*Macromolecules* 1988, *21*, 1571–1579

through the normal $S_N2$ mechanism to form the polymer exclusively consisting of the trans units **6**.

In summary, the polymerization of **3** afforded the polymers having a cis unit content varying from 0 to 100% only with slight modifications of the polymerization conditions. The formation of the cis unit was reasonably interpreted in terms of the $S_N2$ type propagation involving a cyclic trialkyloxonium ion accompanied by oxonium exchange at the penultimate unit of the polymer chain. In the polymerization with lower initial monomer concentrations and at higher temperatures, the polymer consisting of the cis units is predominantly formed by thermodynamic control. In the polymerization with higher initial monomer concentrations and at lower temperatures, the polymer composed of the trans units is preferentially produced under the influence of kinetic control.

**Registry No.** **3**, 92420-59-2; **3** (diol), 34339-25-8; **3** (homopolymer), 114377-67-2; benzyl chloride, 100-44-7.

## References and Notes

(1) Schuerch, C. *Adv. Carbohydr. Chem. Biochem.* **1981**, *39*, 157.
(2) Sumitomo, H.; Okada, M. *Ring-Opening Polymerization*; Ivin, K. J., Saegusa, T., Eds.; Elsevier Applied Science: London, 1984; Vol. I, p 299.
(3) Sumitomo, H.; Okada, M. *Current Topics in Polymer Science*; Ottenbrite, R. M., Utracki, L. A., Inoue, S., Eds.; Carl Hanser Verlag: Munich, 1987; Vol. I, p 15.
(4) Okada, M.; Sumitomo, H.; Hibino, Y. *Polym. J.* **1974**, *6*, 256.
(5) Okada, M.; Sumitomo, H.; Komada, H. *Macromolecules* **1979**, *12*, 395.
(6) Okada, M.; Sumitomo, H.; Sumi, A. *Macromolecules* **1982**, *15*, 1238.
(7) Okada, M.; Sumitomo, H.; Hirasawa, T. *Macromolecules* **1985**, *18*, 2345.
(8) Sumitomo, H.; Okada, M. *Adv. Polym. Sci.* **1978**, *28*, 47.
(9) Sumitomo, H.; Okada, M. *Makromol. Chem., Macromol. Symp.* **1986**, *3*, 265.
(10) Ponomarenko, V. A.; Berman, E. L.; Sakharov, A. M.; Nysenko, Z. N. *Cationic Polymerization and Related Processes*; Goethals, E. J., Ed.; Academic: London, 1984; p 155.
(11) Zachoval, J.; Schuerch, C. *J. Am. Chem. Soc.* **1969**, *91*, 1165.
(12) Okada, M.; Sumitomo, H.; Sumi, A.; Sugimoto, T. *Macromolecules* **1984**, *17*, 2451.
(13) Okada, M.; Sumitomo, H.; Sumi, A. *Carbohydr. Res.* **1985**, *143*, 275.
(14) Although the formulas shown in this paper are of the D configuration, the monomer used is racemic, and therefore the polymers derived therefrom consist of structural units of both D and L configurations.
(15) Sweet, F.; Brown, R. K. *Can. J. Chem.* **1968**, *46*, 2289.
(16) Strivastava, R. M.; Brown, R. K. *Can. J. Chem.* **1970**, *48*, 830.
(17) Murray, T. P.; Sigh, V. P.; Brown, R. K. *Can. J. Chem.* **1971**, *49*, 2131.
(18) The splitting of the signal d′ is presumably due to the different diad placements of the D,L enantiomeric monomeric units in the polymer chain. Similar splittings of the signals are frequently observed in the $^{13}C$ NMR spectra of the polymers from 1 and their derivatives.[2,3,5,6]
(19) Gorin, P. A. J. *Adv. Carbohydr. Chem. Biochem.* **1981**, *38*, 13.
(20) Bock, K.; Pedersen, C. *Adv. Carbohydr. Chem. Biochem.* **1983**, *41*, 27.
(21) Jacobsen, S.; Moles, O. *Acta Chem. Scand., Ser. B* **1981**, *35*, 163.
(22) Gagnaire, D. *Carbohydr. Res.* **1976**, *51*, 140.
(23) Bock, K.; Pedersen, C. *J. Chem. Soc., Perkin Trans. 2* **1974**, 293.
(24) Gagnaire, D.; Voignon, M. *Makromol. Chem.* **1977**, *178*, 2321.
(25) Uryu, T.; Sakamoto, Y.; Hatanaka, K.; Matsuzaki, K. *Macromolecules* **1984**, *17*, 1307.
(26) Penczek, S.; Kubisa, P.; Matyjaszewski, K. *Adv. Polym. Sci.* **1980**, *37*, 1.
(27) Lemieux, R. U.; Morgan, A. R. *Can. J. Chem.* **1965**, *43*, 2205.
(28) Kirby, A. J. *The Anomeric Effect and Related Stereoelectronic Effects at Oxygen*; Springer-Verlag: New York, 1983; p 15.
(29) Penczek, S.; Matyjaszewski, K. *J. Polym. Sci., Polym. Symp.* **1976**, *56*, 255.
(30) Miki, T.; Higashimura, T.; Okamura, S. *J. Polym. Sci., A-1* **1970**, *8*, 157.

---

# Equilibrium Polymerizations of 7,8-Dibenzoyl-, 7,8-Diacetyl-, and 7,8-Dibutoxycarbonyl-7,8-dicyanoquinodimethane and Their Copolymerizations with Styrene: A New Concept on the Mechanism of Alternating Copolymerization

**Shouji Iwatsuki,* Takahito Itoh, Tatsuya Higuchi, and Katsuyuki Enomoto**

*Department of Chemical Research for Resources Faculty of Engineering, Mie University, Kamihama-cho, Tsu 514, Japan.* *Received August 18, 1987*

ABSTRACT: Kinetics of polymerization of 7,8-dibenzoyl-7,8-dicyanoquinodimethane (BzCQ), 7,8-diacetyl-7,8-dicyanoquinodimethane (AcCQ), and 7,8-dibutoxycarbonyl-7,8-dicyanoquinodimethane (BCQ) have been studied in chloroform solutions using 2,2′-azobis(isobutyronitrile) as an initiator. These polymerizations were found to be greatly influenced by depolymerization. The ceiling temperatures and the equilibrium monomer concentrations were determined. The values of enthalpy ($\Delta H$) and entropy changes ($\Delta S$) of the polymerization were found to be $\Delta H$ = 21.6 kJ/mol and $\Delta S$ = 37.5 J/K·mol for BzCQ, $\Delta H$ = 25.4 kJ/mol and $\Delta S$ = 36.9 J/K·mol for AcCQ, and $\Delta H$ = 26.4 kJ/mol and $\Delta S$ = 36.8 J/K·mol for BCQ. These $\Delta S$ values are one-third as large as the corresponding ones (100–130 J/K·mol) for vinyl and related compounds, suggesting one of the features of polymerization of quinodimethane compounds. Their copolymerizations with styrene were carried out at various temperatures to change in copolymerization fashion from random to alternating depending upon whether these quinodimethane compounds are homopolymerizable or not, implying an influence of depolymerization. A new concept on the mechanism of radical alternating copolymerization was proposed.

## Introduction

Previously it was reported that 7,8-dialkoxycarbonyl-7,8-dicyanoquinodimethanes (ACQ),[1-3] carrying two different electron-accepting substituents at each 7- and 8-position, are obtainable as stable crystal at room temperature, are homopolymerizable with free radical and anionic initiators, especially the latter of which such as butyllithium gives a high polymer with molecular weight above some millions, and are copolymerizable with styrene (St) in a random fashion. Very recently 7,8-dibenzoyl-7,8-dicyanoquinodimethane (BzCQ)[4] and 7,8-diacetyl-7,8-dicyanoquinodimethane (AcCQ),[4] carrying electron-ac-

0024-9297/88/2221-1571$01.50/0

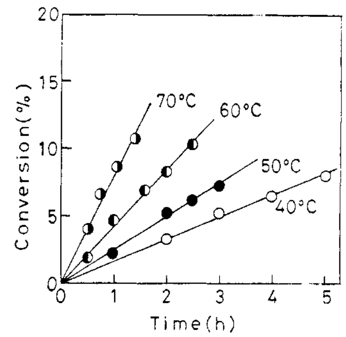

**Figure 1.** Time–conversion curves for the polymerization of BzCQ at various temperatures: 40 (○), 50 (●), 60 (◐), and 70 (◑) °C. [BzCQ] = 0.094 mol/L; [AIBN] = $3.30 \times 10^{-3}$ mol/L.

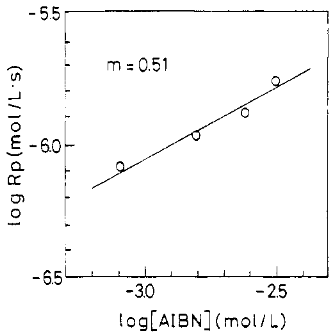

**Figure 2.** A log–log plot of $R_p$ versus [AIBN] for the polymerization of BzCQ in chloroform at 60 °C. [BzCQ] = 0.094 mol/L.

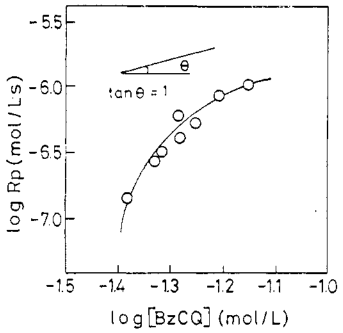

**Figure 3.** A log–log plot of $R_p$ versus [BzCQ] for the polymerization of BzCQ in chloroform at 60 °C. [AIBN] = $3.30 \times 10^{-3}$ mol/L.

cepting acyl groups instead of alkoxycarbonyl groups of ACQ, were successfully prepared as compounds with a polymerizability similar to that of ACQ.

In this work was studied a detailed kinetics of radical polymerizations of BzCQ, AcCQ, and 7,8-dibutoxycarbonyl-7,8-dicyanoquinodimethane (BCQ) to obtain features of the polymerizations of those stable substituted quinodimethane compounds. In addition, copolymerizations of these quinodimethane compounds with St were carried out in detail and their copolymerizations were found to change from a random to an alternating fashion when homopolymerizability of these quinodimethane compounds disappears. A new concept on the mechanism of alternating copolymerization was proposed.

## Experimental Section

**Materials.** BCQ,[3] BzCQ,[4] and AcCQ[4] were prepared according to the methods of the previous papers. St was washed with 2% aqueous sodium hydroxide solution and water, dried over barium oxide, stirred with calcium hydride at room temperature for 6 h, and then distilled under reduced pressure. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol. Chloroform and dichloromethane were refluxed over calcium hydride for 12 h and, then, distilled.

**Homopolymerization Kinetics.** A given amount of monomer such as BzCQ, AcCQ, and BCQ, chloroform as solvent, and AIBN as initiator were placed in an ampule which was degassed completely by the freeze–thaw method (repeatedly 3 times) and sealed. The ampule was set in a bath thermostated at temperatures of 40, 50, 60, or 70 °C for the time of polymerization and then opened. For the cases of BzCQ and AcCQ, the concentration of the compounds was measured spectrophotometrically with absorption bands of 398 and 414 nm, characteristic of BzCQ and AcCQ, respectively. Polymerization rate, $R_p$, was calculated from the amounts of the monomer consumed for a given time. In the case of BCQ, the reaction mixture was poured into excess hexane to precipitate the polymer, which was dried under reduced pressure and weighed. Polymerization rate, $R_p$, was calculated from the weight of the polymer obtained for a given time.

**Copolymerization Procedure.** Given amounts of monomers, chloroform, or dichloromethane as solvent, AIBN as initiator, and two drops of acetic acid as anionic polymerization inhibitor were placed in an ampule, which was degassed completely by the freeze–thaw method (repeatedly 3 times) and sealed. The ampule was placed in a bath thermostated at temperatures of 40, 50, 60, or 70 °C for the time of polymerization and then opened. The reaction mixture was poured into excess hexane to precipitate the copolymer. For purification, the copolymer obtained was dissolved in a small amount of dichloromethane and the resulting solution was poured into excess hexane to precipitate the copolymer again. This procedure was repeated more than 3 times. The copolymer was dried under reduced pressure to constant weight.

**Characterization.** Copolymer composition was established by elemental analysis. The number-average molecular weight ($\bar{M}_n$) of the copolymers was determined by gel permeation chromatography (GPC) with a series of columns, G 2500H and G 3000H, using standard polystyrenes as reference and tetrahydrofuran as eluent.

## Results and Discussion

**Kinetic Study of Radical Polymerization.** Relationships of the polymer yield versus time of polymerization, so-called time–conversion curves, for the homopolymerizations of BzCQ at 40, 50, 60, and 70 °C are shown in Figure 1. The polymer yield increases linearly with time of polymerization at these temperatures of polymerization. For the homopolymerizations of AcCQ at 40, 50, and 60 °C and BCQ at 50, 60, and 70 °C, the time–conversion curves also are found to be linear. A log–log plot of homopolymerization rate, $R_p$, versus initiator concentration, [AIBN], for the polymerization of BzCQ at 60 °C displays a good straight line with a slope of 0.51 as shown in Figure 2. The log–log plots for the polymerizations of AcCQ ([AcCQ] = 0.025 mol/L, AIBN concentration region from $0.29 \times 10^{-3}$ to $1.15 \times 10^{-3}$ mol/L) and BCQ ([BCQ] = 0.014 mol/L, AIBN concentration region from $0.86 \times 10^{-4}$ to $9.20 \times 10^{-4}$ mol/L) also give good straight lines with slopes of 0.49 and 0.48, respectively. It is concluded therefore that these polymerizations are compatible with the conventional radical polymerization rate equation, predicting a square-root dependence on initiator concentration. A log–log plot of polymerization rate, $R_p$, versus monomer concentration, [BzCQ], for the polymerization of BzCQ at 60 °C does not display a straight line as shown in Figure 3. In the monomer concentration range of BzCQ above $6.3 \times 10^{-2}$ mol/L, this plot appears to be a straight line with a slope of 1, whereas in the range below $6.3 \times 10^{-2}$ mol/L, its slope deviates greatly, the less concentration the steeper the slope. In other words, in the high monomer concentration region, the polymerization rate, $R_p$, shows a first-order dependence on monomer concentration as conventional radical polymerization while in the low monomer concentration region it exhibits a much higher order dependence on monomer concentration. The log–log plots of polymerization rate, $R_p$, versus monomer concentration

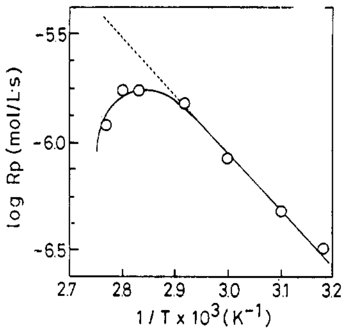

**Figure 4.** Plot of log $R_p$ versus $1/T$ for the polymerization of BzCQ in chloroform. [BzCQ] = 0.069 mol/L; [AIBN] = $3.30 \times 10^{-3}$ mol/L.

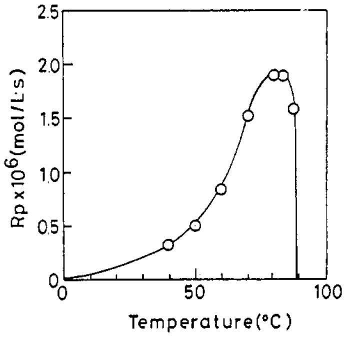

**Figure 5.** Plot of $R_p$ versus $T$ for the polymerization of BzCQ. [BzCQ] = 0.069 mol/L; [AIBN] = $3.30 \times 10^{-3}$ mol/L.

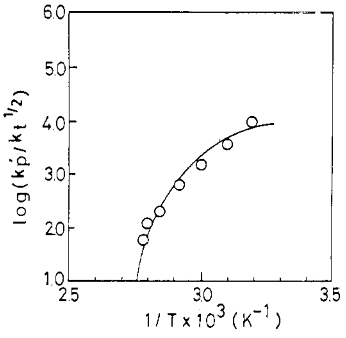

**Figure 6.** Plot of log $(k_p'/k_t^{1/2})$ versus $1/T$ for the polymerization of BzCQ. [BzCQ] = 0.069 mol/L; [AIBN] = $3.30 \times 10^{-3}$ mol/L.

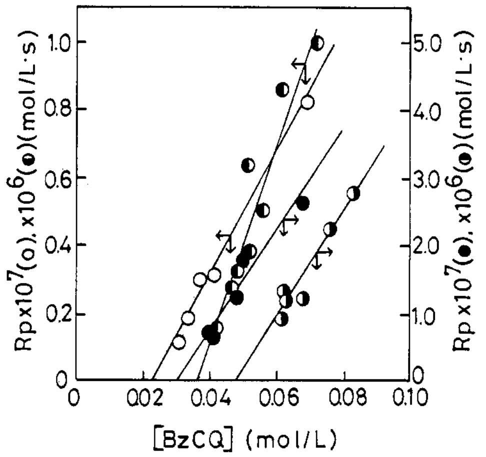

**Figure 7.** Plots of $R_p$ versus [BzCQ] for the polymerization of BzCQ in chloroform at various temperatures: 40 (○), 50 (●), 60 (◐), and 70 (◑) °C. [AIBN] = $3.30 \times 10^{-3}$ mol/L.

for the polymerization at 60 °C of AcCQ (AcCQ concentration region from $1.26 \times 10^{-2}$ to $1.57 \times 10^{-2}$ mol/L, [AIBN] = $1.44 \times 10^{-4}$ mol/L) and of BCQ (BCQ concentration region from $8.53 \times 10^{-3}$ to $1.42 \times 10^{-2}$ mol/L, [AIBN] = $3.04 \times 10^{-4}$ mol/L) show profiles similar to the polymerization of BzCQ. As shown in Figure 4, a plot, so-called Arrhenius plot, of log $R_p$ versus the reciprocal of the absolute polymerization temperature, $1/T$, for the polymerization of BzCQ with monomer concentration of 0.069 mol/L, is a good straight line at the polymerization temperature below 75 °C; from a slope of which apparent overall activation energy of the polymerization of BzCQ was calculated to be 46.9 kJ/mol. On the other hand, at the polymerization temperature above 75 °C it deviates greatly from a straight line, indicating a significant decrease instead of increase in polymerization rate, $R_p$, with temperature of polymerization. Similar plots of log $R_p$ versus $1/T$ for the polymerization of AcCQ with monomer concentration of 0.0177 mol/L and initiator concentration of $1.44 \times 10^{-4}$ mol/L and BCQ with monomer concentration of 0.014 mol/L and initiator concentration of $3.04 \times 10^{-4}$ mol/L showed the same profile, giving good straight lines in the region of polymerization temperature below 70 and 85 °C, respectively, from slopes of which apparent overall activation energies of the polymerizations were calculated to be 54.1 and 42.6 kJ/mol, respectively. However, in the region of polymerization temperature above 70 and 85 °C, values of $R_p$ were found to decrease significantly with temperature. Relationship of polymerization temperature, $T$, versus polymerization rate, $R_p$, for the polymerization of BzCQ with monomer concentration of 0.069 mol/L is shown in Figure 5. $R_p$ increases with polymerization temperature in the region of temperature below 80 °C, whereas it decreases sharply with polymerization temperature in the region of temperature above 80 °C and its extrapolation to the rate of zero gives the polymerization temperature of about 89 °C, above which the polymerization does not take place apparently. Therefore, it is obvious in these polymerizations that both dependences of $R_p$ on monomer concentration and on polymerization temperature seriously deviate from those for the conventional radical polymerization, suggesting a great contribution of depolymerization to those polymerizations at the high temperature and low monomer concentration. The ceiling temperatures, $T_c$, in the radical polymerizations of BzCQ, AcCQ, and BCQ were determined according to the method of Otsu et al.[5] For the polymerization of BzCQ with monomer concentration of 0.069 mol/L, log values of apparent polymerization rate constant, $k_p'/k_t^{1/2}$, where $k_t$ is a rate constant for termination reaction and $k_p'$ an overall rate constant for propagation reaction containing depolymerization, are plotted against reciprocals of absolute polymerization temperatures, $1/T$, as shown in Figure 6. The ceiling temperature, $T_c$, where a slope of the plot becomes perpendicular to the axis of $1/T$, i.e., polymerization rate becomes zero, are found to be 89 °C for the polymerization of BzCQ. From similar plots for the polymerizations of AcCQ with monomer concentration of 0.0177 mol/L and initiator concentration of $1.44 \times 10^{-4}$ mol/L and of BCQ with monomer concentration of 0.014 mol/L and initiator concentration of $3.04 \times 10^{-4}$ mol/L, values of $T_c$ for the polymerizations of AcCQ and BCQ are estimated to be 89 and 103 °C, respectively. Rates, $R_p$, of polymerizations of BzCQ at 40, 50, 60, and 70 °C are plotted against monomer concentration, [BzCQ], as shown in Figure 7 to give a linear relationship, where extrapolation to the rate of zero allows ones to obtain an equilibrium monomer concentration,

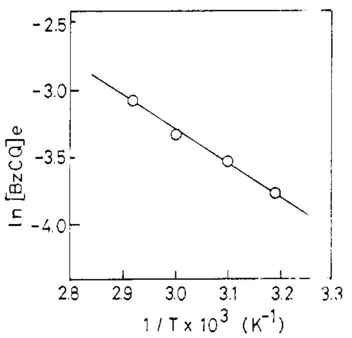

**Figure 8.** Plot of ln $[BzCQ]_e$ versus $1/T$ for the polymerization of BzCQ.

**Table I**
**Equilibrium Monomer Concentration, $[M]_e$, for the Polymerizations of BzCQ, AcCQ, and BCQ**

| temp, °C | $1/T \times 10^3$ | $[M]_e \times 10^3$, mol/L<br>BzCQ | AcCQ | BCQ |
|---|---|---|---|---|
| 40 | 3.19 | 23.6 | 4.98 | |
| 50 | 3.10 | 29.5 | 6.51 | 4.46 |
| 60 | 3.00 | 36.6 | 9.17 | 6.50 |
| 70 | 2.92 | 47.9 | 11.2 | 7.91 |

$[M]_e$, between the polymerization and the depolymerization at respective polymerization temperatures. The values of $[M]_e$ for the polymerizations of BzCQ, AcCQ, and BCQ at respective polymerization temperatures are summarized in Table I. For the polymerization of BzCQ, log, values of $[M]_e$ are plotted against reciprocal of absolute polymerization temperature, $1/T$, as shown in Figure 8 to give a good straight line. For the polymerization of AcCQ and BCQ, similar plots also showed good straight lines. From these linear relationships, $T_c$ values were found to be 88 °C for the polymerization of BzCQ with monomer concentration of 0.069 mol/L, 87 °C for that of AcCQ of 0.0177 mol/L, and 93 °C for that of BCQ of 0.014 mol/L. These values of $T_c$ estimated are in good agreement with the ones obtained according to the method of Otsu et al., indicating that the radical polymerizations of BzCQ, AcCQ, and BCQ consist of only four elementary reactions such as initiation, propagation, termination, and depolymerization, and do not suffer seriously from any other side reactions. The values of $T_c$ for the polymerizations of BzCQ, AcCQ, and BCQ are summarized in Table II, together with the corresponding values of St, methyl methacrylate (MMA), and α-methylstyrene (α-MeSt) for comparison. The relationship between an equilibrium monomer concentration, $[M]_e$, and a reciprocal of ceiling temperature, $1/T_c$, is shown in Figure 8 to be linear as expressed by the equation[6]

$$\ln [M]_e = \Delta H/RT_c - \Delta S/R \tag{1}$$

where $\Delta H$ and $\Delta S$ are enthalpy and entropy changes for polymerization between the monomer and the polymer, respectively, and $R$ is the gas constant. Values of enthalpy change, $\Delta H$, and entropy change, $\Delta S$, for the polymerizations of BzCQ, AcCQ, and BCQ are summarized in Table II, together with ceiling temperature, $T_c$, at a monomer concentration, [M], and also with the corresponding ones of St, MMA and α-MeSt for comparison. It is well-known[6] that entropy changes, $\Delta S$, for polymerization of vinyl and related monomers are relatively insensitive to individual monomer structure within the range 105–130 J/K·mol, whereas enthalpy changes, $\Delta H$, for polymerization vary over a wide range. It can be pointed out that $\Delta S$ values for the BzCQ, AcCQ, and BCQ are as almost constant as about 40 J/K·mol, which is about one-third as large as the corresponding values for vinyl and related monomers, indicating that these quinodimethane compounds fall under a class of monomers different from vinyl and related compounds. Moreover, it is apparent that values of the enthalpy change, $\Delta H$, for the polymerization of BzCQ, AcCQ, and BCQ are much smaller than that of α-MeSt, probably to one of the lowest value of $\Delta H$ among vinyl and related compounds. The polymerization with low enthalpy change is more seriously subjected depolymerization at the higher polymerization temperature or at the lower monomer concentration as expressed obviously in the relationship of eq 1. Values of $T_c$ for the polymerizations of BzCQ, AcCQ, and BCQ with the high monomer concentration of 1.0 mol/L are in the region 300–450 °C, much higher than the corresponding ones for MMA (160 °C) and α-MeSt (7.5 °C), especially AcCQ and BCQ exhibiting values of Tc as high as the one for St (389 °C). On the other hand, in the case of low monomer concentration of $5 \times 10^{-3}$ mol/L, values of $T_c$ drop down as low as room temperature. For the polymerization of these quinodimethane compounds, it is conceivable that in spite of a small change in enthalpy, negative change takes place in free energy change of polymerization because of a much smaller change in entropy.

**Table II**
**Ceiling Temperatures, $T_c$, Enthalpy Changes, $\Delta H$, and Entropy Changes, $\Delta S$, for Polymerizations of BzCQ, AcCQ, BCQ, St, MMA, and α-MeSt**

| monomer | [M], mol | $T_c$, °C | $-\Delta H$, kJ/mol | $-\Delta S$, J/K·mol |
|---|---|---|---|---|
| BzCQ | 0.069 | 88 | 21.6 | 37.5 |
| | 1.0 | 301.5 | | |
| AcCQ | 0.0177 | 87 | 25.4 | 36.9 |
| | 1.0 | 415 | | |
| BCQ | 0.0141 | 93 | 26.4 | 36.8 |
| | 1.0 | 442 | | |
| St | 0.00091 | 150 | 66.5 | 112 |
| | 1.0 | 389 | | |
| MMA | 0.82 | 155.5 | 58.5 | 130 |
| | 1.0 | 160 | | |
| α-MeSt | 0.76 | 0 | 33.5 | 130 |
| | 1.0 | 7.5 | | |

A rate of radical polymerization under consideration of the depolymerization can be obtained in the following reaction scheme:

Initiation

$$I \xrightarrow{k_d} 2R^\bullet \qquad -d[I]/dt = k_d[I] \tag{2}$$

$$R^\bullet + M \xrightarrow{k_i} M^\bullet \qquad d[M^\bullet]/dt = k_i[R^\bullet][M] = 2fk_d[I] \tag{3}$$

where $f$, $k_d$, and $k_i$ are the initiator efficiency, the rate constant for the decomposition of initiator, I, and the rate constant for the initiation reaction, respectively. M refers to monomer.

Propagation

$$M^\bullet + M \underset{k_{-p}}{\overset{k_p}{\rightleftharpoons}} M^\bullet$$

$$-d[M]/dt = k_p[M^\bullet][M] - k_{-p}[M^\bullet] \tag{4}$$

where $k_p$ and $k_{-p}$ are the rate constants for the propagation and the depolymerization reactions, respectively. $M^\bullet$ refers to polymer radical.

Termination

$$2M^\bullet \xrightarrow{k_t} P \qquad -d[M^\bullet]/dt = 2k_t[M^\bullet]^2 \tag{5}$$

where $k_t$ is the rate constant for the termination reaction. At equilibrium, the rate for the propagation reaction is equal to that for the depolymerization.

$$k_p[M]_e = k_{-p} \tag{6}$$

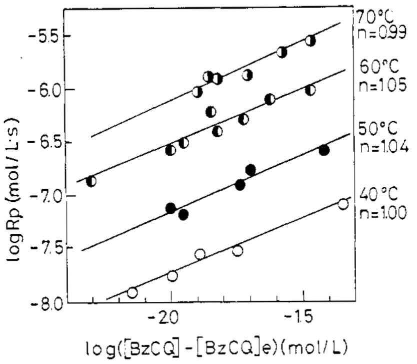

**Figure 9.** log-log plots of $R_p$ versus [BzCQ] − $[BzCQ]_e$ for the polymerization of BzCQ in chloroform at various temperatures: 40 (○), 50 (●), 60 (◐), and 70 (◑) °C. [BzCQ] = 0.069 mol/L; [AIBN] = 3.30 × $10^{-3}$ mol/L.

where $[M]_e$ refers to the equilibrium monomer concentration. By substitution of eq 6 into 4,

$$-d[M]/dt = k_p[M^\bullet]([M] - [M]_e) \quad (7)$$

Assuming the steady state of radical concentration,

$$2fk_d[I] = 2k_t[M^\bullet]^2$$

hence

$$[M^\bullet] = (fk_d[I]/k_t)^{1/2} \quad (8)$$

Combining eq 7 and 8, the overall rate of polymerization is given by the equation:

$$R_p = k_p(fk_d/kt)^{1/2}[I]^{1/2}([M] - [M]_e) \quad (9)$$

Since equilibrium monomer concentration, $[BzCQ]_e$, for the polymerization of BzCQ at 60 °C is 0.0366 mol/L (see Table I), the log–log plot of modified monomer concentration, [BzCQ] − $[BzCQ]_e$, versus rate of polymerization, $R_p$, for the polymerization of BzCQ at 60 °C gives a straight line with a slope of 1.05 in wide monomer concentration range is shown in Figure 9. The corresponding plots at different polymerization temperatures such as 40, 50, and 70 °C also gave straight lines with a slope of about 1.0. Moreover, in the polymerizations of AcCQ and BCQ where equilibrium monomer concentrations, $[AcCQ]_e$ and $[BCQ]_e$, are 9.17 × $10^{-3}$ and 6.50 × $10^{-3}$ mol/L, respectively, log–log plots of modified monomer concentration, [M] − $[M]_e$, versus rate of polymerization, $R_p$, for the polymerizations of AcCQ and BCQ at 60 °C gave straight lines with slopes of 1.00 and 1.01, respectively. Therefore, overall rates of the polymerizations of BzCQ, AcCQ, and BCQ are expressed by the following equations:

$$R_p = k[AIBN]^{0.51}([BzCQ] - [BzCQ]_e)^{1.05} \quad (10)$$

$$R_p = k[AIBN]^{0.49}([AcCQ] - [AcCQ]_e)^{1.00} \quad (11)$$

$$R_p = k[AIBN]^{0.48}([BCQ] - [BCQ]_e)^{1.01} \quad (12)$$

where $k = k_p(fk_d/kt)^{1/2}$ is an overall rate constant for the polymerization reaction. Surely these polymerizations of BzCQ, AcCQ, and BCQ are explained well in terms of the conventional polymerization reaction scheme plus depolymerization.

**Copolymerizations of BzCQ, AcCQ, and BCQ with St.** The results of the copolymerizations of BzCQ with St at 40, 50, and 60 °C, those of AcCQ with St at 40, 50, 60, and 70 °C, and those of BCQ with St at 50, 60, and 70 °C are summarized in Tables III, IV, and V, respectively, and their copolymerization composition diagrams are shown in Figures 10, 11, and 12, respectively. All of those results were treatable without appreciable deviation with the intersection,[7] the integrated copolymerization equation,[7] and the Kelen–Tüdös[8] methods, all of which are based on the terminal model equation of the copolymerization under the prerequisite that a reactivity of a polymer radical is determined only by the terminal monomer unit. It is certain that their copolymerizations take place in a random fashion and accord exactly with the terminal model equation of the copolymerization. The monomer reactivity ratios obtained are listed in Table VI. Since monomer concentrations of these quinodimethane compounds were employed above 0.025 mol/L in those copolymerizations, the copolymerizations of AcCQ and BCQ with St below 60 °C were considered not to be seriously affected by the depolymerization. Alfrey–Price's Q − e values were calculated by using monomer reactivity ratios at 50 °C to be Q = 14.9 and e = +1.07 for AcCQ and Q = 9.3 and e = +0.8 for the BCQ, without influence of the depolymerization. AcCQ and BCQ are much higher conjugative (reactive) monomers than St and are as electron accepting as acrylonitrile and alkyl acrylates.

The log values of monomer reactivity ratios are plotted against the reciprocal of absolute polymerization tem-

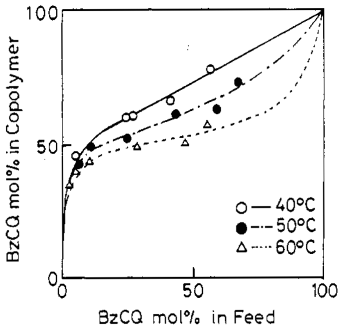

**Figure 10.** Composition diagrams for the copolymerization of the BzCQ–St system at various temperatures: 40 (○), 50 (●), and 60 (△) °C.

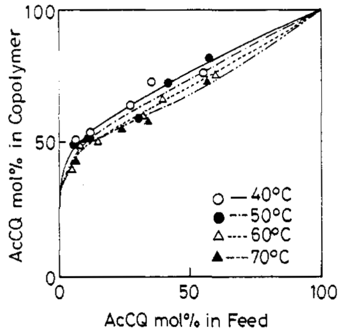

**Figure 11.** Composition diagrams for the copolymerization of the AcCQ–St system at various temperatures: 40 (○), 50 (●), 60 (△), and 70 (▲) °C.

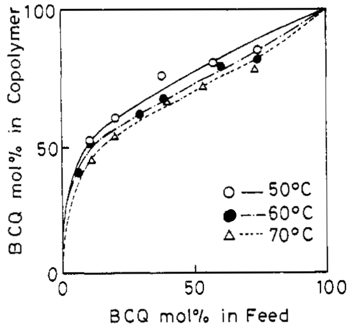

**Figure 12.** Composition diagrams for the copolymerization of the BCQ–St system at various temperatures: 50 (○), 60 (●), and 70 (△) °C.

**Table III**
**Copolymerization[a] of BzCQ with St in Dichloromethane at Various Temperatures**

| | monomer feed | | | | | copolymer compn | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | anal., % | | | | |
| run | BzCQ, mg | St, mg | BzCQ, mol % | time, h | convn, % | H | C | N | BzCQ, mol % | $\bar{M}_n/10^3$[b] |
| | | | | | 40 °C | | | | | |
| 1 | 31.83 | 169.80 | 5.1 | 12.25 | 10.3 | 4.64 | 82.38 | 5.75 | 45.4 | 18 |
| 2 | 80.10 | 70.94 | 24.5 | 12.5 | 8.4 | 4.31 | 81.15 | 6.50 | 60.3 | 17 |
| 3 | 92.17 | 72.50 | 26.8 | 12.5 | 6.0 | 4.29 | 81.07 | 6.53 | 61.0 | 17 |
| 4 | 116.06 | 47.26 | 41.4 | 12.5 | 7.8 | 4.08 | 80.75 | 6.75 | 66.4 | 18 |
| 5 | 153.58 | 33.61 | 56.8 | 12.5 | 9.9 | 3.92 | 80.37 | 7.17 | 78.6 | 17 |
| | | | | | 50 °C | | | | | |
| 6 | 55.55 | 222.25 | 6.1 | 18.5 | 11.5 | 4.57 | 82.90 | 5.58 | 42.7 | 6.8 |
| 7 | 47.08 | 114.07 | 10.6 | 19.5 | 13.8 | 4.59 | 82.31 | 5.97 | 49.4 | 8.6 |
| 8 | 115.25 | 102.74 | 24.4 | 19.0 | 15.2 | 4.57 | 82.25 | 6.13 | 52.4 | 7.4 |
| 9 | 114.32 | 43.43 | 43.1 | 17.5 | 14.7 | 4.51 | 81.32 | 6.55 | 61.5 | 7.6 |
| 10 | 242.55 | 48.83 | 58.8 | 13.5 | 14.1 | 4.21 | 81.51 | 6.64 | 63.6 | 6.6 |
| 11 | 223.00 | 30.97 | 67.4 | 12.5 | 10.5 | 4.07 | 80.79 | 7.01 | 73.7 | 3.1 |
| | | | | | 60 °C | | | | | |
| 12 | 44.39 | 465.28 | 2.7 | 10.0 | 9.1 | 5.04 | 84.25 | 4.95 | 33.8 | 11.6 |
| 13 | 46.92 | 268.03 | 4.8 | 12.0 | 14.7 | 4.94 | 83.27 | 5.27 | 38.4 | 4.0 |
| 14 | 54.65 | 138.26 | 10.2 | 8.5 | 12.4 | 4.86 | 82.81 | 5.63 | 43.5 | 5.6 |
| 15 | 121.34 | 87.70 | 28.5 | 7.0 | 10.0 | 4.26 | 82.87 | 5.92 | 48.4 | 5.4 |
| 16 | 145.47 | 47.47 | 46.8 | 3.5 | 8.0 | 4.44 | 82.80 | 6.00 | 49.9 | 4.6 |
| 17 | 213.84 | 49.14 | 55.6 | 3.5 | 9.3 | 4.29 | 81.56 | 6.36 | 57.2 | 2.7 |

[a] Solvent, 5 mL; initiator, AIBN 1 mg. [b] Determined by GPC; THF eluent.

**Table IV**
**Copolymerization[a] of AcCQ with St in Chloroform at Various Temperatures**

| | monomer feed | | | | | copolymer compn | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | anal., % | | | | | |
| run | AcCO, mg | St, mg | AcCO, mol % | time, h | convn, % | H | C | N | AcCQ, mol % | $\bar{M}_n/10^3$[b] | solvent, mL |
| | | | | | 40 °C | | | | | | |
| 1 | 29.48 | 200.77 | 6.0 | 3.5 | 7.9 | 5.57 | 77.77 | 8.22 | 50.4 | 9.7 | 5 |
| 2 | 30.15 | 98.25 | 11.8 | 3.5 | 8.3 | 4.94 | 76.45 | 8.55 | 53.8 | 3.6 | 5 |
| 3 | 34.88 | 42.13 | 26.6 | 3.5 | 10.2 | 4.78 | 74.95 | 9.26 | 61.9 | 4.5 | 6 |
| 4 | 45.91 | 36.35 | 35.6 | 3.5 | 10.2 | 4.49 | 73.89 | 10.13 | 73.0 | 3.6 | 8 |
| 5 | 57.54 | 20.79 | 54.8 | 3.5 | 9.3 | 4.10 | 72.88 | 10.34 | 76.1 | 2.4 | 10 |
| | | | | | 50 °C | | | | | | |
| 6 | 26.91 | 205.54 | 5.4 | 3.0 | 10.3 | 5.51 | 77.21 | 8.16 | 49.7 | 9.0 | 5 |
| 7 | 29.55 | 97.70 | 11.7 | 1.5 | 9.4 | 4.67 | 77.18 | 8.38 | 52.0 | 6.6 | 5 |
| 8 | 40.24 | 40.93 | 30.1 | 3.5 | 13.5 | 4.59 | 74.66 | 9.00 | 58.8 | 3.5 | 7 |
| 9 | 62.93 | 39.08 | 41.3 | 2.5 | 13.8 | 4.37 | 73.67 | 10.09 | 72.5 | 4.8 | 11 |
| 10 | 64.82 | 21.26 | 57.1 | 2.5 | 8.9 | 3.68 | 72.45 | 10.70 | 81.3 | 2.8 | 11 |
| | | | | | 60 °C | | | | | | |
| 11 | 25.21 | 261.22 | 4.1 | 1.0 | 7.5 | 5.11 | 78.88 | 7.14 | 40.3 | 22.0 | 5 |
| 12 | 36.68 | 199.69 | 8.0 | 1.0 | 10.6 | 5.15 | 77.18 | 8.15 | 49.6 | 9.0 | 6.5 |
| 13 | 37.72 | 96.10 | 14.6 | 1.0 | 10.5 | 5.01 | 76.87 | 8.27 | 50.9 | 5.2 | 6.5 |
| 14 | 42.59 | 43.36 | 30.0 | 1.0 | 7.3 | 4.92 | 75.67 | 9.09 | 59.8 | 3.5 | 7.5 |
| 15 | 51.24 | 35.00 | 39.0 | 1.0 | 6.6 | 4.39 | 73.97 | 9.63 | 66.4 | 3.9 | 9 |
| 16 | 66.22 | 19.73 | 59.5 | 1.0 | 8.7 | 4.43 | 73.27 | 10.30 | 75.5 | 3.5 | 11.5 |
| | | | | | 70 °C | | | | | | |
| 17 | 26.68 | 203.81 | 5.41 | 0.75 | 8.6 | 5.00 | 78.89 | 7.52 | 43.4 | 18.0 | 4.5 |
| 18 | 27.68 | 119.59 | 9.19 | 0.75 | 12.8 | 5.39 | 76.54 | 8.38 | 52.0 | 13.0 | 5.0 |
| 19 | 35.43 | 50.79 | 23.40 | 0.75 | 9.8 | 4.33 | 75.33 | 8.71 | 55.5 | 3.6 | 6 |
| 20 | 44.00 | 37.63 | 33.80 | 0.75 | 10.8 | 4.35 | 75.13 | 9.00 | 58.8 | 3.9 | 7.5 |
| 21 | 56.76 | 19.41 | 56.10 | 0.75 | 14.5 | 4.19 | 73.16 | 10.10 | 72.2 | 2.6 | 10 |

[a] [AcCQ] = 0.024 mol/L; AIBN 0.2 mg. [b] Determined by GPC; THF eluent.

perature for these copolymerizations as shown in Figure 13, where obviously the $r_1$ value of the copolymerization of BzCQ ($M_1$) with St goes down across unity to far below unity with increase in polymerization temperature. On the other hand, in conventional radical copolymerization, it is well-known that monomer reactivity ratios should approach unity with increase in polymerization temperature according to the reaction rate theory, as demonstrated in the radical copolymerization of St with methyl methacrylate by Lewis et al.[9] In the copolymerizations of AcCQ and BCQ ($M_1$) with St, similar behavior can be observed in temperature dependence of the $r_1$ value even though it is not so definite as that for the copolymerization of BzCQ with St. The fact that the $r_1$ value drops down below unity with increase in polymerization temperature contrary to the reaction rate theory of a conventional radical copolymerization, conceivably is closely associated with temperature dependence of the depolymerizations in polymerizations of BzCQ, AcCQ, and BCQ.

In the case of BzCQ, exhibiting the largest participation of depolymerization among these three (quinodimethane) compounds, the sharpest drop of $r_1$ value with temperature

Table V
Copolymerization[a] of BCQ with St in Chloroform at Various Temperatures

| | monomer feed | | | | | copolymer compn | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | anal., % | | | | |
| run | BCQ, mg | St, mg | BCQ, mol % | time, min | convn, % | H | C | N | BCQ, mol % | $\bar{M}_n/10^5$ [b] |
| | | | | | 50 °C | | | | | |
| 1 | 51.80 | 130.35 | 10.5 | 4.5 | 6.8 | 6.41 | 72.10 | 6.10 | 49.8 | 1.4 |
| 2 | 89.84 | 106.46 | 19.9 | 40 | 6.9 | 6.04 | 72.04 | 6.58 | 59.2 | 0.4 |
| 3 | 120.56 | 58.58 | 37.7 | 50 | 9.1 | 6.55 | 70.09 | 7.24 | 76.0 | 3.0 |
| 4 | 200.92 | 43.45 | 57.6 | 45 | 9.8 | 6.25 | 69.50 | 7.39 | 80.6 | 5.4 |
| 5 | 200.19 | 20.23 | 74.4 | 45 | 6.2 | 6.26 | 69.36 | 7.51 | 84.6 | 0.86 |
| | | | | | 60 °C | | | | | |
| 6 | 68.71 | 319.33 | 5.9 | 22 | 3.1 | 6.25 | 73.98 | 5.34 | 37.9 | 4.3 |
| 7 | 50.18 | 131.87 | 10.9 | 20 | 7.4 | 5.86 | 71.98 | 6.11 | 49.9 | 2.1 |
| 8 | 121.05 | 85.79 | 29.4 | 25 | 10.7 | 6.05 | 71.65 | 6.63 | 60.3 | 3.6 |
| 9 | 121.11 | 57.44 | 38.4 | 25 | 10.5 | 6.14 | 70.67 | 6.80 | 64.3 | 3.0 |
| 10 | 201.36 | 39.66 | 59.9 | 30 | 20.0 | 6.00 | 69.52 | 7.31 | 78.1 | 3.9 |
| 11 | 202.50 | 20.92 | 74.0 | 40 | 12.2 | 5.72 | 68.31 | 7.40 | 81.0 | 6.5 |
| | | | | | 70 °C | | | | | |
| 12 | 50.20 | 131.42 | 10.1 | 16 | 19.2 | 5.47 | 71.25 | 5.69 | 43.0 | 0.93 |
| 13 | 86.40 | 106.10 | 19.3 | 15 | 12.3 | 5.23 | 71.15 | 6.22 | 51.9 | 1.1 |
| 14 | 120.78 | 57.26 | 38.3 | 25 | 25.2 | 5.64 | 69.32 | 6.83 | 65.0 | 1.5 |
| 15 | 199.97 | 51.73 | 58.2 | 15 | 20.3 | 5.48 | 68.70 | 7.04 | 70.4 | 2.3 |
| 16 | 201.90 | 22.00 | 72.9 | 10 | 12.3 | 5.35 | 68.03 | 7.27 | 76.9 | 1.3 |

[a] Solvent 10 mL; initiator, AIBN 2 mg. [b] Determined by GPC; THF eluent.

Table VI
Monomer Reactivity Ratios of Copolymerizations of the BzCQ–St, AcCQ–St, and BCQ–St Systems at Various Temperatures

| system | MRR | 40 °C | 50 °C | 60 °C | 70 °C |
|---|---|---|---|---|---|
| BzCQ–St | $r_1$ | 1.78 ± 0.32 | 0.73 ± 0.2 | 0.16 ± 0.12 | |
| | $r_2$ | 0.025 ± 0.01 | 0.021 ± 0.015 | 0.026 ± 0.01 | |
| AcCQ–St | $r_1$ | 2.06 ± 0.23 | 2.02 ± 0.2 | 1.46 ± 0.24 | 1.12 ± 0.32 |
| | $r_2$ | 0.017 ± 0.014 | 0.015 ± 0.01 | 0.021 ± 0.012 | 0.023 ± 0.02 |
| BCZ–St | $r_1$ | | 2.59 ± 0.2 | 1.49 ± 0.16 | 1.21 ± 0.22 |
| | $r_2$ | | 0.030 ± 0.01 | 0.033 ± 0.017 | 0.048 ± 0.015 |

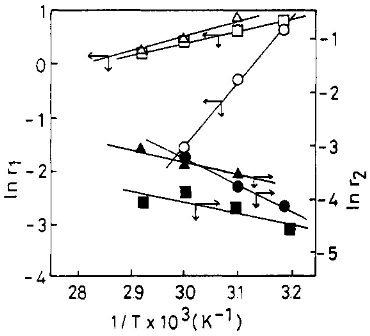

**Figure 13.** Relationships of ln $r_1$ and ln $r_2$ versus $1/T$ for the BzCQ–St ($r_1$ (○), $r_2$ (●)), AcCQ–St ($r_1$ (□), $r_2$(■)), and BCQ–St ($r_1$ (△), $r_2$ (▲)) systems.

of polymerization can be observed. In addition, it is interestingly pointed out that an alternating tendency, $r_1 \times r_2$, of those copolymerizations increases suddenly with temperature of polymerization due to the above-mentioned drop of $r_1$ value with temperature of polymerization. In other words, when the quinodimethane compound is not homopolymerizable due to large participation of depolymerization, it copolymerizes with St in an alternating fashion. It is emphasized, therefore, that the fashion of the copolymerization of the quinodimethane compound with St is determined depending upon whether it is homopolymerizable or not; when it is polymerizable, it copolymerizes in a random fashion, while when it is not polymerizable, it does so in an alternating fashion.

**A New Concept on the Mechanism of Alternating Copolymerization.** Two main classes of mechanisms have been proposed for an alternating copolymerization. The first one mentions that the cross propagations take place much faster than the homopropagation among four kinds of propagations in conventional radical copolymerization; a polymer radical with a terminal monomer unit reacts very fast with a different monomer in comparison with a rate that a polymer radical with a terminal monomer unit reacts with the same monomer. This mechanism is referred to as a free propagating mechanism because any complex formation is not considered between monomer and comonomer. As the reason why the cross propagation is very fast, Alfrey and Price[10] proposed an electrostatic interaction of permanent charges between polymer radical and reacting monomer, as exhibited in Alfrey-Price's well-known $Q,e$ scheme. Walling and Mayo[11] cast doubt on this concept because of no variation of monomer reactivity ratios on dielectric constant of the reaction medium and proposed a contribution of charge-transfer interaction in the transition state of the cross propagation, i.e., charge transfer from polymer radical to monomer (or vice versa) takes place instead of polarization, on the basis of the influence of nuclear substitution on the reactivity of substituted styrene in their copolymerization. As to another mechanism, Bartlett and Nozaki[12] reported a yellow coloration on mixing St and maleic anhydride and proposed a participation of the molecular complex into their alternating copolymerization. The mechanism is called the (charge-transfer) complex mechanism because an alternating copolymerization is regarded as a homopolymerization of the molecular (charge-transfer) complex between donor and acceptor monomers. In a series of our studies[13] on terpolymerizations involving an alternatingly copolymerizable monomer pair, it was pointed out that the experimental results obtained are explained more reasonably in terms of the complex mechanism rather than the free propagating mechanism.

Recently two problems incompatible with the complex mechanism have come out in our studies of polymerization behaviors of electron-accepting quinodimethane compounds. The first problem is on the difference in the polymerization behavior between nonhomopolymerizable compounds such as 7,7,8,8-tetramethoxycarbonylquinodimethane (TMCQ)[14] and 7,7,8,8-tetraethoxycarbonylquinodimethane (TECQ)[15] and homopolymerizable compounds such as BzCQ, AcCQ, and BCQ. The latter three compounds are much more electron accepting than the former two and the latter three are much more subject to charge-transfer interaction with St than the former two. If the charge-transfer complex would play an important role in the alternating copolymerization, the latter three should copolymerize with St in a more highly alternating fashion than the former two. Actually it was found, on the contrary, that the latter three copolymerize with St in a random fashion whereas the former two do in an alternating fashion. The second problem arises from the terpolymerization[14,15] of TMCQ or TECQ, 7,7,8,8-tetracyanoquinodimethane (TCNQ), and St, in which terpolymers obtained always contain 50 mol % TCNQ unit regardless of monomer feed ratios and the remaining parts consist of TMCQ or TECQ and St units, the ratio of which varies with monomer feed ratio. In this terpolymerization it was conceivable that TMCQ or TECQ and St react as donor monomers and TCNQ does as an acceptor monomer. All of monomer pairs such as TMCQ- or TECQ–TCNQ, TMCQ- or TECQ–St, and TCNQ–St among those three monomers are subject to alternating copolymerization and charge-transfer interaction.[14,15] From the standpoint of the complex mechanism, the complex between TMCQ or TECQ and St could not take part in the terpolymerization and the complexes between TMCQ or TECQ and TCNQ and between TCNQ and St would be much more reactive than the complex between TMCQ or TECQ and St. It is conceivable that these explanations are too much a one-sided view.

In a series of works on polymerization of stable, electron-accepting quinodimethane compounds, it is evident that the nonhomopolymerizable compounds such as TCNQ,[16] 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane,[17] 2,5,7,7,8,8-hexacyanoquinodimethane,[18] 11,11,12,12-tetracyanonaphtho-2,6-quinodimethane,[18] TMCQ,[14] and TECQ[15] are alternatingly and spontaneously copolymerizable with St, whereas the homopolymerizable compounds such as BzCQ, AcCQ, and BCQ are randomly copolymerizable with St. It is claimed therefore that the fashion of those copolymerizations with St is not determined by the electron-accepting character of the quinodimethane compounds but is determined depending upon whether the quinodimethane compound is homopolymerizable or not, as described in the preceding section. Moreover it is noteworthy that the copolymerizations of BzCQ, AcCQ, and BCQ with St change from a random to an alternating fashion when a participation of the depolymerization increases in the polymerizations of BzCQ, AcCQ, and BCQ with increasing temperature of polymerization.

An outline of the copolymerizations of BzCQ, AcCQ, and BCQ with St is given as follows: Naturally these quinodimethane compounds are much more highly conjugative (reactive) than St. They add to a propagating polymer radical with terminal St unit about 30 times as fast as St does, as calculated by the monomer reactivity ratios obtained, indicating that the polymer radical with terminal St unit reacts almost exclusively with the quinodimethane compound. Then, the resulting polymer radicals with the terminal quinodimethane unit are reactive with either the quinodimethane compound or St when the temperature of polymerization is below $T_c$ of the polymerization of the quinodimethane compound. Amounts of the quinodimethane compound and St reacted in this propagation are given from the $r_1$ value of the copolymerization, in general the former reacting much faster than the latter. This reactivity is explained well in terms of a reaction rate mechanism[7] similar to that of the conventional copolymerization of vinyl and related monomers. When temperature of polymerization is higher than $T_c$, the copolymerization changes from a random to an alternating fashion because the depolymerization of the quinodimethane participates more intensively in the polymerization. Thereupon it is intended to be pointed out in copolymerization that when a much more highly conjugative (reactive) monomer is not homopolymerizable owing to a participation of its depolymerization, the copolymerization takes place in an alternating fashion, whereas when it is homopolymerizable, the random copolymerization occurs. The homopolymerization character of the more highly conjugative (reactive) monomer of the monomer pair should be an important key to determine the fashion of the copolymerization.

Besides, it was pointed out in previous papers on alternating terpolymerizations of donor–donor–acceptor monomer[19] and donor–acceptor–acceptor monomer[20] systems that the reactivity of the monomer and the factor for the rate-determining process must be different between the random and alternating copolymerizations. In the random copolymerization, it is well-known that the reactivity of monomer is determined by both factors, conjugative (general reactivity) and polar effects, as expressed by the semiempirical equation of Alfey–Price's $Q,e$ scheme.[10] On the other hand, in the alternating copolymerization the monomer reactivity is controlled exclusively by the polar effect.[19] In addition, it is presumedly correlated with the product of polar values of donor and acceptor monomers, similar to the relationship of the Coulomb equation.[20] Furthermore, the monomer reactivity in the alternating copolymerization was found to be not compatible with quantum-theoretical parameters such as conjugation stabilization energy,[21] which, on the other hand, is related well with the monomer reactivity of the conventional random copolymerization.[22,23] Therefore it is conceivable that the rate-determining transition state of the alternating copolymerization is quite different from that of the random copolymerization, in which a polymer radical and a coming monomer are brought so close together that their electron clouds begin to overlap, the second perturbation taking place. Probably, in the alternating copolymerization it should be a state in which the polymer radical and the monomer are so far apart that Coulombic electrostatic attraction is dominant. Among possible addition processes in the copolymerizations of BzCQ, AcCQ, and BCQ with St, it is reasonably considered that, when the copolymerizations begin to occur in an alternating fashion, the addition reaction of the polymer radical with terminal quinodimethane unit to St monomer is the slowest reaction as the rate-determining process 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. This slowest addition should take place via a rate-determining transition state different from the productlike one of the conventional radical copolymerization as described above. Probably charge-transfer interaction between the polymer radical and St has to play an exclusive role in this addition, indicating one of the features of the alternating copolymerization.

For the case of the terpolymerization of TMCQ (TECQ), TCNQ, and St, since TCNQ is the most highly conjugative (reactive) monomer, the polymer radicals of terminal monomer unit other than TCNQ unit react exclusively with TCNQ due to their reaction energetic profiles and the resulting polymer radical of terminal TCNQ unit reacts with either TMCQ (TECQ) or St under favor of strong charge-transfer interaction between the polymer radical and the monomers. Therefore, the terpolymer always consists of 50 mol % of TCNQ unit regardless of monomer feed ratios. Probably this is a reasonable explanation.

Finally, a new concept is proposed on the mechanism of the radical alternating copolymerization as follows: (1) The first point is the fact that the more highly conjugative (reactive) monomer between copolymerizable monomer pair is not homopolymerizable, probably due to participation of the depolymerization. (2) The second point is the fact that the resulting polymer radical, which is considered as very stable, unreactive, undergoes cross propagation under favor of strong charge-transfer interaction with the comonomer due to a great difference in polarity between the two reacting species, corresponding to the rate-determining process of the alternating copolymerization. The reactivity of the alternating copolymerization is different from that of the conventional radical copolymerization and is determined exclusively with the polar character of the polymer radical and the monomer.

**Registry No.** BzCQ, 110458-74-7; AcCQ, 110458-72-5; BCQ, 99214-01-4; AIBN, 78-67-1; (BzCQ)(St) (alternating copolymer), 114132-86-4; (AcCQ)(St) (alternating copolymer), 114132-88-6; (BCQ)(St) (alternating copolymer), 114132-89-7; St, 100-42-5.

## References and Notes

(1) Iwatsuki, S.; Itoh, T.; Nishihara, K.; Furuhashi, H. *Chem. Lett.* **1982**, 517.
(2) Hall, H. K., Jr.; Cramer, R. J.; Mulvaney, J. E. *Polym. Bull.* **1982**, 165.
(3) Iwatsuki, S.; Itoh, T.; Sawada, H.; Iwai, T. *Macromolecules* **1985**, *18*, 2726.
(4) Iwatsuki, S.; Itoh, T.; Higuchi, T. *Macromolecules* **1987**, *20*, 2671.
(5) Yamada, B.; Sugiyama, S.; Mori, S.; Otsu, T. *J. Macromol. Sci., Chem.* **1987**, *A15*, 339.
(6) Dainton, F. S.; Ivin, K. J. *Quart. Rev.* **1958**, *12*, 61.
(7) Mayo, F. R.; Lewis, F. M. *J. Am. Chem. Soc.* **1944**, *66*, 1694.
(8) Kelen, T.; Tüdös, F. *J. Macromol. Sci., Chem.* **1975**, *A9*, 1.
(9) Lewis, F. M.; Walling, C.; Cummings, W.; Briggs, E. R.; Mayo, F. R. *J. Am. Chem. Soc.* **1940**, *70*, 1519.
(10) Alfrey, Jr. T.; Price, C. C. *J. Polym. Sci.* **1947**, *2*, 101.
(11) Walling, C.; Briggs, E. R.; Wolfstirn, K. B.; Mayo, F. R. *J. Am. Chem. Soc.* **1948**, *70*, 1537.
(12) Bartlett, P. D.; Nozaki, K. *J. Am. Chem. Soc.* **1946**, *68*, 1495.
(13) Iwatsuki, S.; Yamashita, Y. *Prog. Polym. Sci., Jpn.* **1971**, *2*, 1–48.
(14) Iwatsuki, S.; Itoh, T. *Macromolecules* **1980**, *13*, 983.
(15) Iwatsuki, S.; Itoh, T.; Yokotani, I. *Macromolecules* **1983**, *16*, 1817.
(16) Iwatsuki, S.; Itoh, T.; Horiuchi, K. *Macromolecules* **1978**, *11*, 497.
(17) Iwatsuki, S.; Itoh, T. *Macromolecules* **1982**, *15*, 347.
(18) Iwatsuki, S.; Itoh, T.; Saito, H.; Okada, J. *Macromolecules* **1983**, *16*, 1571.
(19) Iwatsuki, S.; Itoh, T.; Shimizu, M.; Ishikawa, S. *Macromolecules* **1983**, *16*, 1407.
(20) Iwatsuki, S.; Itoh, T.; Sato, T. *Macromolecules* **1986**, *19*, 1800.
(21) Iwatsuki, S.; Itoh, T.; Ishiguro, K. *Macromolecules* **1987**, *20*, 939.
(22) Yonezawa, T.; Hayashi, K.; Nagata, C.; Okamura, S.; Fukui, K. *J. Polym. Sci.* **1954**, *14*, 312.
(23) Coulson, C. A.; Longuet-Higgins, H. C. *Proc. R. Soc. London, A* **1948**, *195*, 188.

---

# Studies on Chitin. 13. New Polysaccharide/Polypeptide Hybrid Materials Based on Chitin and Poly(γ-methyl L-glutamate)

**Keisuke Kurita,* Akira Yoshida, and Yoshiyuki Koyama**

*Department of Industrial Chemistry, Faculty of Engineering, Seikei University, Musashino-shi, Tokyo, Japan.*

*Received July 14, 1987*

ABSTRACT: A new type of polysaccharide/polypeptide hybrid material, chitin derivatives having polypeptide side chains, was prepared by the graft copolymerization of γ-methyl L-glutamate *N*-carboxy anhydride (NCA) onto water-soluble chitin in water/ethyl acetate. The polymerization proceeded quite smoothly, and both the conversion and grafting efficiency were very high owing to the homogeneous polymerization conditions which became feasible by making use of the water-soluble characteristic of the partially deacetylated chitin. The length of the polypeptide chains was easily regulated by the amount of NCA, and the graft copolymers with side chains of various lengths were obtained reproducibly. The results of solubility tests, infrared spectroscopy, and X-ray analysis of the copolymers were largely dependent on the side-chain length, and influence of α-helix formation by the side chains was evident. The ester groups of the side chains were transformed into carboxylate groups by alkaline hydrolysis, and the resulting copolymers exhibited remarkable water solubility.

## Introduction

Chitin is the most abundant natural amino polysaccharide and estimated to be produced annually almost as much as cellulose. It has become of great interest not only as an underutilized resource but as a new functional material of high potential in various fields, and the recent progress in chitin chemistry is quite noteworthy. Special attention has been given to the chemical modifications of chitin as one of the most probable means to realize its full potential. Reactions with chitin have been carried out mostly on solid chitin owing to the lack of solubility in ordinary solvents. A partially deacetylated chitin with about 50% deacetylation prepared by homogeneous hydrolysis was, however, found to be soluble in water.[1,2] This water-soluble chitin has a great advantage as a starting material for modifications, since the water solubility allows smooth reactions under mild conditions.

We have attempted to develop various modes of efficient modification reactions on chitin.[3-8] Among the modifications yet undeveloped, graft copolymerization on chitin is very attractive, being capable of affording novel hybrid materials based on this polysaccharide, although only a few papers reported the graft copolymerization on chitin, using vinyl monomers, with low grafting efficiencies.[9,10] In a

0024-9297/88/2221-1579$01.50/0