Macromolecules **1993,** *26,* 5539–5542

Preparation and Characterization of Telechelic Poly(methyl methacrylate). 2. Anionic Polymerization with a Difunctional Initiator Derived from 4-[2-(*tert*-Butyldimethylsiloxy)ethyl]-α-methylstyrene

Masatoshi Ohata,[*,1a] **Shouji Ikeda,**[1a] **Shin-ichi Akatani,**[1b] **and Yoshinobu Isono**[1b]

Department of Materials Science and Technology, Nagaoka University of Technology, Nagaoka, Niigata 940-21, Japan, and Research Center, Nippon Paint Company, Ltd., Neyagawa, Osaka 572, Japan

Received February 15, 1993; Revised Manuscript Received July 7, 1993[⊗]

ABSTRACT: Novel telechelic poly(methyl methacrylate) having OH and COOH groups in the chain was prepared by anionic polymerization with the difunctional initiator made by the reaction betweem 4-[2-(*tert*-butyldimethylsiloxy)ethyl]-α-methylstyrene and sodium napththalene, followed by termination with carbon dioxide and hydrolysis of the *tert*-butyldimethylsiloxy group. The resulting polymer was characterized by osmometry, GPC, ^{1}H NMR, and potentiometric titration. OH groups were introduced quantitatively, but the number of the terminal COOH groups per molecule was 1.7 ● 0.1 which is less than the theoretical value, 2. The latter result was because part of the initiator was doubly charged and the rest had one charge plus a nonactive end, and/or the initiation efficiency in the reaction between the initiator and methyl methacrylate was low. The characterization assures that the multifunctionality of the polymer necessary for self-cross-linking is presented.

Introduction

We have reported in the preceding papers[2–4] that unsymmetrical telechelic poly(methyl methacrylate)s [poly(MMA)s] can be prepared by anionic polymerization with monofunctional initiators bearing potential functional groups, followed by functional termination. The initiators were derived from 4-[2-(*tert*-butyldimethylsiloxy)ethyl]-α-methylstyrene (abbreviated as 1) or 4-[2-(*tert*-butyldimethylsiloxy)ethyl]-α-phenylstyrene, and the terminator was carbon dioxide. The resulting polymers showed fairly narrow molecular weight distributions and had a hydroxyl group at one end of the chain and a carboxyl group at the other end. The polymers are expected to be useful for solvent-free powder paints due to the following points: (a) high weathering resistance, (b) high transparency, and (c) definite pour point. In order to obtain hard coating through cross-linking, however, one needs a multifunctional cross-linking reagent.

It is well-known that a telechelic polymer can be prepared with a difunctional initiator[5–7] as well as a monofunctional one. For example, we can use α-methylstyrene (α-MeSt) to obtain a difunctional initiator. We have reported that the thermodynamic parameters for the propagation of 1 are close to those of α-MeSt.[2] Hence, it may be considered that 1 can react with sodium naphthalene to give a difunctional initiator (abbreviated as 2). When a monomer is anionically polymerized with 2 and terminated with carbon dioxide, the resulting polymer will have carboxyl groups at chain ends and hydroxyl groups at the central part of the chain. Such a multifunctional polymer is self-cross-linkable.

The purpose of this paper is to prepare a double-functional telechelic poly(MMA) having carboxyl and hydroxyl groups with 2 and to characterize the number of functional groups (–COOH and –OH) in a step-by-step fashion.

Experimental Section

Initiators. The precursor of the initiator, 4-[2-(*tert*-butyldimethylsiloxy)ethyl-α-methylstyrene (1), was prepared in the same way as has been reported previously.[2] 1 was purified with *sec*-butylmagnesium bromide in three stages by distillation in a sealed glass apparatus under a pressure of 1×10^{-3} Pa or lower after being dried over calcium hydride. The purified 1 was further distilled and diluted to about 10–20 v/v % with purified THF just prior to use.

Difunctional initiator, 2, was prepared by the reaction between 1 and solution naphthalene in purified THF. The reaction was carried out at 273 K for 0.5 h and then at 195 K for 0.5 h in a glass apparatus having break-seals under high vacuum (1×10^{-3} Pa or lower). 2 was prepared just prior to polymerization.

Monomers and Solvents. THF used for the preparation of the initiator and the polymerization was purified in the same way as has been reported previously.[8,9] Methyl methacrylate (MMA) and α-methylstyrene (α-MeSt) were purified by distillation from calcium hydride and the sodium salt of *n*-octylbenzophenone, respectively, as have been reported elsewhere.[2,9,10] The monomers were redistilled carefully and diluted to about 10–20 v/v % with purified THF just prior to polymerization. Carbon dioxide (purity, 99.99% or higher) packed in a glass ampule equipped with a break-seal was obtained from Takachiho Syoji Co., Ltd.

Polymerization. The preparation of the initiator and anionic polymerizations were carried out at 195 K in a sealed glass apparatus equipped with break-seals under a pressure of 1×10^{-3} Pa or lower, using essentially the same procedures as have been reported previously.[2,10] The sodium salt of the end-carboxylated poly(MMA) was prepared by the reaction of living poly(MMA) with carbon dioxide at 195 K for 0.5 h. After being quenched with a small amount of methanol, poly(MMA) and poly(α-MeSt) samples were precipitated from THF solution into excesses of *n*-hexane and methanol, respectively. The precipitated samples were further purified by reprecipitation in benzene/*n*-hexane or benzene/methanol systems. The purified polymers were freeze-dried from the benzene solutions for 24 h.

Introduction of Carboxyl and Hydroxyl Groups. The sodium salt of the end-carboxylated poly(MMA) dissolved in benzene was acidified by being shaken with 0.1 N hydrochloric acid. After the hydrochloric acid had been removed by a saturated aqueous solution of sodium chloride, the end-carboxylated poly-

---

[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1993.

0024-9297/93/2226-5539$04.00/0

Table I. Polymerization of MMA with 2[a]

sample code	amt of NaphNa[b] (mmol)	amt of 1 (mmol)	amt of MMA (mmol)	conv (%)	$10^{-3}M_k$[c]	$10^{-3}\bar{M}_n$	GPC $10^{-3}\bar{M}_n$	GPC $\bar{M}_w/\bar{M}_n$	tacticity[d] (%) I	tacticity[d] (%) H	tacticity[d] (%) S
MA-1	3.5_3	6.3_8	100	100	6.7	7.0	6.6	1.3_1	10	40	50
MA-2[e]	3.5_7	8.9_5	96.4	100	6.8	7.2	6.8	1.3_8	8	36	56

[a] Condition of polymerization: temp, 195 K; time, 30 min; conc, ca. 7%. [b] Sodium naphthalene. [c] Kinetic molecular weight, calculated from the ratios of the amounts of 1 and MMA to NaphNa. [d] I: isotactic. H: heterotactic. S: syndiotactic. [e] End-carboxylated poly(MMA).

(MMA) [abbreviated as C-PMMA] dissolved in acetone was purified by precipitation into a mixture of methanol/water (1/2 by volume ratio).

Hydrolysis of the *tert*-butyldimethylsiloxy group was carried out by bubbling hydrogen chloride gas into a ca. 2 w/v % acetone solution of C-PMMA for 2 h at 298 K. Purification procedures were the same as in C-PMMA.

Molecular Characterization. The number-average molecular weight, $\bar{M}_n$, and the molecular weight distribution, $\bar{M}_w/\bar{M}_n$, were measured by gel permeation chromatography (GPC) at 298 K using a HLC-803D instrument (Tosoh Ltd.) equipped with refractive index (RI) and ultraviolet absorption (UV) detectors. The columns were a set of G4000H8 and G3000H8 or a set of three G4000H8 (Tosoh Ltd.), which were calibrated with standard poly(styrene)s. THF was used as an eluent.

The absolute values of $\bar{M}_n$ of poly(MMA), C-PMMA, and the resulting telechelic poly(MMA) were determined by vapor pressure osmometry (VPO) in toluene at 343 K with a Corona type 117 instrument. The apparatus constant was determined with a standard poly(styrene) ($\bar{M}_n = 1.04 \times 10^4$, $\bar{M}_w/\bar{M}_n = 1.02$). It was experimentally confirmed that association between carboxyl groups at the chain ends hardly took place under our experimental conditions.[2]

The average number of carboxyl groups at the chain ends was estimated by potentiometric titration by the same method as was reported previously.[2]

^{1}H NMR and ^{13}C NMR spectra were obtained at room temperature in $CDCl_3$ with a JEOL GX-270 FT-NMR spectrometer (270.05 and 67.80 MHz for ^{1}H and ^{13}C NMR, respectively). Chemical shifts were referred to chloroform (7.25 and 76.9 ppm for ^{1}H and ^{13}C NMR, respectively) in $CDCl_3$.

Results

The results of the polymerization of MMA with 2 are listed in Table I. The values in stereoregularity of the resulting poly(MMA)s are also listed in Table I. In the sample MA-2, the living end of poly(MMA) was allowed to react with carbon dioxide before quenching. When 1 was added to sodium naphthalene in THF at 273 K, the color of the solution changed immediately from green to dark red, indicating formation of 2. The vessel was moved quickly into a bath at 195 K and kept at that temperature for 0.5 h. When MMA was added, the dark red color disappeared immediately, showing an initiation reaction of MMA. The polymer yields were quantitative, but the values of $\bar{M}_n$ determined by VPO were higher than those of the kinetic molecular weight, M_k, which are calculated from the molar ratios of 1 and MMA to sodium naphthalene. This may be due to the two side reactions; the attack of 2 on the silyl ether of the 1 unit[7,11] and that of the ester group of MMA.[12] These effects will be discussed in the next section.

Figure 1 shows the GPC chromatogram of the sample MA-2. MA-1 also showed a similar curve. The signals by refractive index and UV absorption at 254 nm were observed in the same range of elution volume, indicating the existence of the unit of 1 in the poly(MMA) samples.

Figure 2 shows the ^{1}H NMR spectrum of the sample MA-2 after acidification. Signals at 0.9, 1.1, 1.2, and 3.6 ppm are assigned to the α-methyl protons of the syndiotactic, heterotactic, and isotactic triads and methoxy protons in MMA, respectively. The ones at 0 and 6.5–7.5 ppm were assigned to the CH_3–Si and phenyl protons in 1, respectively. The one due to the *tert*-butyl protons in 1 overlaps with that of the α-methyl protons of the syndiotactic triad. The weak one appearing at around 2.7 ppm is due to the $-CH_2C_6H_4$ in 1. However, the signal due to the $-CH_2O$ in 1 overlaps with that of the methoxy protons in MMA.

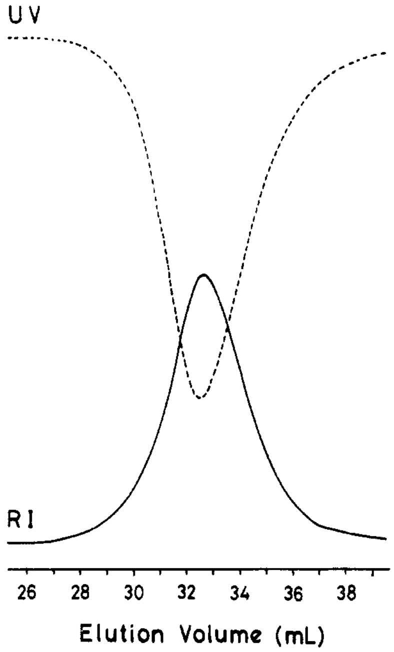


Figure 1. GPC chromatogram of poly(MMA), MA-2. The solid and broken curves show the signals by RI and UV (254 nm) detectors, respectively. Columns were G3000H8 and G4000H8 combined in series. The carrier was THF at 298 K. Flow rate, 1 mL/min; concentration, 0.1 g/dL.

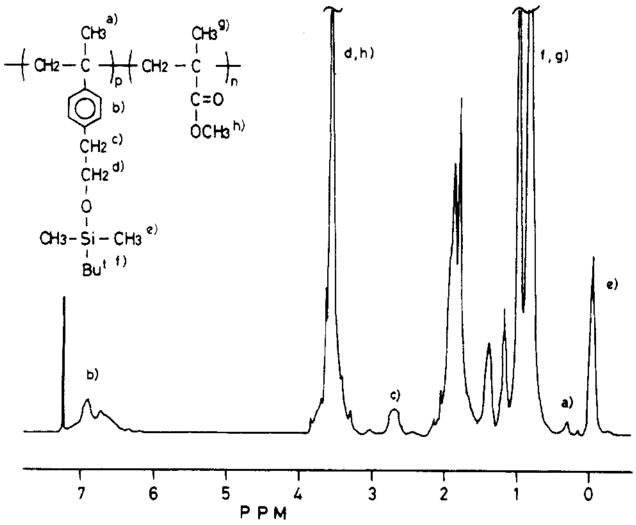


Figure 2. ^{1}H NMR spectrum of poly(MMA), acidified MA-2. The solvent was $CDCl_3$.

The average number of 1 units per molecule, N_1, can be estimated from the signal intensity ratio, i.e., the intensity ratio of the phenyl to the CH_3–O protons or that of the CH_3–Si to the CH_3–O protons, and the value of $\bar{M}_n$ by VPO. These values are listed in Table II. The estimated

Table II. Characterization of Poly(MMA)

sample code	ave no. of 1 units per molecule, N_1							ave no. of -COOH groups per molecule	
		found							
	theor[a]	phenyl[b]	CH_3Si[c]	$(1-d)f$	x_{di}	x_{mono}	x_{zero}	theor[d] (F_1)	found[e] (N_C)
MA-1	3.6	3.5	3.5	0.78	0.61	0.34	0.05	1.6	
MA-2	5.0	5.0	4.6	0.74	0.55	0.38	0.07	1.6	1.7 ± 0.1

[a] Calculated from the amount of 1 and sodium naphthalene. [b] Estimated from the ^1H NMR signal intensity ratio of the phenyl to the methoxy protons. [c] Estimated from the ^1H NMR signal intensity ratio of the CH_3Si to the methoxy protons. [d] Functionality of initiator (see Discussion). [e] Estimated from the total number of carboxyl groups per unit weight of the sample measured by potentiometric titration and the value of $\bar{M}_n$ by VPO.

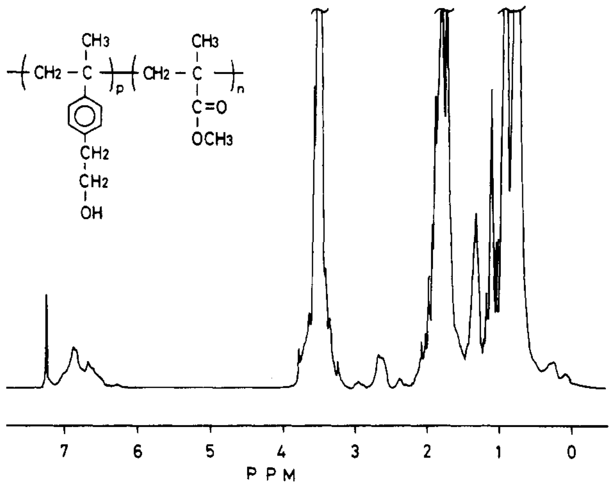


Figure 3. ^1H NMR spectrum of poly(MMA), acidified and deprotected MA-2. The solvent was $CDCl_3$.

values of N_1 for both samples are in good agreement with the values expected for the ratio of the amounts of 1 to sodium naphthalene. It is, hence, clear that 1 is oligomerized quantitatively with sodium naphthalene and that the *tert*-butyldimethylsilyl groups remain during the polymerization and acidification processes.

The average number of carboxyl groups per molecule, N_C, was estimated from the value of $\bar{M}_n$ by VPO and the number of carboxyl groups per unit weight of the sample, which was determined by potentiometric titration. The value of N_C was 1.7 ± 0.1 which is less than the theoretical value, 2.

Figure 3 shows the ^1H NMR spectrum of the sample MA-2 after deprotection of the blocking group in 1. Only the signal at 0 ppm assigned to CH_3Si disappeared, and the signal intensity ratio of methoxy to α-methyl protons in MMA showed no change. These results show a complete elimination of the *tert*-butyldimethylsilyl group without the hydrolysis of the ester group in poly(MMA).

The value of $\bar{M}_n$ of the deprotected MA-2 was determined to be 7.0×10^3 by VPO, showing no change in the degree of polymerization. This suggests no cleavage occurred in the main chain through the hydrolysis of the *tert*-butyldimethoxysiloxy group.

These results confirm that the resulting polymer MA-2 has hydroxyl and carboxyl groups in the chain.

Discussion

Table III. Polymerization of α-MeSt with 2[a]

sample code	amt of NaphNa (mmol)	amt of 1 (mmol)	amt of α-MeSt (mmol)	conv (%)	$10^{-4}M_k$[b]	$10^{-4}\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]
MS-1	0.43_4	2.7_7	90.0	100	5.3	5.3	1.1_0

[a] Condition of polymerization: temp, 195 K; time, 1 h; conc, 5.2%. [b] Kinetic molecular weight, calculated from the ratios of the amounts of α-MeSt and 1 to NaphNa. [c] Estimated by GPC on the basis of calibration with standard poly(styrene)s.

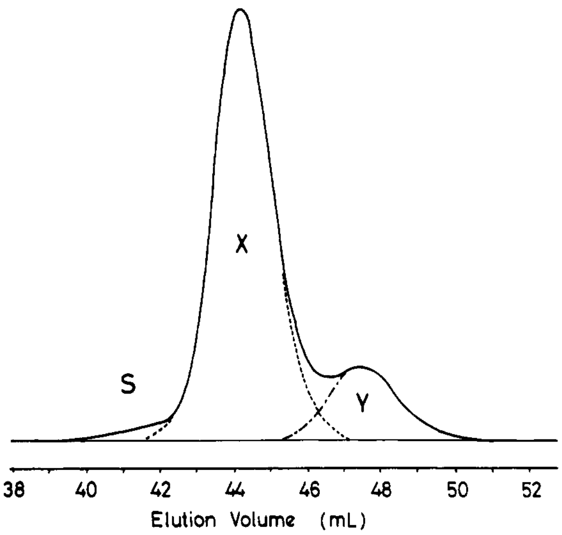


Figure 4. GPC chromatogram of poly(α-MeSt), MS-1. The meanings of X, Y, and S are mentioned in the text. Columns were three G4000H8 combined in series. Other measurement conditions were the same as in Figure 1.

There may be three reasons why the value of N_C was less than 2. The first is that part of the initiator is doubly charged and the rest has one charge plus a noneactive end.[13-16] The second is low initiation efficiency in the reaction between 2 and MMA. The third is deactivation of the living end during the polymerization. If the first and/or the second are the reasons, the sample should have a bimodal molecular weight distribution. Unfortunately, we cannot judge this point from Figure 1, because poly(MMA) does not have a sharp molecular weight distribution, even if the sample is prepared by anionic polymerization.[10]

It has been reported that the propagation reaction of α-MeSt in anionic polymerization proceeds quantitatively and the resulting polymer has a sharp molecular weight distribution.[6] Furthermore, we have reported that the thermodynamic parameters for the polymerization of 1 are close to those of α-MeSt.[2] Incidentally, it has been known that the ^{13}C NMR chemical shift of the β-carbon of a monomer is a measure of the reactivity of the monomer.[17] The chemical shift of the β-carbon of monomer 1 appeared at 111.7 ppm which is very close to that of α-MeSt (112.3 ppm). These facts suggest that the thermodynamic and the chemical properties of 1 are similar to those of α-MeSt and the initiation efficiency in the reaction between 2 and α-MeSt is not low. Hence, we tried to polymerize α-MeSt with 2, in order to examine the possibility of the first reason.

Table III shows the result of polymerization of α-MeSt with 2 in THF. The polymer yield was quantitative. Figure 4 shows the GPC chromatogram of the sample MS-1. The curve has bimodal peaks though the peak at the higher molecular weight side has a shoulder. Hence, the curve

Table IV. Characterization of Poly(α-MeSt) and 2

sample code	area fraction			peak X		peak Y	
	S	X	Y	$10^{-4}\bar{M}_n{}^a$	$\bar{M}_w/\bar{M}_n{}^a$	$10^{-4}\bar{M}_n{}^a$	$\bar{M}_w/\bar{M}_n{}^a$
MS-1	0.01_9	0.81_9	0.16_2	6.1	1.0_3	3.1	1.0_3

^{a} Estimated by GPC on the basis of calibration with standard poly(styrene)s.

was resolved into three parts, X, Y, and S, as shown by broken and dot-dashed lines in Figure 4. The area fractions of the three parts and the values of $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of the peaks X and Y estimated on the basis of calibration with standard poly(styrene)s are listed in Table IV. The area fraction of the shoulder S is only 0.02.

Each of the two fractions X and Y has a very narrow moleclar weight distribution. The value of $\bar{M}_n$ of the fraction X is 2 times higher than that of the fraction Y. These suggest that the bimodal distribution is not due to deactivation of the living end during the polymerization but due to the presence of two kinds of initiator, i.e., difunctional and monofunctional initiators, and/or imperfect initiation.

Effective functionality, F_I, is defined by

$$F_I = (2x_{di} + x_{mono})/(x_{di} + x_{mono}) \quad (1)$$

where x_{di} and x_{mono} are molar fractions of difunctional and monofunctional initiators, respectively.

Let d be the probability that one active site of the initiator, 2, is deactivated due to side reactions such as the cleavage of silyl ether during the preparation of the initiator, and let f be the initiation efficiency in the reaction between 2 and MMA. Then x_{di}, x_{mono}, and x_{zero} are expressed in terms of d and f as

$$x_{di} = (1 - d)^2 f^2 \quad (2)$$

$$x_{mono} = 2(1 - d)f\{1 - (1 - d)f\} \quad (3)$$

$$x_{zero} = 1 - x_{di} - x_{mono} \quad (4)$$

where x_{zero} is the molar fraction of the initiator having no effective initiation site. It can be seen from eqs 1–3 that F_I depends on d and f as

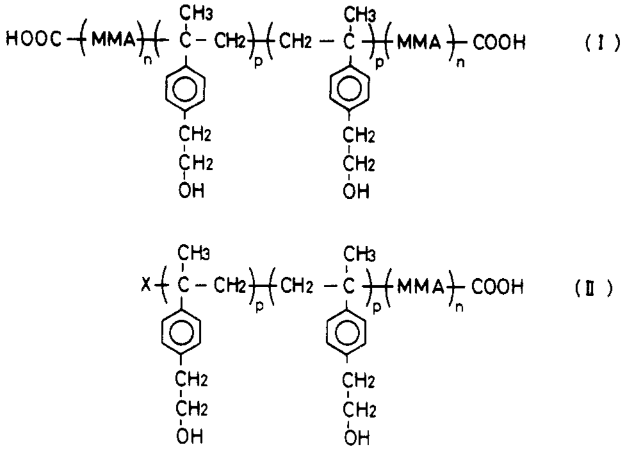
$$F_I = \frac{2}{2 - (1 - d)f} \quad (5)$$

The number-average molecular weight, $\bar{M}_n$, of poly(MMA) is expressed as

$$\bar{M}_n = \frac{2n_{MMA}m_{MMA}}{n_{NaphNa}(x_{di} + x_{mono})} + \frac{2n_1 m_1}{n_{NaphNa}} \quad (6)$$

where n_{MMA}, n_{NaphNa}, and n_1 are the number of moles of MMA monomer, sodium naphthalene, and 1, respectively, and m_{MMA}, and m_1 are the molecular weights of MMA and 1, respectively. From the given amounts of monomer and initiator and the value of $\bar{M}_n$ listed in Table I, we can estimate the values of $(1 - d)f$, x_{di}, x_{mono}, and x_{zero} as shown in Table II. Using eq 5 and the values of $(1 - d)f$, we obtain the value of F_I to be 1.6, which agrees with the value observed, 1.7 ± 0.1. Therefore, we may conclude that the value of the functionality of the end carboxyl groups which is smaller than the theoretical one is not due to deactivation of the living end during polymerization of MMA but due to the existence of two types of initiators, that is, mono- and difunctional ones, and/or a low initiation efficiency in the reaction between 2 and MMA.

Scheme I. Structure of the Telechelic Poly(MMA)s



It is confirmed that the sample MA-2 consists of two types of polymers. One has carboxyl groups at both ends and several hydroxyl groups at the center of the chain as shown by structure I in Scheme I. The other has a carboxyl group at one end and several hydroxyl groups at the other end (structure II in Scheme I). Hence, it is clear that we have successfully prepared the new type of reactive poly(MMA) having the functionality necessary for self-crosslinking.

Acknowledgment. This work was supported in part by a Grant-in-Aid for Developmental Scientific Research (No. 63850156) from the Ministry of Education, Science, and Culture, Japan.

References and Notes

(1) (a) Nippon Paint Co., Ltd. (b) Nagaoka University of Technology.
(2) Ohata, M.; Ikeda, S.; Akatani, S.; Isono, Y. *Macromolecules* **1992**, *25*, 5131.
(3) Ohata, M.; Isono, Y. *Jpn. Polym. Sci. Technol.* **1992**, *49*, 801.
(4) Ohata, M.; Isono, Y. *Polymer* **1993**, *34*, 1546.
(5) Brody, H.; Richards, D. H.; Szwarc, M. *Chem. Ind. (London)* **1958**, 1473.
(6) Morton, M. In *Anionic Polymerization: Principles and Practice*; Academic Press: New York, 1983; pp 93 and 233.
(7) Hirao, A.; Yamamoto, A.; Takenaka, K.; Yamaguchi, K.; Nakahama, S. *Polymer* **1987**, *28*, 303.
(8) Fujimoto, T.; Ozaki, N.; Nagasawa, M. *J. Polym. Sci., Part A* **1965**, *3*, 2259.
(9) Kase, T.; Imahori, M.; Kazama, T.; Isono, Y.; Fujimoto, T. *Macromolecules* **1991**, *24*, 1714.
(10) Zhang, H.; Ishikawa, H.; Ohata, M.; Kazama, T.; Isono, Y.; Fujimoto, T. *Polymer* **1992**, *33*, 828.
(11) Gilman, H.; Smart, G. N. R. *J. Org. Chem.* **1950**, *15*, 720.
(12) Warzelhan, V.; Höcker, H.; Schulz, G. V. *Makromol. Chem.* **1978**, *179*, 2221.
(13) McCormick, H. W. *J. Polym. Sci.* **1959**, *138*, 327.
(14) Wenger, F. *Makromol. Chem.* **1963**, *14*, 151.
(15) Hostalka, H.; Figini, R. V.; Schulz, G. V. *Makromol. Chem.* **1964**, *71*, 198.
(16) Roovers, J.; Toporowski, P. M. *Macromolecules* **1981**, *14*, 1174.
(17) Kennedy, J. P.; Marechal, E. In *Carbocationic Polymerization*; Wiley: New York, 1982; p 339.