaniline that because BF_3·Et_2O as a very strong Lewis acid is capable of doing coordination to cyano and ester groups, **4** could be activated so as to be more readily subject to nucleophilic attack with some basic compound, which could not be identified in this polymerization system, to polymerize via an anionic mechanism.

There should be two kinds of monomer unit placements in the polymerization of **4** owing to the chemical structure with different exocyclic atoms, i.e., 1,6 or head-to-tail placement (structure A) and 1,1 or head-to-head placement (structure B) as shown in the following:



structure A



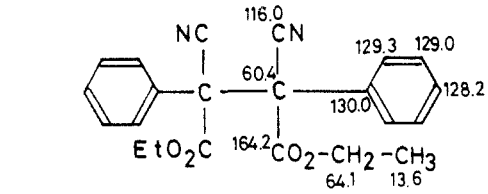
structure B

The mode of the monomer unit placement in poly-**4a** was determined by ^{13}C NMR spectroscopy. Compounds **8** and **9** were prepared as model compounds carrying head-to-head and head-to-tail placements, respectively. Found values of ^{13}C NMR chemical shift are expressed in ppm at the side of each carbon in the chemical structures of **8**

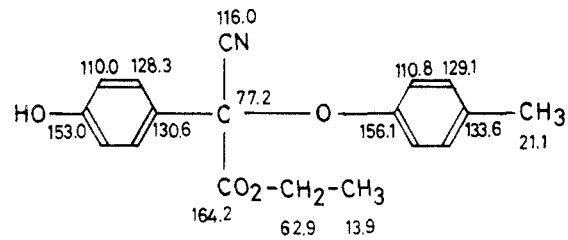
Table II
Homopolymerization of 7-(Alkoxycarbonyl)-7-cyano-1,4-benzoquinone Methides (4a–d)

run no.	benzoquinone methide/mg	initiator	[M]/[I]	solv.	[M]/(mol/L)	temp/°C	time/h	conv/%	$\bar{M}_n \times 10^{-3}$
				4a (R = Et)					
1	20.8	none		bulk		60	16	27	48
2	20.0	AIBN	1	bulk		60	17	98	35
3	22.6	AIBN	1	toluene	0.3	60	16	77	2.7
4	30.0	pyridine	470	bulk		60	108	89	110
5	33.0	pyridine	430	toluene	0.8	60	5	100	35
6	30.0	BF_3·OEt_2	18	$CHCl_3$	0.3	rt	23	25	0.7
				4b (R = Me)					
7	18.6	AIBN	1	toluene	0.3	60	11	68	1.6
8	15.3	pyridine	430	toluene	0.8	60	5	88	66
9	30.0	BF_3·OEt_2	17	$CHCl_3$	0.3	rt	42	46	0.7
				4c (R = *i*Pr)					
10	21.0	AIBN	1	toluene	0.3	60	11	65	3.0
11	32.2	pyridine	370	toluene	0.7	60	5	100	45
12	30.0	BF_3·OEt_2	16	$CHCl_3$	0.2	rt	41	14	0.9
				4d (R = Bu)					
13	20.8	AIBN	1	toluene	0.3	60	11	8	2.3
14	30.0	pyridine	340	toluene	0.7	60	5	100	68
15	29.0	BF_3·OEt_2	14	$CHCl_3$	0.2	rt	41	25	0.9

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



Compound 8



Compound 9

Figure 2. Chemical shift values of carbons for model compounds 8 and 9.

and 9 in Figure 2. The chemical shift values of benzyl carbon for compounds 8 and 9 were found to be 60.4 and 77.2 ppm, respectively, apart enough to distinguish between 8 and 9. The benzyl carbon of poly-**4a** appeared at 77.2 ppm, supporting the hypothesis that poly-**4a** consists of 1,6 or head-to-tail monomer unit placement rather than 1,1 or head-to-head placement and that **4a** polymerizes in an addition mode of 1,6 or head-to-tail monomer unit placement anionically as well as radically.

^1H NMR and ^{13}C NMR spectra of poly-**4a** (run no. 4) prepared in bulk with pyridine are shown in parts a and b of Figure 3, respectively. Poly-**4a** (run no. 2) obtained in bulk with AIBN also afforded similar spectra. Each peak in the ^1H NMR spectrum of poly-**4a** (run no. 4) was assignable to each proton of the chemical structure illustrated in the figure. 2,6-Dimethyl-7,7-bis(trifluoromethyl)-1,4-benzoquinone methide[2] and 7,7-bis(trifluoromethyl)-1,4-benzoquinone methide (**2**)[9] were reported to polymerize in the same addition mode.

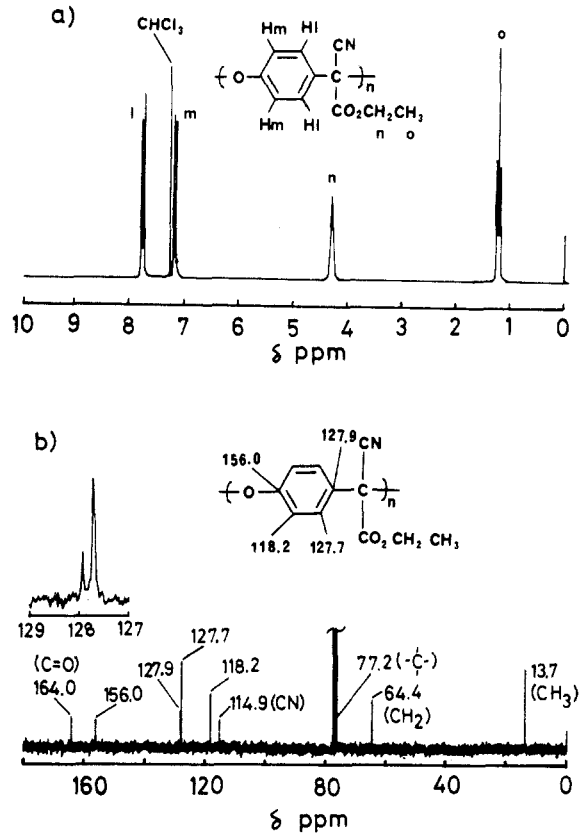


Figure 3. ^1H NMR (a) and ^{13}C NMR (b) spectra of poly-**4a** (run no. 4) in chloroform-*d*.

Unsubstituted 1,4-benzoquinone methide (**1**) spontaneously reacts to give 1,2-bis(4′-hydroxyphenyl)ethane,[1] suggesting that a coupling reaction takes place at its 7-exocyclic carbon. When electron-accepting groups are introduced at the 7 position, the substituted 1,4-benzoquinone methides such as **4a**, 2,6-dimethyl-7,7-bis(trifluoromethyl)-1,4-benzoquinone methide, and 7,7-bis(trifluoromethyl)-1,4-benzoquinone methide (**2**) become stable enough to obtain as pure compounds and simultaneously become polymerizable in 1,6 or head-to-tail monomer unit placement through forming a linkage between exocyclic oxygen and exocyclic carbon. It may well be considered that an anionic addition occurs in a

Table III
Copolymerization[a] of 7-Cyano-7-(ethoxycarbonyl)-1,4-benzoquinone Methide (4a) with Styrene in Toluene at 60 °C

	monomer feed							copolym composn: elem anal.				
run no.	4a/mg	St/mg	4a/(mol %)	AIBN/mg	toluene/mL	time/h	conv/%	% H	% C	% N	4a/(mol %)	$\bar{M}_n$[b] × 10^{-3}
1	50.4	436.0	5.6	1.0	6.2	57.0	1.4	5.72	73.23	4.95	56.7	1.7
2	24.5	102.8	10.9	5.0	0.5	8.0	16.7	4.51	66.30	4.85	62.1	2.0
3	25.1	48.7	20.9	8.6	0.5	4.5	5.0	5.13	69.53	5.72	71.3	1.4
4	49.1	61.1	29.2	5.3	2.0	18.0	3.0	5.41	68.32	5.93	75.9	1.6
5	50.5	30.2	46.1	8.3	1.0	8.2	6.4	4.98	67.72	6.16	81.0	1.3
6	184.0	51.5	64.7	13.8	3.6	23.5	5.4	4.91	66.73	6.40	86.8	3.0

[a] A polyethylene ampule was used. Polymerization was carried out under nitrogen. [b] Determined by GPC using tetrahydrofuran as an eluent and standard polystyrenes as reference.

way that an anion attacks the exocyclic carbon site of 1,4-benzoquinone methide to form a more stable phenolate anion, followed by subsequent additions to give a polymer with 1,6 or head-to-tail placement. When resonance-stabilizing substituents are introduced on the carbon at the 7 position, the carbon radical at the 7 position becomes less reactive so that a coupling reaction no longer takes place between them and furthermore a difference in polarity between the exocyclic carbon and the exocyclic oxygen begins to play an important role even in radical addition to afford 4 to polymerize in 1,6 or head-to-tail placement rather than the coupling reaction between exocyclic carbon atoms.

Poly-**4a** (run no. 4) are capable of being cast from dichloromethane solution to give a tough film. Results of TG-DTA and DSC measurements of poly-**4a** are shown in parts a and b of Figure 4, respectively. It began to be subject to weight loss at ca. 120 °C, and the weight loss from 120 to 190 °C amounted to 36%, which approximately corresponds to the weight percent of the ethoxycarbonyl group to the **4a** unit. The glass transition temperature (T_g) of poly-**4a** was 57.5 °C as shown in Figure 4b.

Copolymerization of 4a with Styrene. Copolymerization of **4a** with styrene in the presence of AIBN as an initiator were carried out in toluene at 60 °C using a polyethylene ampule. Copolymers were obtained as white powder, and their values of the number-average molecular weight were in the range of 1.3–3.0 × 10^3. The results of the copolymerizations are summarized in Table III, and the copolymerization composition curve is shown in Figure 5. The results were rationally analyzed according to the intersection[12] and Kelen–Tüdös[13] methods to obtain monomer reactivity ratios: r_{4a} = 3.4 ± 0.2 and r_{St} = 0.01 ± 0.08 at 60 °C, indicating that the copolymerization takes place in a random fashion. On the other hand, 7,7-dicyano-1,4-benzoquinone methide (**3**) was copolymerized with styrene in an alternating fashion.[4] This difference in copolymerization fashion probably corresponds to the difference in homopolymerizability of homopolymerizable **4a** and nonpolymerizable 7,7-dicyano-1,4-benzoquinone methide (**3**),[4] and it can be explained in terms of our mechanism[14] of alternating copolymerization in connection with equilibrium polymerization behavior. Alfrey–Price's Q and e values of **4a** were calculated on the basis of the monomer reactivity ratios to be 23 and 1.04, respectively, indicating that **4a** is highly conjugative (highly reactive) and electron-accepting similar to BCQ (Q = 9.3, e = 0.8)[14] and AcCQ (Q = 14.9, e = 1.07).[14]

Conclusion

7-(Alkoxycarbonyl)-7-cyano-1,4-benzoquinone methides **4** (R = Me, Et, *i*Pr, and Bu) were successfully prepared as pure, isolable crystals. Compound **4a** underwent acid-catalyzed 1,6-addition with phenol or *N*,*N*-dimethylaniline

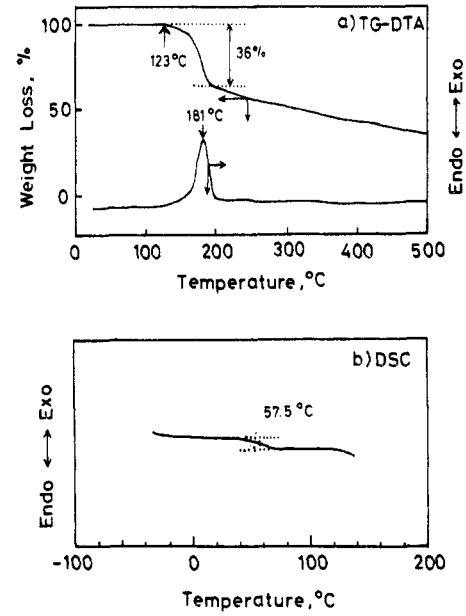


Figure 4. Thermal analysis of poly-**4a** at an elevating rate of temperature of 10 °C/min under nitrogen: (a) TG-DTA curves and (b) DSC curve.

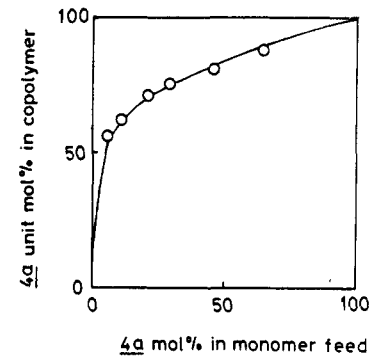


Figure 5. Copolymerization composition curve for the copolymerization of **4a** with styrene in toluene at 60 °C.

to give the 1:1 adducts. The addition reaction of **4a** with hydrogen chloride indicated that reactivity of **4a** is almost equivalent to that of 2,6-dimethyl-7,7-bis(trifluoromethyl)-1,4-benzoquinone methide rather than that of 7,7-dicyano-1,4-benzoquinone methide (**3**). When dissolved in basic aprotic polar solvents such as acetone, acetonitrile, tetrahydrofuran, *N*,*N*-dimethylformamide, and dimethyl sulfoxide, **4a** spontaneously polymerized to give oligomer. Compounds **4** were homopolymerizable with radical, anionic, and even cationic initiators. In other words, it was hard to keep **4** as a monomer without great care. When pyridine was used as an initiator, poly-**4a** was obtained with a high molecular weight of 1.1 × 10^5. Poly-**4a** was found to consist of 1,6 or head-to-tail monomer unit placement. Compound **4a** was copolymerizable with

styrene in a random fashion in the presence of AIBN to obtain the monomer reactivity ratios: $r_{4a} = 3.4 \pm 0.2$ and $r_{St} = 0.01 \pm 0.08$ at 60 °C and Q and e values of **4a** of $Q = 23$ and $e = 1.04$. Compounds **4** were highly conjugative (highly reactive) and electron-accepting.

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