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Molecular Weight Distribution of Branched Polystyrene: Propagation of Poisson Distribution

Jinsook Ryu, Kyuhyun Im, Wonjae Yu, Jaiwook Park, and Taihyun Chang*

Department of Chemistry and Center for Integrated Molecular Systems, Pohang University of Science and Technology, Pohang 790-784, Korea

Kwanyoung Lee and Namsun Choi

Kumho Petrochemical R&D Center, Korea Kumho Petrochemical Co., Ltd., P.O. Box 64, Yuseong, Daejeon 305-600, Korea

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Introduction

Living anionic polymerization has been used for decades to prepare many useful polymers, in particular the polymers of very narrow molecular weight distribution (MWD).[1] According to the early theoretical work of Flory,[2] an "ideal" living anionic polymerization should yield a polymer with a Poisson distribution of chain length

$$n_i = \frac{\nu^{i-1}\mathrm{e}^{-\nu}}{(i-1)!} \tag{1}$$

in which n_i stands for the number 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.

Experimental verification of the theoretical prediction had to wait long until a good experimental tool became available to precisely measure the MWD of the polymers of very narrow MWD. The MWD of polymers has been commonly measured by size exclusion chromatography (SEC), but SEC overestimates the MWD of the polymers of very narrow MWD significantly due to the inherent band broadening effect.[3] Recently, Lee et al. reported that the MWD of polystyrenes (PS) prepared by anionic polymerization is very close to the Poisson distribution based on their MWD measurement by temperature gradient interaction chromatography (TGIC).[3,4] TGIC suffers from the band broadening effect much less than SEC. However, there was another obstacle in verifying the Flory's prediction; that is the "ideal" polymerization condition. An "ideal" living anionic polymerization should proceed under the 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 greater than the propagation rate.[2] Since it was practically impossible to avoid all side reactions in real situation, Lee et al. synthesized a set of PS of different molecular weights from a single batch polymerization to keep the nonideal aspects of the polymerization as identical as possible for all PS samples.[5] The MWD measured by TGIC was very close to the Poisson distribution, but there existed a small but finite discrepancy, which was attributed to the "nonideal" process in the anionic polymerization.

In this study we report on the MWD measurements of branched polymers. The branched PS employed in this study were prepared by linking polystyryl anions with chlorodimethylsilylstyrene (CDMSS), which links the polystyryl anions to yield a series of branched polymers with different number of branches.[6] The MWD of the branched PS cannot be measured precisely by a chromatographic method due to the lack of appropriate calibration standard materials. Instead, we employed the matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI−TOF MS) method. Recent advances of MALDI−TOF MS have made it possible to rigorously analyze relatively high molecular weight polymers.[7−9] Although the MALDI−TOF method still cannot fully cope with polymers of wide MWD, it is now well established that MALDI−TOF MS is able to measure the precise MWD for very narrowly dispersed and relatively low molecular weight polymers.[10−12] By combining TGIC fractionation and MALDI−TOF MS analysis, we were able to unambiguously confirm how the MWD of the branched polystyrenes changes as the number of branches increases.

Experimental Section

Branched polystyrenes (PS) were prepared by coupling polystyryl anion with 4-chlorodimethylsilylstyrene (CDMSS).[13] 4-Chlorodimethylsilylstyrene (CDMSS) was prepared following the literature procedure and stored at −25 °C in a drybox filled with argon gas. Styrene was distilled from calcium hydride under reduced pressure. Tetrahydrofuran and cyclohexane were distilled from sodiobenzophenone. Methanol was degassed with argon gas. Styrene, tetrahydrofuran, cyclohexane, and methanol were transferred into a drybox filled with argon gas and purified again by passing through a column filled with activated neutral alumina (Merck, 70−230 mesh) that was baked for 24 h at 250 °C in vacuo. Purified styrene was stored at −25 °C in the drybox. All the preparation procedure including termination of living anion was carried out in the drybox. Polystyryl anion was prepared by adding 0.38 mL (0.49 mmol) of *sec*-BuLi (Aldrich, 1.3 M in cyclohexane) to a solution of styrene (1.5 mL) in cyclohexane (15 mL) and THF (40.6 μL) at 60 °C. The solution was stirred for 30 min at 60 °C. A 5.0 mL aliquot of the polystyryl anion solution was transferred into another flask taken for the branching reaction. CDMSS (18.6 mg, 0.09 mmol) was added all at once to the solution with stirring at 60 °C. The molar ratio of CDMSS to the polystyryl anion was about 0.65. Stirring was continued for 30 min at 60 °C before the termination by adding a few drops of dried methanol. PS precursor was prepared by quenching

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* Corresponding author: Tel +82-54-279-2109; Fax +82-54-279-3399; e-mail tc@postech.edu.

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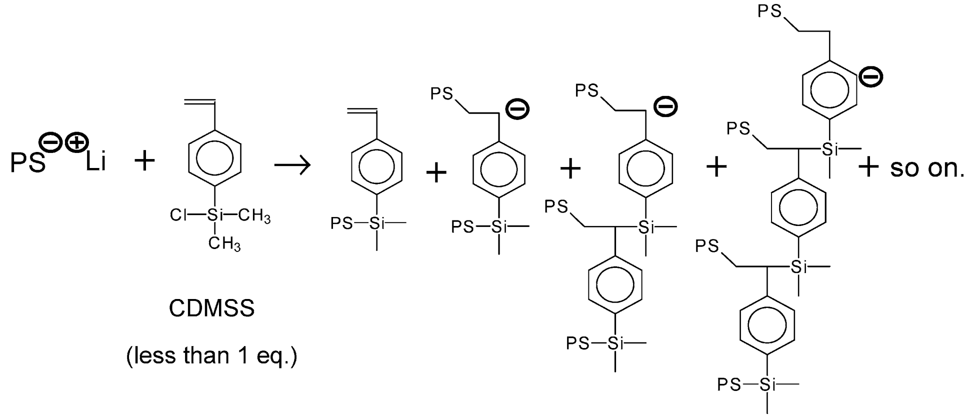
Scheme 1. Reaction Scheme and Possible Products from the Linking Reaction of Polystyryl Anions with 4-Chlorodimethylsilylstyrene (CDMSS)[a]



[a] Each PS chain contains one *sec*-butyl initiator moiety. There are other possible isomeric structures formed from the reaction of branched PS anions with the double bond in CDMSS.[6].

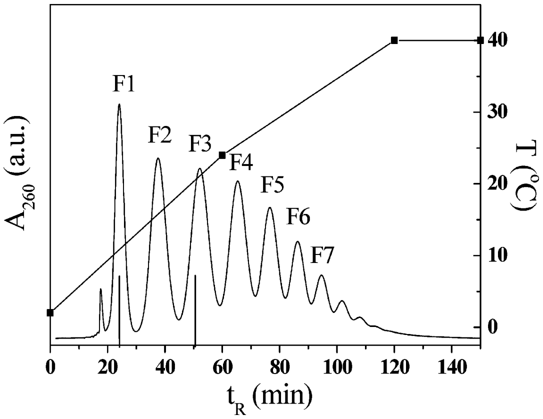


Figure 1. Temperature gradient interaction chromatogram of the branched polystyrene (PS). The small vertical bars indicate the elution time range to collect a fraction of the 2-branch PS for the MALDI−TOF MS measurements. Column: Zorbax C18 bonded silica, 100 Å, 250 × 9.3 mm, eluent: CH_2Cl_2/CH_3CN (55/45, v/v), flow rate: 0.7 mL/min. Temperature program is shown in the plot.

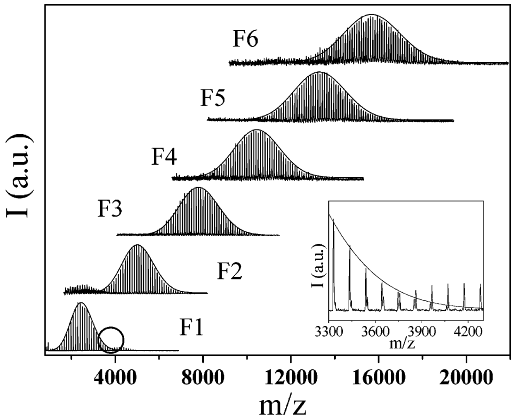


Figure 2. MALDI−TOF MS spectra of the six TGIC fractions of branched PS from 1 to 6 branches. The solid lines are the Poisson functions at the corresponding number-average molecular weight. In the inset, the expanded mass spectrum of F1 (circled region) is displayed to show the overlap region of 1-branch and 2-branch PS and the fit to the Poisson function.

the polystyryl anion solution with methanol. The branched PS prepared from this polymerization/coupling reaction is shown in Scheme 1.

For the reversed phase (RP)−TGIC fractionation of the branched PS, a C18 bonded silica column (Zorbax C18, 5 μm particle size, 100 Å pore, 250 × 9.3 mm) was used. The mobile phase was a CH_2Cl_2/CH_3CN mixture (55/45, v/v, Duksan) at a flow rate of 0.7 mL/min. The TGIC separation condition of the branched PS was reported earlier in detail.[13] The MALDI−TOF MS spectra were taken with a spectrometer equipped with a nitrogen laser (λ = 337 nm), a pulsed ion extraction, and a reflector (Bruker, Reflex III).[14,15] Polymer solutions were prepared in THF at a concentration of 5 mg/mL. The matrix 1,8-dihydroxy-9(10*H*)-anthracenone (dithranol, Aldrich, 97%) was dissolved in THF at a concentration of 20 mg/mL. A 5 μL aliquot of the polymer solution was mixed with 50 μL of the matrix solution and 1.5 μL of a silver trifluoroacetate (AgTFA, Aldrich, 98%) solution (1 mg/mL) in THF. A 0.5 μL portion of the final solution was deposited onto a sample target plate and allowed to dry in air at room temperature.

Results and Discussion

Figure 1 displays the RP−TGIC chromatogram of the branched PS with the temperature program. It shows well-resolved peaks representing the branched polymers with different number of the branches. As reported earlier, such a high resolution is due to the contribution of the nonpolar groups in the branched PS: the dimethylsilyl groups in the branching unit as well as the *sec*-butyl initiator groups.[13] As the number of branches increases, the number of the nonpolar groups increases, which in turn increases the RP−TGIC retention synergistically with increasing molecular weight. Despite such a good resolution, the molecular weight distribution cannot be determined precisely from the chromatogram since a reliable calibration curve cannot be constructed for the branched polymers. Therefore, each branched PS was collected by TGIC fractionation, and the MWD of each branched PS was measured by MALDI−TOF MS. Two vertical bars in Figure 1 represent a typical elution time range to collect a fraction of the branched PS for the MALDI−TOF MS measurements.

Figure 2 displays the MALDI−TOF MS spectra of six branched PS with the number of branches from one (precursor PS) to six. Each branched PS fraction was collected over the excessive elution time range as shown in Figure 1 not to distort the MWD of the branched PS. It should contain some amount of adjacent branched PS; however, as shown in the inset of Figure 2, their MALDI−TOF mass peaks do not overlap with the peaks of the main envelope since the adjacent branched PS contain different numbers of CDMSS and *sec*-butyl moieties.[13] The peaks from the neighboring species were removed to show the clearer peak envelops of the branched PS, except for the overlap regions of 1- and 2-branch PS, which are left for visual aid. The quality of the mass spectra gradually deteriorates as the number of branches (i.e., molecular weight) increases, but near complete resolution of each *mer* was achieved up to 6-branch PS.

The MWD of the branched polymers is the convolution products of MWD of the precursor PS anion. If we know MWD of the 1-branch PS (equivalent to the precursor polystyryl anion with one CDMSS end group), we can self-convolute the distribution numerically to predict MWD of the 2-branch PS. The MWD of the 3-branch PS is the convolution product of the 2-branch PS with 1-branch PS, and so on. The solid curves in Figure 2 are the Poisson functions located at the corresponding average molecular weight. Fortunately, the MWD of the 1-branch PS is very well matched with the Poisson distribution. Therefore, it is not necessary to carry out the numerical convolution since the convolution of a Poisson function with another Poisson function results in a Poisson function.[16] It is apparent in Figure 2 that all the branched PS have Poisson distributions from the near perfect match of the MALDI−TOF MS peak envelops with the solid curves representing the Poisson distribution located at the corresponding average molecular weight.

Then a question why the branched PS shows such a near perfect propagation of the Poisson distribution arises as the linking reaction proceeds. As mentioned in the Introduction, all branches in all branched PS must have the same MWD as the polystyryl anion precursor. Even though some side reactions including the undesired termination occur during the linking reaction, TGIC fractionates each branched PS with an intact number of branches, and the possible byproducts do not contaminate the fractions. Therefore, once the polystyryl anions have a Poisson distribution, all the branched polymers prepared by this type of linking reaction must have a Poisson distribution. In contrast, in the case of linear PS, a more strict "ideal" condition is required during the anionic polymerization to ensure the Poisson distribution.[5] In conclusion, the experimental results of this study unequivocally confirm to us that the polymers prepared by anionic polymerization have a Poisson distribution and the branched polymers obtained by linking such polymer anion precursors also have a Poisson distribution.

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References and Notes

(1) Hsieh, H. L.; Quirk, R. P. *Anionic Polymerization: Principles and Practical Applications*; Marcel Dekker: New York, 1996.
(2) Flory, P. J. *J. Am. Chem. Soc.* **1940**, *62*, 1561.
(3) Chang, T. *Adv. Polym. Sci.* **2003**, *163*, 1.
(4) Chang, T.; Lee, W.; Lee, H. C.; Park, S.; Ko, C. *Macromol. Chem. Phys.* **1999**, *200*, 2188.
(5) Lee, W.; Lee, H.; Cha, J.; Chang, T.; Hanley, K. J.; Lodge, T. P. *Macromolecules* **2000**, *33*, 5111.
(6) Knauss, D. M.; Al-Muallem, H. A.; Huang, T. Z.; Wu, D. T. *Macromolecules* **2000**, *33*, 3557.
(7) McEwen, C. N.; Peacock, P. M. *Anal. Chem.* **2002**, *74*, 2743.
(8) Hanton, S. D. *Chem. Rev.* **2001**, *101*, 527.
(9) Pasch, H.; Ghahary, R. *Macromol. Symp.* **2000**, *152*, 267.
(10) Montaudo, G.; Montaudo, M. S.; Puglisi, C.; Samperi, F. *Rapid Commun. Mass Spectrom.* **1995**, *9*, 453.
(11) Zhu, H. H.; Yalcin, T.; Li, L. *J. Am. Soc. Mass Spectrom.* **1998**, *9*, 275.
(12) Guttman, C. M.; Wetzel, S. J.; Blair, W. R.; Fanconi, B. M.; Girard, J. E.; Goldschmidt, R. J.; Wallace, W. E.; VanderHart, D. L. *Anal. Chem.* **2001**, *73*, 1252.
(13) Im, K.; Park, S.; Cho, D.; Chang, T.; Lee, K.; Choi, N. *Anal. Chem.* **2004**, *76*, 2638.
(14) Park, S.; Cho, D.; Ryu, J.; Kwon, K.; Chang, T.; Park, J. *J. Chromatogr. A* **2002**, *958*, 183.
(15) Hong, J.; Cho, D.; Chang, T.; Shim, W. S.; Lee, D. S. *Macromol. Res.* **2003**, *11*, 341.
(16) Perrin, C. L. *Mathematics for Chemists*; Wiley-Interscience: New York, 1970.

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