Equilibrium Polymerization of 7-(Alkoxycarbonyl)-7-cyano-1,4-benzoquinone Methides, Substituent Effect on Polymerizability, and Copolymerization with Styrene

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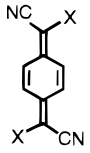
ABSTRACT: Polymerization kinetics of 7-(alkoxycarbonyl)-7-cyano-1,4-benzoquinone methides with alkoxy groups such as methoxy (**3a**), butoxy (**3b**), isopropoxy (**3c**), and *sec*-butoxy (**3d**) was investigated in chloroform in the presence of 2,2′-azobis(isobutyronitrile) (AIBN) as an initiator. Their polymerizations were found to be typical equilibrium polymerization reactions, and on the basis of this polymerization behavior, the thermodynamic parameters of polymerization such as the enthalpy (ΔH) and entropy (ΔS) of polymerization were determined. To get information about the substituent effect on the homopolymerizability of 7-(alkoxycarbonyl)-7-cyano-1,4-benzoquinone methides, the ΔH values were compared with the substituent parameters for the alkyl group of the alkoxy substituents by means of a linear free energy relationship and the homopolymerizability was found to be determined mainly by the steric hindrance of the alkoxy groups. The copolymerization of **3a** with styrene in chloroform with AIBN as an initiator was carried out above and below the equilibrium monomer concentration of **3a**. Above the equilibrium monomer concentration of **3a**, **3a** copolymerized with styrene in a random fashion to afford the monomer reactivity ratios, r_1(**3a**) = 4.70 ± 0.85 and r_2(styrene) = 0.01 ± 0.01 at 60 °C. Alfrey−Price's Q and e values of **3a** were calculated to be $Q = 32$ and $e = +1.05$, respectively, indicating that **3a** is a highly conjugative (reactive) and electron-accepting monomer. On the other hand, below the equilibrium monomer concentration of **3a**, **3a** copolymerized with styrene in a perfectly alternating fashion. The change from random fashion to alternating one for this copolymerization was explained well in connection with the equilibrium polymerization behavior of **3a**.

Introduction

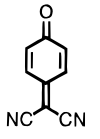
Substituted quinodimethanes bearing two different electron-withdrawing substituents such as the cyano group and the alkoxycarbonyl or acyl groups (**1a** and



1a X = COOR (R = Me, Et, Bu)
1b X = COR (R = Me, Et, iPr, Ph)
1c X = SR (R = Et, Ph)

1b) and bearing an electron-withdrawing cyano group and an electron-donating alkylthio group (**1c**) at positions 7 and 8 are isolable as pure crystals at room temperature and homopolymerizable with anionic and radical initiators.[1−7] These substituted quinodimethanes have exhibited polymerization behavior different from that of the conventional vinyl monomers. The detailed kinetic studies of the radical polymerizations for the substituted quinodimethanes indicated that their polymerizations are typical equilibrium polymerization reactions, and it was found that the values of the entropy of polymerization are almost constant, one-third as large as those of conventional vinyl monomers, and the values of the enthalpy of polymerization are much smaller compared to the corresponding ones for vinyl monomers.[5,7] The substituent effect on the homopolymerizability of the substituted quinodimethanes, especially **1b**, indicated that the polymerizability is exclusively determined by the steric hindrance of the acyl substituents at positions 7 and 8.[6] Moreover, it was pointed out that, on the copolymerization of the substituted quinodimethanes with styrene, the copolymerization fashion (alternating or random) significantly depends upon whether these substituted quinodimethanes are homopolymerizable or not.

Substituted 1,4-benzoquinone methides have shown polymerization behaviors similar to the substituted quinodimethanes in some aspects. For example, 7-dicyano-1,4-benzoquinone methide (**2**) is not homopoly-



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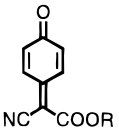

3a : R = Me
3b : R = Bu
3c : R = iPr
3d : R = sBu

merizable with a radical initiator but copolymerizable with styrene in an alternating fashion,[8] and 7-(alkoxycarbonyl)-7-cyano-1,4-benzoquinone methides (**3a**−**c**) are homopolymerizable with anionic and radical initiators and copolymerizable with styrene in a random fashion.[9] However, for these substituted 1,4-benzoquinone methides, detailed polymerization studies such as polymerization kinetics, substituent effect on the polymerizability, and determination of the equilibrium monomer concentrations and the thermodynamic parameters have not been carried out. To make clear whether the polymerization behavior observed for the substituted quinodimethanes is a remarkable feature of the polymerization of the quinonoid family or not, it

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is useful to study the polymerization of the substituted 1,4-benzoquinone methides in detail. 7-(Alkoxycarbonyl)-7-cyano-1,4-benzoquinone methides are considered to be suitable candidates for this purpose because they are isolable as crystals at room temperature, homopolymerizable with a radical initiator, and copolymerizable with styrene.[9]

In this work, in addition to 7-(methoxycarbonyl)-, 7-(butoxycarbonyl)-, and 7-(isopropoxycarbonyl)-7-cyano-1,4-benzoquinone methides (**3a**, **3b**, and **3c**) reported previously, 7-(*sec*-butoxycarbonyl)-7-cyano-1,4-benzoquinone methide (**3d**) was prepared as a new monomer, and the polymerization behavior of **3a**−**d**, especially concerning the kinetics of the radical homopolymerization, the substituent effect on the polymerizability, and the fashion of the copolymerization with styrene, were investigated.

Experimental Section

Melting points are uncorrected. The copolymer composition was established by elemental analysis. The number-average molecular weights, M_n, of the copolymers were determined by gel permeation chromatography (GPC) using standard polystyrenes as a reference and tetrahydrofuran as an eluent without correction. ^{1}H NMR measurement was carried out in chloroform-*d* with tetramethylsilane as an internal standard. A Yanaco MP-53 was used for measuring the melting point, a Yanaco CHN Corder MT-3 for elemental analysis, a GPC Tosoh HLC-803D with a series of Tosoh TSK-gel G2000H and G2500H columns, for measuring the number-average molecular weight, a JEOL JNM-EX 270 FT NMR spectrometer for ^{1}H NMR spectroscopy, a JASCO IR-700 spectrometer for infrared spectroscopy, and a UVIDEC-430B spectrometer for UV−vis spectroscopy, respectively.

Materials. Styrene (bp 52 °C (30 mmHg)) was washed with a 2% aqueous sodium hydroxide 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 then distilled under reduced pressure. Chloroform was refluxed over calcium hydride for 24 h and then distilled. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol.

sec-Butyl cyanoacetate (bp 109 °C (22 mmHg)) was prepared in a 61.5% yield from the reaction of cyanoacetyl chloride[10] with *sec*-butyl alcohol. 7-Cyano-7-(methoxycarbonyl)-1,4-benzoquinone methide (**3a**), 7-cyano-7-(butoxycarbonyl)-1,4-benzoquinone methide (**3b**), and 7-cyano-7-(isopropoxycarbonyl)-1,4-benzoquinone methide (**3c**) were prepared according to the methods reported previously.[9]

Synthesis of 7-(*sec*-Butoxycarbonyl)-7-cyano-1,4-benzoquinone Methide (3d). 4-[Cyano(*sec*-butoxycarbonyl)-methylene]cyclohexanone. 1,4-Cyclohexanedione monoethylene ketal (17 g, 108.6 mmol) and *sec*-butyl cyanoacetate (16.9 g, 119.7 mmol) were refluxed in the presence of 0.7 g of ammonium acetate and 3.5 mL of acetic acid in 250 mL of toluene using a Dean−Stark water separator to isolate water formed for 44 h. The reaction mixture was washed twice with 100 mL of water and dried over anhydrous magnesium sulfate. It was placed under reduced pressure to remove toluene to give a yellow viscous material, to which was added 350 mL of a 2% aqueous sulfuric acid solution, and then refluxed for 1.5 h. After cooling, the reaction mixture was extracted with chloroform (400 mL × 3). The extracts were combined, washed twice with 100 mL of water, dried over anhydrous magnesium sulfate, and then placed under reduced pressure to remove toluene to give 24.4 g (95.3% yield) of 4-[cyano(*sec*-butoxycarbonyl)methylene]cyclohexanone as a yellow oil. IR (neat): ν_{C-H} 2934, ν_{CN} 2204, $\nu_{C=O}$ 1690, $\nu_{C=C}$ 1571, ν_{C-O} 1234, 1083 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.96 (m, 1H), 3.41 (t, J = 6.93 Hz, 2H), 3.13 (t, J = 6.93 Hz, 2H), 2.57 (m, 4H), 1.67 (m, 2H), 1.31 (d, J = 6.27 Hz, 3H), 0.96 (t, J = 7.43 Hz, 3H).

7-Cyano-7-(*sec*-butoxycarbonyl)-1,4-benzoquinone Methide (3d). 4-[Cyano(*sec*-butoxycarbonyl)methylene]cyclohexanone (2.97 g, 12.6 mmol) was dissolved in 1200 mL of chloroform, and then into the resulting solution were added 24.1 g of activated manganese dioxide (Aldrich Co.) and 24.1 g of 3A molecular sieves. The mixture was refluxed with stirring for 40 min, cooled, and then filtered. The orange filtrate was placed under reduced pressure to remove chloroform 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 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 0.84 g (28.7% yield) of **3d** as orange needles: mp 57.5−58.0 °C. IR (KBr): ν_{C-H} 2936, ν_{CN} 2198, $\nu_{C=O}$ 1682, $\nu_{C=C}$ 1610, 1588, ν_{C-O} 1234, 1072 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.57 (d, J = 7.92 Hz, 1H), 7.72 (d, J = 7.59 Hz, 1H), 6.61 (d, J = 8.24 Hz, 1H), 6.53 (d, J = 8.25 Hz, 1H), 5.05 (m, 1H), 1.69 (m, 2H), 1.36 (d, J = 6.27 Hz, 3H), 0.99 (t, J = 7.59 Hz, 3H). UV ($CHCl_3$) 320 nm (ϵ = 3.06 × 10^4). Anal. Calcd for $C_{13}H_{13}NO_3$: C, 78.35; H 6.59; N, 7.03; O, 8.03. Found: C, 78.14; H, 6.62; N, 7.08; O, 8.16.

Homopolymerization. A given amount of **3a**−**d** as a monomer was weighed out in a 10- or 5-mL volumetric flask, to which 1 or 5 mL of AIBN solution in chloroform of known concentration as an initiator was added, and then the flask was filled to its meniscus with chloroform to obtain monomer and initiator solutions with a given concentration. A 1-mL aliquot was pipetted into each ampule, which was degassed completely by the freeze−thaw method (repeated three times) and sealed. Each ampule was set in a bath thermostated at 50, 55, 60, 65, 70, or 80 °C for the time of polymerization and then opened. A fixed volume of an aliquot of the polymerization mixture was taken out of each ampule and then added into the flask containing a given volume of chloroform, followed by filling to its meniscus with chloroform in order to obtain the solution for measurement. The resulting solution was measured spectrophotometrically to obtain the concentration of unreacted monomer by using absorption bands of 320 nm (ϵ = 3.35 × 10^4), 320 nm (ϵ = 3.26 × 10^4), 320 nm (ϵ = 3.23 × 10^4), and 320 nm (ϵ = 3.06 × 10^4) characteristic of **3a**, **3b**, **3c**, and **3d**, respectively. The polymerization rate, R_p, was calculated from the amounts of monomer consumed as a function of time.

Copolymerization. Given amounts of **3a** as a monomer, styrene as a comonomer, AIBN as an initiator, and chloroform as a solvent were placed in an ampule. By adjusting an amount of chloroform, the monomer concentration of **3a** was maintained at a fixed value (0.30 and 0.06 mol/L). The ampule was degassed by the freeze−thaw method (repeated three times) and sealed. It was set 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 deposit a polymeric product. The dissolution−precipitation process was repeated more than three times for purification. Dichloromethane and hexane were used as a solvent and a precipitant, respectively. The purified product was dried under reduced pressure until a constant weight was attained.

Results and Discussion

Kinetics of Radical Homopolymerization. We chose **3a** as a representative monomer for the kinetic studies of the polymerization of the substituted 1,4-benzoquinone methides because it has the smallest alkoxy substituent, a methyl group. The polymerization rates, R_p, in the presence of AIBN for **3a** were measured at 50, 55, 60, 65, 70, and 80 °C. The plots of time versus conversion for the homopolymerization of **3a** are shown in Figure 1. The conversion increases linearly with the time of polymerization without an induction period in all cases except for 80 °C, at which no polymerization of **3a** occurred. The R_p values can be obtained from the slopes of the straight kinetic plots. The log−log plot of

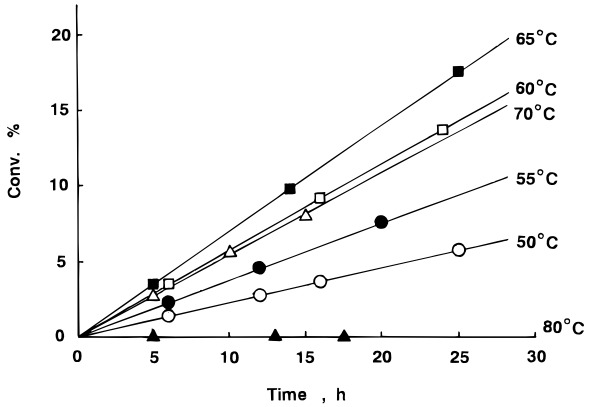

Figure 1. Plots of time versus conversion for the polymerization of **3a** in chloroform at 50 (○), 55 (●), 60 (□), 65 (■), 70 (△) and 80 (▲) °C, with a [**3a**] of 0.30 mol/L and a [AIBN] of 3.0×10^{-2} mol/L.

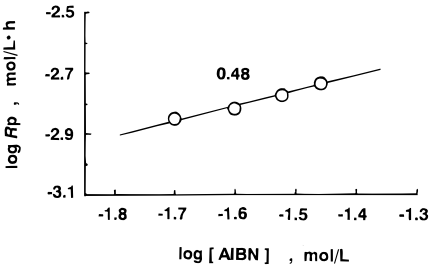

Figure 2. log−log plot of R_p versus [AIBN] in chloroform at 60 °C, with a [**3a**] of 0.30 mol/L.

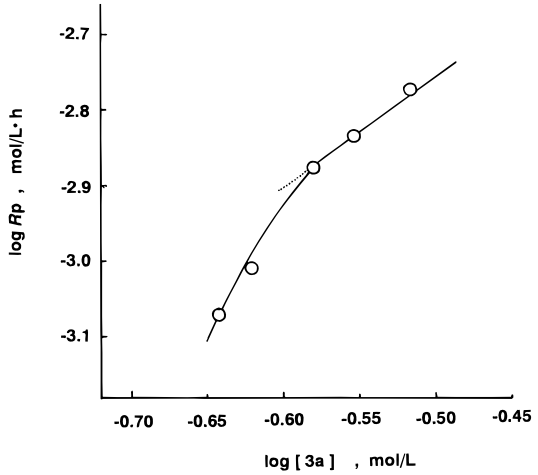

Figure 3. log−log plot of R_p versus [**3a**] in chloroform at 60 °C, with a [AIBN] of 3.0×10^{-2} mol/L.

R_p versus initiator concentration, [AIBN], for the polymerization of **3a** at 60 °C displayed a good straight line with a slope of 0.48 ± 0.03, as shown in Figure 2, indicating that the radical polymerization of **3a** is compatible with a conventional radical polymerization rate equation,[11] predicting a square-root dependence on initiator concentration. The log−log plot of R_p versus monomer concentration for the polymerization of **3a** at 60 °C does not display a straight line, as shown in Figure 3. In the region of the monomer concentration higher than 0.26 mol/L **3a**, this plot appears to be a straight line with a slope of 1.0 ± 0.1, while in the region of the monomer concentration lower than 0.26 mol/L **3a**, its slope deviates greatly: the lower the monomer concentration, the steeper the slope. In other words, in the high monomer concentration region, the R_p shows

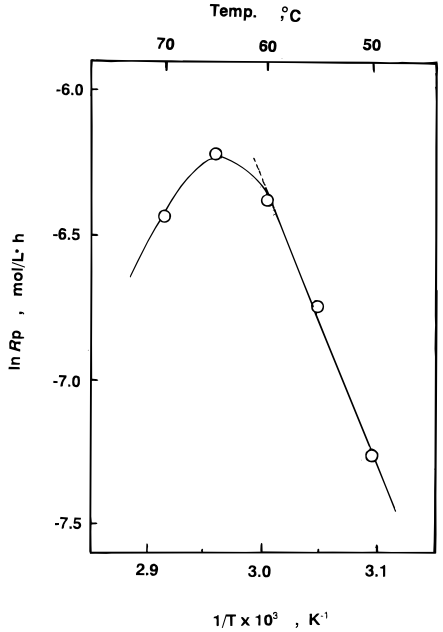

Figure 4. Arrhenius plot for the polymerization of **3a**, with a [**3a**] of 0.30 mol/L and with a [AIBN] of 3.0×10^{-2} mol/L.

a first-order dependence on monomer concentration as a conventional radical polymerization, whereas in the low monomer concentration region, it exhibits a much higher order dependence on monomer concentration. The Arrhenius plot of ln R_p versus the reciprocal of the absolute polymerization temperature, $1/T$, for the polymerization of **3a** at a monomer concentration of 0.30 mol/L is shown in Figure 4. The plot displays a good straight line in the region of the polymerization temperature below 60 °C, from a slope of which an apparent overall activation energy of the polymerization is estimated to be 78.9 ± 0.6 kJ/mol. On the other hand, in the region of the polymerization temperature above 65 °C, it deviates greatly from the straight line, indicating a significant decrease instead of an increase in the polymerization rate with the polymerization temperature. Therefore, it is obvious in this polymerization that both dependencies of the R_p on the monomer concentration and on the polymerization temperature are seriously different from those for the conventional radical polymerization, suggesting a great contribution of the depolymerization to the polymerization of **3a** at the high temperature and in the low monomer concentration. The polymerization rates, R_p, in the polymerization of **3a** at 50, 55, and 60 °C are plotted against the monomer concentrations of **3a**. Linear plots are obtained, as shown in Figure 5, and the extrapolation of the plots to the polymerization rate of zero gives equilibrium monomer concentrations, $[M]_e$, between the polymerization and the depolymerization at different polymerization temperatures. The $[M]_e$ values at different polymerization temperatures for the polymerization of **3a** are summarized in Table 1, together with the corresponding ones for the polymerizations of 7,8-dibenzoyl-7,8-dicyanoquinodimethane (BzCQ),[5] 7,8-bis(butoxycarbonyl)-7,8-dicyanoquinodimethane (BCQ),[5] and 7,8-bis(phenylthio)-7,8-dicyanoquinodimethane (PSCQ)[7] for comparison. Some plots of the R_p versus monomer concentrations for the polymerizations of **3b**−**d** at 50, 55, and 60 °C with monomer concentrations of 0.24−0.33 mol/L **3b** and an AIBN concentration of 3.0×10^{-2} mol/L for **3b**, 0.22−0.36 mol/L **3c** and an AIBN concentration of

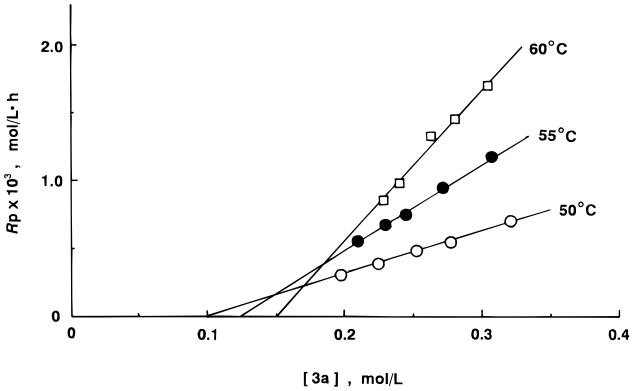

Figure 5. Relationship of R_p versus monomer concentration [**3a**] in chloroform at 50 (○), 55 (●), and 60 (□) °C, with a [AIBN] of 3.0×10^{-2} mol/L.

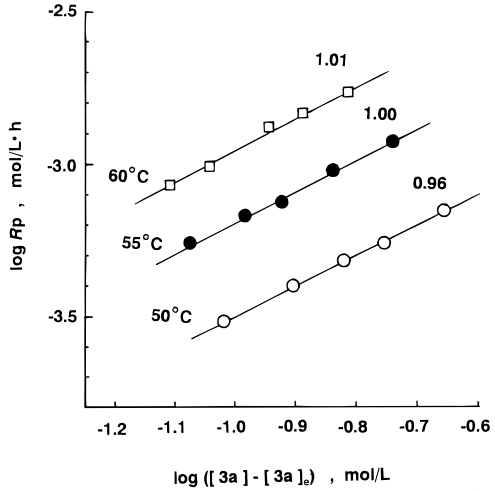

Figure 6. log−log plots of R_p versus ([**3a**] − [**3a**]$_e$) in chloroform at 50 (○), 55 (●), and 60 (□) °C, with a [AIBN] of 3.0×10^{-2} mol/L.

Table 1. Equilibrium Monomer Concentrations, [M]$_e$, of 3a−d, BzCQ, BCQ, and PSCQ

	10^{-3}[M]$_e$, mol/L						
temp, °C	**3a** (Me)	**3b** (Bu)	**3c** (iPr)	**3d** (sBu)	BzCQ	BCQ	PSCQ
50	101	147	178	200	29.5	4.46	9.2
55	126	174	211	243			
60	150	216	259	286	36.6	6.5	12.0

3.0×10^{-2} mol/L for **3c**, and 0.35−0.46 mol/L **3d** and an AIBN concentration of 3.0×10^{-2} mol/L for **3d**, respectively, gave good straight lines, and the [M]$_e$ values for **3b**−**d** were obtained according to the same procedure. All the [M]$_e$ values for **3a**−**d** are summarized in Table 1. The log−log plots of the effective monomer concentration, ([M] − [M]$_e$), versus R_p at various temperatures for the polymerization of **3a** give straight lines with slopes of 1.01 ± 0.05, as shown in Figure 6, different from the profile in Figure 3. The polymerization rate for **3a** at 60 °C is able to be expressed by the following equation

$$R_p = k[\mathrm{AIBN}]^{0.48\pm0.03}([\mathbf{3a}] - [\mathbf{3a}]_e)^{1.01\pm0.05} \quad (1)$$

where k is an apparent rate constant for the polymerization. This equation is identical to eq 2 for the rate of the radical polymerization under consideration of the depolymerization,[5] where f, k_d, k_p, k_t, [I], [M], and [M]$_e$ are the initiator efficiency, the rate constants for the decomposition of initiator, the propagation reaction, and the termination reaction, the initiator concentration, the monomer concentration, and the equilibrium monomer concentration, respectively. It was concluded, therefore, that the polymerization of **3a** can be explained well in terms of the radical polymerization under serious influence of the depolymerization, as well as those of homopolymerizable substituted quinodimethanes[5,7] such as BzCQ, BCQ, and PSCQ.

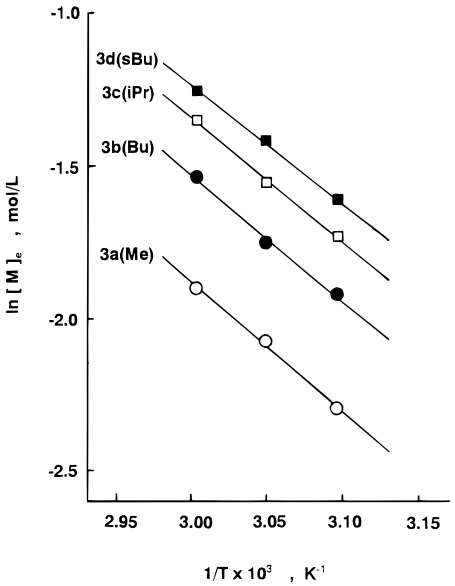

Figure 7. Plots of ln [M]$_e$ versus $1/T$ for the polymerization of **3a**−**d**, with a [AIBN] of 3.0×10^{-2} mol/L.

$$R_p = k_p(fk_d/k_t)^{1/2}[\mathrm{I}]^{1/2}([\mathrm{M}] - [\mathrm{M}]_e) \quad (2)$$

It is known that a ln value of an equilibrium monomer concentration, [M]$_e$, is related to a ceiling temperature, T_c, of polymerization according to eq 3,[12] where ΔH and

$$\ln [\mathrm{M}]_e = \Delta H/RT_c - \Delta S/R \quad (3)$$

ΔS are the enthalpy of polymerization and the entropy of polymerization, respectively, and R is the gas constant. The ln [M]$_e$ values were plotted against the reciprocal of the absolute polymerization temperature, $1/T$, for **3a**−**d**. Good straight lines are obtained, as shown in Figure 7. The slopes and intercepts of the lines give the ΔH and ΔS values for the polymerizations of **3a**−**d**. Their values obtained for **3a**−**d** are summarized in Table 2. The ΔH values for the polymerizations of **3a**−**d** vary with the change of the alkoxy group of **3a**−**d**, while the ΔS values are almost constant within the 85−90 J/(mol·K) range. Previously, we reported that substituted quinodimethanes such as 7,8-diacyl-7,8-dicyanoquinodimethanes (**1b**)[6] and 7,8-bis(alkylthio)-7,8-dicyanoquinodimethanes (**1c**)[7] have almost constant ΔS values of about 40 J/(mol·K), which are smaller than the corresponding values [105−130 J/(mol·K)][11] for vinyl and related monomers. The ΔS values for the polymerizations of **3a**−**d** are largely different from the corresponding values for the substituted quinodimethanes reported previously, probably being due to the difference in the structures between the 1,4-benzoquinone methides and the quinodimethanes, as the polymerization rates for both systems are measured by the same procedure.

Table 2. Enthalpy (Δ*H*) of Polymerization and Entropy (Δ*S*) of Polymerization for 3a−d and Substituent Constants

monomer	−Δ*H*, kJ/mol	−Δ*S*, J/(mol·K)	σ*	σ	*Es*	ΔΔ*H*, kJ/mol	ΔΔ*H* − 3*Es*, kJ/mol
3a (Me)	35.4	90.5	0.00	−0.17	0.00	0.0	0.00
3b (Bu)	34.4	90.5	−0.13	−0.151	−0.39	−1.0	+0.17
3c (iPr)	33.5	89.4	−0.19	−0.197	−0.47	−1.9	−0.49
3d (sBu)	32.0	85.6	−0.21	−0.12	−1.13	−3.4	−0.01

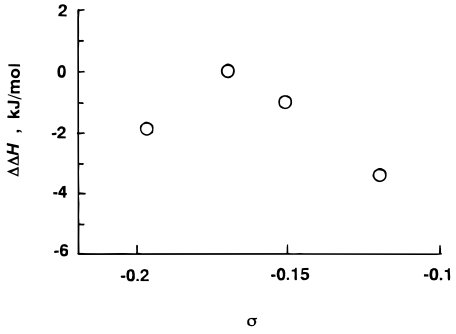

Figure 8. Hammett plot of ΔΔ*H* versus σ for the polymerization of **3a**−**d**.

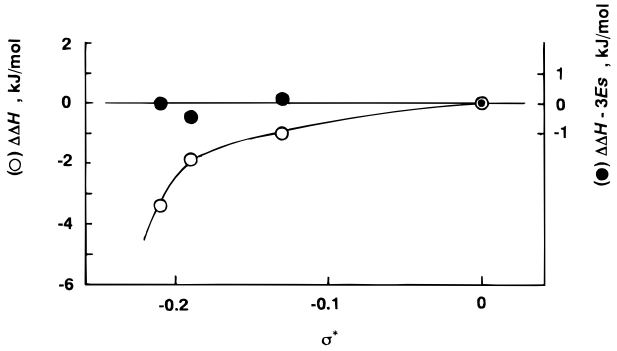

Figure 9. Hammett plot (○) of ΔΔ*H* versus σ* and Taft plot (●) of ΔΔ*H* − 3*Es* versus σ* for the polymerizations of **3a**−**d**.

Substituent Effect on Polymerizability. To get information about the influence of the alkoxy groups at position 7 on the polymerizability of the substituted 1,4-benzoquinone methides, the Δ*H* values for the polymerizations of **3a**−**d** were examined by means of a linear free energy relationship such as the Hammett equation (4)[13] and the Taft equation (5)[13] where ρ is a constant

$$\Delta H = \rho\sigma \tag{4}$$

$$\Delta H = \rho^*\sigma^* + \delta Es \tag{5}$$

for the specific reaction, σ is a polar substituent constant, generally referred to as the Hammett substituent constant, ρ* is a constant giving the susceptibility of the reaction to the polar effect, σ* is a polar substituent constant of the substituent group to the methyl group, *Es* is a steric effect parameter of substituents, and δ is a constant giving the susceptibility of the reaction to the steric effect. In Table 2 are listed the values of σ, σ*, and *Es* for the alkyl groups (R)[13] of the alkoxy (RO) substituents at position 7 of the substituted 1,4-benzoquinone methides. Here, for the polymerizations of **3a**−**d**, the Δ*H* value of **3a**, which has a methyl group as the alkyl group of the alkoxy substituent, is taken as the standard one and the ΔΔ*H* values are given as the differences between the Δ*H* value of **3a** and the Δ*H* values of **3b**, **3c**, and **3d**. To get quantitative information, a Hammett plot was made, as shown in Figure 8. A linear correlation is not obtained between the ΔΔ*H* values and Hammett constants σ for different substituents. The plot (○) of ΔΔ*H* versus σ* also does not display a linear correlation, as shown in Figure 9. However, if the steric hindrance is taken into account by subtracting 3*Es* from the ΔΔ*H* values, the plot (●) of ΔΔ*H* − 3*Es* versus σ* becomes a straight line with zero slope; i.e., ρ* = 0. It is obvious, therefore, that the free energy of polymerization for the substituted 1,4-benzoquinone methides (**3a**−**d**) is dependent only upon the steric hindrance of the substituents and is not influenced any more by the polar effect of the substituents; that is, the homopolymerizability of **3a**−**d** is exclusively determined by the steric hindrance of the alkoxy groups. This conclusion is in agreement with that from studies of the substituted quinodimethanes such as the 7,8-diacyl-7,8-dicyanoquinodimethanes and the 11,12-bis(alkylthio)-11,12-dicyano-2,6-naphthoquinodimethanes, though the contribution (3*Es*) of the steric hindrance on the polymerizability of the substituted 1,4-benzoquinone methides is smaller compared to those of the substituted quinodimethanes such as 7,8-diacyl-7,8-dicyanoquinodimethanes (4*Es*)[6] and 11,12-bis(alkylthio)-11,12-dicyano-2,6-naphthoquinodimethanes (10*Es*),[14] probably due to the different chemical structures. Therefore, the steric hindrance effect of substituents at the exocyclic positions on the polymerizability is probably one important feature for the polymerization of the quinonoid family.

Copolymerization of 3a with Styrene. The copolymerization of **3a** with styrene in the presence of AIBN was carried out in chloroform at 60 °C with two different monomer concentrations ([**3a**] = 0.30 and 0.06 mol/L) above and below the equilibrium monomer concentration of **3a** ([**3a**]$_e$ = 0.150 mol/L at 60 °C; see Table 1). All copolymers were obtained as white powders, which are soluble in benzene, dichloromethane, acetone, chloroform, and tetrahydrofuran but insoluble in hexane. The results of the copolymerizations are summarized in Table 3, and their copolymerization composition diagrams are shown in Figure 10. The copolymerization at a given monomer concentration of 0.30 mol/L above the equilibrium monomer concentration of **3a** took place in a random fashion, while the copolymerization at a given monomer concentration of 0.06 mol/L below the equilibrium monomer concentration of **3a** occurred in an alternating fashion. The results of the copolymerization at a given monomer concentration above the equilibrium monomer concentration of **3a** were analyzed according to the curve-fitting,[15] the intersection,[16] and Kelen−Tüdös methods[17] to obtain the monomer reactivity ratios: r_1(**3a**) = 4.70 ± 0.85 and r_2(styrene) = 0.01 ± 0.01 at 60 °C. Since the monomer concentration of 0.30 mol/L of **3a** in this copolymerization is much higher than its equilibrium monomer concentration, the copolymerization of **3a** with styrene at 60 °C can be regarded to take place without influence of the depolymerization. Thus, Alfrey−Price's *Q* and *e* values of **3a** were calculated on the basis of the monomer reactivity ratios to be 32 and +1.05, respectively, indicating that **3a** is a highly conjugative (reactive) and electron-accepting monomer. The fashion of the copolymerization of **3a**

Table 3. Copolymerizations of 3a with Styrene at Two Different Monomer Concentrations of 3a in Chloroform at 60 °C

run no.	monomer feed **3a**	monomer feed St	[**3a**], mol %	amt of solv, mL	amt of AIBN, mg	time, h	conv, %	elemental anal. % C	elemental anal. % N	copolym comp **3a**, mol%	$10^{-3}M_n$
					[**3a**] = 0.30 mol/L						
1	56.6	601.1	4.9	0.5	5.4	24	8.0	72.07	5.15	55.7	2.6
2	39.9	196.6	10.0	0.5	3.7	12	7.4	69.60	5.52	61.7	2.0
3	61.3	140.3	19.2	1.0	5.9	12	13.9	68.52	6.28	75.5	1.6
4	61.0	75.8	30.5	1.0	2.3	12	6.5	67.12	6.22	74.3	1.6
5	88.9	72.3	40.5	1.5	3.4	12	6.8	68.51	6.30	75.8	2.3
6	117.0	67.8	48.8	2.0	4.5	12	7.8	66.78	6.76	85.2	1.3
7	115.1	39.5	61.6	2.0	4.2	12	7.6	65.37	7.03	91.2	1.25
8	145.9	38.8	67.5	2.5	5.2	12	4.3	65.39	7.05	91.6	1.15
					[**3a**] = 0.06 mol/L						
9	51.1	545.2	4.9	4.0	1.3	24	4.0	69.65	5.03	53.6	1.6
10	47.2	228.5	10.3	4.0	1.0	64	6.6	70.56	5.10	54.9	1.25
11	53.0	116.0	20.1	4.5	1.1	64	5.7	68.04	5.18	56.2	1.25
12	50.9	63.8	30.7	4.5	2.3	62	10.0	73.37	4.81	50.5	2.20
13	79.8	44.9	49.4	7.0	2.0	64	6.1	70.39	5.02	53.7	1.25
14	90.7	31.2	61.5	8.0	4.1	63.5	10.8	73.24	4.76	49.8	1.45

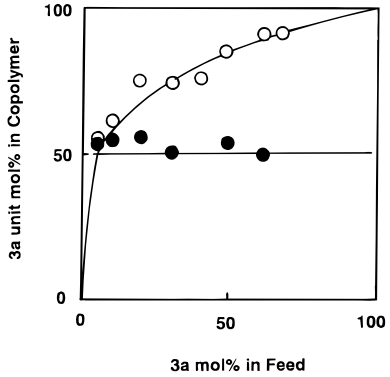

Figure 10. Copolymerization composition curves of **3a** with styrene in chloroform, with a [**3a**] of 0.30 mol/L (○) and 0.06 mol/L (●).

with styrene was found to change from random to alternating, when the **3a** concentration of 0.30 mol/L in monomer feed was reduced to 0.06 mol/L, at which **3a** does not homopolymerize due to the serious influence of the depolymerization. Previously, we reported that nonhomopolymerizable **2** could copolymerize with styrene in a perfectly alternating fashion.[8] Therefore, it is worth noting that the difference in the copolymerization fashion is determined depending on whether **3a** is homopolymerizable or not. That is, it indicates that this polymerization behavior could also be explained well in terms of the alternating copolymerization mechanism[5,18] proposed for the copolymerization of the substituted quinodimethanes with styrene. The mechanism is explained on the basis of the following scheme:

$$\sim\text{BQM}\bullet + \text{BQM} \rightleftarrows \sim\text{BQM}\bullet$$

$$\sim\text{BQM}\bullet + \text{St} \rightarrow \sim\text{St}\bullet$$

$$\sim\text{St}\bullet + \text{BQM} \rightarrow \sim\text{BQM}\bullet$$

$$\sim\text{St}\bullet + \text{St} \rightarrow \sim\text{St}\bullet$$

Substituted 1,4-benzoquinone methides (BQM) are much more conjugative (reactive) than styrene (St). Therefore, the polymer radical with the terminal St unit reacts almost exclusively with BQM. Then, the resulting polymer radical with the terminal BQM unit reacts with either BQM or St when the monomer concentration of BQM in the feed is higher than its equilibrium monomer concentration, leading to a random copolymerization. When the monomer concentration of BQM in the feed is lower than its equilibrium monomer concentration, the addition reaction of the resulting polymer radical with the terminal BQM unit to the BQM monomer does not occur because of the depolymerization. Here, the addition reaction of the resulting polymer radical with the terminal BQM unit to the St monomer is the slowest reaction because the most conjugative (least reactive) polymer radical reacts with the least conjugative (least reactive) monomer, corresponding to the most disadvantageous reaction in view of reaction energetic theory. However, the resulting polymer radical with the terminal BQM unit could undergo a cross-propagation reaction in favor of a strong charge-transfer interaction with the St monomer due to a great difference in polarity between the two reacting species, leading to an alternating copolymerization.

In summary, the kinetics for the polymerizations of 7-(alkoxycarbonyl)-7-cyano-1,4-benzoquinone methides was investigated in detail and their polymerizations were found to be a typical equilibrium polymerization reaction. On the basis of the equilibrium polymerization behavior, the ΔH and ΔS values for polymerizations of **3a**−**d** were determined. It was found that the ΔS values were almost constant regardless of the alkoxy substituents and the polymerizability of **3a**−**d** was significantly dependent upon the ΔH values. The ΔH values were analyzed by means of a linear free energy relationship such as the Taft equation, and the polymerizability of **3a**−**d** was found to be determined mainly by the steric hindrance of the substituents and to be independent of the polar effect. The change from random fashion to alternating for the copolymerization of **3a** with styrene above and below the equilibrium monomer concentrations of **3a** could be explained well in connection with the equilibrium polymerization behavior of **3a**. The polymerization behavior observed for the substituted 1,4-benzoquinone methides was very similar to that observed for the substituted quinodimethanes. It is concluded therefore that the polymerization behavior observed for both monomers is a general feature for the quinonoid family.

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