



# Kinetic and thermodynamic characteristics of anionic living-equilibrium polymerization for (*p*-Isopropenylphenethyl)poly( $\alpha$ -methylstyrene) macromonomer

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## ARTICLE INFO

### Article history:

Received 2 July 2010

Received in revised form

6 August 2010

Accepted 14 August 2010

Available online 21 August 2010

### Keywords:

Anionic living-equilibrium polymerization of macromonomers

A ceiling temperature

Kinetic and thermodynamic characteristics of equilibrium polymerization

## ABSTRACT

The anionic living-equilibrium polymerization (ALEP) of (*p*-isopropenylphenethyl)poly( $\alpha$ -methylstyrene) macromonomer (PMStM) was studied: PMStM was simultaneously purified and initiated above a ceiling temperature ( $T_c$ ) and then propagated below  $T_c$ . Three PMStMs ( $M_n = 1.77 \times 10^3$ ,  $3.65 \times 10^3$ , and  $5.36 \times 10^3$ ) were prepared by the coupling of poly( $\alpha$ -methylstyryllithium) with *p*-isopropenylphenethyl chloride, and were polymerized to produce polymacromonomers, (PMSt) $_m$  ( $m = 9.5$ ,  $4.1$ , and  $3.5$ ) by *n*-BuLi in *d*<sub>8</sub>-THF at temperatures below  $-10^\circ\text{C}$  under high vacuum via ALEP. From kinetic studies using a  $^1\text{H}$  NMR technique, the propagation rate constant ( $0.240$ ,  $0.110$ , and  $0.079 \text{ l mol}^{-1} \text{ s}^{-1}$ ) at  $-78^\circ\text{C}$  was found to be proportional to a reciprocal of  $M_n$  of PMStM, and its  $M_n$  dependence was discussed based on a simple diffusion-controlled theory. The thermodynamic characteristics of  $\Delta H_{\text{MSt}}$  ( $-7.48$ ,  $-6.73$ , and  $-3.82 \text{ kJ mol}^{-1}$ ) and  $\Delta S_{\text{MSt}}$  ( $-26.8$ ,  $-24.1$ , and  $-13.7 \text{ J mol}^{-1} \text{ K}^{-1}$ ) were determined from a kinetic analysis, and their  $M_n$  dependence was also discussed. The  $T_c$  values for the three PMStM, including  $\alpha$ -methylstyrene, were found to be the same ( $6.0^\circ\text{C}$ ).

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## 1. Introduction

Anionic living polymerization of macromonomers with a styryl group at one end [1,2] is useful for preparing non-linear block copolymers such as hetero-arm star block copolymers [3,4], block-graft copolymers [5], and rod-linear block copolymers [6,7]. However, there was an experimental problem to be solved: namely, purification of the macromonomers [1,2]. Some techniques have been reported to solve this problem and to prepare the interesting block copolymers [8] using the carefully purified macromonomers [9–11]. Hadjichristidis et al. have solved the problem by synthesizing and polymerizing the styrenic macromonomers in the same reactor without isolating them [1,12]. By the *in situ* anionic polymerization of the styrenic macromonomers without previous isolation, many complex macromolecular architectures, having macromonomers as building blocks, have been synthesized by them [12,13]. We have proposed another technique of purifying the styrenic macromonomers that is similar to that of purifying common monomers [14]. That is, the THF solution of the styrenic macromonomer and a cross-linked polystyrene particle containing benzophenone sodium ( $\text{R}-\text{C}_6\text{H}_5-\text{CO}-\text{C}_6\text{H}_5\text{Na}^+$ ) as a purging

reagent was stirred for 48 h and the purified macromonomer was then separated from the suspension by a glass filter under high vacuum [2,14,15].

This paper provides a different method of purifying and polymerizing the macromonomers [16–18] by using a concept of anionic living-equilibrium polymerization (ALEP) [19–21]. In order to study the ALEP of the macromonomers, an  $\alpha$ -methylstyrenic macromonomer has to be prepared. We first prepared a (*p*-isopropenylphenethyl)poly( $\alpha$ -methylstyrene) macromonomer [16] (PMStM) having an  $\alpha$ -methylstyrene group ( $\text{CH}_2=\text{C}(\text{CH}_3)-\text{C}_6\text{H}_4-$ ) at one end of the poly( $\alpha$ -methylstyrene) (PMSt). The reason that the main chain of PMStM is not polystyrene (PSt) but PMSt is to avoid the complexity of molecular characterization of the final product of polymacromonomer due to the heterogeneity of composition using a technique of light scattering. After a common purification of PMStM, *n*-butyllithium (*n*-BuLi) was introduced to the THF solution of PMStM at  $-15^\circ\text{C}$  under high vacuum. The *n*-BuLi purges the impurities included in the solution and simultaneously initiates the PMStM. After 30 min at  $-15^\circ\text{C}$ , the solution was lowered to  $-78^\circ\text{C}$ , which is below a ceiling temperature ( $T_c$ ), to propagate the PMStM to produce polymacromonomer, (PMSt) $_m$ . This technique has been named ALEP of macromonomers [17,18].

A few attempts have been made at a kinetic study of the anionic polymerization of macromonomers. The ALEP of PMStM is available

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for carrying out it, because the propagation starts from all initiators at the same time and no termination can occur when the polymerization solution is cooled to below  $T_c$  as quickly as possible. In addition, many kinetic studies of the same sample would be carried out at different temperatures using a technique of  $^1\text{H}$  NMR measurements; namely, after finishing a kinetic study at a certain temperature, the  $(\text{PMSt})_m$  polymacromonomer was converted to PMStM by raising the temperature above  $T_c$ , and then the next kinetic study was carried out at a different temperature. The present paper provides the kinetic and thermodynamic characteristics of PMStM via ALEP, and the dependences of them on the  $M_n$  of PMStM are also discussed.

## 2. Experimental

### 2.1. *p*-Isopropenylphenethyl chloride ( $\text{CH}_2=\text{C}(\text{CH}_3)-\text{C}_6\text{H}_4-\text{CH}_2\text{CH}_2\text{Cl}$ , IPPC)

IPPC, which is a coupling reagent for preparing PMStM macromonomer, was prepared as follows: *p*-Chloroacetophenone ( $\text{CH}_3\text{CO}-\text{C}_6\text{H}_4-\text{Cl}$ ) was reacted with the Grignard reagent of methyl chloride and magnesium turnings to produce *p*-isopropenylphenethyl chloride ( $\text{CH}_2=\text{C}(\text{CH}_3)-\text{C}_6\text{H}_4-\text{Cl}$ ) according to previous methods [22,23]. *p*-Isopropenylphenethyl chloride (100 g) and methyl iodide (2 g) in THF (200 ml) was added to magnesium turnings (16.3 g) at  $75^\circ\text{C}$  under high vacuum, and the mixture was refluxed for 2 h to produce a Grignard reagent. Ethylene oxide (50 ml) dried over calcium hydride ( $\text{CaH}_2$ ) in tetrahydrofuran (THF, 100 ml) was added to the Grignard reagent at  $0^\circ\text{C}$  under high vacuum, and was then allowed to react for 1 h. The product was hydrolyzed by hydrochloric acid, extracted with diethyl ether, concentrated, and distilled under reduced pressure ( $97-98^\circ\text{C}/3\text{ mmHg}$ ) to yield *p*-isopropenylphenethyl alcohol ( $\text{CH}_2=\text{C}(\text{CH}_3)-\text{C}_6\text{H}_4-\text{CH}_2\text{CH}_2\text{OH}$ , IPPA, 67 g, yield: 64%). To the IPPA (65 g) in carbon tetrachloride, triphenylphosphine [24,25] (110 g) was added, refluxed for 2 h, extracted with petroleum ether, concentrated, and distilled under reduced pressure ( $85-86^\circ\text{C}/3\text{ mmHg}$ ) to yield IPPC (62 g, yield: 87%). The IPPC was distilled twice and its purity was checked by  $^1\text{H}$  NMR. Subsequent purification was carried out at  $10^{-6}\text{ mmHg}$  in an all-glass apparatus equipped with break seals. IPPC was twice purified with  $\text{CaH}_2$ , distilled, and then diluted with carefully purified THF for anionic polymerization.

### 2.2. Reagents

*n*-Butyllithium (*n*-BuLi) was purchased and diluted with purified *n*-heptane. The concentration of the initiator was determined by titration with a standard HCl solution.  $\alpha$ -Methylstyrene was dried over  $\text{CaH}_2$  under a pressure of  $10^{-6}\text{ mmHg}$  and purified with octylbenzophenone sodium complex ( $\text{C}_8\text{H}_{17}-\text{C}_6\text{H}_4-\text{CO}-(\text{C}_6\text{H}_5)\text{Na}^+$ ) [22,23]. THF used for preparation of the macromonomers and deuterated THF ( $d_8$ -THF) used for polymerization were dried with sodium metal, distilled under high vacuum with anthracene sodium complex, and then purified by distillation from a mixture of  $\alpha$ -methylstyrene sodium complex. *n*-Heptane used for dilution of the initiator was dried with sodium metal, distilled under high vacuum with sodium metal, and then purified by distillation from a mixture of 1, 1-diphenylhexyllithium and *n*-BuLi.

### 2.3. Purification of the macromonomers

The PMStM macromonomers were dissolved in THF and precipitated in excess methanol to remove IPPC, which was not reacted with poly( $\alpha$ -methylstyryllithium). After drying under a high vacuum, each of the benzene solutions of the resultant

PMStM was introduced to an ampoule with a break seal, freeze-dried under a vacuum for 10 h, and sealed off by flame. The freeze-dried macromonomers were further dried under a pressure of  $10^{-6}\text{ mmHg}$  for 48 h, diluted with carefully purified  $d_8$ -THF, and sealed off by flame.

### 2.4. $^1\text{H}$ NMR measurements for kinetic and thermodynamic studies

Fig. 1 shows the apparatus for preparing the polymerization solution of the PMStM macromonomer. After the apparatus was evacuated to  $10^{-6}\text{ mmHg}$  and washed with a THF solution of  $\alpha$ -methylstyrene sodium complex, a heptane solution of *n*-BuLi (0.014 N, 3–8 ml) was introduced into the reactor. *n*-Heptane was collected in a flask and sealed off by flame. After cooling at  $-15^\circ\text{C}$ , the  $d_8$ -THF solution of PMStM (10 ml) was introduced into the reactor. The polymerization solution was sufficiently stirred at  $-15^\circ\text{C}$  to purge the impurities included in the polymerization solution and to initiate the PMStM. Part of the polymerization solution (0.60 ml) was transferred into NMR sample tubes and sealed off. The remaining polymerization solution was polymerized at  $-78^\circ\text{C}$  for 100 h. The resulting polymacromonomers were used to determine the weight, conversion, and molecular characteristics. The polymerization techniques were almost the same as those employed in previous studies conducted by the present authors [26].

The kinetic studies were carried out as follows: The polymerization solution was kept at  $-10^\circ\text{C}$  in an NMR instrument and the depropagation was checked by  $^1\text{H}$  NMR signals. The temperature was then decreased to a given temperature. It took less than 1 min for the polymerization solution to reach a constant temperature. The propagation rates were determined by following the conversion of polymacromonomers as a function of time. That is, the  $^1\text{H}$  NMR intensities of a vinyl group of isopropenyl group for PMStM (5.05 ppm and 5.33 ppm shown in Fig. 2) was measured as a function of time and normalized by the  $^1\text{H}$  NMR intensities of all

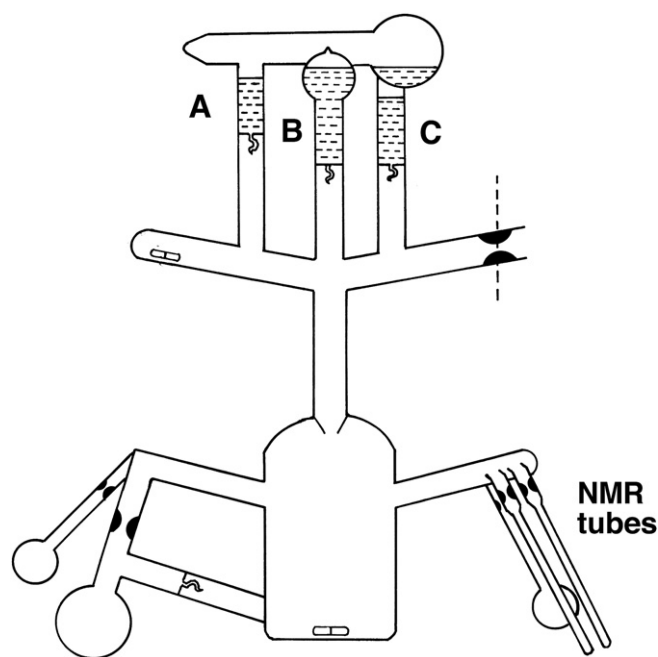


Fig. 1. A glass apparatus for preparing the sample solution used for the kinetic and thermodynamic measurements by the  $^1\text{H}$  NMR technique. The symbols represent the following: A, THF solution of  $\alpha$ -methylstyrene sodium complex; B,  $d_8$ -THF solution of PMStM; C, *n*-heptane solution of *n*-BuLi.

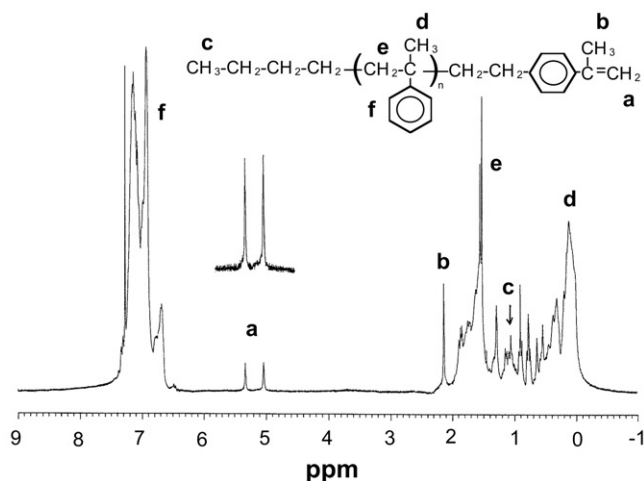


Fig. 2. A  $^1\text{H}$  NMR spectrum of the (*p*-isopropenylphenethyl)poly( $\alpha$ -methylstyrene) macromonomer (PMStM-1). The signals are assigned on the figure.

signal. The resultant value is presented by  $I_t$ . The conversion of polymacromonomers was calculated by  $(I_0 - I_t)/I_0$ , where  $I_0$  was the corresponding  $^1\text{H}$  NMR intensities of the polymerization solution kept at  $-10^\circ\text{C}$ . After the conversion of the (PMSt) $_m$  polymacromonomers reached an equilibrium state at which the corresponding  $^1\text{H}$  NMR intensities was presented by  $I_e$ , the equilibrium macromonomer concentrations  $[\text{PMStM}]_e$  were determined at that temperature from  $[\text{PMStM}]_0 \times (I_e/I_0)$ , where  $[\text{PMStM}]_0$  was the initial molar concentration of PMStM. After the measurements were finished, the temperature of the polymerization solution was raised to  $-10^\circ\text{C}$  for complete depropagation. These procedures were repeated for three PMStM macromonomers having different molecular weights from  $-10^\circ\text{C}$  to  $-78^\circ\text{C}$ . The spectra were observed with JEOL GX-270 FT NMR spectrometer: pulse repetition time, 7 s; accumulated scans, 16–64 times for the kinetic study or 256 times for determining the  $[\text{PMStM}]_e$ .

## 2.5. Molecular characterization

The number-average molecular weights ( $M_n$ ) of the macromonomers were determined by vapor pressure osmometry (VPO; Model 117, Hitachi, Tokyo, Japan) in Bz at  $30^\circ\text{C}$ , and the  $M_w/M_n$  values were determined by GPC (Model CCPD, Tosoh Co., Tokyo, Japan) using standard polystyrenes. Molecular characterization of the (PMSt) $_m$  polymacromonomers was carried out in THF using a GPC in conjunction with a low-angle laser light scattering

(GPC-LALLS) detector (Model LS-8000, Tosoh Co.) and RI detector (RI-8010, Tosoh Co.). For the GPC measurements, two high-resolution columns (G2500H, G3000H, G400H and GMH-M, 7.8 mm  $\times$  60 cm; Tosoh Co.) were connected in a series. Special analysis was required to determine  $M_n$  and  $M_w$  values of the (PMSt) $_m$  polymacromonomers using GPC-LALLS [15,27].

## 3. Results and discussion

### 3.1. Synthesis of (*p*-isopropenylphenethyl)poly( $\alpha$ -methylstyrene) macromonomer ( $\text{CH}_2=\text{C}(\text{CH}_3)-\text{C}_6\text{H}_4-\text{CH}_2\text{CH}_2-\text{C}(\text{CH}_3)=\text{CH}_2$ ) $\text{C}_6\text{H}_5-\text{CH}_2]_n-\text{C}_4\text{H}_9$ , PMStM)

The apparatus for preparing PMStM is similar to that shown in Fig. 1. After the apparatus was evacuated to  $10^{-6}$  mmHg and sealed off, it was washed inside with a THF solution of  $\alpha$ -methylstyrene sodium complex, which was afterward taken back into a flask and sealed off. *n*-BuLi was introduced into the reactor followed by a THF solution of  $\alpha$ -methylstyrene, which was maintained at  $-15^\circ\text{C}$ . The polymerization solution was sufficiently stirred at  $-15^\circ\text{C}$  for 20 min to purge the impurities included in the polymerization solution and to simultaneously initiate the  $\alpha$ -methylstyrene. The polymerization solution was inserted in a cold bath at  $-78^\circ\text{C}$  to propagate the  $\alpha$ -methylstyrene. This polymerization technique is the same as that used in the polymerization of PMStM; namely, ALEP.

After 1 h of polymerization, a THF solution of IPPC ([IPPC]/[*n*-BuLi] = 3.2–3.9) was added to the THF solution of poly( $\alpha$ -methylstyryllithium) (PMSt $^-$ ) at  $-78^\circ\text{C}$ . The PMSt $^-$  instantly changed its color from red to colorless to produce the PMStM macromonomer. The polymerization conditions and results are shown in Table 1. Each of the GPC chromatograms of three PMStM samples was uniform and sharp and had no shoulder at a higher  $M_n$  side that could be attribute to a dimer of poly( $\alpha$ -methylstyrene) (PMSt). This finding suggests that the coupling reaction of the PMSt $^-$  with IPPC occurs selectively and that of the PMSt $^-$  with the isopropenyl group of the produced PMStM does not occur [16,28].

Fig. 2 shows the  $^1\text{H}$  NMR spectrum of the resultant PMStM. As compared with a  $^1\text{H}$  NMR spectrum of PMSt, the vinyl protons of the isopropenyl group ( $\text{CH}_2=\text{C}(\text{CH}_3)-$ ) for PMStM were observed at 5.05 ppm and 5.33 ppm, and the methyl protons of that were observed at 2.11 ppm. IPPC also has the vinyl protons of the isopropenyl group at the same  $^1\text{H}$  NMR positions as those of PMStM, and further ethyl protons of a phenethyl group ( $-\text{C}_6\text{H}_4-\text{CH}_2-\text{CH}_2-\text{Cl}$ ) at 3.01 ppm and 3.68 ppm where the respective peak intensity is twice that of the corresponding vinyl protons. As the ethyl protons of the phenethyl group for the IPPC were not observed at 3.01 ppm and 3.68 ppm in Fig. 1, the vinyl

Table 1  
Preparation<sup>a</sup> and characterization of (*p*-isopropenylphenethyl)poly( $\alpha$ -methylstyrene) macromonomers (PMStM).

Polymers	Monomer g	THF ml	$10^{-3}M_k^b$	[IPPC]/[ <i>n</i> -BuLi] <sup>c</sup>	$10^{-3}M_n$			$M_w/M_n$		$f_c^h$
					VPO <sup>d</sup>	GPC <sup>e</sup>	NMR <sup>f</sup>	GPC <sup>e</sup>	VPO/LALLS <sup>g</sup>	
PMStM-1	8.2	180	1.67	2.3	1.74	1.77	1.79	1.09	1.12	0.97
PMStM-2	9.7	190	3.45	2.9	3.65	3.65	3.72	1.09	1.10	0.98
PMStM-3	10.4	210	5.30	2.9	5.60	5.36	5.65	1.08	1.09	0.99

<sup>a</sup>  $\alpha$ -Methylstyrene was anionically initiated by *n*-BuLi in THF at  $-15^\circ\text{C}$  for 20 min under a pressure of  $10^{-6}$  mmHg and then propagated at  $-78^\circ\text{C}$  for 1–2 h.

<sup>b</sup> Kinetic molecular weights determined from the amounts of monomer and initiator.

<sup>c</sup> The molar ratio of *p*-isopropenylphenethyl chloride (IPPC) as a deactivator to *n*-BuLi as an initiator.

<sup>d</sup> Determined by the vapor pressure osmometry ( $M_n^{\text{VPO}}$ ).

<sup>e</sup> PSt-reduced molecular weight ( $M_n^{\text{PSt}}$ ) was determined by GPC using standard PSts. Then, ( $M_n^{\text{PMSt}}$ ) was determined from  $M_n^{\text{PSt}}[\eta]_{\text{PSt}} = M_n^{\text{PMSt}}[\eta]_{\text{PMSt}}$ , where  $[\eta]_{\text{PSt}}/[\eta]_{\text{PMSt}} = 0.94$ .

<sup>f</sup> Calculated from the ratio of benzene to isopropenyl groups determined from the NMR measurements ( $M_n^{\text{NMR}}$ ).

<sup>g</sup> A special analysis using GPC in conjunction with a low-angle laser light scattering detector ( $M_w^{\text{LALLS}}$ ) [2,27].

<sup>h</sup> Coupling efficiency determined by  $M_n^{\text{VPO}}/M_n^{\text{NMR}}$ .

protons of the isopropenyl group at 5.05 ppm and 5.33 ppm were assigned to those of not IPPC but PMStM. From the ratio of the  $^1\text{H}$  NMR intensities of all signals to that of the vinyl group, a number-average molecular weight ( $M_n^{\text{NMR}}$ ) can be calculated. Thus, the coupling efficiency ( $f_c$ ) can be determined as  $f_c = M_n^{\text{VPO}}/M_n^{\text{NMR}}$ . As shown in Table 1, three well-defined PMStM macromonomers having different  $M_n$ , narrow molecular weight distributions, and  $f_c = 0.97$ – $0.99$  were prepared.

### 3.2. Anionic living-equilibrium polymerization (ALEP) of PMStM macromonomers

When the  $d_8$ -THF solution of PMStM was added to  $n$ -butyllithium at  $-15^\circ\text{C}$ , its color changed immediately from colorless to red. The red color corresponds to the production of poly( $\alpha$ -methylstyryllithium) carbanion. After stirring for 20 min at  $-15^\circ\text{C}$ , part of the  $d_8$ -THF solution of  $n$ -BuLi and PMStM was transferred into NMR sample tubes and sealed off by flame. The remaining polymerization solution was cooled and kept at  $-78^\circ\text{C}$  for 100 h to produce  $(\text{PMSt})_m$  polymacromonomers. The polymerization conditions and results for the three PMStM having different  $M_n$  are shown in Table 2.

Fig. 3 shows a representative GPC chromatogram of the product for PMStM-1, where two peaks were observed: one is due to PMStM-1 macromonomer and the other is due to  $(\text{PMSt-1})_m$  polymacromonomers. Although the ALEP is well known, attention should be directed to PMStM-1 and  $(\text{PMSt-1})_m$  that coexist in THF at  $-78^\circ\text{C}$  under high vacuum at a state of ALEP. A part of PMStM-1 was polymerized to produce the living  $(\text{PMSt-1})_m^-$  carbanion of polymacromonomer and the residual PMStM-1 remained unreacted at  $-78^\circ\text{C}$  even after a long polymerization time, because the polymerization rate was equal to the depolymerization rate at the state of ALEP. When the polymerization temperature of  $-78^\circ\text{C}$  was raised to a different temperature and kept there for a long time, the GPC peaks due to the  $(\text{PMSt-1})_m^-$  and the residual PMStM-1 decreased and increased, respectively. Thus the yield of the  $(\text{PMSt-1})_m^-$  was found to depend on the polymerization temperature. The yield of the polymacromonomers will be discussed in detail in the next section of “thermodynamic studies on ALEP of PMStM”. In conclusion, the GPC peak of PMStM-1 in Fig. 3 is not due to poly( $\alpha$ -methylstyrene) without an  $\alpha$ -methylstyrene group at one end and due to the unreacted PMStM-1 that coexisted with  $(\text{PMSt-1})_m^-$  terminated by some impurities, but the unreacted PMStM-1 that coexisted with the living  $(\text{PMSt-1})_m^-$  carbanion.

As shown in Table 2, each  $M_n^{\text{LALLS}}$  value determined by GPC-LALLS of the resultant three  $(\text{PMSt})_m$  polymacromonomers is larger than the corresponding  $M_n^{\text{GPC}}$  value determined by GPC using standard PSTs. This finding provides evidence that the resultant

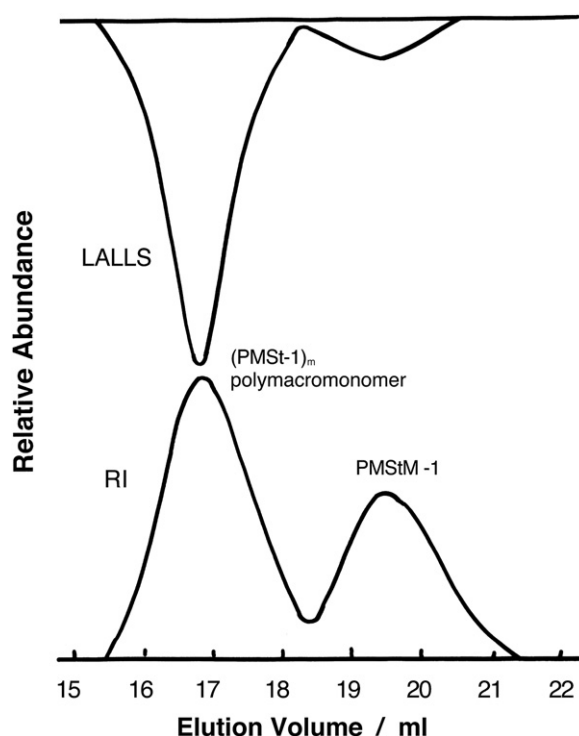


Fig. 3. GPC chromatograms of the product prepared via anionic living-equilibrium polymerization (ALEP) of PMStM-1 by  $n$ -BuLi in THF at  $-78^\circ\text{C}$  using the RI and LALLS detectors. One is a peak due to the PMStM-1 macromonomer and the other is a peak due to the  $(\text{PMSt-1})_m$  polymacromonomer.

product is not linear polymers but non-linear polymers such as comb-shaped polymers. It has been shown that polymacromonomers, regular comb polymers with dense side chains, are sometimes called “bottle-brush polymers” or “brushlike polymers” and behave like stiff chains in dilute solution [29,30]. However, when the degree of polymerization of  $(\text{PMSt})_m$  polymacromonomers is low (for example,  $m = 3$ – $6$ ), the polymacromonomers are supposed to behave like star polymers. It is well known that the molecular dimensions of the star polymers are smaller than those of the linear polymers having the same molecular weights as those of the star polymers. This behavior can be explained by the  $g_{\text{star}}$  value, defined as  $g_{\text{star}} = \langle S^2 \rangle_{\text{star}} / \langle S^2 \rangle_{\text{linear}} = (3m - 2)/m^2$ , where  $\langle S^2 \rangle$  and  $m$  are the mean-square radius of gyration and the number of arms, respectively [31,32]. Thus, the  $(\text{PMSt})_m$  polymacromonomers similar to the star polymers having narrow molecular weight distributions were prepared.

**Table 2**  
Anionic living-equilibrium polymerization<sup>a</sup> (ALEP) of PMStM macromonomers.

Polymers	$10^{-3}M_n$ of PMStM	PMStM <sup>b</sup>	$d_8$ -THF	$10^3[\text{I}]$	$[\text{PMStM}]/[\text{I}]^c$	Yield %	$10^{-3}M_n$		$M_w/M_n$	$m^f$	$f_i^g$	$10^3[\text{LE}]^h$
		g	ml	mol l <sup>-1</sup>			GPC <sup>d</sup>	LALLS <sup>e</sup>	LALLS <sup>e</sup>			
PMStM-1	1.77	0.70	9.0	7.50	5.8	62.0	10.1	16.8	1.10	9.5	0.38	2.85
PMStM-2	3.65	0.72	8.2	14.8	1.6	60.9	12.9	15.0	1.07	4.1	0.24	3.55
PMStM-3	5.36	0.70	8.1	5.33	3.0	31.4	15.7	18.8	1.07	3.5	0.27	1.44

<sup>a</sup> PMStM macromonomers were anionically initiated by  $n$ -BuLi in  $d_8$ -THF at  $-15^\circ\text{C}$  for 20 min under a pressure of  $10^{-6}$  mmHg and then propagated at  $-78^\circ\text{C}$  for 100 h.

<sup>b</sup> The weights were corrected by [the amount of PMStM used]  $\times f_c$ , where  $f_c$  is the coupling efficiency of the PMStM.

<sup>c</sup> The molar ration of PMStM to  $n$ -BuLi; namely, kinetic number of side chains of  $(\text{PMSt})_m$  polymacromonomers.

<sup>d</sup> PST-reduced molecular weight ( $M_n^{\text{PST}}$ ) was determined by GPC using standard PSTs. Then,  $M_n^{\text{PMSt}}$  was determined from  $M_n^{\text{PST}}[\eta]_{\text{PST}} = M_n^{\text{PMSt}}[\eta]_{\text{PMSt}}$ , where  $[\eta]_{\text{PST}}/[\eta]_{\text{PMSt}} = 0.94$ .

<sup>e</sup> A special analysis using GPC in conjugation with a low-angle laser light scattering detector ( $M_n^{\text{LALLS}}$  and  $M_w^{\text{LALLS}}$ ) [2,27].

<sup>f</sup> Number of side chains of the produced  $(\text{PMSt})_m$  polymacromonomers corresponding to the degree of polymerization of PMStM.

<sup>g</sup> Initiation efficiency determined by  $(\text{Yield} \times [\text{PMStM}]/[\text{I}])/m$ .

<sup>h</sup> Effective molar concentration of the living end determined by  $[\text{LE}] = f_i [\text{I}]$ .



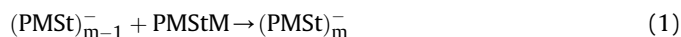
The initiation efficiency ( $f_i$ ) for ALEP of PMStM was found to be below. This lack of efficiency can be explained in part by the uncompleted purification of PMStM macromonomer [2,14,33,34]. In addition, the amount of  $n$ -BuLi used in this polymerization ( $4 \times 10^{-5} - 9 \times 10^{-5}$  mol) was less than half of that used for the common polymerization condition; namely, when 10 g polymer with  $M_n = 5 \times 10^4$  is prepared, the amount of  $n$ -BuLi is  $20 \times 10^{-5}$  mol. Although this problem will be discussed in future elsewhere, the effective concentration of living end ([LE]) can be determined from the apparent concentration of initiator ([I]) by [LE] =  $f_i$  [I]. The [LE] values corrected thus were used for the kinetic study.

Supplemental explanation of the low numbers of side chains of the produced (PMSt) $_m$  polymacromonomers is as follows, where  $m = 3.3-9.5$ . The lower initiator concentrations are necessary for preparing (PMSt) $_m$  having the higher  $m$  values. However, the lower initiator concentrations must be higher than the concentrations of the impurities involved in the polymerization solution. The  $f_i$  values were low as mentioned above, and hence it was difficult to precisely control the higher  $m$  values more than 10 in the present study.

### 3.3. Kinetic studies on ALEP of PMStM

Typical examples of the living-equilibrium polymerization are an anionic polymerization of  $\alpha$ -methylstyrene derivatives [19,35] and a coordination polymerization of  $n$ -hexyl isocyanate [36,37]. But there has been no study regarding ALEP of macromonomers. In order to clarify the relationship between the molecular weight and the propagation rate constant, three PMStM macromonomers were polymerized in the  $^1\text{H}$  NMR tubes. The conversion of the (PMSt) $_m$  polymacromonomers was determined from a decrease in the  $^1\text{H}$  NMR intensity of a vinyl group of isopropenyl group for PMStM.

According to the living polymerization, the propagation rate can be expressed as follows:



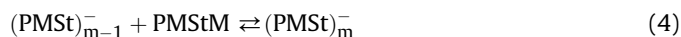
$$-d[\text{PMStM}]/dt = k_p[\text{LE}][\text{PMStM}] \quad (2)$$

where  $k_p$  is the propagation rate constant; [PMStM] and [LE] are the molar concentrations of the PMStM and the living ends, respectively. As [LE] remains constant during the propagation, the kinetic equation of the living polymerization of PMStM can be obtained as follows:

$$\ln([\text{PMStM}]_0/\text{PMStM}) = k_p[\text{LE}]t \quad (3)$$

where [PMStM] $_0$  is the initial molar concentration of the PMStM. Fig. 4 shows the plots of the left-side term of Eq. (3) against the [LE] $t$ , when PMStM-2 was propagated at  $-78^\circ\text{C}$ . The plots do not show a straight line even on the lower conversion side of the (PMSt) $_m$  polymacromonomers. At large limiting [LE] $t$  values, the conversion curve will be asymptotic to the value of  $([\text{PMStM}]_0 - [\text{PMStM}]_e)/[\text{PMStM}]_0$ , which is also described in Fig. 4, where [PMStM] $_e$  is the equilibrium molar concentration of the PMStM. It is concluded that the propagation did not follow the simple first-order rate equation expressed by Eq. (3).

On the other hand, the propagation rate of ALEP of PMStM can be expressed as follows [19,20]:



$$-d[\text{PMStM}]/dt = k_p[\text{LE}][\text{PMStM}] - k_d[\text{LE}] \quad (5)$$

where  $k_d$  is the depropagation rate constant. After the equilibrium is attained, the PMStM concentration reaches to the equilibrium

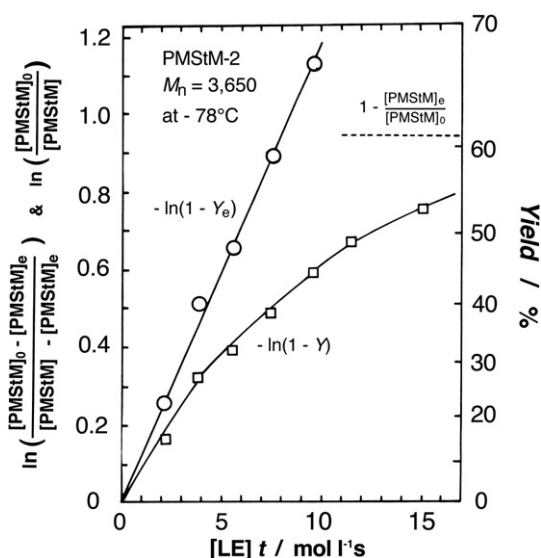


Fig. 4. The simple first-order plots and the corrected first-order plots using [PMStM] $_e$  for ALEP of PMStM-2 by  $n$ -BuLi in THF at  $-78^\circ\text{C}$  measured by the  $^1\text{H}$  NMR technique.

PMStM concentration. According to Eq. (5), the [PMStM] $_e$  is given in the following:

$$[\text{PMStM}]_e = k_d/k_p \quad (6)$$

Therefore, Eq. (5) can be expressed by using [PMStM] $_e$

$$-d[\text{PMStM}]/dt = k_p[\text{LE}]( [\text{PMStM}] - [\text{PMStM}]_e ) \quad (7)$$

Thus, the kinetic equation of ALEP can be obtained as follows:

$$\ln([([\text{PMStM}]_0 - [\text{PMStM}]_e) / ([\text{PMStM}] - [\text{PMStM}]_e)) = k_p[\text{LE}]t \quad (8)$$

Fig. 4 also shows the plots of the left-side term of Eq. (8) against the [LE] $t$ . As a straight line was observed, it is concluded that the propagation follows a mechanism of ALEP expressed by Eq. (5). The difference in the conversion of (PMSt) $_m$  polymacromonomers between the two curves is due to the difference between  $1 - ([\text{PMStM}]/[\text{PMStM}]_0)$  by Eq. (3) and  $1 - ([([\text{PMStM}] - [\text{PMStM}]_e) / ([\text{PMStM}]_0 - [\text{PMStM}]_e))$  by Eq. (8).

Fig. 5 shows the temperature dependence of the propagation behavior for PMStM-3 at  $-60^\circ\text{C}$  and at  $-78^\circ\text{C}$ . To clarify this point, the left-side terms of Eq. (8) were plotted against  $t$ . Fig. 6 shows the  $M_n$  dependence of the propagation behavior for three PMStM macromonomers at  $-78^\circ\text{C}$ . As the [LE] of the three propagations differ, the left-side terms of Eq. (8) were plotted against [LE] $t$ . From the slopes of the straight lines in Fig. 6, the  $k_p$  values were determined. The kinetic results are described in Table 3. The  $k_p$  values decreased with increasing molecular weight ( $M_n$ ) of PMStM.

### 3.4. The dependence of $k_p$ on the $M_n$ of PMStM

Fig. 7 shows the plots of  $k_p$  against the  $M_n$  of PMStM, with the results for  $\alpha$ -methylstyrene also plotted as a reference. As shown in Fig. 7, the  $k_p$  is proportional to a reciprocal of  $M_n$  of PMStM: namely,  $k_p \sim M_n^{-1}$ . According to simple diffusion-controlled theory [38], the propagation of PMStM consists of 2 processes. (i) One is the diffusion of PMStM into the vicinity of the living (PMSt) $_m^-$ . The diffusion of PMStM is important for the discussion because the (PMSt) $_m^-$  polymacromonomer is too large to diffuse for a short time under consideration, compared with PMStM. (ii) Another is an effective collision between the vinyl group of PMStM and the living end of

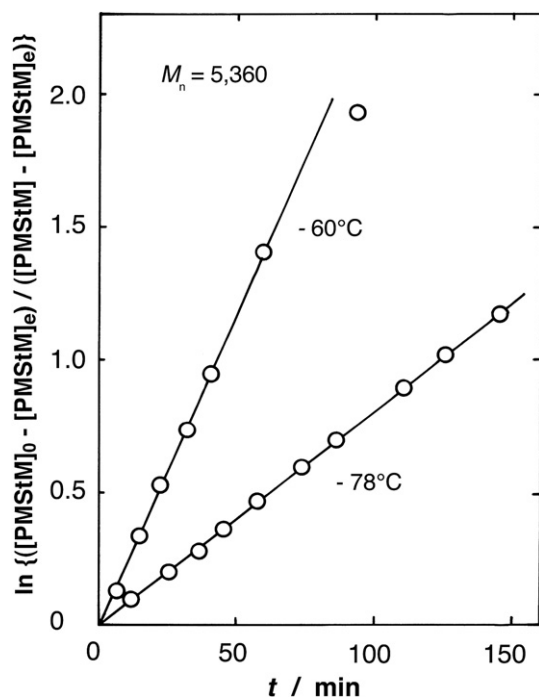


Fig. 5. The corrected first-order plots using  $[PMStM]_e$  for ALEP of PMStM-3 by  $n$ -BuLi in THF at  $-60$  °C and  $-78$  °C.

$(PMStM)_m^-$ . The effective collision of PMStM is important for the discussion because the  $(PMStM)_m^-$  polymacromonomer is also too large to change its position, as compared with PMStM. When the diameters of PMStM and the vinyl group of PMStM are  $L$  and  $d$ , respectively, the probability of the effective collision should be  $d/L$ . In other words, the second process corresponds to steric hindrance between the two reactive sites.

Hence,  $k_p \sim D(d/L)$ , where  $D$  is the diffusion constant of PMStM. The  $d$  does not depend on the  $M_n$  of PMStM. In the case of  $\theta$  solvent,  $D \sim M_n^{-0.5}$  and  $L \sim \langle R^2 \rangle^{0.5} \sim M_n^{0.5}$ . Thus,  $k_p \sim D L^{-1} \sim M_n^{-0.5} (M_n^{0.5})^{-1} \sim M_n^{-1}$  although the present discussion is simple and adequately approximated, the  $M_n$  dependence of  $k_p$  shown in Fig. 7 might be explained as described above.

During the propagation of macromonomers (increasing the molecular weights of polymacromonomers), the steric hindrance, which arises from the conformation of the branched living chain, is expected to be getting larger. However, in the case of polymerization of common monomers, the steric hindrance between the monomer and the growing oligomer at an initial polymerization stage might be the same as that between the monomer and the growing polymer at the final polymerization stage. Thus, the steric hindrance is due to the steric interaction of the two reactive sites as a first approximation. Similarly the steric hindrance between PMStM and the branched living end of  $(PMStM)_m^-$  might not be

**Table 3**  
Propagation rate constants of the PMStM macromonomers by  $n$ -BuLi in THF via ALEP.

Macromonomers	$10^{-3}M_n$ of PMStM	$k_p$		$10^{-3} \Delta E_a$
		$l\text{ mol}^{-1}\text{ s}^{-1}$		$J\text{ mol}^{-1}$
		$-60\text{ }^{\circ}\text{C}$	$-78\text{ }^{\circ}\text{C}$	
PMStM-1	1.77		0.240	
PMStM-2	3.65	0.282	0.110	33.2
PMStM-3	5.36	0.269	0.0790	41.6
$\alpha$ -methylstyrene <sup>a</sup>	0.118		3.60	50.7

<sup>a</sup> The results were reported in the reference No. [19] and [20].

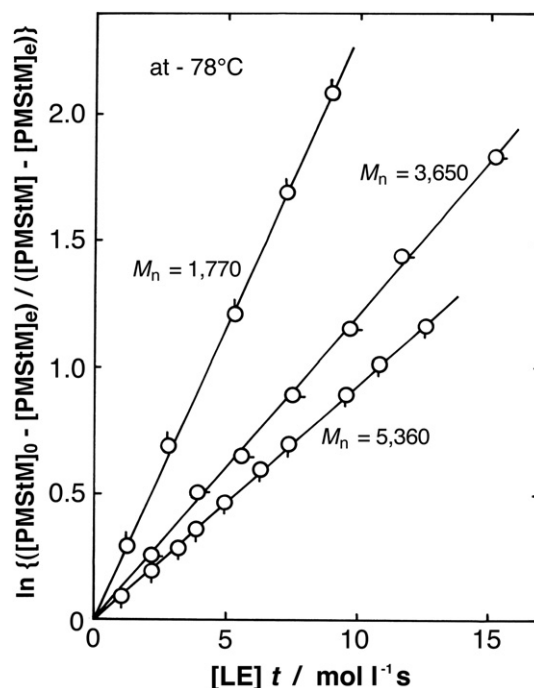


Fig. 6. The corrected first-order plots using  $[PMStM]_e$  for ALEP of the three PMStM macromonomers by  $n$ -BuLi in THF at  $-78$  °C.

affected by the difference in the conformation of the branched living  $(PMStM)_m^-$  due to an increase in  $m$  (a number of side chains) of the growing branched  $(PMStM)_m^-$ . Therefore, the  $k_p$  shows constant values that depend on the  $M_n$  of PMStM. This finding is in accord with the straight line of the corrected first-order plots using  $[PMStM]_e$  as shown in Fig. 4.

### 3.5. Thermodynamic studies on ALEP of PMStM

According to Eq. (4), the equilibrium constant ( $K$ ) for ALEP can be given as

$$K = \frac{[(PMStM)_m^-]}{[(PMStM)_{m-1}^-][PMStM]_e} = 1/[PMStM]_e \quad (9)$$

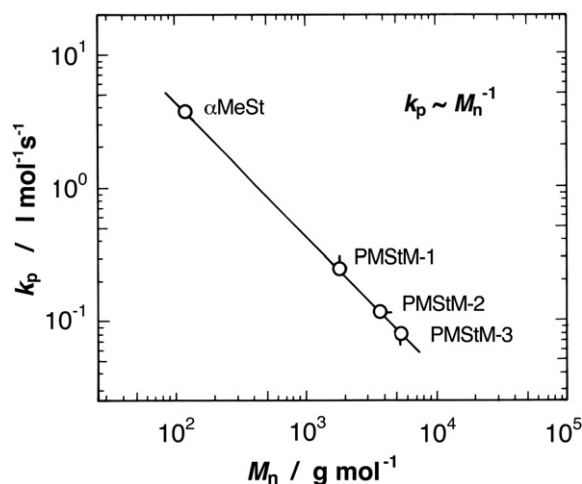


Fig. 7. The dependence of  $k_p$  on the  $M_n$  of PMStM for ALEP of the three PMStM macromonomers by  $n$ -BuLi in THF at  $-78$  °C. The result of  $\alpha$ -methylstyrene is also described in the figure.

The molar Gibbs free energy of the propagation ( $\Delta G_{\text{PMStM}}$ ) can be calculated from  $K$  and  $[\text{PMStM}]_e$  as

$$\Delta G_{\text{PMStM}} = -RT \ln K = RT \ln [\text{PMStM}]_e \quad (10)$$

Therefore, the following equations at the equilibrium state can be obtained as [14,16]

$$\ln [\text{PMStM}]_e = \Delta G_{\text{PMStM}} / RT = (\Delta H_{\text{PMStM}} / RT) - (\Delta S_{\text{PMStM}} / R) \quad (11)$$

$$T_c^{\text{PMStM}} = \Delta H_{\text{PMStM}} / \Delta S_{\text{PMStM}} \quad (12)$$

where  $\Delta H_{\text{PMStM}}$  and  $\Delta S_{\text{PMStM}}$  are the changes in enthalpy and entropy of the propagation of PMStM, respectively;  $T_c$  is the ceiling temperature when  $\Delta G_{\text{PMStM}} = 0$  or  $[\text{PMStM}]_e = 1 \text{ mol l}^{-1}$ .

The  $[\text{PMStM}]_e$  values were determined by  $^1\text{H}$  NMR measurements at different propagation temperatures for the three PMStM. Plots of  $\ln [\text{PMStM}]_e$  against  $1/T$  are shown in Fig. 8, which follows Eq. (11). From the slopes and intercepts of the three straight lines, the  $\Delta H_{\text{PMStM}}$  and  $\Delta S_{\text{PMStM}}$  were determined. The thermodynamic characteristics estimated thus are shown in Table 4. The magnitudes of the  $\Delta H_{\text{PMStM}}$  increase with decreases in the  $M_n$  of PMStM, and approach that of  $\alpha$ -methylstyrene. In contrast, the  $\Delta S_{\text{PMStM}}$  changes in positive or negative values with varying  $M_n$  of PMStM, and hence the  $T_c$  also changes in positive or negative values. The negative  $T_c$  values are difficult to understand. Additional analysis is therefore necessary to elucidate the ALEP of PMStM.

Attention should be directed to  $[\text{PMStM}]_e$ . When the  $[\text{PMStM}]_e$  values of the three PMStMs differ at the same propagation temperature, this finding contains two physical meanings; one is the  $M_n$  dependence of PMStM, and the other is the concentration dependence of PMStM. Even if the  $[\text{PMStM}]_e$  values for the three PMStMs are the same, their concentrations differ more than 3 times. For example, the  $T_c$  can be defined as the temperature at which  $[\text{PMStM}]_e = 1.0$ . In the case of  $[\text{PMStM-3}]_e = 1$ , PMStM-3 of 5360 g should be dissolved in 1 L solution, which would be impossible to prepare. This finding allows the concept of equilibrium monomer concentration to be developed for the equilibrium macromonomer concentration. For discussing only the  $M_n$  dependence of thermodynamic characteristics, the concentration

dependence should be excluded as much as possible. That is, the molar concentration of a  $\alpha$ -methylstyrene monomeric unit for PMStM ( $[\text{MSt}]$ ) should be used as a substitute for the molar concentration of PMStM: namely,  $[\text{PMStM}]_e = [\text{MSt}]_e / n$ , where  $n$  is the degree of polymerization of PMStM. Thus, Eqs. (10) and (11) for PMStM change to the following equations for the MSt monomeric unit.

$$\Delta G_{\text{PMStM}} = RT \ln \{ [\text{MSt}]_e / n \} = RT \ln [\text{MSt}]_e - RT \ln n \quad (13)$$

Therefore,

$$\begin{aligned} \ln [\text{MSt}]_e &= \Delta G_{\text{PMStM}} / RT + \ln n \\ &= (\Delta H_{\text{PMStM}} / RT) - (\Delta S_{\text{PMStM}} / R - \ln n) \\ &= (\Delta H_{\text{MSt}} / RT) - (\Delta S_{\text{MSt}} / R) \end{aligned} \quad (14)$$

where the  $\Delta H_{\text{MSt}}$  and  $\Delta S_{\text{MSt}}$  are the changes in enthalpy and entropy of the propagation of PMStM using  $[\text{MSt}]_e$ : namely,  $\Delta H_{\text{MSt}} = \Delta H_{\text{PMStM}}$  and  $\Delta S_{\text{MSt}} = \Delta S_{\text{PMStM}} - R \ln n$ . Hence, the  $T_c^{\text{MSt}}$  can be determined as,

$$T_c^{\text{MSt}} = \Delta H_{\text{MSt}} / \Delta S_{\text{MSt}} \quad (15)$$

Plots of  $\ln [\text{MSt}]_e$  against  $1/T$  for the three PMStM are shown in Fig. 9, which follows Eq. (14). From the slopes and intercepts of three straight lines, the  $\Delta H_{\text{MSt}}$  and  $\Delta S_{\text{MSt}}$  were determined. The thermodynamic characteristics estimated thus are also shown in Table 4.

There is doubt as to whether the ALEP of macromonomers is an effective method for preparing well-defined polymacromonomers. The reason is that as shown in Fig. 3, the unreacted PMStM is included in the final products and subsequently should be removed from the mixture so as to isolate  $(\text{PMSt})_m$  polymacromonomers. Though the unreacted PMStM can be efficiently separated from the mixture by fractionation, it is better that most of the PMStM can be polymerized to produce the corresponding polymacromonomers. The yield of  $(\text{PMSt})_m$  polymacromonomers ( $Y$ ) is as follows:

$$\begin{aligned} Y/\% &= 100 \{ 1 - ([\text{PMStM}]_e / [\text{PMStM}]_0) \} \\ &= 100 \{ 1 - ([\text{MSt}]_e / [\text{MSt}]_0) \} \end{aligned} \quad (16)$$

For example, when  $\alpha$ -methylstyrene with an initial concentration of 5.0 wt% is polymerized at  $-78^\circ\text{C}$ ,  $[\text{MSt}]_0$  is  $0.44 \text{ mol l}^{-1}$ ,  $[\text{MSt}]_e$  is  $2 \times 10^{-3} \text{ mol l}^{-1}$  as shown in Fig. 9, and the  $Y$  becomes 99.5%. This is a well-known result for  $\alpha$ -methylstyrene derivatives where the  $Y$  is not 100% but close to 100%. When PMStM-1 with an initial concentration of 7.7 wt% was polymerized at  $-78^\circ\text{C}$ ,  $[\text{MSt}]_0$  was  $0.66 \text{ mol l}^{-1}$ ,  $[\text{MSt}]_e$  was  $0.25 \text{ mol l}^{-1}$  as shown in Fig. 9, and the  $Y$  became 62%. This finding was shown in Table 2 and Fig. 3. If PMStM-1 with an initial concentration of 20 wt% is polymerized at  $-90^\circ\text{C}$  (mp of THF is  $-108.5^\circ\text{C}$ ),  $[\text{MSt}]_0$  is  $1.7 \text{ mol l}^{-1}$ ,  $[\text{MSt}]_e$  is  $0.17 \text{ mol l}^{-1}$ , and the  $Y$  would become 90%. Though the  $Y$  is still less than 100%, it should increase by raising the initial concentration and lowering the polymerization temperature. This is an interesting method of increasing the  $Y$  to approach 100%, and subsequently of preparing well-defined polymacromonomers without removal of the unreacted macromonomers.

### 3.6. The dependence of $\Delta H_{\text{MSt}}$ and $\Delta S_{\text{MSt}}$ on the $M_n$ of PMStM

Fig. 10 shows the dependence of  $\Delta H_{\text{MSt}}$  and  $\Delta S_{\text{MSt}}$  on the  $M_n$  of PMStM. Both values increase with an increase in the  $M_n$ , and will be asymptotic to the value of zero. For PMStM having a limiting high  $M_n$ , both values can be expected to be zero, where the polymerization of PMStM does not proceed, so there is no exothermic reaction and no decrease in entropy.

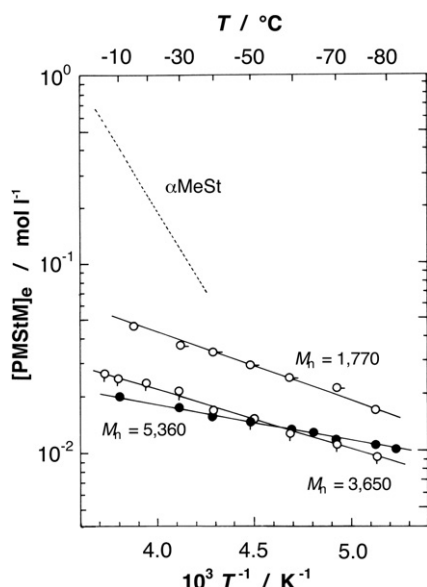


Fig. 8. Temperature dependence of the equilibrium PMStM concentration ( $[\text{PMStM}]_e$ ) for ALEP of the three PMStM macromonomers by  $n\text{-BuLi}$  in THF. The result of  $\alpha$ -methylstyrene is also described in the figure. From the slopes and intercepts of the straight lines,  $\Delta H_{\text{PMStM}}$  and  $\Delta S_{\text{PMStM}}$  were determined.

**Table 4**Thermodynamic characteristics of the PMStM macromonomers by *n*-BuLi in THF via ALEP.

Macromonomers	$10^{-3}M_n$ of PMStM	Eq. (11) <sup>a</sup>			Eq. (14) <sup>b</sup>		
		$10^{-3}\Delta H_{\text{PMStM}}$ J mol <sup>-1</sup>	$\Delta S_{\text{PMStM}}$ J mol <sup>-1</sup> K <sup>-1</sup>	$T_C^{\text{PMStM}}$ °C	$10^{-3}\Delta H_{\text{MSt}}$ J mol <sup>-1</sup>	$\Delta S_{\text{MSt}}$ J mol <sup>-1</sup> K <sup>-1</sup>	$T_C^{\text{MSt}}$ °C
PMStM-1	1.77	-7.48	-4.30	1470	-7.48	-26.8	6.0
PMStM-2	3.65	-6.73	4.41	Negative	-6.73	-24.1	6.1
PMStM-3	5.36	-3.82	18.0	Negative	-3.82	-13.7	5.7
$\alpha$ -methylstyrene <sup>c</sup>	0.118	-33.5	-120	6.0	-33.5	-120	6.0

<sup>a</sup> Determined from the slopes and intercepts of the plots of  $\ln[\text{PMStM}]_e$  against  $T^{-1}$ ; namely, using the molar concentration of the equilibrium PMStM macromonomer ( $[\text{PMStM}]_e$ ).

<sup>b</sup> Determined from the slopes and intercepts of the plots of  $\ln[\text{MSt}]_e$  against  $T^{-1}$ ; namely, using the molar concentration of the monomeric unit of the PMStM macromonomer ( $[\text{MSt}]_e$ ). That is,  $[\text{MSt}] = n[\text{PMStM}]$ , where  $n$  is the degree of polymerization of PMStM.

<sup>c</sup> The results were reported in the reference No. [19] and [20].

The  $\Delta H_{\text{MSt}}$  may be due to a difference in the bond energy converted from the isopropenyl group (a C=C double bond) to the isopropyl one (a C–C single bond). Taking into account that  $\Delta H_{\text{MSt}} = \Delta H_{\text{PMStM}}$ , it seems strange that  $\Delta H_{\text{MSt}}$  depends on the  $M_n$  of PMStM. However, in the case of  $\alpha$ -methylstyrene, the difference in the bond energy converted from the C=C double bond (612 kJ mol<sup>-1</sup>) to the C–C single bond (348 kJ mol<sup>-1</sup>) is -264 kJ mol<sup>-1</sup> [32]. This value is much different from the  $\Delta H_{\text{MSt}}$  one of  $\alpha$ -methylstyrene (-33.5 kJ mol<sup>-1</sup>). The difference between the two values should not be considered strange because the standard reaction enthalpy can be calculated from the standard enthalpy of formation but can not from the mean bond enthalpy. In other word, the  $\Delta H_{\text{MSt}}$  might contain a difference in the interaction between the resultant (PMSt)<sub>m</sub><sup>-</sup>, PMStM, and solvent, in addition to the difference in the mean bond enthalpy. Thus, the  $M_n$  dependence of  $\Delta H_{\text{MSt}}$  does not appear to be strange and is likely affected by some interaction not yet identified well.

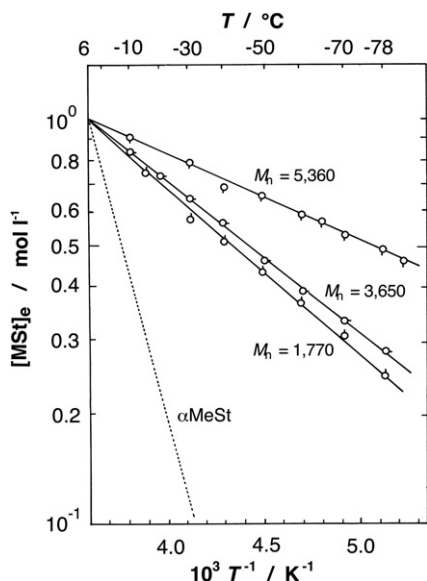
On the other hand, the  $M_n$  dependence of  $\Delta S_{\text{MSt}}$  can be expected to be observed without special analysis. In the propagation,  $\Delta S_{\text{MSt}}$  should be a negative value that corresponds to an entropy change from a free chain of PMStM to a side chain of the poly-macromonomer like the comb polymer or to an arm of the star

polymer. With an increase in the  $M_n$  of PMStM, the magnitude of  $\Delta S_{\text{MSt}}$  became a small value corresponding to a small entropy change from PMStM to a side chain of polymacromonomers. The  $M_n$  dependence shown in Fig. 10, which is quite easy to understand, is reported herein for the first time.

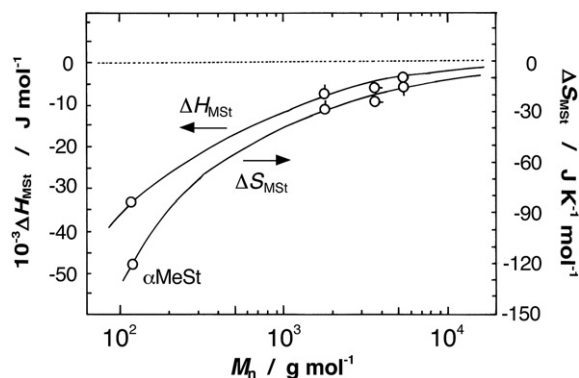
The most striking finding is that the  $T_C^{\text{MSt}}$  (6.0 °C) for the three PMStM including  $\alpha$ -methylstyrene exhibit the same values. As shown in Fig. 10,  $M_n$  dependence of  $\Delta H_{\text{MSt}}$  is similar to that of  $\Delta S_{\text{MSt}}$ , even though their values and dimensions differ. Let us suppose a function of the  $M_n$  dependence for  $\Delta H_{\text{MSt}}$  and  $\Delta S_{\text{MSt}}$  as  $f(n)$ . Therefore, both thermodynamic characteristics can be described as  $\Delta H_{\text{MSt}} \sim \Delta H_0 f(n)$  and  $\Delta S_{\text{MSt}} \sim \Delta S_0 f(n)$ , where  $\Delta H_0$  and  $\Delta S_0$  are constants and can be substituted for the corresponding constants of  $\alpha$ -methylstyrene, and  $n$  is the degree of polymerization of the PMStM macromonomer. Thus,  $T_C^{\text{MSt}} = \Delta H_{\text{MSt}}/\Delta S_{\text{MSt}} = \Delta H_0 f(n)/\Delta S_0 f(n) = \Delta H_0/\Delta S_0$ . The resultant  $T_C^{\text{MSt}}$  did not comprise the  $f(n)$ ; namely, the  $T_C^{\text{MSt}}$  did not depend on  $M_n$  of PMStM but was the same as that of the  $\alpha$ -methylstyrene. The present explanation of  $T_C^{\text{MSt}} = 6.0$  °C is simple and might be reasonably accurate as a first approximation.

On the other hand, though the  $T_C^{\text{MSt}}$  is based on the calculations of  $\Delta H_{\text{MSt}}/\Delta S_{\text{MSt}}$ , the chemical meaning of the  $T_C^{\text{MSt}}$  may be related to the polymerization and depolymerization of the monomer. All the macromonomers and  $\alpha$ -methylstyrene have the same  $\alpha$ -methylstyryl groups, which undergo the propagation. So, the  $T_C^{\text{MSt}}$  should be directly related to the chemical structure of the  $\alpha$ -methylstyryl groups. It might not be surprise that all the  $T_C^{\text{MSt}}$  values are almost the same.

A comment regarding  $f(n)$  must be made, as follows. It is convenient to consider that an isopropenyl group at an end of



**Fig. 9.** Temperature dependence of the equilibrium monomeric concentration of PMStM ( $[\text{MSt}]_e$ ) for ALEP of the three PMStM macromonomers by *n*-BuLi in THF. The result of  $\alpha$ -methylstyrene is also described in the figure. From the slopes and intercepts of the straight lines,  $\Delta H_{\text{MSt}}$  and  $\Delta S_{\text{MSt}}$  were determined. The  $T_C^{\text{MSt}}$  of the four samples exhibit the same values.



**Fig. 10.** The dependence of  $\Delta H_{\text{MSt}}$  and  $\Delta S_{\text{MSt}}$  on the  $M_n$  of PMStM for ALEP of the three PMStM macromonomers determined by the plots of  $\ln[\text{MSt}]_e$  against  $T^{-1}$ . The result of  $\alpha$ -methylstyrene is also described in the figure.



PMStM reacts with  $(\text{PMSt})_{m-1}^-$ . Some changes might be produced at a given monomeric unit in the PMStM chain. The influence should decrease with increases in the length ( $l$ ) between the reacted site and the given monomeric unit; namely, the influence might be described using a correlation function of  $C(l)$ . As is well known, a simple correlation function is  $C(l) \sim e^{-l}$ . As the  $l$  is proportional to  $n$ ,  $f(n) \sim C(l) \sim C(n) \sim e^{-n}$ . Although this speculation is simple, it is useful for understanding the  $M_n$  dependence of  $\Delta H_{\text{PMStM}}$  and  $\Delta S_{\text{PMStM}}$ ; namely,  $\Delta H_{\text{PMStM}} \sim \Delta H_0 e^{-n}$  and  $\Delta S_{\text{PMStM}} \sim \Delta S_0 e^{-n}$ . The details will be discussed in future elsewhere.

We must check the kinetic characteristics using  $[\text{MSt}]_e$  for substitution of  $[\text{PMStM}]_e$ . Eq. (8) was led using  $[\text{PMStM}]_e$ , and that treatment is general and correct, where  $[\text{PMStM}]_0 = [\text{MSt}]_0/n$ ,  $[\text{PMStM}]_e = [\text{MSt}]_e/n$ , and  $[\text{PMStM}] = [\text{MSt}]/n$ . Thus, Eq. (8) is deformed to

$$\ln \left( \frac{[\text{MSt}]_0 - [\text{MSt}]_e}{[\text{MSt}] - [\text{MSt}]_e} \right) = k_p [\text{LE}] t \quad (17)$$

The plots of the left-side term of Eq. (17) against  $[\text{LE}]t$  are the same as those in Eq. (8). Hence, the two  $k_p$  values determined by Eqs. (8) and (17) do not differ as expected.

#### 4. Conclusions

Three well-defined PMStM macromonomers ( $M_n = 1.77 \times 10^3$ ,  $3.65 \times 10^3$ , and  $5.36 \times 10^3$ ) with narrow molecular weight distribution ( $M_w/M_n = 1.09$ ,  $1.09$ , and  $1.08$ ) and high coupling efficiency ( $f_c = 0.97$ ,  $0.98$ , and  $0.99$ ) were prepared by the coupling of  $\text{PMSt}^-$  with IPPC in THF at  $-78^\circ\text{C}$  under high vacuum. PMStM was polymerized to produce  $(\text{PMSt})_m$  ( $m = 9.5$ ,  $4.1$ , and  $3.5$ ) poly-macromonomers by  $n\text{-BuLi}$  in  $d_8\text{-THF}$  at temperatures below  $-10^\circ\text{C}$  under high vacuum via anionic living-equilibrium polymerization (ALEP): namely, PMStM was simultaneously purified and initiated above a ceiling temperature ( $T_c$ ) and then propagated below  $T_c$ . Although the initiation efficiency was low ( $f_i = 0.38$ ,  $0.24$ , and  $0.27$ ),  $[\text{LE}]$  was determined by  $[\text{LE}] = f_i [\text{I}]$  for kinetic studies, where  $[\text{I}]$  is the apparent molar concentration of  $n\text{-BuLi}$ .

Kinetic studies of ALEP of PMStM were carried out using a  $^1\text{H}$  NMR technique. Propagation of PMStM followed not a simple first-order rate equation but a first-order rate equation of the living-equilibrium polymerization. The  $k_p$  values ( $0.240$ ,  $0.110$ , and  $0.079 \text{ l mol}^{-1} \text{ s}^{-1}$ ) of the three PMStM at  $-78^\circ\text{C}$  were found to be proportional to a reciprocal of  $M_n$  of PMStM; namely,  $k_p \sim M_n^{-1}$ . The  $M_n$  dependence of  $k_p$  might be explained by a simple diffusion-controlled theory. The thermodynamic characteristics of  $\Delta H_{\text{PMStM}}$ ,  $\Delta S_{\text{PMStM}}$ , and  $T_c^{\text{PMStM}}$  determined using  $[\text{PMStM}]_e$  seemed strange, but those of  $\Delta H_{\text{PMSt}}$  ( $-7.48$ ,  $-6.73$ , and  $-3.82 \text{ kJ mol}^{-1}$ ),  $\Delta S_{\text{PMSt}}$  ( $-26.8$ ,  $-24.1$ , and  $-13.7 \text{ J mol}^{-1} \text{ K}^{-1}$ ), and  $T_c^{\text{PMSt}}$  ( $6.0$ ,  $6.1$ , and  $5.7^\circ\text{C}$ ) determined using  $[\text{MSt}]_e$  seemed reasonable and were easily understood. The  $M_n$  dependence of  $\Delta H_{\text{PMSt}}$  and  $\Delta S_{\text{PMSt}}$  might be explained by a simple correlation function of  $C(n) \sim e^{-n}$ . The  $T_c^{\text{PMSt}}$

for the three PMStM including  $\alpha$ -methylstyrene was found to exhibit the same values ( $6.0^\circ\text{C}$ ).

It is known that the  $M_w/M_n$  value of the poly( $\alpha$ -methylstyrene) prepared via ALEP is less than  $1.008$ , that may be the smallest  $M_w/M_n$  value in those so far reported [39]. As the ALEP was found to be useful in polymerizing the  $\alpha$ -methylstyrenic macromonomers in the present study, the precise synthesis of the branched macromolecular architectures using ALEP of the macromonomers would be advanced.

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