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Kinetic and Thermodynamic Characteristics of Anionic Living-Equilibrium

Polymerization for (*p*-Isopropenylphenethyl)poly(α -methylstyrene) Macromonomer

Kazunori Se*, Masaaki Suzuki

Department of Materials Science and Engineering, Graduate School of Engineering,

University of Fukui,

Bunkyo 3-9-1, Fukui 910-8507, Japan

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* Corresponding author. Tel: +81-776-27-8957; Fax: +81-776-27-8767

E-mail address: se@matse.u-fukui.ac.jp (K. Se).

ABSTRACT

The anionic living-equilibrium polymerization (ALEP) of (*p*-isopropenylphenethyl)poly(α -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 ($M_n=1.77\times 10^3$, 3.65×10^3 , and 5.36×10^3) were prepared by the coupling of poly(α -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*₈-THF at temperatures below -10°C under high vacuum *via* ALEP. From kinetic studies using an ^1H NMR technique, the propagation rate constant ($0.240, 0.110$, and $0.079 \text{ l mol}^{-1} \text{ s}^{-1}$) at -78°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 ΔH_{MSt} ($-7.48, -6.73$, and $-3.82 \text{ kJ mol}^{-1}$) and ΔS_{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 α -methylstyrene, were found to be the same (6.0°C).

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 site* anionic polymerization of the styrenic macromonomers without previous isolation, many complex macromolecular architectures, having macromonomers as building blocks, has 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 ($\text{R-C}_6\text{H}_5\text{-CO-C}_6\text{H}_5\text{Na}^+$) 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 α -methylstyrenic macromonomer has to be prepared. We first prepared a (*p*-isopropenylphenethyl)poly(α -methylstyrene) macromonomer [16] (PMStM) having an α -methylstyrene group ($\text{CH}_2=\text{C}(\text{CH}_3)\text{-C}_6\text{H}_4\text{-}$) at one end of the poly(α -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*-buthyllithium (*n*-BuLi) was introduced to the THF solution of PMStM at -15°C under high vacuum. The *n*-BuLi purges the impurities included in the solution and simultaneously initiates the PMStM. After 30 minutes at -15°C, the solution was lowered to -78°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 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 ¹H NMR measurements ; namely, after finishing a kinetic study at a certain temperature, the (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 ($CH_2=C(CH_3)-C_6H_4-CH_2CH_2Cl$, IPPC)

IPPC, which is a coupling reagent for preparing PMStM macromonomer, was prepared as follows: *p*-Chloroacetophenon ($CH_3CO-C_6H_4-Cl$) was reacted with the Grignard reagent of methyl chloride and magnesium turnings to produce *p*-isopropenylphenyl chloride ($CH_2=C$

(CH₃)-C₆H₄-Cl) according to previous methods [22, 23]. *p*-Isopropenylphenyl chloride (100 g) and methyl iodide (2 g) in THF (200 ml) was added to magnesium turnings (16.3 g) at 75°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 (CaH₂) in tetrahydrofuran (THF, 100 ml) was added to the Grignard reagent at 0°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°C/3 mmHg) to yield *p*-isopropenylphenethyl alcohol (CH₂=C(CH₃)-C₆H₄-CH₂CH₂OH, IPPA, 67g, 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°C/3 mmHg) to yield IPPC (62 g, yield: 87%). The IPPC was distilled twice and its purity was checked by ¹H NMR. Subsequent purification was carried out at 10⁻⁶mmHg in an all-glass apparatus equipped with break seals. IPPC was twice purified with CaH₂, 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. α -Methylstyrene was dried over CaH₂ under a pressure of 10⁻⁶ mmHg and purified with octylbenzophenone sodium complex (C₈H₁₇-C₆H₄-CO(C₆H₅)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 α -methyl styrene 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(α -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} mmHg for 48 h, diluted with carefully purified d_8 -THF, and sealed off by flame.

2.4. ^1H 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} mmHg and washed with a THF solution of α -methyl styrene sodium complex, a heptane solution of *n*-BuLi (0.014N, 3-8ml) was introduced into the reactor. *n*-Heptane was collected in a flask and sealed off by flame. After cooling at -15°C , the d_8 -THF solution of PMStM (10 ml) was introduced into the reactor. The polymerization solution was sufficiently stirred at -15°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°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°C in a NMR instrument and the depropagation was checked by ¹H NMR signals. The temperature was then decreased to a given temperature. It took less than 1 minute 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 ¹H 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 ¹H NMR intensities of all 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 ¹H NMR intensities of the polymerization solution kept at -10°C. After the conversion of the (PMSt)_m polymacromonomers reached an equilibrium state at which the corresponding ¹H NMR intensities was presented by I_e , the equilibrium macromonomer concentrations ([PMStM]_e) were determined at that temperature from $[PMStM]_0 \times (I_e / I_0)$, where $[PMStM]_0$ was the initial molar concentration of PMStM. After the measurements were finished, the temperature of the polymerization solution was raised to -10°C for complete depropagation. These procedures were repeated for three PMStM macromonomers having different molecular weights from -10°C to -78°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 258 times for determining the [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°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 x 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(α -methylstyrene) macromonomer

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 α -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 α -methylstyrene, which was maintained at -15°C. The polymerization solution was sufficiently stirred at -15°C for 20 minutes to purge the impurities included in the polymerization solution and to simultaneously initiate the α -methylstyrene. The polymerization solution was inserted in a cold bath at -78°C to propagate the α -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(α -methylstyryllithium) (PMSt⁻) at -78°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(α -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 ¹H NMR spectrum of the resultant PMStM. As compared with a ¹H NMR spectrum of PMSt, the vinyl protons of the isopropenyl group (CH₂=C(CH₃)-) 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 ¹H NMR positions as those of PMStM, and further ethyl protons of a phenethyl group (-C₆H₄-CH₂-CH₂-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 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 ¹H NMR intensities of all signals to that of the vinyl group, a number-average molecular weight (M_n^{NMR}) can be calculated. Thus, the coupling efficiency (f_c) can be determined as $f_c = M_n^{VPO}/M_n^{NMR}$. 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*-buthyllithium at -15°C, it's color changed immediately from colorless to red. The red color corresponds to the production of poly(α -methylstyryllithium) carbanion. After stirring for 20 minutes at -15°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°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°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°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°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 a 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(α -methylstyrene) without an α -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^{LALLS} value determined by GPC-LALLS of the resultant three $(\text{PMSt})_m$ polymacromonomers is larger than the corresponding M_n^{GPC} value determined by GPC using standard PSTs. This finding provides evidence that the resultant 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 (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_{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 (PMSt)_m polymacromonomers similar to the star polymers having narrow molecular weight distributions were prepared.

The initiation efficiency (f_i) for ALEP of PMStM was found to be low. 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 (4×10^{-5} - 9×10^{-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 20×10^{-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 $[\text{LE}] = f_i [\text{I}]$. 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 α -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 ^1H NMR tubes. The conversion of the $(\text{PMSt})_m$ polymacromonomers was determined from a decrease in the ^1H 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; $[\text{PMStM}]$ and $[\text{LE}]$ are the molar concentrations of the PMStM and the living ends, respectively. As $[\text{LE}]$ 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 $[\text{PMStM}]_0$ is the initial molar concentration of the PMStM. **Fig. 4** shows the plots of the left-side term of Eq. (3) against the $[\text{LE}]t$, when PMStM-2 was propagated at -78°C . The plots do not show a straight line even on the a lower conversion side of the $(\text{PMSt})_m$ polymacromonomers. At large limiting $[\text{LE}]t$ 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 $[\text{PMStM}]_e$ 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 PMStM concentration. According to Eq. (5), the $[\text{PMStM}]_e$ is given in the following:

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

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

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

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 $[\text{LE}]t$. 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 $(\text{PMSt})_m$ 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°C and at -78°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°C . As the $[\text{LE}]$ of the three propagations differ, the left-side terms of Eq. (8) were plotted against $[\text{LE}]t$. From the slopes of the straight lines in Figure 6, the k_p

values were determined. The kinetic results are described in **Table 3**. The k_p values decreased with increasing the 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 α -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 $(\text{PMSt})_m^-$. The diffusion of PMStM is important for the discussion because the $(\text{PMSt})_m^-$ 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 $(\text{PMSt})_m^-$. The effective collision of PMStM is important for the discussion because the $(\text{PMSt})_m^-$ polymacromonomer is also too large to change its position, as compared with PMStM. When the diameters of the vinyl group of PMStM and PMStM are d and L , 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 θ 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 $(\text{PMSt})_m^-$ might not be affected by the difference in the conformation of the branched living $(\text{PMSt})_m^-$ due to an increase in m (a number of side chains) of the growing branched $(\text{PMStM})_m^-$. 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 $[\text{PMStM}]_e$ 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

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

The molar Gibbs free energy of the propagation (ΔG_{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 ΔH_{PMStM} and ΔS_{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 ^1H 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 ΔH_{PMStM} and ΔS_{PMStM} were determined. The thermodynamic characteristics estimated thus are shown in **Table 4**. The magnitudes of the ΔH_{PMStM} increase with decreases in the M_n of PMStM, and approach that of α -methylstyrene. In contrast, the ΔS_{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 liter 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 α -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 ΔH_{MSt} and ΔS_{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^{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 ΔH_{MSt} and ΔS_{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 α -methylstyrene with an initial concentration of 5.0wt % is polymerized at -78°C , $[\text{MSt}]_0$ is 0.44 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 α -methylstyrene derivatives where the Y is not 100% but close to 100%. When PMStM-1 with an initial concentration of 7.7wt % was polymerized at -78°C , $[\text{MSt}]_0$ was 0.66 mol l^{-1} , $[\text{MSt}]_e$ was 0.25 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°C (mp of THF is -108.5°C), $[\text{MSt}]_0$ is 1.7 mol l^{-1} , $[\text{MSt}]_e$ is 0.17 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 ΔH_{MSt} and ΔS_{MSt} on the M_n of PMStM

Fig. 10 shows the dependence of ΔH_{MSt} and ΔS_{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.

The ΔH_{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 ΔH_{MSt} depends on the M_n of PMStM. However, in the case of α -methylstyrene, the difference in the bond energy converted from the C=C double bond (612 kJmol^{-1}) to the C-C single bond (348 kJmol^{-1}) is -264 kJmol^{-1} [32]. This value is much different from the ΔH_{MSt} one of α -methylstyrene (-33.5 kJmol^{-1}). 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 ΔH_{MSt} might contain a difference in the interaction between the resultant $(\text{PMSt})_m^-$, PMStM, and solvent, in addition to the difference in the mean bond enthalpy. Thus, the M_n dependence of ΔH_{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 ΔS_{MSt} can be expected to be observed without special analysis. In the propagation, ΔS_{MSt} should be a negative value that corresponds to an entropy change from a free chain of PMStM to a side chain of the polymacromonomer like the comb polymer or to an arm of the star polymer. With an increase in the M_n of PMStM, the magnitude of ΔS_{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 Figure 10, which is a quite easy to understand, is reported herein for the first time.

The most striking finding is that the T_C^{MSt} (6.0°C) for the three PMStM including α -methylstyrene exhibit the same values. As shown in Fig. 10, M_n dependence of ΔH_{MSt} is similar to that of ΔS_{MSt} , even though their values and dimensions differ. Let us suppose a function of the M_n dependence for ΔH_{MSt} and ΔS_{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 ΔH_0 and ΔS_0 are constants and can be substituted for the corresponding constants of α -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^{MSt} did not comprise the $f(n)$; namely, the T_C^{MSt} did not depend on M_n of PMStM but was the same as that of the α -methylstyrene. The present explanation of $T_C^{\text{MSt}} = 6.0^\circ\text{C}$ is simple and might be reasonably accurate as a first approximation.

On the other hand, though the T_C^{MST} is based on the calculations of $\Delta H_{\text{MSt}} / \Delta S_{\text{MSt}}$, the chemical meaning of the T_C^{MST} may be related to the polymerization and depolymerization of the monomer. All the macromonomers and α -methylstyrene have the same α -methylstyryl groups, which undergo the propagation. So, the T_C^{MST} should be directly related to the chemical structure of the α -methylstyryl groups. It might not be surprise that all the T_C^{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 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 ΔH_{MSt} and ΔS_{MSt} ; namely, $\Delta H_{\text{MSt}} \sim \Delta H_0 e^{-n}$ and $\Delta S_{\text{MSt}} \sim \Delta S_0 e^{-n}$. 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 ($M_n = 1.77 \times 10^3$, 3.65×10^3 , and 5.36×10^3) 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 PMSt^- with IPPC in THF at -78°C under high vacuum. PMStM was polymerized to produce $(\text{PMSt})_m$ ($m = 9.5$, 4.1 , and 3.5) polymacromonomers by $n\text{-BuLi}$ in $d_8\text{-THF}$ at temperatures below -10°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), $[LE]$ was determined by $[LE] = f_i [I]$ for kinetic studies, where $[I]$ is the apparent molar concentration of n -BuLi.

Kinetic studies of ALEP of PMStM were carried out using a 1H 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 l mol^{-1} s^{-1}) of the three PMStM at $-78^\circ C$ 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 ΔH_{PMStM} , ΔS_{PMStM} , and T_C^{PMStM} determined using $[PMStM]_e$ seemed strange, but those of ΔH_{MSt} ($-7.48, -6.73$, and -3.82 kJ mol^{-1}), ΔS_{MSt} ($-26.8, -24.1$, and -13.7 J mol^{-1} K^{-1}), and T_C^{MSt} ($6.0, 6.1$, and $5.7^\circ C$) determined using $[MSt]_e$ seemed reasonable and were easily understood. The M_n dependence of ΔH_{MSt} and ΔS_{MSt} might be explained by a simple correlation function of $C(n) \sim e^{-n}$. The T_C^{MSt} for the three PMStM including α -methylstyrene was found to exhibit the same values ($6.0^\circ C$).

It is known that the M_w/M_n value of the poly(α -methylstyren) 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 α -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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Figure Captions

- Fig. 1** A glass apparatus for preparing the sample solution used for the kinetic and thermodynamic measurements by the ^1H NMR technique. The symbols represent the following: A, THF solution of α -methylstyrene sodium complex; B, d_8 -THF solution of PMStM; C, n -heptane solution of n -BuLi.
- Fig. 2** A ^1H NMR spectrum of the (*p*-isopropenylphenethyl)poly(α -methylstyrene) macromonomer (PMStM-1). The signals are assigned on the figure.
- Fig. 3** GPC chromatograms of the product prepared *via* anionic living-equilibrium polymerization (ALEP) of PMStM-1 by n -BuLi in THF at -78°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 (PMSt-1)_m polymacromonomer.
- Fig. 4** The simple first-order plots and the corrected first-order plots using $[\text{PMStM}]_e$ for ALEP of PMStM-2 by n -BuLi in THF at -78°C measured by the ^1H NMR technique.
- Fig. 5** The corrected first-order plots using $[\text{PMStM}]_e$ for ALEP of PMStM-3 by n -BuLi in THF at -60°C and -78°C .
- Fig. 6** The corrected first-order plots using $[\text{PMStM}]_e$ for ALEP of the three PMStM macromonomers by n -BuLi in THF at -78°C .
- 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 α -methylstyrene is also described in the figure.
- Fig. 8** Temperature dependence of the equilibrium PMStM concentration ($[\text{PMStM}]_e$) for ALEP of the three PMStM macromonomers by n -BuLi in THF. The result

of α -methylstyrene is also described in the figure. From the slopes and intercepts of the straight lines, ΔH_{PMStM} and ΔS_{PMStM} were determined.

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 α -methylstyrene is also described in the figure. From the slopes and intercepts of the straight lines, ΔH_{MSt} and ΔS_{MSt} were determined.

The T_c^{MSt} of the four samples exhibit the same values.

Fig. 10 The dependence of ΔH_{MSt} and ΔS_{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 α -methylstyrene is also described in the figure.

Fig. 1 A glass apparatus for preparing the sample solution used for the kinetic and thermodynamic measurements by the ^1H NMR technique. The symbols represent the following: A, THF solution of α -methylstyrene sodium complex; B, d_8 -THF solution of PMS StM ; C, n -heptane solution of n -BuLi.

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

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

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.

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

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 α -methylstyrene is also described in the figure. From the slopes and intercepts of the straight lines, ΔH_{PMStM} and ΔS_{PMStM} were determined.

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 α -methylstyrene is also described in the figure. From the slopes and intercepts of the straight lines, the ΔH_{MSt} and ΔS_{MSt} were determined. The T_c^{MSt} of the four samples exhibit the same values.

Fig. 10 The dependence of ΔH_{MSt} and ΔS_{MSt} on the M_n of PMStM for ALEP of the three PMStM macromonomers determined by the plots of $\ln[\text{MSt}]_c$ against T^{-1} . The result of α -methylstyrene is also described in the figure.

Table 1.

Preparation^a and characterization of (*p*-isopropenylphenethyl)poly(α -methylstyrene) macromonomers (PMStM).

Polymers	Mono	THF	$10^{-3}M_k^b$	[IPPC]/[	$10^{-3}M_n$			M_w/M_n		f_C^h
	mer			n -BuLi] ^c						
	g	ml			VPO ^d	GPC ^e	NMR ^f	GPC ^e	VPO/L	
	ALLS ^g									
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

^a α -Methylstyrene was anionically initiated by *n*-BuLi in THF at -15°C for 20 minutes under a pressure of 10^{-6} mmHg and then propagated at -78°C for 1 - 2 h.

^b Kinetic molecular weights determined from the amounts of monomer and initiator.

^c The molar ration of *p*-isopropenylphenethyl chloride (IPPC) as a deactivator to *n*-BuLi as an initiator.

^d Determined by the vapor pressure osmometry (M_n^{VPO}).

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

^f Calculated from the ratio of benzene to isopropenyl groups determined from the NMR measurements (M_n^{NMR}).

^g A special analysis using GPC in conjugation with a low-angle laser light scattering detector (M_w^{LALLS}) [2, 27].

^h Coupling efficiency determined by M_n^{VPO}/M_n^{NMR} .

Table 2.

Anionic living-equilibrium polymerization^a (ALEP) of PMStM macromonomers.

Polymers	$10^{-3}M_n$	PMS	d_8 -T	$10^3[I]$	[PM	Yield	$10^{-3}M_n$	M_w/M_n	m^f	f_I^g	$10^3[L$	
	of	tM ^b	HF		StM]						E] ^h	
	PMStM				/[I] ^c							
		g	ml	mol l ⁻¹		%	GPC ^d	LALLS ^e	LALLS ^e		mol l ⁻¹	
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

^a PMStM macromonomers were anionically initiated by *n*-BuLi in d_8 -THF at -15°C for 20 minutes under a pressure of 10^{-6} mmHg and then propagated at -78°C for 100 h.

^b The weights were corrected by [the amount of PMStM used] $\times f_c$, where f_c is a coupling efficiency of the PMStM.

^c The molar ration of PMStM to *n*-BuLi; namely, kinetic number of side chains of (PMSt)_m polymacromonomers.

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

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

^f Number of side chains of the produced (PMSt)_m polymacromonomers corresponding to the degree of polymerization of PMStM.

^g Initiation efficiency determined by (Yield $\times$ [PMStM]/[I])/m.

^h Effective molar concentration of the living end determined by $[LE] = f_1 [I]$.

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		$10^{-3} \Delta E_a$
		$l \text{ mol}^{-1} \text{ s}^{-1}$		
		-60°C	-78°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
α -methylstyrene ^a	0.118		3.60	50.7

^a The results were reported in the reference No. [19] and [20].

Table 4.

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

Macromonomers	$10^{-3}M_n$ of PMStM	Eq. (11) ^a			Eq. (14) ^b		
		$10^{-3}\Delta H_{\text{PMStM}}$	ΔS_{PMStM}	T_c^{PMStM}	$10^{-3}\Delta H_{\text{MSt}}$	ΔS_{MSt}	T_c^{MSt}
		J mol ⁻¹	J mol ⁻¹ K ⁻¹	°C	J mol ⁻¹	J mol ⁻¹ K ⁻¹	°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
α -methylstyrene ^c	0.118	-33.5	-120	6.0	-33.5	-120	6.0

^a 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 ($[\text{PMStM}]_e$).

^b 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.

^c The results were reported in the reference No. [19] and [20].