

Kinetic Studies on the Cationic Polymerization of 1,3-Dioxolane Initiated with Methyl Fluorosulfonate

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ABSTRACT: The cationic polymerization of 1,3-dioxolane (DOL) initiated with methyl fluorosulfonate was investigated in deuteriochloroform (CDCl_3) or nitromethane- d_3 (CD_3NO_2) at five different temperatures ranging from -20 to 5°C by means of ^1H - and ^{13}C -NMR spectroscopy. Only an ester growing species was observed in CDCl_3 solution throughout the polymerization, while the simultaneous presence of ester and ionic species was confirmed in CD_3NO_2 solution, except in the final stage of the polymerization where the ionic species was barely detectable. Kinetic analysis of the polymerization in CDCl_3 gave the rate constant of propagation, which varied from 0.7×10^{-2} (-20°C) to 2.3×10^{-2} $\text{l/mol} \cdot \text{s}$ (5°C). The activation enthalpy ΔH_p^\ddagger and the activation entropy ΔS_p^\ddagger for the polymerization in CDCl_3 were evaluated from the temperature dependence of the k_p values: $\Delta H_p^\ddagger = 6.1 \pm 0.4$ kcal/mol and $\Delta S_p^\ddagger = -42 \pm 1$ $\text{cal/mol} \cdot \text{deg}$. On the basis of these results, the mechanism of the polymerization of DOL by superacid derivatives is discussed in comparison with that for tetrahydrofuran.

KEY WORDS Kinetics / 1,3-Dioxolane / Methyl Fluorosulfonate / Ester Growing Species / Rate of Propagation / Ring-Opening Polymerization / Nuclear Magnetic Resonance /

The cationic polymerization of cyclic ethers by using superacid derivatives as initiators has been extensively studied by many workers.¹⁻¹¹ In most of these studies, ester-type growing species, which were generally in equilibrium with normal ionic growing species, were observed by means of ^1H - and ^{19}F -NMR spectroscopy. Kinetic analyses on the basis of quantitative determination of both ester and ionic species were performed under a wide variety of conditions, particularly in the polymerization of tetrahydrofuran (THF), and valuable information on the structures and reactivities of these growing species, as well as on solvent effects, has been accumulated. The coexistence of ionic and covalent growing species was also confirmed in the cationic polymerization of vinyl monomers¹²⁻¹⁴ and cyclic iminoethers.¹⁵

On the contrary, there have been few studies on the polymerization of cyclic acetals with superacids and their derivatives,¹⁶ and the simultaneous presence of the ionic and covalent growing species has never been reported. From the facts that the growing species in the cationic polymerization of cyclic

acetals initiated with triethyloxonium salts have an oxycarbenium ionic character¹⁷⁻¹⁹ and that they are relatively unstable compared with the trialkyloxonium ionic growing species in the polymerization of THF under similar conditions, it is expected that the growing species of cyclic acetals in their polymerization initiated with superacid derivatives would be stabilized by the formation of ester species with counter anions and that the polymerization proceeds predominantly through such ester species.

In this paper we describe the kinetic analysis of the cationic polymerization of 1,3-dioxolane (DOL) initiated with methyl fluorosulfonate by means of ^1H - and ^{13}C -NMR spectroscopy, and discuss the mechanism of the polymerization.

EXPERIMENTAL

Materials

1,3-Dioxolane was prepared by the method of Astle, *et al.*,²⁰ dried over sodium metal followed by calcium hydride, and fractionally distilled. bp $75-76^\circ\text{C}$. Commercial methyl fluorosulfonate

(CH₃OSO₂F) was purified by distillation. bp 92–94°C. The deuteriochloroform (CDCl₃) and nitromethane-*d*₃ (CD₃NO₂) used as the polymerization solvents were dried over anhydrous sodium sulfate and distilled. bp: CDCl₃, 60°C, CD₃NO₂, 101°C. Benzene, which was used as an internal standard for the determination of monomer and active species by ¹H-NMR spectroscopy, was dried over sodium metal and distilled. bp, 80°C.

Polymerization

The desired amounts of DOL, solvent, benzene, and CH₃OSO₂F were taken in this order into an NMR sample tube at room temperature under a nitrogen atmosphere. The sample tube was then cooled to liquid nitrogen temperature and sealed off. In the polymerization of DOL initiated with CH₃OSO₂F, an induction period was observed. It was confirmed by ¹H-NMR spectroscopy that the concentrations of DOL and CH₃OSO₂F during the induction period were equal to their initial concentrations, *i.e.*, the initiation was not preceded by any side-reaction. The concentrations of the residual DOL and the growing species during the polymerization were directly determined by means of ¹H-NMR spectroscopy. The limit and accuracy of the measurement of the concentration of the growing species are estimated to be 1 × 10⁻³ mol/l and ± 10%, when 1 × 10⁻² mol/l of benzene is used as the internal standard. ¹H- and ¹³C-NMR spectra were recorded on a JNM FX-100 Fourier transform spectrometer working at 100 MHz for proton and at 25 MHz for carbon.

RESULTS

Figure 1 shows a typical ¹H-NMR spectrum of the polymerization system in CDCl₃ at 0°C. The assignments of the signals are given in the structural formula in Figure 1. The signal a appearing at δ 5.5 ppm is reasonably assigned to the asterisked terminal-methylene protons of the ester species **2** both from the chemical shift of CH₃OSO₂F (δ 4.2 ppm) and from the deshielding effect of an alkoxy group.

The trialkyloxonium ion **1**, if present, should exhibit the signal of the asterisked ring methylene protons adjacent to the two oxygen atoms near δ 7 ppm. However, no corresponding signal was actually observed in this region. Furthermore, there appeared

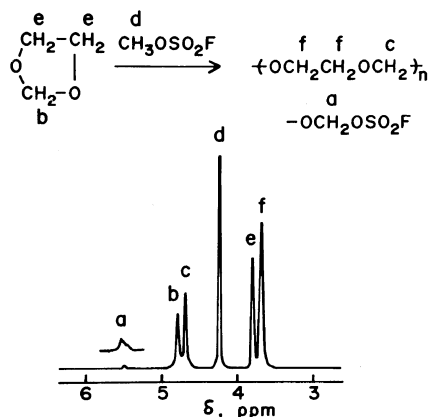
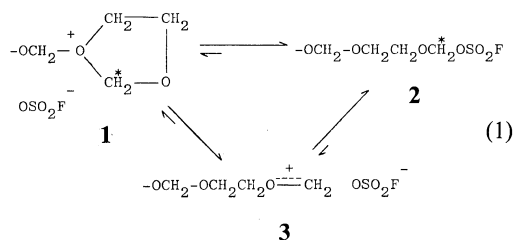


Figure 1. ¹H-NMR spectrum of 1,3-dioxolane polymerization system: [DOL]₀, 4.32 and [CH₃OSO₂F]₀, 3.75 mol/l; solvent, CDCl₃; temp, 0°C; time, 20 min.



no signal due to the terminal-methylene proton of the oxycarbenium ion **3**, which had been confirmed by our previous studies to show its characteristic signal near δ 11 ppm.¹⁷⁻¹⁹

Figure 2 shows the ¹³C-NMR spectrum of the polymerization system of DOL initiated with CH₃OSO₂F. The signal a at δ 108 ppm is assignable to the terminal-methylene carbon in the ester growing species **2**. This assignment of signal a was confirmed by the fact that the methylene carbon of CH₃OCH₂OSO₂F formed in the reaction of dimethoxymethane with CH₃OSO₂F showed the same chemical shift, δ 108 ppm. The assignments of the other signals are shown in Figure 2.

The ¹H-NMR spectrum of the polymerization system of DOL initiated with CH₃OSO₂F in CD₃NO₂ is shown in Figure 3. When compared with the spectrum in Figure 1, a new signal a was observed at δ 10.5 ppm. From the chemical shift of the terminal-methylene protons in 3-ethoxypropoxy-methylum tetrafluoroborate, which is formed in the reaction of 1,3-dioxane with triethyloxonium tetrafluoroborate,^{17,18} the signal a in Figure 3 can be assigned to the terminal-methylene protons in **3**. In

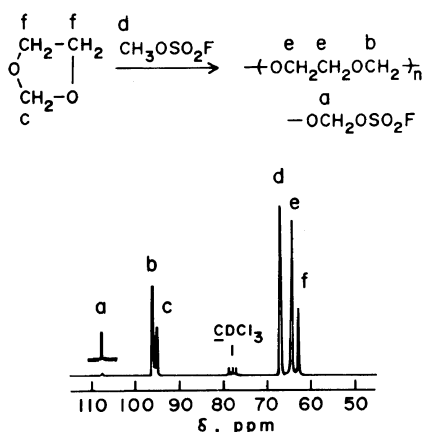


Figure 2. ^{13}C -NMR spectrum of 1,3-dioxolane polymerization system: $[\text{DOL}]_0$, 4.32 and $[\text{CH}_3\text{OSO}_2\text{F}]_0$, 3.75 mol/l; solvent, CDCl_3 ; temp, 0°C .

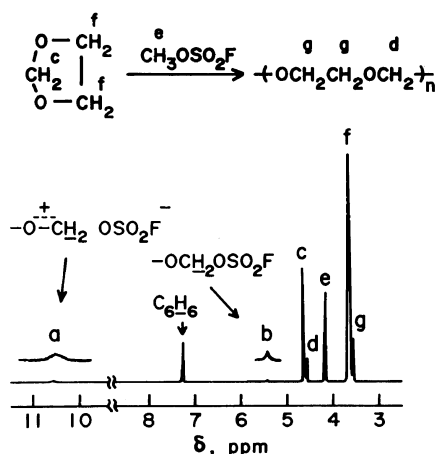


Figure 3. ^1H -NMR spectrum of 1,3-dioxolane polymerization system: $[\text{DOL}]_0$, 5.69 and $[\text{CH}_3\text{OSO}_2\text{F}]_0$, 2.09 mol/l; solvent, CD_3NO_2 ; temp, 0°C ; time, 2 h.

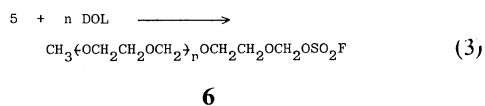
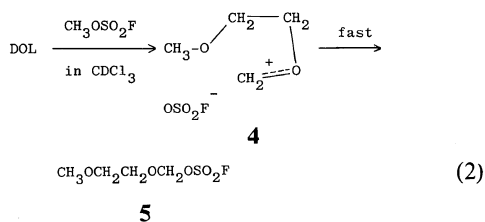
this system there appears a signal b due to the ester growing species, and hence the simultaneous presence of the ester and ionic growing species was identified. On the other hand, no signal ascribable to the oxycarbenium ion was detected in CDCl_3 solution, indicating that the propagation in the polymerization of DOL initiated with $\text{CH}_3\text{OSO}_2\text{F}$ in CDCl_3 proceeds exclusively through the ester growing species.

In the polymerization of DOL in CD_3NO_2 solution, the concentration of the ionic species was comparable with that of the ester species at the first stage of the polymerization. With increase in the

polymerization time, however, the concentration of the ionic species gradually decreased and in contrast that of the ester species increased. At the final stage of the polymerization, the ionic species was hardly detectable. On the contrary, only an ionic species was reportedly observed in the polymerization of THF initiated with $\text{C}_2\text{H}_5\text{OSO}_2\text{F}$ in CD_3NO_2 at 0°C .⁸ Such differences in the polymerization behavior between DOL and THF in CD_3NO_2 solution can be explained in terms of the difference in the stability of the ionic growing species. As the oxycarbenium ion in the polymerization of DOL is less stable than the trialkyloxonium ionic species in the polymerization of THF, it would appear that the former is eventually transformed to the more stable ester species.

The difference in the growing species between the polymerization of DOL in CDCl_3 and CD_3NO_2 solutions may be ascribable to the difference in their solvation abilities. As the polarity of CD_3NO_2 is higher than that of CDCl_3 , the ionic species in CD_3NO_2 solution can be stabilized efficiently by solvation. Hence, the ionic species solvated with CD_3NO_2 molecules are conceivably transformed into the relatively stable ester species more slowly than that in CDCl_3 solution.

On the basis of the assignments of ^1H -NMR spectrum in Figure 1, the polymerization scheme is represented as follows.



Therefore, the bimolecular rate equation for the polymerization is given by eq 4

$$-\frac{d[\text{DOL}]}{dt} = k_p[\text{P}^*]([\text{DOL}] - [\text{DOL}]_e) \quad (4)$$

where k_p is the rate constant of propagation. $[\text{P}^*]$ and $[\text{DOL}]$ are the concentrations of propagating species and monomer, respectively, and $[\text{DOL}]_e$ is the monomer concentration at equilibrium. Equation 4 is integrated with respect to time to give eq 5

$$\alpha \equiv \ln \frac{[\text{DOL}]_{t_1} - [\text{DOL}]_e}{[\text{DOL}]_{t_2} - [\text{DOL}]_e} = k_p \int_{t_1}^{t_2} [\text{P}^*] dt \quad (5)$$

where $[\text{DOL}]_{t_1}$ and $[\text{DOL}]_{t_2}$ are the monomer concentrations at time t_1 and t_2 , respectively.

Figure 4 illustrates the time dependences of $[\text{DOL}]$ and $[\text{P}^*]$ in the polymerization of DOL at -5°C in CDCl_3 . In this system a significantly long induction period was observed. This clearly indicates that a very slow initiation reaction takes place between DOL and $\text{CH}_3\text{OSO}_2\text{F}$, in comparison with the propagation rate.

In Figure 5, α in eq 5 was plotted against the integrated value of $[\text{P}^*]$ from t_1 to t_2 , evaluated by graphical integration on the time- $[\text{P}^*]$ curve. From the slope of the straight line passing through the origin, the k_p value was calculated to be $1.3 \times 10^{-2} \text{ l/mol} \cdot \text{s}$ at -5°C in CDCl_3 where $[\text{DOL}]_e$

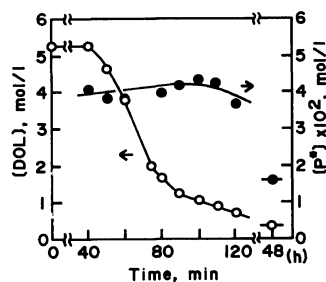


Figure 4. Concentrations of 1,3-dioxolane and active species vs. time: $[\text{DOL}]_0$, 5.29 and $[\text{CH}_3\text{OSO}_2\text{F}]_0$, 3.01 mol/l; solvent, CDCl_3 ; temp, -5°C .

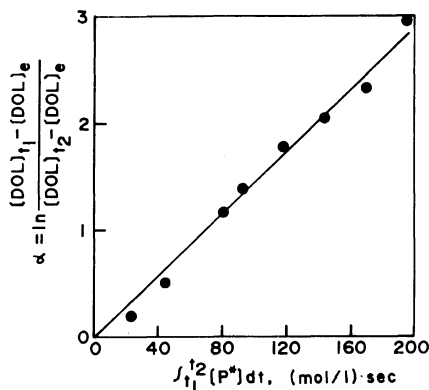


Figure 5. Relationship between α and $\int_{t_1}^{t_2} [\text{P}^*] dt$: $[\text{DOL}]_0$, 5.29 and $[\text{CH}_3\text{OSO}_2\text{F}]_0$, 3.01 mol/l; solvent, CDCl_3 ; temp, -5°C .

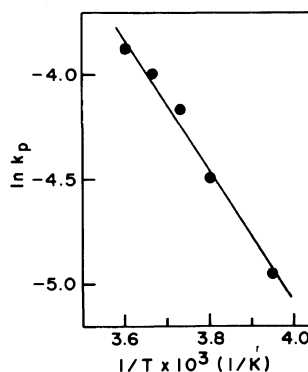


Figure 6. Relationship between $\ln k_p$ and $1/T$ in 1,3-dioxolane polymerization: solvent, CDCl_3 ; initiator, $\text{CH}_3\text{OSO}_2\text{F}$.

Table I. Rate constants and activation parameters

	Temp, $^\circ\text{C}$	DOL ^a	THF ^b
$k_p \times 10^2$, l/mol·s	5	2.3	
	0	1.8	0.090
	-5	1.3	
	-10	1.1	
	-20	0.7	
ΔH_p^\ddagger , kcal/mol		6.1 ± 0.4	8
ΔS_p^\ddagger , cal/mol·deg		-42 ± 1	-42

^a Solution polymerization in CDCl_3 ; initiator, $\text{CH}_3\text{OSO}_2\text{F}$.

^b Reference 7 (solution polymerization in CCl_4 ; initiator, $\text{C}_2\text{H}_5\text{OSO}_2\text{F}$).

was 0.46 mol/l. Similarly, the k_p values at four other temperatures were obtained.

As shown in Figure 6, the Arrhenius plots for the k_p values gave a straight line, from which the activation energy, ΔE_p^\ddagger , was estimated to be $6.6 \pm 0.4 \text{ kcal/mol}$.

The kinetic parameters for the polymerization of DOL initiated with $\text{CH}_3\text{OSO}_2\text{F}$ in CDCl_3 are listed in Table I, together with the reported values for the polymerization of THF under comparable conditions.⁷

DISCUSSION

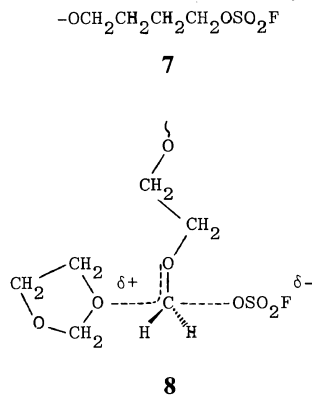
As described in the foregoing section, only the ester growing species was detected in the polymerization mixture in CDCl_3 . It might be speculated,

however, that there is an undetectable amount of the ionic growing species, through which the propagation actually proceeds because of its much greater reactivity than that of the ester growing species. In this connection, a k_p value of 140 ± 25 l/mol·s was reported for the polymerization in methylene chloride at 25°C initiated with triphenylmethyl salts and 1,3-dioxolan-2-ylum salts with AsF_6^- and SbF_6^- anions.²¹ If such extraordinarily highly reactive ionic growing species existed in the present system, the observed rate of polymerization could be accounted for by only 10^{-5} mol/l of the ionic species. Such a low concentration of the ionic species is, of course, undetectable by NMR technique, and hence, the speculation above cannot be ruled out.

However, it seems reasonable to postulate that the propagation proceeds through the ester growing species for the following two reasons. The first is the large negative value of the activation entropy for the propagation. This point will be described later. The second is the finding that a random copolymer was formed in the copolymerization of DOL and THF with the use of $\text{CH}_3\text{OSO}_2\text{F}$. Previously, one of the authors found that the attempted copolymerization of DOL and THF initiated with triethyloxonium tetrafluoroborate gave rise to a homopolymer mixture, and explained this anomaly in terms of oxonium ion exchange at the growing chain end.²² Therefore, the formation of a random copolymer when $\text{CH}_3\text{OSO}_2\text{F}$ was used as an initiator can be taken as a strong indication, although not conclusive evidence, of the occurrence of the propagation by the ester growing species. The details of the copolymerization experiments will be reported in a forthcoming publication.

The rate constant of propagation k_p for the polymerization of DOL initiated with $\text{CH}_3\text{OSO}_2\text{F}$ in CDCl_3 at 0°C is 1.8×10^{-2} l/mol·s. The k_p value for the polymerization of THF initiated with $\text{C}_2\text{H}_5\text{OSO}_2\text{F}$ in CCl_4 at 0°C is 0.90×10^{-3} l/mol·s, where only the ester growing species is present.⁷ Such a difference in the k_p values between DOL and THF is reflected in their activation enthalpies for the propagation. The ΔH_p^\ddagger value for DOL was about 2 kcal/mol smaller than that for THF. In view of the fact that the basicity of THF is higher than that of DOL,²³ the difference in the observed k_p values (therefore ΔH_p^\ddagger values) probably arises from the difference in the reactivities of the corresponding ester growing species, **6** and **7**. In the transition state

of propagation **8**, the developed positive charge on the terminal-methylene carbon is resonance-stabilized by the alkoxy participation in the polymerization of DOL, while such stabilization can not be realized for THF. This is another way of saying that **6** takes such a charge-separated transition state more readily than **7** in the rate-determining step.



Furthermore, it seems very likely that the growing species of THF **7** is solvated by basic monomer molecules more tightly than that of DOL **6**. This factor is also responsible, at least partly, for the reduction of the reactivity of **7** in comparison with that of **6**.

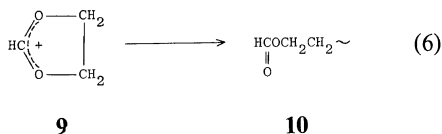
The $-\Delta S_p^\ddagger$ values, 42 cal/mol·deg for both monomers, are significantly larger than those for usual ionic polymerization, e.g., 26 cal/mol·deg for the polymerization of THF initiated with boron trifluoride.²⁴ A large value of $-\Delta S^\ddagger$ and therefore a small frequency factor A^\ddagger are characteristic of dipole-dipole S_N2 reactions producing ionic species, e.g., the Menshutkin reaction. Therefore, the observed $-\Delta S_p^\ddagger$ value ($A_p^\ddagger = 3.3 \times 10^3$ l/mol·s) supports the proposal that the polymerization of DOL initiated with $\text{CH}_3\text{OSO}_2\text{F}$ proceeds through the reaction of the ester growing species with monomer.

The apparent k_p values in CD_3NO_2 where both ionic and ester growing species were detected, were only two or three times larger than the k_p values in CDCl_3 . Considering the aforementioned k_p value, 140 ± 25 l/mol·s for the polymerization through the ionic species,²¹ the apparent k_p value in CD_3NO_2 is very small. However, the reported value was determined for kinetic measurements with $[\text{Initiator}]_0 = [\text{Growing species}] \approx 10^{-4}$ mol/l, while in this study the measurements were made for a much higher concentration of the growing species, $3\text{--}4 \times 10^{-2}$ mol/l. Therefore, it seems probable that

the ionic growing species in the present system are in a state of higher aggregates, thus possessing lower reactivity. This is supported by the facts that, in the polymerization of THF initiated with derivatives of fluorosulfonic and trifluoromethanesulfonic acids, the proportion of macroions monotonically increases with the concentration of living ends (sum of macroesters and macroions at equilibrium) due to the stabilization by aggregation, and that the k_p^\pm values for the ionic species decrease as the concentration of living ends increases.^{8,9}

In this system, the concentration of the growing species was very small, compared with the initial concentration of the initiator, as shown in Figure 4. This finding is an indication that the rate constant of initiation k_i is much smaller than the k_p value. Moreover, the concentration of the growing species decreased slightly with increase in the polymerization time, suggesting that some sort of termination of the ester species, although uncertain, might occur in this polymerization. In fact, it was confirmed by means of ¹H-NMR spectroscopy that complicated cleavage reactions of the polymer chains took place, in particular in CD₃NO₂ solution, when the reaction mixture was allowed to stand for a long time after the polymerization had reached its equilibrium.

In order to interpret the induction period observed in the polymerization in CDCl₃, we attempted to determine the rate constant of initiation k_i : The polymerization of DOL initiated with CH₃OSO₂F was carried out in CDCl₃ at 0°C with monomer concentration lower than the equilibrium monomer concentration. In this case also, the ester growing species was observed. However, the rate of the formation of the ester growing species was very small, and, moreover, hydride abstraction from monomer by the ester species occurred to form 1,3-dioxolan-2-ylum ion **9**, which was in turn readily transformed to formate derivatives **10**.



Consequently an accurate k_i value in this polymerization system could not be determined.

From the foregoing results and discussion, it is concluded that the polymerization of DOL initiated

with CH₃OSO₂F involves only the ester growing species in CDCl₃ solution, while it involves the oxycarbenium ionic species in addition to the ester species in CD₃NO₂ solution, except in the final stage of the polymerization.

REFERENCES

1. S. Kobayashi, H. Danda, and T. Saegusa, *Bull. Chem. Soc. Jpn.*, **46**, 3214 (1973).
2. S. Kobayashi, T. Saegusa, and Y. Tanaka, *Bull. Chem. Soc. Jpn.*, **46**, 3220 (1973).
3. S. Smith and A. J. Hubin, *J. Macromol. Sci., Chem.*, **7**, 1339 (1973).
4. K. Matyjaszewski and S. Penczek, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 1905 (1974).
5. S. Kobayashi, H. Danda, and T. Saegusa, *Macromolecules*, **7**, 415 (1974).
6. S. Kobayashi, T. Ashida, and T. Saegusa, *Bull. Chem. Soc. Jpn.*, **47**, 1233 (1974).
7. S. Kobayashi, K. Morikawa, and T. Saegusa, *Macromolecules*, **8**, 386 (1975).
8. T. Saegusa and S. Kobayashi, *J. Polym. Sci., Polym. Symp.*, No. 56, 241 (1976).
9. S. Penczek and K. Matyjaszewski, *J. Polym. Sci., Polym. Symp.*, No. 56, 255 (1976).
10. K. Matyjaszewski and S. Penczek, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 247 (1977).
11. A. M. Buyle, K. Matyjaszewski, and S. Penczek, *Macromolecules*, **10**, 269 (1977).
12. A. Gandini and P. H. Plesch, *Eur. Polym. J.*, **4**, 55 (1968).
13. D. C. Pepper, *Makromol. Chem.*, **175**, 1077 (1974).
14. T. Higashimura and T. Masuda, *Polym. J.*, **5**, 275 (1973).
15. T. Saegusa, *Makromol. Chem.*, **175**, 1199 (1974).
16. P. S. Raman and V. Mahadevan, *Makromol. Chem.*, **175**, 2339 (1974).
17. Y. Yokoyama, M. Okada, and H. Sumitomo, *Makromol. Chem.*, **176**, 795 (1975).
18. Y. Yokoyama, M. Okada, and H. Sumitomo, *Makromol. Chem.*, **178**, 529 (1977).
19. Y. Yokoyama, M. Okada, and H. Sumitomo, *Makromol. Chem.*, **179**, 1393 (1978).
20. M. J. Astle, J. A. Zaslowsky, and P. G. Lafyatis, *Ind. Eng. Chem.*, **46**, 787 (1954).
21. S. Penczek, *Makromol. Chem.*, **175**, 1217 (1974).
22. Y. Yamashita, S. Kozawa, K. Chiba, and M. Okada, *Makromol. Chem.*, **135**, 75 (1970).
23. S. Iwatsuki, N. Takigawa, M. Okada, Y. Yamashita, and Y. Ishii, *J. Polym. Sci., Part B*, **2**, 549 (1964).
24. T. Saegusa, S. Matsumoto, M. Motoi, and H. Fujii, *Macromolecules*, **5**, 236 (1972).