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Synthesis and Polymerization Behavior of 7-Cyano-7-(phenyl)benzoquinone Methide

Takahito Itoh,* Eriko Nakanishi, Masayuki Okayama, and Masataka Kubo

Department of Chemistry for Materials, Faculty of Engineering, Mie University, 1515 Kamihama-cho, Tsu-shi, Mie 514-8507, Japan

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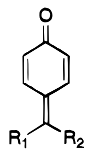
ABSTRACT: A novel captodatively substituted benzoquinone methide, 7-cyano-7-(phenyl)benzoquinone methide (**3**), was synthesized successfully as an isolable crystal at room temperature. **3** polymerized spontaneously on dissolving it in highly polar, basic solvents such as DMSO and DMF. The acid-catalyzed 1,6-addition reaction of **3** was investigated. Acid-catalyzed 1,6-addition reactions of **3** with phenol and *N,N*-dimethylaniline afforded 1:1 adducts. In the reaction with hydrogen chloride, a 1,6-addition adduct was also formed. Homopolymerizations of **3** and 7,7-di(cyano)benzoquinone methide (**1a**) with radical, anionic, and cationic initiators were investigated. **3** and **1a** are homopolymerizable with an anionic initiator but not with radical and cationic ones. **3** is copolymerizable spontaneously with styrene in an alternating fashion. The copolymer structure of **3** with styrene was determined on the basis of the spectral data of model compounds and the polymerization mechanism was discussed.

Introduction

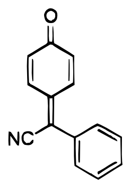
Unsubstituted quinodimethane is unstable to give its polymer spontaneously at room temperature.[1] However, captive substitution on exocyclic methylenes in the highly reactive unsubstituted quinodimethane with electron-withdrawing substituents such as cyano, ester, and acyl groups lowers its reactivity (polymerizability), resulting in highly electron-accepting substituted quinodimethanes[2−10] isolable as crystals at room temperature. Captodative substitution on exocyclic methylenes in the quinodimethane structure with both electron-withdrawing substituents and electron-donating substituents such as alkylthio and phenyl groups also affords isolable substituted quinodimethanes, being close to neutral in polarity.[11−13] We have studied the polymerization behaviors of these isolable and treatable substituted quinodimethanes.[3−5,7−13] Interesting polymerization behaviors such as equilibrium polymerizations, alternating copolymerizations, and changes in the polymerization mode from random to alternating copolymerization, according to its substitution mode and bulkiness of substituents, were found for the substituted quinodimethanes, and it was proven that they are a new class of monomers different from vinyl and related compounds.[14]

Unsubstituted benzoquinone methide,[15] being a member of the quinonoid family, is unstable, giving dimeric compounds and oligomers at room temperature like an unsubstituted quinodimethane. Substitution of hydrogen atoms on exocyclic methylene with electron-withdrawing substituents such as cyano and/or ester groups or with electron-donating substituents such as phenyl and dithioethylene groups afforded the corresponding substituted benzoquinone methides as isolable crystals at room temperature because of reduced polymerizability: e.g., 7,7-di(cyano)benzoquinone methide (**1a**),[16] 7-(alkoxycarbonyl)-7-cyanobenzoquinone methides (**1b**),[17,18] 7,7-bis(alkoxycarbonyl)benzoquinone methides (**1c**),[19] 7,7-di(phenyl)benzoquinone methide (**2a**),[20] and 4-(1′,3′-dithiolan-2′-ylidene)-2,5-cyclohexadien-1-one (**2b**).[21] Polymerization behaviors of these captively substituted benzoquinone methides **1a**−**c**, have been investigated.[17−19,22] It was found that **1a** is not homopolymerizable with radical initiator, but copolymerizable with styrene in an alternating fashion, and both **1b** and **1c** are homopolymerizable with radical and anionic initiators and copolymerizable with styrene and *p*-methoxystyrene in a random fashion except for **1c** with a bulky isopropyl group, which exhibited a polymerization behavior similar to **1a**. In analogy with captodatively substituted quinodimethanes, captodative substitution on the exocyclic methylene in the reactive unsubstituted benzoquinone methide is expected to afford the substituted benzoquinone methide isolable as crystals at room temperature. Captodatively substituted benzoquinone methides have not been synthesized yet, and also their polymerization behaviors are of interest in comparison with those of captively substituted benzoquinone methides.

In this work, 7-cyano-7-(phenyl)benzoquinone methide (**3**) as one of the novel captodatively substituted benzoquinone methides was successfully synthesized as an isolable crystal, and some of its chemical properties and polymerizations were investigated.



1a: R_1=R_2=CN
1b: R_1=CN, R_2=COOR
1c: R_1=R_2=COOR
2a: R_1=R_2=Ph
2b: R_1=R_2=SCH_2CH_2S



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Experimental Section

Monomer Synthesis. 4-[1′-Cyano-1′-(phenyl)methylene]-1,4-dioxaspiro[4.5]decane (4). 1,4-Cyclohexanedione monoethylene ketal (11.84 g, 75.8 mmol) and phenylacetonitrile (8.88 g, 75.8 mmol) were dissolved in 120 mL of ethanol, and to the resulting solution was added 7.58 g (75.8 mmol) of

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* Corresponding Author. Telephone: +81(Japan)-59-231-9410. Fax: +81(Japan)-59-231-9410. E-mail: itoh@chem.mie-u.ac.jp.

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a 40% sodium hydroxide aqueous solution, and then the mixture was stirred for at room temperature for 3 days. A 200 mL aliquot of water was added to the reaction mixture, and the resulting solution was extracted with 100 mL of diethyl ether three times. The extracts were combined, washed with 100 mL of water, and dried over anhydrous magnesium sulfate. The filtrate was placed under reduced pressure to remove solvents to afford a pale yellow solid, which was recrystallized from hexane to give 15.92 g (82.2% yield) of **4** as white needles: mp 63.4−65.4 °C; IR (KBr) ν_{CH} 3018−2990, ν_{CH} 2922−2858, ν_{CN} 2182, $\nu_{C=C}$ 1594, ν_{C-O} 1115, 1085 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.40−7.35 (m, 3H), 7.30−7.27 (m, 2H), 4.00 (s, 2H), 3.99 (s, 2H), 2.87 (t, J = 6.60 Hz, 4H), 2.50 (t, J = 6.60 Hz, 2H), 1.89 (t, J = 6.60 Hz, 2H), 1.70 (t, J = 6.60 Hz, 2H). Anal. Calcd for $C_{16}H_{17}NO_2$: H, 6.72; C, 75.27; N, 5.48; O, 12.53. Found: H, 6.84; C, 75.33; N, 5.27; O, 12.56.

4-[1′-Cyano-1′-(phenyl)methylene]cyclohexanone (5). **4** (12.68 g, 62.1 mmol) was added to 240 mL of a 2% aqueous sulfuric acid solution, and the resulting suspension was refluxed for 1 h and then, after cooling, extracted with four times with 100 mL of chloroform. The extracts were combined, washed with 100 mL of water and 100 mL of saturated sodium carbonate aqueous solution, and dried over anhydrous magnesium sulfate and then placed under reduced pressure to remove solvent to give a pale yellow oil, which was dissolved in a small amount of benzene. The resulting solution was passed through a silica gel column by using benzene as an eluent. The yellow elution band was collected and placed under reduced pressure to remove solvent to obtain 10.2 g (83% yield) of **5** as a yellow oil: IR (NaCl) ν_{CH} 3016−2986, ν_{CH} 2926−2868, ν_{CN} 2190, $\nu_{C=O}$ 1681, $\nu_{C=C}$ 1588, $\nu_{C=C}$ 1466 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.44−7.33 (m, 3H), 7.32−7.31 (m, 2H), 3.10 (t, J = 6.60 Hz, 2H), 2.76 (t, J = 6.60 Hz, 2H), 2.62 (t, J = 6.60 Hz, 2H), 2.44 (t, J = 6.60 Hz, 2H). Anal. Calcd for $C_{14}H_{13}NO$: H, 6.21; C, 79.59; N, 6.63; O, 7.57. Found: H, 6.34; C, 79.36; N, 6.64; O, 7.66.

7-Cyano-7-(phenyl)benzoquinone Methide (3). **5** (3.41 g, 16.7 mmol) was dissolved in 100 mL of benzene and then into the resulting solution were added 14.5 g (167 mmol) of activated manganese dioxide and 14.5 g of 3A molecular sieves. The mixture was refluxed with stirring for 24 h, cooled, and then filtered. The orange filtrate was placed under reduced pressure to remove solvent to give a dark orange solid, which was dissolved in a small amount of benzene. The resulting solution was passed through a silica gel column by using benzene as an eluent. The orange elution band was collected and placed under reduced pressure to remove solvent to obtain an orange solid, which was recrystallized from a mixed solution of hexane and dichloromethane to give 0.67 g (20% yield) of **3** as orange needles: mp 113.0−114.0 °C; IR (KBr) ν_{CH} 3020, ν_{CN} 2184, $\nu_{C=O}$ 1598, $\nu_{C=C}$ 1581, $\nu_{C=C}$ 1534, $\nu_{C=C}$ 1486 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.85 (dd, J = 9.89 and 2.64 Hz, 1H), 7.54 (s, 5H), 7.48 (dd, J = 10.23 and 2.64 Hz, 1H), 6.62 (dd, J = 9.89 and 1.98 Hz, 1H), 6.49 (dd, J = 10.23 and 1.98 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 186.4 (C=O), 139.6 (Ar), 136.9, 134.4, 131.9 (>C=), 131.4, 131.3, 131.2 (Ar), 130.4 (Ar), 129.3 (Ar), 124.0 (>C=), 117.1 (CN); UV−vis (CHCl$_3$) λ_{max} = 362 (ϵ = 2.48 × 10^4) nm. Anal. Calcd for $C_{14}H_9NO$: H, 4.39; C, 81.14; N, 6.76; O, 7.71. Found: H, 4.52; C, 80.83; N, 6.72; O, 7.93.

Adduct Formation of 3. With Phenol. **3** (100.8 mg, 0.486 mmol) and phenol (102.0 mg, 1.084 mmol) were dissolved in 10 mL of tetrahydrofuran (THF), and then 3 drops of acetic acid were added. The orange color changed to pale yellow color immediately. After being allowed to stand at room temperature for 13 h, the reaction mixture was placed under reduced pressure to remove solvent to give a viscous pale yellow 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 pale yellow elution band was collected and placed under reduced pressure to remove solvent to afford a pale yellow solid, which was recrystallized from toluene to give 132.5 mg (90.4% yield) of 1-cyano-1-phenyl-1,1-di(4-hydroxyphenyl)methane (**6**) as white needles: mp 168−169.5 °C; IR (KBr) ν_{OH} 3298, ν_{CH} 3020, ν_{CH} 2988, ν_{CN} 2226, $\nu_{C=C}$ 1670, $\nu_{C=C}$ 1582, $\nu_{C=C}$ 1565, $\nu_{C=C}$ 1485 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.35−7.32 (m, 3H), 7.23−7.20 (m, 2H), 7.06 (d, J = 8.91 Hz, 4H), 6.79 (d, J = 8.91 Hz, 4H), 4.91 (s, 2H). Anal. Calcd for $C_{20}H_{15}NO_2$: H, 5.02; C, 79.71; N, 4.65; O, 10.62. Found: H, 5.09; C, 80.07; N, 4.55; O, 10.29.

With *N,N*-Dimethylaniline. **3** (101.2 mg, 0.488 mmol) and phenol (500.1 mg, 4.13 mmol) were dissolved in 10 mL of THF, and then 507.7 mg (8.45 mmol) of acetic acid was added. After being allowed to stand at room temperature for 4.5 h, the reaction mixture was poured into 50 mL of ice−water and then extracted three times with 50 mL of chloroform. The extracts were combined, washed with water and dried over anhydrous magnesium sulfate, and then placed under reduced pressure to remove solvent to give a brown solid, 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 yellow elution band was collected and placed under reduced pressure to remove solvent to afford 65.6 mg (40.9% yield) of 1-cyano-1-phenyl-1-(4′-hydroxyphenyl)-1-[4″-(*N,N*-dimethylamino)phenyl]methane (**7**) as yellow solids: mp 226.0−228.6 °C; IR (KBr) ν_{OH} 3336, ν_{CH} 3040, ν_{CH} 2880, ν_{CN} 2220, $\nu_{C=C}$ 1578, $\nu_{C=C}$ 1485, $\nu_{C=C}$ 1421 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.34−7.30 (m, 3H), 7.25−7.21 (m, 2H), 7.02 (d, J = 8.9 Hz, 2H), 6.90 (d, J = 8.9 Hz, 2H), 6.79 (d, J = 8.9 Hz, 2H), 6.66 (d, J = 8.9 Hz, 2H), 2.95 (s, 6H). Anal. Calcd for $C_{22}H_{20}N_2O$: H, 6.14; C, 80.46; N, 8.53; O, 4.87. Found: H, 5.97; C, 80.09; N, 8.59; O, 5.35.

With Hydrogen Chloride. **3** (109.6 mg, 0.529 mmol) was dissolved in 10 mL of dichloromethane, and then dry hydrogen chloride was bubbled through the resulting solution for 30 min. The orange color of the solution changed to yellow gradually on bubbling. The yellow solution was concentrated to about 1 mL in volume and passed through a silica gel column by using dichloromethane as an eluent. The yellow band was collected and placed under reduced pressure to remve solvent to obtain 85.8 mg (66.6% yield) of 1-cyano-1-chloro-1-phenyl-1-(hydroxyphenyl)methane (**8**) as a yellow oil: IR (NaCl) ν_{OH} 3374, ν_{CH} 3020−2990, ν_{CN} 2220, ν_{C-Cl} 631 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.45 (s, 2H), 7.36 (d, J = 5.9 Hz, 3H), 7.29 (d, J = 8.9 Hz, 2H), 6.81 (d, J = 8.9 Hz, 2H), 6.33 (s, 1H). Anal. Calcd for $C_{14}H_{10}NOCl$: H, 4.14; C, 69.00; N, 5.75; O, 6.56; Cl 14.55. Found: H, 4.25; C, 69.13; N, 5.91; O, 6.25; Cl, 14.46.

Model Compounds. 1-Phenyl-1-phenoxyethane (12). Sodium metal (0.10 g, 4.35 mmol) was dissolved in 30 mL of ethanol, and into the resulting solution was dissolved 0.41 g (4.36 mmol) of phenol and then 0.80 g (4.32 mmol) of α-bromoethylbenzene was added and the mixture refluxed for 2 h. The reaction mixture was placed under reduced pressure to remove solvents to give a solid and a viscous oil, to which was added 30 mL of water. The resulting solution was extracted three times with 30 mL of chloroform, and the extracts were dried over anhydrous magnesium sulfate. The filtrate was placed under reduced pressure to afford a pale yellow oil, 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 second elution band was collected and placed under reduced pressure to remove solvent to give 246.2 mg (28.4% yield) of **12** as a colorless oil: IR (NaCl): ν_{CH} 3018−2936, ν_{CH} 2886, $\nu_{C=C}$ 1567, $\nu_{C=C}$ 1466, $\nu_{C=C}$ 1426, ν_{C-O} 1220 and 1071, σ_{C-H} 739 and 687 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.27−6.73 (m, 10H), 5.17 (q, J = 6.60 Hz, 1H), 1.51 (d, J = 6.60 Hz, 3H); ^{13}C NMR (CDCl$_3$) δ 158.0 (Ar), 143.2 (Ar), 128.5 (Ar), 127.3 (Ar), 125.5 (Ar), 120.6 (Ar), 115.9 (Ar), 75.8 (CH), 24.4 (CH$_3$). Anal. Calcd for $C_{14}H_{14}O$: C, 84.80; H, 7.13; O, 8.07. Found: C, 84.51; H, 7.20; O, 8.29.

1-Phenyl-2-phenoxyethane (13). **13** was obtained as a colorless oil in 19.5% yield from β-bromoethylbenzene in a process similar to that for **12**: IR (NaCl) ν_{CH} 3016−2904, ν_{CH} 2832, $\nu_{C=C}$ 1568, $\nu_{C=C}$ 1470, $\nu_{C=C}$ 1420, ν_{C-O} 1225 and 1025, σ_{C-H} 737 and 683 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.34−6.87 (m, 10H), 4.14 (t, J = 6.60 Hz, 2H), 3.09 (t, J = 6.60 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ 158.8 (Ar), 138.3 (Ar), 129.4 (Ar), 129.0 (Ar), 128.5 (Ar), 120.7 (Ar), 114.5 (Ar), 68.5 (CH$_2$), 35.8 (CH$_2$). Anal. Calcd for $C_{14}H_{14}O$: C, 84.80; H, 7.13; O, 8.07. Found: C, 84.60; H, 7.23; O, 8.17.

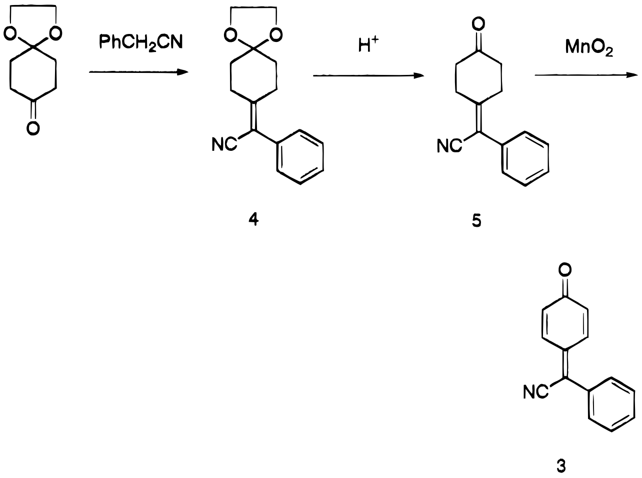
1-Cyano-1,1,2-triphenylpropane (14). Commercial sodium hydride (60% in oil) was washed twice with hexane and dried reduced pressure to obtain 0.37 g (15.4 mmol) of sodium hydride in a powder state, to which 50 mL of THF was added under nitrogen. Into this mixture was added 0.50 g (2.59 mmol) of phenylacetonitrile and the resulting mixture refluxed for 30 min. Into the resulting solution was added 0.48 g (2.59 mmol) of α-bromoethylbenzene and the resulting mixture refluxed for 4 h. The reaction mixture was cooled to room temperature and placed under reduced pressure to remove solvents to give white solids, to which was added 30 mL of water. The resulting solution was extracted three times with 30 mL of chloroform, and the extracts were combined, washed with water, and dried over anhydrous magnesium sulfate. The filtrate was placed under reduced pressure to afford a white 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 first elution band was collected and placed under reduced pressure to remove solvent to give 348.4 mg (35.5% yield) of **14** as white needles: mp 89.5−91.0 °C; IR (KBr) ν_{CH} 3018−2990, ν_{CH} 2938, ν_{CN} 2214, $\nu_{C=C}$ 1570, $\nu_{C=C}$ 1468, $\nu_{C=C}$ 1426, σ_{C-H} 737 and 688 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.67−7.02 (m, 15H), 3.88 (q, J = 6.90 Hz, 1H), 1.57 (d, J = 6.90 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 140.4 (Ar), 139.4 (Ar), 138.8 (Ar), 128.8 (Ar), 128.5 (Ar), 128.3 (Ar), 128.2 (Ar), 128.0 (Ar), 127.8 (Ar), 127.8 (Ar), 127.4 (Ar), 127.0 (Ar), 126.8 (Ar), 126.7 (Ar), 121.3 (CN), 58.9 (>C<), 46.6 (CH), 18.3 (CH_3). Anal. Calcd for $C_{22}H_{19}N$: C, 88.84; H, 6.45; N, 4.71. Found: C, 88.74; H, 6.51; N, 4.75.

1-Cyano-1,1,3-triphenylpropane (15). **15** was obtained as yellow solids in 35.5% yield from β-bromoethylbenzene in a process similar to that for **14**: mp 89.5−92.0 °C; IR (KBr) ν_{CH} 3018−2988, ν_{CH} 2930, ν_{CN} 2215, $\nu_{C=C}$ 1568, $\nu_{C=C}$ 1465, $\nu_{C=C}$ 1424, σ_{C-H} 738 and 685 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.57−7.09 (m, 15H), 2.75−2.64 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 140.6 (Ar), 139.9 (Ar), 130.1 (Ar), 128.9 (Ar), 128.6 (Ar), 128.3 (Ar), 128.0 (Ar), 126.8 (×2, Ar), 126.3 (×2, Ar), 122.8 (CN), 51.7 (>C<), 42.7 (CH_2), 32.0 (CH_2). Anal. Calcd for $C_{22}H_{19}N$: C, 88.84; H, 6.45; N, 4.71. Found: C, 88.89; H, 6.43; N, 4.68.

Materials. 7,7-Di(cyano)benzoquinone methide (**1a**) was prepared according to the method reported by Hyatt.[16] 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. Styrene [bp 52 °C (30 mmHg)] was washed with a 2% sodium hydroxide aqueous solution and water and dried over anhydrous magnesium sulfate for 1 day. Its supernatant was dried again over calcium hydride with stirring at room temperature for 12 h and distilled under reduced pressure. Benzene (bp 80 °C) was washed in sequence with concentrated sulfuric acid, water, a 5% aqueous sodium hydroxide solution, and again water, dried over anhydrous calcium chloride, refluxed over sodium metal for 12 h, and then distilled. Dichloromethane (40 °C), chloroform (bp 61 °C), acetonitrile (bp 82 °C), and acetone (bp 56 °C) were refluxed over calcium hydride for 12 h and then distilled. Tetrahydrofuran (THF) (bp 65 °C) was refluxed over lithium aluminum hydride for 12 h and distilled, and then the distillate was distilled again over benzophenone−sodium. *N*,*N*-Dimethylformamide (DMF) [bp 70 °C (10 mmHg)] and dimethyl sulfoxide (DMSO) [bp 68 °C (10 mmHg)] were dried over 3 Å molecular sieves for 1 day and then distilled under reduced pressure. Boron trifluoride diethyl etherate ($BF_3 \cdot Et_2O$) [bp 50 °C (50 mmHg)] and 4-methoxyphenol [bp 90 °C (5 mmHg)] were distilled under reduced pressure under nitrogen. Tetrabutylammonium perchlorate (Aldrich Co.) was dried under reduced pressure at 150 °C for 12 h. Potassium *tert*-butoxide was dried under reduced pressure at 80 °C for 24 h and then used without purification.

Polymerization Procedure. Radical Polymerization. Given amounts of **3**, styrene as a comonomer, AIBN as a radical initiator if necessary, and benzene as a solvent were placed in a glass ampule, which was degassed by the freeze−thaw method (repeatedly three times) and sealed. It 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 cycles of a redissolution−reprecipitation method. Chloroform and hexane were used as a solvent and a precipitant, respectively. The product obtained was dried under reduced pressure at room temperature until a constant weight was reached.

Scheme 1



Ionic Polymerization. The polymerization was carried out with the apparatus reported previously.[5] A given amount of **1a** or **3** as a monomer was placed in the apparatus, which was filled with nitrogen. Into it was introduced a given amount of solvent such as dichloromethane or THF 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 $BF_3 \cdot Et_2O$ or potassium 4-methoxyphenoxide, prepared from 4-methoxyphenol and potassium *tert*-butoxide, in THF solution was injected by a syringe. After a given time of the reaction, 2 drops of acetic acid were added to the reaction mixture, which then was poured into excess hexane for **1a** and isopropyl ether for **3** to deposit a polymeric product. The rest of the procedure was carried out similarly to the above-mentioned radical polymerization.

Measurements. All melting points were obtained with a Yanaco MP-53 melting point apparatus. Elemental analyses were performed on a Yanaco CHN Corder MT-3. The number-average molecular weights, M_n, of the homopolymers and copolymers were measured on a gel permeation chromatography (GPC) Tosoh HLC-803D with a series of Tosoh TSK-gel G2000H, G2500H, G3500H, and G4000H columns, calibrated with standard polystyrenes as a reference, with THF as an eluent. ^{1}H NMR spectra were taken on a JEOL JNM-EX 270 FT NMR spectrometer in chloroform-*d* or acetone-d_6 with tetramethylsilane as an internal standard. Infrared and UV−vis spectra were obtained with a JASCO IR-700 spectrometer and a UVIDEC-430B spectrometer, respectively.

Reduction potentials of monomers were measured on a Yanaco cyclic voltammetric analyzer VMA-010 at room temperature at a scanning rate of 100 mV/s using dichloromethane as a solvent containing tetrabutylammonium perchlorate (0.1 mol/L) as the supporting electrolyte, and Ag/AgCl, glassy carbon, and platinum wire were used as reference, working, and counter electrodes, respectively.

Results and Discussion

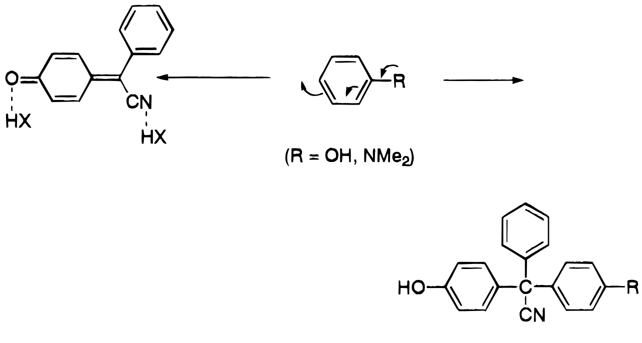
Monomer Synthesis. Monomer **3** was prepared successfully by the synthetic route shown in Scheme 1. **4** was obtained as white needles in 82% yield by the reaction of 1,4-cyclohexanedione monoethylene ketal with phenylacetonitrile in the presence of sodium hydroxide. The deprotection reaction of **4** with a 2% aqueous sulfuric acid solution yielded **5** in 83% yield, which was readily oxidized with activated manganese dioxide to afford **3** in 20% yield as orange needles. IR, ^{1}H and ^{13}C NMR spectra, and elemental analysis

Table 1. Values of First Reduction Potentials, E_1, of Substituted Benzoquinone Methides[a]

benzoquinone methides	E_1/V
1a	−0.55
1b(Et)	−0.28
3	−0.12

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

Scheme 2



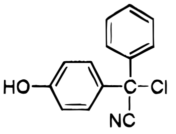
6: R = OH
7: R = NMe$_2$

values strongly suggested the chemical structure of 7-substituted benzoquinone methide.

The electron-accepting property of **3** was estimated as the value of the first reduction potentials, E_1, by cyclic voltammetry. The value of **3** is shown in Table 1, together with the corresponding values of **1a** and **1b** with an ethoxy group for comparison. It is obvious that **3** is weaker in its electron-accepting property than **1a** and **1b**(Et) as expected from the difference in the electron-withdrawing character among cyano (Hammett's substituent constant, $\sigma_p = +0.66$),[23] ethyl ester ($\sigma_p = +0.45$),[23] and phenyl ($\sigma_p = -0.01$)[23] groups and the number of them, and it is close to neutral. Therefore, this order could be explained well by the inductive effect of the substituents.

Addition Reaction of 3. Acid-catalyzed 1,6-addition reactions of **3** with phenol and *N,N*-dimethylaniline afforded the one-to-one adducts, **6** and **7**, respectively. The possible reaction mechanism is shown in Scheme 2, similar to that for corresponding reactions of **1a** and **1b** reported previously.[16,17]

Also, **3** is capable of reacting with hydrogen chloride to form the isolable, stable one-to-one adduct (**8**), in contrast to **1b** which reacts with hydrogen chloride to give the unstable corresponding adduct.



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Homopolymerization. The stability of **3** was examined in various solvents such as benzene, chloroform, acetonitrile, acetone, THF, DMF, and DMSO. When dissolved in DMF and DMSO, the color of solutions of **3** gradually changed from orange to yellow, and after 48 h, the solutions were subject to GPC, the chromatograms of which exhibited only one peak of the oligomers of **3** with a molecular weight of 500−2000 in DMSO and with a molecular weight of 400−1300 in DMF and no peak of monomer **3**. However, the color of **3** did not change in benzene, chloroform, acetonitrile, acetone, and THF solutions and their GPC chromatograms after 48 h showed only one peak as the monomer state. For comparison, the stability of **1a** was also examined in benzene, chloroform, acetonitrile, acetone, and THF. The color of **1a** did not change in benzene, chloroform, and THF solutions and their GPC chromatograms after 24 h exhibited only one peak as the monomer state, but oligomerization of **1a** took place in acetone and acetonitrile solutions to give polymers with molecular weights of 600−3500 and 600−1500, respectively. The highly polar, basic solvents induce oligomerizations of both **1a** and **3** as well as **1b**, which polymerized easily in polar, basic solvents such as acetonitrile, acetone, THF, DMF, and DMSO.[17] The difference in polymerization behavior among **1a**, **1b**(Et), and **3** could be attributed to the difference in their electron-accepting character; i.e., $E_1 = -0.55$ V for **1a**, −0.28 V for **1b**(Et), and −0.12 V for **3**.

Homopolymerization of **3** was attempted with the radical initiator AIBN at 60 °C, the cationic initiator $BF_3 \cdot Et_2O$ at 0 °C, and the anionic initiator potassium 4-methoxyphenoxide at 0 °C in order to investigate the polymerizability. The polymerization results are summarized in Table 2. It can be pointed out from the table that **3** is homopolymerizable with anionic initiator but not with radical and cationic ones. For comparison, the polymerization of **1a** was also examined with same initiators under similar conditions. The anionic initiator induced the polymerization of **1a** to give a polymer, but the cationic and radical ones did not. Previously, it was reported that **1b** is homopolymerizable with radical and anionic initiators but not with cationic one.[17] The polymerization behavior of **3** is similar to that of **1a** rather than **1b**.

The polymer of **3** (run no. 3 in Table 2) was obtained as a pale yellow powder, which was soluble in benzene, chloroform, and THF but insoluble in hexane and isopropyl ether. Its IR spectrum showed absorption bands at 3360 cm^{-1} due to the hydroxy group, at 2230 cm^{-1} due to the cyano group, at 1574 and 1477 cm^{-1} due to the carbon−carbon double bond of phenyl and phenylene groups, and at 1204 and 1160 cm^{-1} due to the ether linkage and showed absorption bands at 1598 cm^{-1} due to the carbonyl group and at 1534 cm^{-1} due to the exocyclic carbon−carbon double bond in monomer **3** that disappeared in the polymer, indicative of aromatization upon the polymerization of **3**. Its ^{1}H NMR spectrum in chloroform-*d* is shown in part a of Figure 1, where peaks at 3.8 ppm and at 7.8−6.6 ppm are

Table 2. Homopolymerizations of 1a and 3

run no.		monomer, mg	initiator, mmol	[monomer]/[initiator]	solvent, mL	temp, °C	time, h	yield, mg	convn, %	$M_n/10^3$
1	**3**	51.8	AIBN, 0.033	7.6	benzene, 5	60	6	0		
2	**3**	101.5	$BF_3 \cdot Et_2O$, 0.024	20	dichloromethane, 5	0	6	0		
3	**3**	103.6	KOPhOMe, 0.005	100	THF, 5	0	3	49.1	44.4	2.6
4	**1a**	78.5	AIBN, 0.016	10	benzene, 3	60	6	0		
5	**1a**	157.6	$BF_3 \cdot Et_2O$, 0.05	20	dichloromethane, 3	0	6	0		
6	**1a**	157.2	KOPhOMe, 0.01	100	THF, 3	0	3	44.6	27.5	1.5

Scheme 3

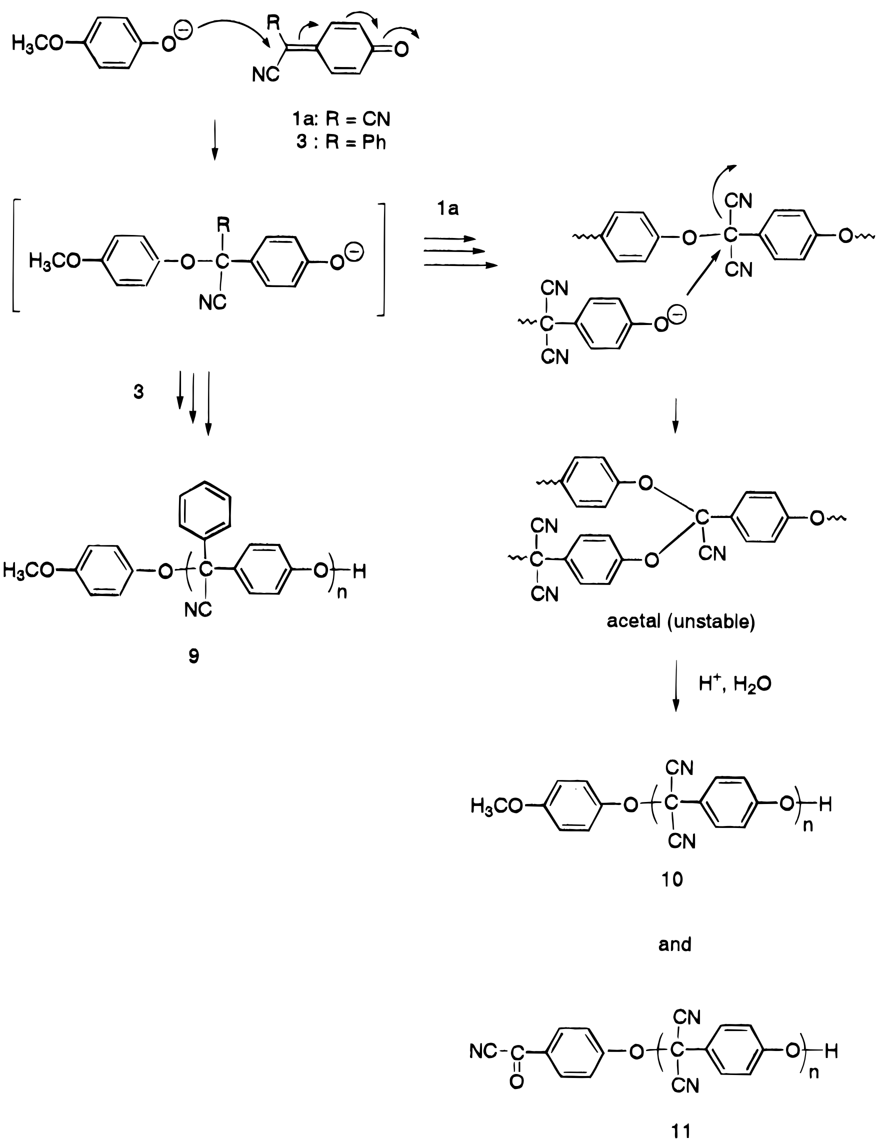


Table 3. Spontaneous Copolymerization of 3 with Styrene (St) in Benzene at 60 °C

run no.	monomer feed			solv, mL	time, day	yield, mg	convn, %	elemental anal.			copolym compn[a]	$M_n/10^3$
	3, mg	St, mg	**3**, mol %					% H	% C	% N	**3**, mol %	
1	100.0	248.8	16.8	1	7	15.3	4.4	5.47	84.58	4.74	54.1	7.6
2	101.1	104.0	32.8	1	5	9.4	4.6	5.42	84.61	4.63	52.2	7.3
3	200.2	108.3	48.2	2	7	5.1	1.7	5.13	84.60	4.80	55.2	3.0
4	300.1	73.9	67.1	3	7	17.6	4.7	5.65	84.10	4.78	54.8	4.7
5	502.0	43.5	85.3	5	5	15.2	2.8	5.43	84.84	4.67	52.9	3.4

[a] Calculated from nitrogen content.

assigned to the methoxy protons of the initiator unit and the aromatic protons of **3** and the initiator units, respectively. The molecular weight of the polymer of **3** was estimated from the peak area ratio of methoxy protons to aromatic protons to be 2700 (DP = 12.6), which is close to the value (2600, DP = 11.9) estimated from GPC measurement as a polystyrene standard. This indicates that the polymerization takes place in such a way that 4-methoxyphenoxide anion attacks the exocyclic cyano(phenyl)methylene carbon site of **3** to form phenoxide anion via aromatization, followed by subsequent addition to give a polymer (**9**) with head-to-tail monomer unit placement.

The polymer of **1a** (run no. 6 in Table 2) was obtained as a pale green powder, which was soluble in acetone and THF but insoluble in benzene, chloroform, hexane, and isopropyl ether. Its IR spectrum showed absorption bands at 3372 cm^{-1} due to the hydroxy group, at 2234 cm^{-1} due to the cyano group, at 1574 and 1477 cm^{-1} due to the carbon−carbon double bond of phenyl and phenylene groups, and at 1204 and 1160 cm^{-1} due to the ether bond. An additional peak was observed at 1688 cm^{-1} due to the carbonyl group in the polymer, which is assigned to the carbonyl of the cyanobenzoyl group (1695 cm^{-1}).[2] Its ^1H NMR spectrum in acetone-d_6 is shown in part b of Figure 1, where peaks at 3.8 ppm

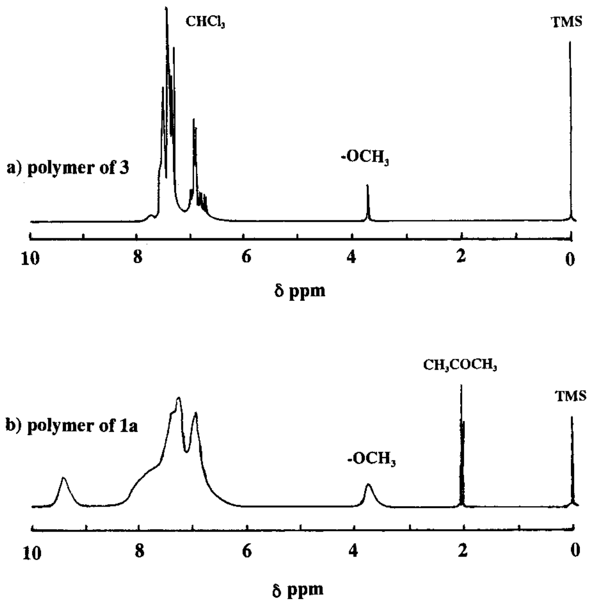


Figure 1. ^{1}H NMR spectra of (a) the polymer of **3** (run no. 3 in Table 2) in chloroform-*d* and (b) the polymer of **1a** (run no. 6 in Table 2) in acetone-d_6.

and at 8.4−6.7 ppm are assigned to the methoxy protons due to the initiator unit and aromatic protons of **1a** and the initiator units, respectively. The molecular weight of the polymer of **1a** could be estimated from the peak area ratio of methoxy protons to aromatic protons to be 7500 (DP = 47.3). However, its molecular weight measured by GPC (polystyrene standard) is found to be 1500 (DP = 8.8) and is much lower than that obtained by NMR measurement, indicating that the isolated polymer contains a large amount of polymer without an initiator unit at its terminus. A possible mechanism for the polymerizations of **1a** and **3** initiated with potassium 4-methoxyphenoxide is summarized in Scheme 3.

For **1a**, the attack of a growing phenoxide anion on the more electron deficient quarternary carbon in the polymer main chain during propagation reaction might take place easily, resulting in unstable acetals, which would be decomposed by a contaminant water in the reaction system or with the acid added to stop the polymerization to produce a mixture of a polymer (**10**) with an initiator moiety at its terminus and a polymer (**11**) with cyanobenzoyl group unit in its terminus.

Copolymerization of 3 with Styrene. The spontaneous copolymerization of **3** with styrene was carried out in benzene at 60 °C with a concentration of 0.48 mmol/L of **3**. The polymers were obtained as white solids, and the M_n values were in the range of 4000−7300. The results are summarized in Table 3, and the copolymer composition curve is shown in Figure 2. The copolymers obtained were always composed of about 50 mol % of the **3** unit regardless of monomer feed ratios.

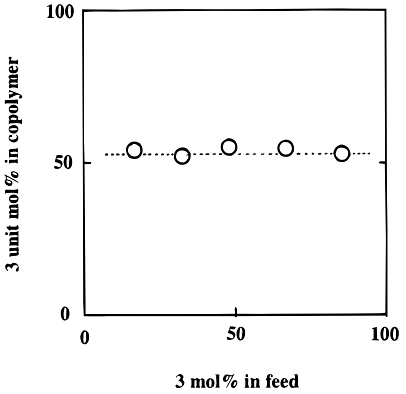


Figure 2. Copolymerization composition curve for the copolymerization of **3** with styrene at 60 °C in benzene.

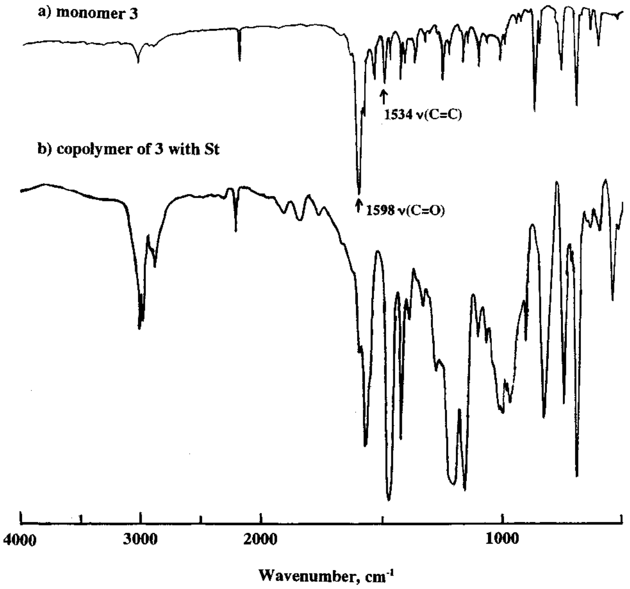


Figure 3. IR spectra of (a) monomer **3** (KBr) and (b) the copolymer of **3** with styrene (film).

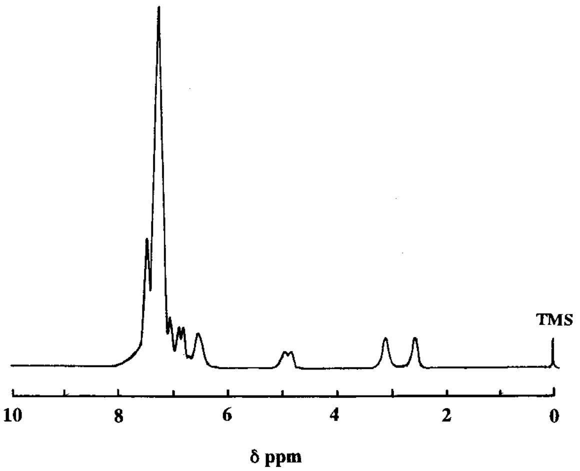
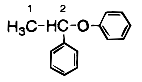
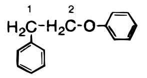
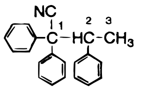
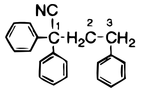
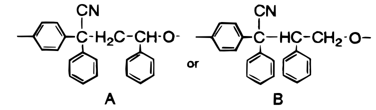


Figure 4. ^{1}H NMR spectrum of the copolymer of **3** with styrene in chloroform-*d*.

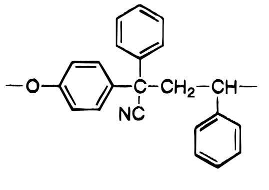
Parts a and b of Figure 3 illustrate IR spectra of the monomer **3** and the copolymer of **3** with styrene, respectively. Monomer **3** shows absorption bands at 1598 cm^{-1} due to the carbonyl group and at 1534 cm^{-1} due to the exocyclic carbon−carbon double bond, but both absorption bands disappeared in the copolymer, indicating that **3** reacts at its exocyclic carbon and oxygen sites with styrene like **1a**.[22] The ^{1}H NMR spectrum of the copolymer (run no. 1 in Table 3) is shown in Figure 4, where the methine and methylene protons of the styrene unit in the copolymer appear at 4.9 and 3.2−2.6 ppm, respectively, indicating that they are much more subject to deshielding than the corresponding ones of polystyrene, generally appearing in the 1−2 ppm region.[24] Presumably, the deshielding arises from electron withdrawal by the neighboring oxygen atom and the cyano(phenyl)methylene group, indicating that the styrene unit is linked directly to **3** on both. There-

Table 4. ^{1}H and ^{13}C NMR Chemical Shift Values of Model Compounds (12−15) and Copolymer

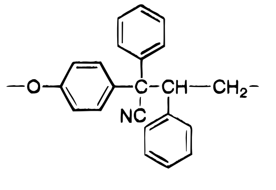
model compounds and copolymer	carbon, ppm 1	2	3	CN	proton, ppm CH	CH_2	CH_3
12 	24.4	75.8			5.18(q)		1.51(d)
13 	35.8	68.5				4.14(t), 3.09(t)	
14 	58.9	46.6	18.3	121.3	3.88(q)		1.57(d)
15 	51.7	42.7	32.0	122.8		2.75-2.64(m)	
	$>\underline{C}<$,	$>\underline{C}H$-,	-$\underline{C}H_2$-,	$\underline{C}N$	$C\underline{H}$	$C\underline{H}_2$	
	48.9	81.0	48.0	119.4	4.9	3.1 2.6	

fore, the copolymer of **3** with styrene is really alternating.

There are two possible structures (structure A and structure B) for an alternating copolymer of **3** with styrene.



Structure A



Structure B

To determine which one is formed, we prepared four model compounds and their chemical shift values were compared with those of the alternating copolymer obtained. The chemical shift values of aliphatic protons, aliphatic carbons, and cyano carbon of the model compounds (**12**−**15**) are summarized in Table 4, together with the corresponding values for the alternating copolymer of **3** with styrene. As aromatic peaks in the spectrum of the copolymer did not give us any information for the orientation of the units because of serious overlapping of the peaks, the chemical shift values of aliphatic protons and aliphatic carbons were used for determination of the orientation. According to the proton chemical shift values in Table 4, the methine and methylene protons of the copolymer would be observed at 5.18 ppm and 2.75−2.64 ppm for structure A and at 3.88 and 4.14 ppm for structure B, respectively. As shown in Figure 4, methine and methylene protons appear at 4.9 and 3.1−2.6 ppm, respectively, which are in fair agreement with chemical shift values expected for structure A rather than for structure B. Moreover, quarternary, methine, and methylene carbons of the alternating copolymer are expected to appear at 51.7, 75.8, and 42.7 ppm for structure A and at 58.8, 46.6, and 68.5 ppm for structure B, respectively, according to carbon chemical shift values of the model compounds in Table 4. In the ^{13}C NMR spectrum of the alternating copolymer, three peaks due to aliphatic carbons were observed at 48.9, 81.0, and 48.0 ppm, which could be assigned to quarternary, methine, and methylene carbons, respectively. The ^{13}C NMR spectral data obviously indicate that this alternating copolymer also has structure A.

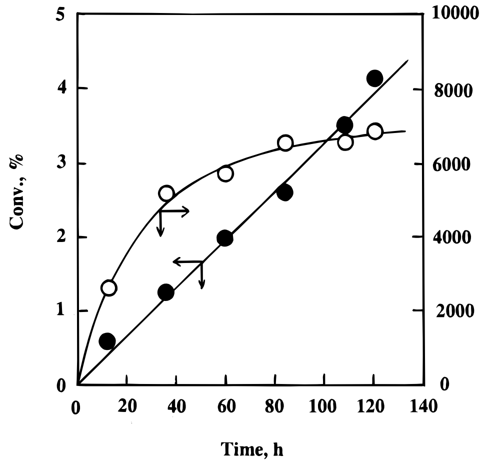
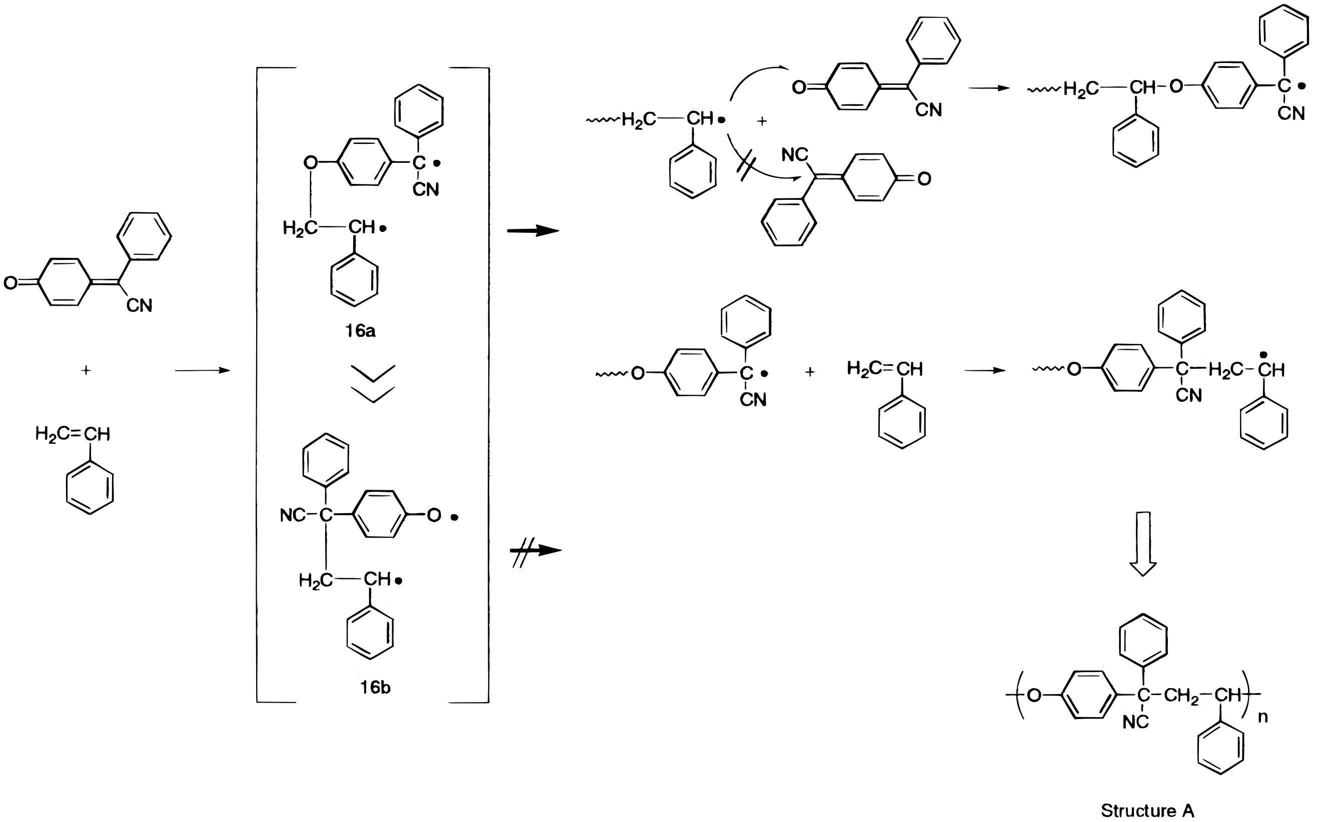


Figure 5. Time−conversion and time−M_n plots for the spontaneous copolymerization of **3** ([**3**] = 0.46 mol/L) with styrene ([styrene] = 0.47 mol/L) in benzene (3 mL) at 60 °C.

Hall et al.[25−27] have proposed the bond-forming initiation theory to explain spontaneous polymerizations for the electron-rich olefins/electrophilic olefins, the electron-rich dienes/electrophilic olefins, and the electron-rich olefins/electrophilic quinodimethanes systems. The initiating species were proposed to be tetramethylene, hexamethylene, and *p*-phenylenetetramethylene intermediates, respectively, which may be either diradicals, leading to alternating copolymers, or zwitterions, leading to homopolymers of electron-rich olefins and dienes. Moreover, for a *p*-phenylenetetramethylene intermediate, it was considered to lean much more toward the diradical side rather than the zwitterion side, because of the incorporated phenylene group, compared with tetramethylene and hexamethylene intermediates. In analogy to the above-mentioned systems, an initiating

Scheme 4



species in the spontaneous polymerization for the electron-rich olefins/electron-accepting benzoquinine methide system might be a *p*-phenyleneoxytrimethylene intermediate, which would be diradical because of an alternating copolymer formation in the spontaneous copolymerization of **3** with styrene and incorporated phenyl and phenylene groups. The orientation of the donor monomer in a diradical initiating species is known from Hall's works.$^{25-27}$ Thus, two different diradical *p*-phenyleneoxytrimethylene intermediates (**16a** and **16b**) as an initiating species are possible, according to the structure of **3**. The formation of **16a** is considered to be favored over **16b** in the initiation reaction, because of much better stabilization of the carbon radical by the captodative effect^{28} compared to the oxygen one. When the diradical intermediate **16a** is formed, two propagation modes are possible: one is a diradical coupling and another is a chain addition; that is, the diradical acts as an initiator. To obtain information about the propagation mode, spontaneous copolymerization of **3** with styrene was carried out in benzene at 60 °C at different polymerization times at the fixed ratio of [**3**]/[styrene] = 1. The conversion and the molecular weight of the obtained copolymers as a function of time are shown in Figure 5. Conversion increases linearly with time, and the molecular weight of the copolymers increases at the beginning, but immediately (at higher conversion than 4%) reaches a molecular weight of about 7000 and afterward seems to be constant, being similar to a conventional radical copolymerization. This indicates that the propagation mode is in favor to a chain addition rather than a diradical coupling. If the diradical coupling reaction of **16a** could take place, the alternating copolymer with structure B is formed and it is not agreement with the alternating polymer with structure A as determined on the basis of NMR spectral data. When the propagation would occur via the chain addition, copolymerization should be governed by formation of the most stable radical and the least steric hindrance. As to the mechanism shown in Scheme 4, a growing styryl radical (obviously with the phenyl on the terminal carbon) can attack the monomer **3** either on the carbonyl side or at the cyano(phenyl)methylene carbon side. The former is favored sterically and also from the standpoint of the stable radical formation by captodative effect. The second possibility is very difficult sterically, with two phenyl groups on adjacent carbons, though slightly favored electronically, and will be greatly disfavored. The resulting cyano(phenyl)benzyl radical can attack the styrene monomer on the methylene carbon side in a known manner. This chain addition mode in the propagation step could lead to the alternating copolymer with structure A.

In conclusion, a novel captodatively substituted benzoquinone methide, 7-cyano-7-(phenyl)benzoquinone methide (**3**), was synthesized successfully as an isolable crystal at room temperature and its polymerization was investigated. When **3** was dissolved in highly polar, basic solvents such as DMSO and DMF, its spontaneous polymerization occurred. Acid-catalyzed 1,6-addition reactions of **3** with phenol and *N*,*N*-dimethylaniline afforded 1:1 adducts. Also, **3** reacted with hydrogen chloride to give a a stable 1,6-addition product. **1a** and **3** homopolymerized with the potassium 4-methoxyphenoxide initiator, but did not with the AIBN and $BF_3 \cdot Et_2O$ ones. **3** copolymerized spontaneously with styrene to give an alternating copolymer, the structure of which was determined on the basis of the chemical shifts values of model compounds. The polymerization mechanism leading to the alternating copolymer could be explained well by both diradical intermediate formation in the initiation step by the bond-forming initiation mechanism and chain addition like a conventional radical copolymerization in the propagation step.

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