

Molecular Weight Distribution of Polystyrene Made by Anionic Polymerization

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ABSTRACT: A set of polystyrenes of varying molecular weights was synthesized by anionic polymerization under identical conditions, and their molecular weight distributions were critically examined. Polymerization of styrene was initiated with 2-butyllithium in cyclohexane at 45 °C. During the polymerization, seven aliquots of the reaction mixture were taken out at various reaction times using a cannula and terminated. The polymerization time varying molecular weights and molecular weight distributions of the polystyrenes were analyzed by temperature gradient interaction chromatography (TGIC) as well as size exclusion chromatography. The molecular weight distribution of the polystyrene approaches the Poisson distribution in the late stages of the polymerization, in accordance with the early prediction of Flory. We also confirmed that the molecular weight distribution of polystyrenes determined by TGIC is close to the true value.

Introduction

Living anionic polymerization has been used for decades to prepare many useful polymers, in particular polymers of very narrow molecular weight distribution (MWD).^{1–6} According to the early theoretical work of Flory,^{7,8} an “ideal” living anionic polymerization should yield a polymer with a Poisson distribution of chain lengths

$$w_i = \frac{i\nu^{i-1}e^{-\nu}}{(\nu+1)(i-1)!} \quad (1)$$

in which w_i stands for the weight fraction of the i -mer. The Poisson distribution has an asymptotic M_w/M_n (weight-average molecular weight/number-average molecular weight) value of $1 + 1/\nu$ where ν is the number-average degree of polymerization. Experimentally, the MWD of anionically polymerized polymers has been commonly measured by size exclusion chromatography (SEC), and typical M_w/M_n values have been in the range 1.01–1.10, where even 1.01 is significantly larger than the value anticipated by the Poisson distribution for high molecular weight polymers. With the advent of new characterization techniques, the validity of the M_w/M_n values determined by SEC has been questioned: Giddings and co-workers found a much lower M_w/M_n value for polystyrene (PS) standards made by anionic polymerization from thermal field flow fractionation analysis.⁹ Shortt¹⁰ and Wyatt and Villalpando¹¹ also pointed out the possibility of a much lower M_w/M_n value for PS from the analysis of the radius of gyration distribution by SEC coupled with multiangle light scattering detection. Recently, Chang and co-workers have also reported much lower M_w/M_n values by temperature gradient interaction chromatography (TGIC) for poly(methyl

methacrylate),¹² polyisoprene,¹³ and PS.^{14,15} However, no experimental method has been established to measure the precise M_w/M_n of anionically polymerized polymers, and the theoretical prediction of Flory has not been proven experimentally. The M_w/M_n values determined by SEC are commonly used although SEC overestimates the M_w/M_n value significantly due to the band broadening effect.^{16,17}

An “ideal” living anionic polymerization proceeds under conditions in which no side reactions of the propagating polymeric anions occur to maintain the living character of the growing species, and the initiation rate is much greater than the propagation rate.¹⁷ Although it is practically impossible to attain the ideal situation in real experiments, it is possible to synthesize a set of polystyrenes of different molecular weight under identical experimental conditions in order to rigorously examine Flory’s theoretical prediction. In this study, we prepared a set of PS samples with different molecular weights by collecting a number of aliquots at different polymerization times from a single batch polymerization. This keeps the nonideal aspects of the polymerization as identical as possible. The MWD of these PS samples were critically analyzed and compared with Flory’s theoretical prediction.

Experimental Section

Materials. Styrene monomer (99%, Aldrich) was first treated with CaH₂ powder (95%, Aldrich) for a few days to remove dissolved water. It was further purified by stirring with dibutylmagnesium (1.0 M in heptane, Aldrich) for 2 h at room temperature. A desired amount of the purified styrene was distilled into a monomer buret by vacuum distillation, and the exact amount of the monomer was determined by weighing. The polymerization solvent, cyclohexane (99%, A.C.S. reagent, Aldrich), was stirred over concentrated sulfuric acid (95–98%, A.C.S. reagent, Aldrich) for 1 week to remove unsaturated impurities before it was transferred to the distillation flask. It was refluxed under Ar for 1 h to remove dissolved gases, and then 5 mL each of *n*-butyllithium (2.0 M in cyclohexane,

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Aldrich) and styrene were injected through a rubber septum to remove additional impurities. The mixture was then refluxed for 2–3 h to ensure complete conversion of styrene to polystyryl anion. The persistence of a deep orange color due to the polystyryl anion indicated that the purity was sufficient for anionic polymerization. 2-Butyllithium (1.3 M in cyclohexane, Aldrich) was used as an initiator without further purification. 2-Propanol (99.5%, A.C.S. reagent, Aldrich) was degassed under vacuum by repeating freeze–thaw cycle several times and then used as the terminating agent. Mobile phases in chromatographic analysis were HPLC grade (Aldrich) tetrahydrofuran (THF), methylene chloride (CH_2Cl_2), and acetonitrile (CH_3CN). They were used without further purification.

Anionic Polymerization. Styrene was polymerized under a purified Ar atmosphere. The anionic polymerization apparatus was similar to the design of Ndoni et al. employing a positive pressure of Ar gas, gastight fittings, and Teflon stopcocks to minimize the possibility of contamination by air while avoiding glass blowing and break seals.¹⁸ Details of a modified apparatus were reported previously.¹⁹ Purified cyclohexane was directly distilled into the reaction vessel under Ar atmosphere.

The polymerization reactor was immersed in a thermostated water bath to maintain the reaction temperature at 45 °C. The desired amount (2.4×10^{-4} mol) of the initiator, 2-butyllithium in hexane, was added by a gastight syringe to the cyclohexane solvent (500 mL) in the reaction vessel, and the polymerization was initiated by adding purified styrene monomer (15.06 g). During the polymerization aliquots of the reaction mixture (50 mL) were transferred to Ar-filled Erlenmeyer flasks through a cannula at different reaction times and terminated by injecting a small amount of degassed 2-propanol. The elapsed time between the introduction of styrene to the reactor and termination was recorded. Polystyrenes were precipitated from each aliquot in a 1/3 (v/v) mixture of 2-propanol/methanol and characterized by SEC and TGIC.

Chromatographic Analysis. The SEC system consisted of an HPLC pump (LDC, CM 3200), six-port sample injector (Rheodyne, 7125), a variable wavelength UV/vis absorption detector (TSP, Spectra 100) operated at the wavelength of 260 nm, and two PS gel columns (PL-mixed C, mixed bed, 300 × 8 mm). The eluent was THF, and the column temperature was kept at 40 °C using a column oven (Eppendorf, TC-50). PS samples in THF (50 μL of 1.0 mg/mL) were injected, and the flow rate of the eluent was 1.0 mL/min. The M_w and MWD were calculated by calibration with eight different PS standards with molecular weights between 1200 and 970 000.

The TGIC system was essentially the same as that of SEC except for the column and the column temperature control. The temperature of the separation column was controlled by circulating fluid from a programmable bath/circulator (NESLAB, RTE-111) through a column jacket. One reversed phase silica column (Nucleosil C18, 100 Å, 250 × 2.1 mm) was used, and the eluent was a 57/43 (v/v) mixture of $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$. A UV/vis detector (LDC, Spectromonitor 3200) was used as the concentration detector. The column temperature was programmed to change in five segments of linear ramp between 5 and 30 °C during the TGIC elution. For MWD calculations, a calibration curve was constructed using the same set of PS standards as in the SEC calibration.

Results and Discussion

Figure 1 displays the SEC chromatograms of the PS obtained at various polymerization reaction times and the calibration curve. The calibration curve of $\log M_w$ vs retention time (t_R) is linear across the molecular weight range of interest. The t_R of the PS decreased as the polymerization time increased, which indicates a progressive increase in molecular weight. The M_w and M_w/M_n values determined by SEC are listed in Table 1. The M_w/M_n values of the 7 PS samples determined by SEC are in the range of typical values for commercial standards.

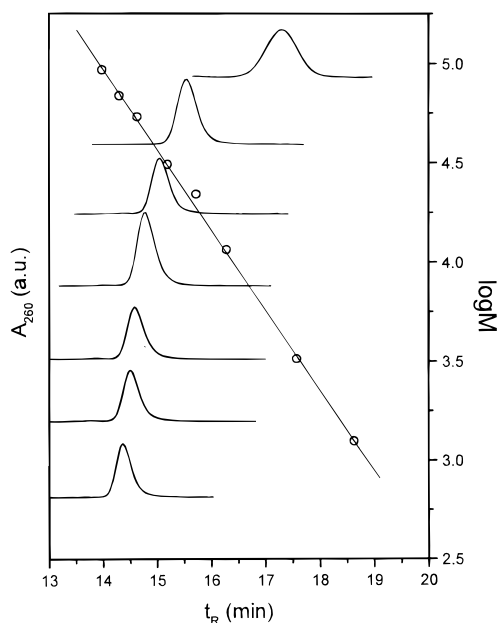


Figure 1. SEC chromatograms of the PS obtained at various polymerization reaction times: from the top, 238 s, 888 s, 1626 s, 2296 s, 3098 s, 4220 s, and 14345 s. Calibration curve made by eight PS standards are also shown.

Table 1. Molecular Weight and Molecular Weight Distribution of Polystyrenes

sample code	polymerization time (s)	$M_w (\times 10^3)$		M_w/M_n		Poisson distribution
		SEC	TGIC	SEC	TGIC	
PS-1	238	4.3	4.0	1.08	1.06	1.02
PS-2	888	21.3	21.0	1.04	1.02	1.003
PS-3	1626	35.0	34.4	1.05	1.02	1.002
PS-4	2296	42.9	43.4	1.05	1.01	1.002
PS-5	3098	50.4	50.2	1.05	1.008	1.002
PS-6	4220	56.0	55.2	1.05	1.006	1.002
PS-7	14345	62.0	62.0	1.05	1.005	1.002

Figure 2 displays the TGIC chromatograms of the same polymers together with the calibration curve made with the same PS standards as in the SEC analysis. The calibration plot of M_w vs t_R was fitted to a fifth-order polynomial function. Using the calibration curve shown in the plot, M_w and M_w/M_n values were determined, and the results are summarized in Table 1. The M_w/M_n values determined by TGIC are systematically much smaller than those from SEC analysis, as reported earlier.¹⁴ In addition, the M_w/M_n values decrease with increasing molecular weight in accordance with a Poisson distribution.⁸

To visually compare the MWD measured by the two characterization methods with the Poisson distribution, we converted the t_R axis in the chromatograms shown in Figures 1 and 2 to a degree of polymerization (i) axis. Since t_R is not directly proportional to the molecular weight, we must modify the SEC and TGIC chromatograms in order to convert $w(t_R)$ to $w(M)$. If t_R is a function of M , i.e., $t_R = f(M)$, the conversion can be done according to eq 2.

$$w(t_R) dt_R = w(M) dM,$$

$$w(M) = w(t_R) \frac{dt_R}{dM} = w(t_R) f'(M) \quad (2)$$

Since the SEC calibration curve of $\log M$ vs t_R is linear, $w(t_R)$ or $w(\log M)$ can be converted to $w(i)$ or $w(M)$ simply by the following relationship.²⁰

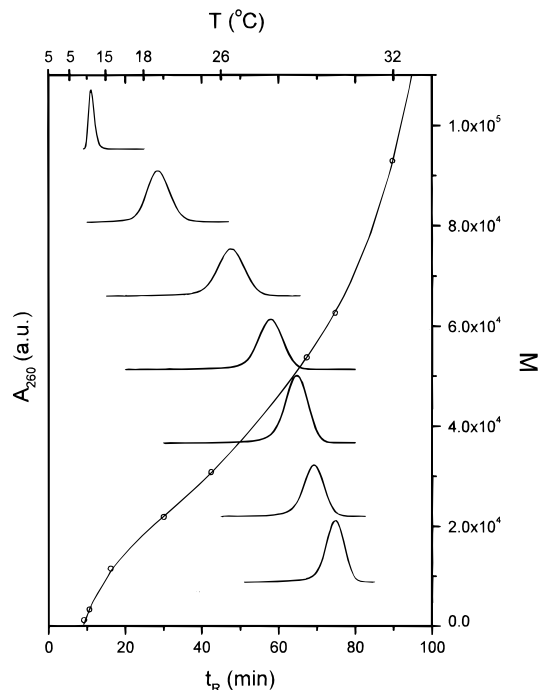


Figure 2. TGIC chromatograms of the same PS set of Figure 1 and the calibration curve. The column temperature was programmed to change in five segments of linear ramp between 5 and 30 °C during the TGIC elution. The initial and final temperatures of each segment shown in the upper abscissa.

$$w(M) \propto \frac{w(\log M)}{M} \quad (3)$$

For TGIC, the transformation was done with the fifth-order polynomial calibration function. Figure 3 displays the converted weight fractions, $w(i)$, determined by SEC (dashed line) and TGIC (solid line). The theoretical Poisson distributions matching the most probable value of each distribution are also plotted as dotted lines for comparison. The MWDs determined by SEC are much wider than the Poisson distributions. This is mainly attributable to the band broadening in SEC.^{16,17} In contrast, the MWD determined by TGIC is close to the Poisson distribution, but there still exists a finite discrepancy between them. The departure of the MWD determined by TGIC from the Poisson distribution may arise from two causes: the band broadening effect in TGIC and the nonideal polymerization condition.

The concept of band broadening correction in chromatographic systems was first proposed by Tung.²¹ Equation 4 represents Tung's integral equation, which relates the experimentally obtained chromatogram, $F(v)$, to the band broadening corrected chromatogram, $W(v)$ (corresponding to real MWD), through the broadening function, $G(v-y)$.

$$F(v) = \int W(y) G(v-y) dy \quad (4)$$

The aim of the band broadening correction is to obtain $W(y)$ by deconvoluting $F(v)$, which requires determination of the broadening function $G(v-y)$. The broadening function $G(v-y)$ represents the experimentally broadened peak shape of a monodisperse species.²² The conceptually simplest approach is to obtain the elution peak of a monodisperse sample, which is impossible for synthetic polymers. As a substitute for a monodisperse

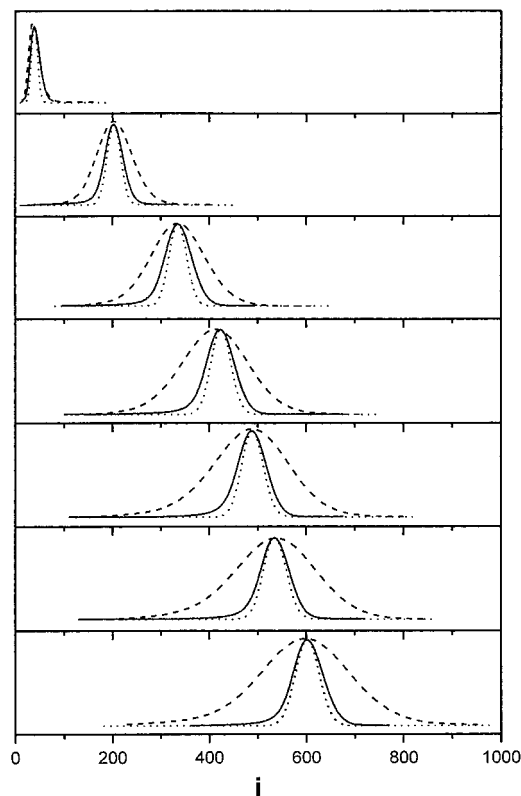


Figure 3. Weight fraction (w_i) vs degree of polymerization (i) plot of SEC (dashed lines) and TGIC (solid lines) characterization results of the PS set. The SEC and TGIC chromatograms represent the integrated regions to calculate the M_w/M_n values listed in Table 1. Theoretical Poisson distributions matching the most probable value of MWD are also plotted with dotted lines.

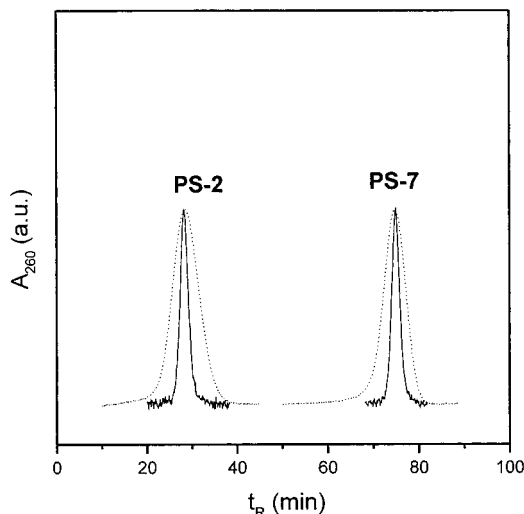


Figure 4. TGIC chromatograms of one-drop fraction (solid lines) taken from PS-2 and PS-7. For comparison, TGIC chromatograms of PS-2 and PS-7 before fractionation are plotted with dotted lines.

sample, we collected one drop of eluate at the peak position of the TGIC elution peaks of PS2 and PS7. We selected one low and one high molecular weight sample to determine the possible molecular weight dependence of the broadening function. The one-drop fractions were resubjected to TGIC analysis. Figure 4 shows the TGIC chromatograms of the collected fractions together with the elution peaks of the parent polymers. Since the elapsed retention time during the collection of one drop was about 8 s, which would be essentially a delta

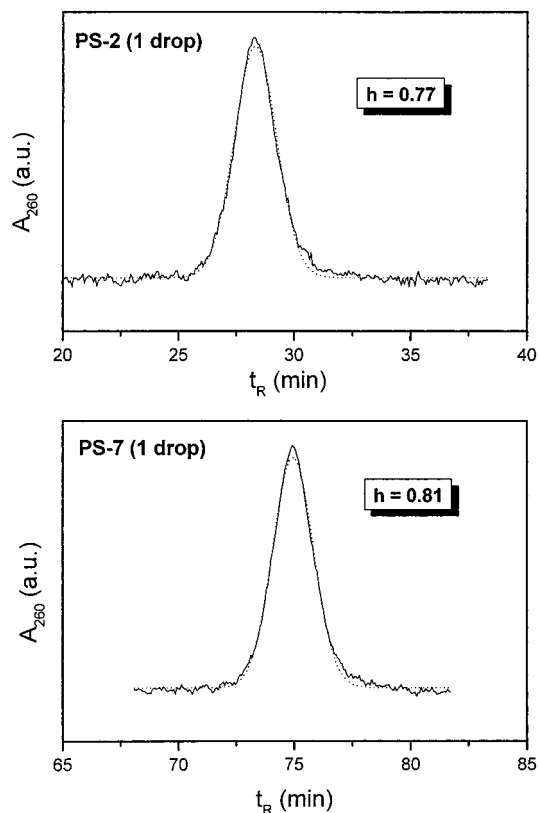


Figure 5. Fit of the TGIC chromatogram of the one drop fractions shown in Figure 4 to the Gaussian function. Resolution factor $h \approx 0.8$ is similar in both cases.

function in the chromatogram shown, the elution peaks of the collected fraction are apparently broadened significantly.

The function $G(v-y)$ presumably has a Gaussian form.^{21–25} Employing this form of the broadening function, it can be represented by eq 5.

$$F(v) = \int W(y) \left\{ \left\langle \frac{h}{\sqrt{\pi}} \right\rangle \exp[-h^2(v-y)^2] \right\} dy \quad (5)$$

We fitted the chromatograms of the one-drop fractions to the Gaussian function to determine the resolution factor h . The elution peaks of the fractions are described well by the Gaussian function (Figure 5). The resulting resolution factor h does not depend strongly on molecular weight, with similar values of ca. 0.8 for both PS-2 and PS-7. We then simulated the broadened form of the Poisson function by convoluting it with the Gaussian function ($h = 0.8$), instead of deconvoluting $F(v)$ to $W(y)$. For the simulation, we divided the Poisson function to thin slices and computed the broadened Gaussian function of each slice. The band broadened Poisson function can then be obtained by summing up the broadened slices, as shown in Figure 6a. The number of slices was increased until the shape of the resulting sum of the broadened slices became constant. The result is compared with the initial Poisson function as well as TGIC chromatogram of PS-7 in Figure 6b. This correction does not significantly broaden the Poisson function. Consequently, we conclude that the band broadening effect of TGIC is not the major cause of the discrepancy between the MWD determined by TGIC and the Poisson distribution. This also suggests that the M_w/M_n values in Table 1 determined by TGIC are very close to the true values. Note that since the elution peaks of the

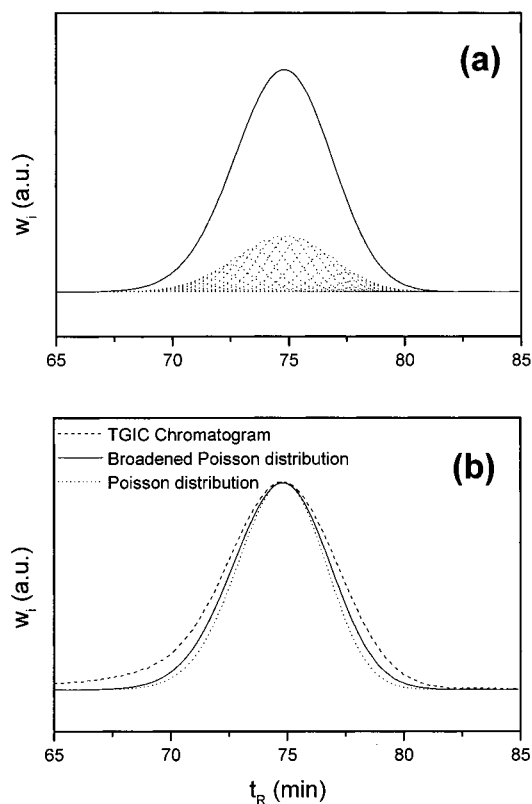


Figure 6. (a) Convolution of a Poisson distribution (approximated with 30 sliced columns) corresponding to PS-7 with the Gaussian band broadening function with the resolution factor, $h = 0.8$. Dotted lines are the broadened slices, and the solid line is the sum of the broadened slices. (b) Comparison of the three different distributions represented in elution time axis: The dashed line is the raw TGIC chromatogram of PS-7, the dotted line is the Poisson distribution, and the solid line is the broadened Poisson distribution by the convolution of the Poisson function shown in (a).

parent PS in Figure 4 are already affected somewhat by band broadening, the one-drop fractions do not represent simply the polymeric species of the corresponding bandwidth (i.e., 8 s in t_R or 20 890–20 980 (PS-2), 62 400–62 490 (PS-7) in molecular weight according to the calibration curve) but contain more species heterogeneous in molecular weight. Therefore, the broadening function obtained from the one-drop fraction already overestimates the band broadening of TGIC separation process itself, and the real band broadening correction should be even less than we estimated.

We therefore conclude that the deviation of MWD from the Poisson distribution is mostly due to the nonideal polymerization condition. We speculate that nonideality occurs primarily in the initial stage of the polymerization, i.e., inhomogeneous solution during the monomer addition, not fast enough initiation reaction relative to propagation, etc. Therefore, we examined the progress of the deviation from the Poisson distribution as the polymerization proceeds, by convoluting the TGIC elution peak of a PS with the Poisson function to obtain the ideal MWD of subsequent aliquots. In other words, we assumed that each mer in the previous distribution [PS- k] propagated following the Poisson distribution to result in the next distribution [PS- $(k+1)$]. The dashed lines in Figure 7 are the simulated MWDs obtained by this process. PS-1 is the Poisson function itself since the polymerization starts from a delta function (initiator). These peaks match the experimentally obtained TGIC

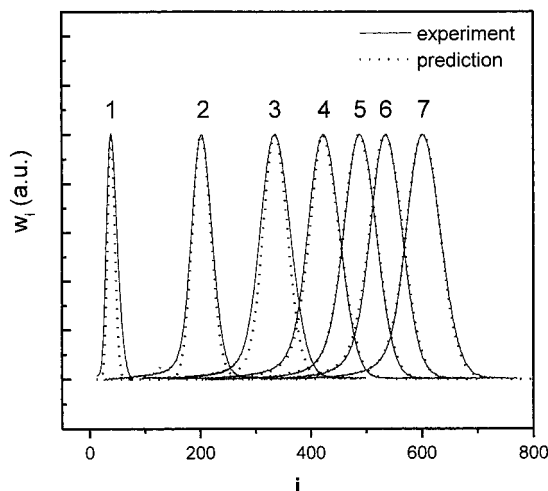


Figure 7. Simulated TGIC chromatograms assuming propagation of MWD according to the Poisson distribution. In the figure, solid lines represent the TGIC chromatograms, and the dotted lines are the simulated chromatograms.

chromatograms (solid lines) very closely, especially with increasing molecular weight which indicates that the later stage propagation follows Flory's prediction well.

The effect of the different initiation and propagation rates on MWD for a living polymerization was studied earlier by Gold²⁶ and Nanda and Jain.²⁷ According to their results, the final M_w/M_n is a function of $[M]_0/[I]_0$ (k_i/k_p). For the polymerization of PS with 2-butyllithium in cyclohexane at 45 °C, k_i/k_p was reportedly larger than 10, and $[M]_0/[I]_0$ in this experiment was about 600.^{28,29} In this case, the effect of the different initiation and propagation rates on MWD is negligible.¹⁷ Therefore, the inhomogeneity of the solution at the initial stage of polymerization seems to be the main cause for the deviation.

In summary, SEC and TGIC analyses were performed on a set of PS samples synthesized anionically under identical polymerization conditions in order to investigate their true MWD's and to compare with the Poisson distribution predicted by Flory. We confirmed from the evaluation of the band broadening of TGIC that the MWD measured by TGIC is close to the true MWD of anionically polymerized PS. Furthermore, the slightly broad MWD of PS relative to the Poisson distribution arises mainly from nonideal factors in the early stage of anionic polymerization. The MWD follows the Poisson distribution very well during the later stages of polymerization.

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