Fractionation of Block Copolymers Prepared by Anionic Polymerization into Fractions Exhibiting Three Different Morphologies

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ABSTRACT: In this study we fractionated polystyrene-*block*-polyisoprene diblock copolymers (PS-*b*-PI) prepared by anionic polymerization into fractions which have a narrower distribution in molecular weight as well as in chemical composition. The strategy was to use two-dimensional HPLC: reversed phase HPLC to fractionate PI block and normal phase HPLC to fractionate PS block with a minimal effect of the other block. The working principle of the separation method was confirmed for a low molecular weight PS-*b*-PI (2.4 kg/mol). With the aid of matrix assisted laser desorption/ionization mass spectrometry, we found that the separation method could resolve each *mer* of the PS-*b*-PI. We extended the application to a high molecular weight diblock copolymer (24 kg/mol) and established the method as a promising tool to further fractionate block copolymers into molecular species better defined in molecular weight as well as in composition. We observed a significant variation in average molecular weight as well as in composition of the fractionated samples. These variations were large enough to show different morphologies for the fractions taken from the same mother block copolymer.

1. Introduction

Block copolymers exhibit a rich morphological variation in molecular scale, which attracts considerable interest due to their potential applicability for the emerging nanotechnology.[1−7] Block copolymers for the studies on their fundamental properties as well as on the possible applications of the self-assembled supramolecular structure are commonly prepared by anionic polymerization. Anionic polymerization is the best available method to yield the polymers of narrow molecular weight distribution (MWD) and predictable molecular weight.[8,9] They are often regarded as “monodisperse” although the MWD of each block is far from the rigorous meaning of the term.

The molecular weight distribution of synthetic polymers is commonly measured by size exclusion chromatography (SEC).[10,11] However, the resolution of SEC is not high enough to measure a correct distribution for many polymers prepared by anionic polymerization.[12] Interaction chromatography (IC) has been known to provide a much higher resolution for the MWD analysis of such polymers.[13] Recently Lee et al. did a systematic analysis using IC on the molecular weight distribution of a set of polystyrenes prepared from a single batch anionic polymerization.[14] They showed that the true MWD was much narrower than that measured by SEC and was quite close to the Poisson distribution as predicted by Flory a long time ago.[15] Nonetheless the polymers prepared by anionic polymerization still have a finite MWD. Consequently each block of a block copolymer has finite MWD, which leads to a chemical composition distribution (CCD) in a whole ensemble of block copolymer molecules. How the heterogeneities would affect the final property of the materials has not been elucidated.

The precise characterization of a copolymer having both MWD and CCD is much more complicated than the analysis of a homopolymer. The ultimate goal is to construct a two-dimensional, one in molecular weight and the other in chemical composition, distribution map. An attractive method for the purpose is the two-dimensional liquid chromatography (2D-LC), in which two different chromatographic separation methods are used in sequence.[16−18] If one of the two separation methods is sensitive to one molecular characteristic while not to the other, and vice versa, it would be possible to construct such a 2D distribution map. Many of the copolymer analyses have been done in this way combining an IC method, commonly in the form of solvent gradient LC for the separation according to the chemical composition, and SEC for the separation with respect to the molecular weight.[16,19] This method has proven to be useful for the analysis of a copolymer having wide CCD and MWD, but not for block copolymers with both narrow MWD and CCD mainly due to the low resolution of SEC.

Another approach is the liquid chromatography at the chromatographic critical condition (LCCC).[18,20,21] At the LCCC condition of a homopolymer, the entropic size exclusion effect and the enthalpic interaction effect compensate each other, and the molecular weight dependence of the chromatography retention disappears. Therefore, at the LCCC condition of a block for a block copolymer, the block becomes “chromatographically invisible” and the other “visible” block solely determines the chromatography retention of the block copolymer. If the MWD of each block were characterized in this way, the information equivalent to 2D map of MWD and CCD can be obtained. The method has worked well for low molecular weight block copolymers in which the interaction of the visible block with the stationary phase is stronger than the invisible block and the separation of the visible block is done by the IC

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mechanism.[22,23] For the analysis of high molecular weight block copolymers, however, the separation of the visible block has to be done by the SEC mechanism since the separation condition is fixed at the LCCC condition of the invisible block.[18,24] In such a fixed isocratic and isothermal elution condition, it is difficult to elute high molecular weight polymers by IC separation mechanism.[25] Therefore, the LCCC separation usually suffers from the low resolution of SEC. Furthermore, the precision of the method has been questioned.[26,27]

Therefore, one needs a method of higher resolution for both MWD and CCD for precise characterization and/or fractionation of block copolymers. In this study, we employed the 2D-LC method: normal phase liquid chromatography (NPLC) for one dimension and reversed phase liquid chromatography (RPLC) dimension for the other dimension. The strategy is to separate one block in terms of its molecular weight with a minimal effect of the other block, which is like the concept of the LCCC method. However, in this case there is more freedom in choosing the separation condition at which isocratic and isothermal elution for the narrowly dispersed block copolymer is possible. This idea is not new and has been already applied for the separation of low molecular weight diblock copolymers having a high polarity contrast between two blocks: alcohol ethoxylates[28] or poly(ethylene oxide)-*block*-poly(propylene oxide).[29] In this study we applied the method for the separation of polystyrene-*block*-polyisoprene diblock copolymers (PS-*b*-PI), which has been used extensively for the morphological study of block copolymers. The polarity contrast in PS-*b*-PI is subtler than the above examples, but we found that suitable IC conditions could be established for the separation of individual blocks with little effect from the presence of the other block. We extended the application to high molecular weight block copolymers and established the method as a promising tool to further fractionate block copolymers into molecular species better defined in molecular weight as well as in composition.

2. Experimental Section

Materials. PS-*b*-PI diblock copolymers were prepared by sequential anionic polymerization at 45 °C under Ar atmosphere using *sec*-butyllithium (Aldrich) and cyclohexane (Aldrich) as an initiator and a solvent, respectively. After the polymerization of styrene block was completed, isoprene monomer was added for the polymerization of the PI block. Details of the apparatus and the polymerization procedure were reported previously.[27,30] The block copolymers were precipitated in methanol and characterized with SEC and ^{1}H NMR spectroscopy. Two PS-*b*-PI polymers of average molar masses of 2.4 kg/mol (30.4 wt % PI content, $M_w/M_n = 1.06$) and 24 kg/mol (34.8 wt % PI content, $M_w/M_n = 1.01$) were prepared and their molecular characteristics were determined by SEC and ^{1}H NMR (Bruker, DPX-300).

For the SEC analysis, two PS gel columns (Polymer Lab., PL-mixed C) were used and the eluent was tetrahydrofuran (THF, Duksan, HPLC grade). The temperature of the column was kept at 40 °C using a column oven (Eppendorf, TC-50). Chromatograms were recorded with a multiangle laser light scattering detector (Wyatt, mini-DAWN) and a refractive index detector (Wyatt, Opti-Lab).

HPLC. The HPLC apparatus consists of a solvent delivery pump (Polymer Lab. LC 1150), a six-port sample injector (Rheodyne, 7125) equipped with a 100 μL injection loop, and a variable wavelength UV/vis absorption detector (Spectra-Series, UV 100). For the NPLC separation of the low molecular weight PS-*b*-PI, a diol-bonded column (Nucleosil Diol, 100 Å, 250 × 7.8 mm) and a mixture of isooctane/THF (97/3, v/v) were used as the stationary phase and the mobile phase, respectively. The sample concentration was 10 mg/mL, and the flow rate of the mobile phase was 0.5 mL/min. The temperature of the column was controlled by circulating fluid from a programmable bath/circulator (Neslab, RTE−111) through a homemade column jacket. The chromatograms were recorded with a UV absorption detector operating at a wavelength of 260 nm. The RPLC system is essentially the same as that of NPLC system except for the column (LUNA C18, 100 Å pore, 250 × 4.6 mm) and the mobile phase (CH_2Cl_2/CH_3CN, 53/47, v/v). HPLC grade CH_3CN (Duksan), CH_2Cl_2 (Duksan), and ACS grade isooctane (JUNSEI) were used, and the eluent mixtures were filtered through a 0.2 μm pore membrane filter (Bio-Rad) before use.

For the fractionation of the high molecular PS-*b*-PI we used larger bore columns (100 × 22 mm for NPLC and 70 × 22 mm for RPLC), different compositions of the mobile phases (isooctane/THF, 70/30 in volume for the NPLC and CH_2Cl_2/CH_3CN, 75/25 in volume for RPLC), higher flow rates (1.5 and 1.2 mL/min in NPLC and RPLC, respectively), and higher sample concentration (140 mg/mL).

MALDI−TOF MS. A Bruker REFLEX III mass spectrometer equipped with a nitrogen laser ($\lambda = 337$ nm), a pulsed ion extraction, and a reflector was used. This instrument was operated at an accelerating potential of 20 kV in reflector mode. Polymer solutions were prepared in HPLC grade THF at a concentration of 1 g/L. The matrix, 1,8-dihydroxy-9(10*H*)-anthracenone (dithranol, Aldrich), was dissolved in THF at a concentration of 15 g/L. A 5 μL aliquot of the polymer solution was mixed with 50 μL of the matrix solution and 1 μL of a silver trifluoroacetate solution (1 g/L in THF), respectively. 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.

Small-Angle X-ray Scattering. PS-*b*-PI specimens for small-angle X-ray scattering (SAXS) analysis contain 0.3 wt % 2,6-di-*tert*-butyl-4-methylphenol. The antioxidant was added to the toluene solution of the polymers and the solvent was slowly evaporated for 1 day at room temperature and then further evaporated under vacuum at 50 °C for 1 day. Then the polymer samples were annealed at 110 °C for 24 h and slowly cooled to room temperature. SAXS measurements were carried out at the synchrotron SAXS facility in the Pohang Light Source (PLS), Pohang, Korea.[31] The wavelength (λ) of the X-ray beam was 1.608 Å and the energy resolution ($\Delta\lambda/\lambda$) was 1.5×10^{-2}. The beam size was smaller than 1 × 1 mm, and the sample-to-detector distance was 160 cm. Scattering profiles were obtained at room temperature and then corrected for absorption and air scattering.

3. Results and Discussion

We first demonstrate the separation method with a low molecular weight PS-*b*-PI for the fractionation of individual block since the fractionation result can be easily confirmed by MALDI−TOF MS. To separate a block copolymer by IC with high resolution, a proper separation condition needs to be selected first. For the separation according to the PS block length, a diol-bonded silica and an isooctane/THF mixture (97/3, v/v) were used as stationary and mobile phases, respectively. The eluent is a good solvent for PI chains, and the PI block shows little interaction with the polar stationary phase. Therefore, homo-PI would elute in the SEC regime while PS block has a sufficient interaction with the stationary phase to yield high resolution by the IC separation mechanism.[32] Figure 1 displays the NPLC chromatograms of the low molecular weight PS-*b*-PI recorded by a UV detector. To enhance the resolution, the temperature of the column was raised in three steps from 3 to 65 °C as shown in the plot. The technique named as temperature gradient interaction chromatography (TGIC) has proven to be an efficient method to

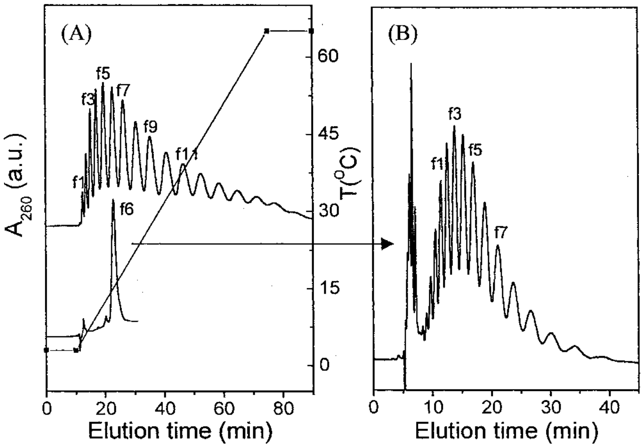

Figure 1. 2D-LC separation of a low molecular weight PS-*b*-PI (2.4 kg/mol, 30.4% PI content): (A) NP-TGIC chromatograms of the PS-*b*-PI (top) and a fraction, f6 (bottom), which separates PS-*b*-PI in terms of the PS block length only (the temperature program is also shown in the plot); (B) RPLC chromatogram of the NP-TGIC fraction, f6, which separates in terms of the PI block length only. It elutes as a single peak in NP-TGIC, but shows multiple peaks in RPLC, indicating that it contains homogeneous PS block lengths (eight monomer units) but various PI block lengths.

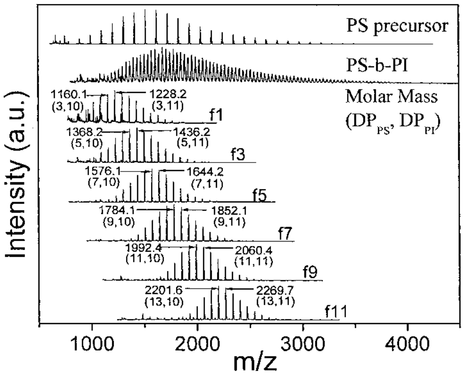

Figure 2. MALDI−TOF mass spectra of the PS precursor, the low molecular weight PS-*b*-PI and six fractions collected from NP-TGIC fractionation as shown in Figure 1A. The spectrum of PS precursor represents MWD of the PS block while the spectra of the six fractions represents MWD of PI block since they have homogeneous PS block length. The molecular weights and the degrees of polymerization of PS (DP_{PS}) and PI block (DP_{PI}) are shown for several peaks.

separate various polymers according to the molecular weight.[13,33] The PS-*b*-PI is resolved very well.

A fraction, for example, f6, was collected and subjected to NPLC separation once again to confirm the purity. As shown in the bottom chromatogram of Figure 1A, the fraction elutes as a single peak, which is a PS-*b*-PI polymer having a homogeneous PS length. To confirm the argument, MALDI−TOF mass spectra of several fractionated PS-*b*-PI polymers are compared in Figure 2. The top spectrum is for the PS precursor taken before the polymerization of PI block. It shows an equally spaced series of the peaks, and the spacing is equivalent to the mass of a styrene monomer unit, 104 g/mol. The second mass spectrum is obtained from the mother block copolymer before the fractionation and it has a far more number of peaks due to the addition of the PI block. The weight-average molecular weight is calculated as 2.4 kg/mol, which is consistent with the SEC analysis result, 2.4 kg/mol. The bottom 6 mass spectra correspond to the fractions collected from the NPLC fractionation as shown in Figure 1A. The mass spectrum of each fraction consists of a series of peaks spaced by 68 (the monomer unit mass of PI) indicating that the spectrum shows the molecular weight distribution of PI block at a constant number of PS repeating units. The peaks between the two adjacent MALDI−TOF mass spectra are shifted by 208 g/mol, which is twice as much as the monomer unit mass of PS. Combining these results we can confirm that the NPLC fractionation was done in terms of PS length only and the repeating unit of PS increased from 3 to 13 from fraction 1 to fraction 11. Also the measured molecular weight is in good agreement with the calculated molecular weight: 104.15 × *n* (*n* styrene units) + 68.12 × *m* (*m* isoprene units) + 58.12 (end groups: *sec*-butyl group from the initiator and one hydrogen from the termination by alcohol) + 107.87 (Ag^+ ion). For an example, with $n = 3$ and $m = 11$, the molar mass of the PS-*b*-PI was found to be 1228.2 compared to the calculated mass of 1227.8.

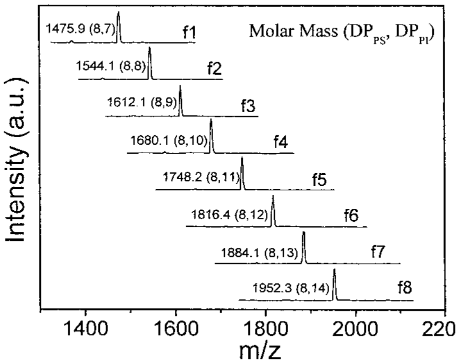

Figure 3. MALDI−TOF MS spectra of the low molecular weight PS-*b*-PI fractionated by both NP-TGIC and RPLC mode as illustrated in Figure 1. The single mass peak of the fractions indicates that they are truly monodisperse block copolymers. The molecular mass and the degree of polymerization of PS (DP_{PS}) and PI block (DP_{PI}) are shown for each spectrum.

To fractionate the PI block, RPLC was used: C18 bonded silica and a mixture of CH_2Cl_2/CH_3CN (53/47, v/v) as a mobile and stationary phase, respectively. In this polar mobile phase and nonpolar stationary phase HPLC condition, the situation is reversed and the PI block has a stronger interaction with the stationary phase than PS. The solvent quality of the eluent is good enough for PS to elute in the SEC regime while PI elutes in the IC regime.[34] When the fraction, f6, was subjected to RPLC separation at 20 °C, the block copolymers are separated in terms of PI block length as shown in Figure 1B. The multiple peaks at the short elution time (5−8 min) are due to the additives including the antioxidant and impurity in the eluent, which was concentrated during the fraction collection, drying, and redissolution process.[35] The resolved individual peaks were collected again and their absolute molecular weight was determined by MALDI−TOF MS. Figure 3 displays the MALDI−TOF mass spectra of the RPLC fractions. The MALDI−TOF mass spectrum for each fraction shows a single mass peak containing eight styrene units and different number of isoprene units indicating that the individual block of the low molecular PS-*b*-PI was completely resolved.

Applying the same fractionation principle, the individual block of a high molecular weight PS-*b*-PI was fractionated. Figure 4 shows a 2D-LC fractionation process similar to that in Figure 1. To fractionate the PI block, we used a RPLC system operated at 15 °C with

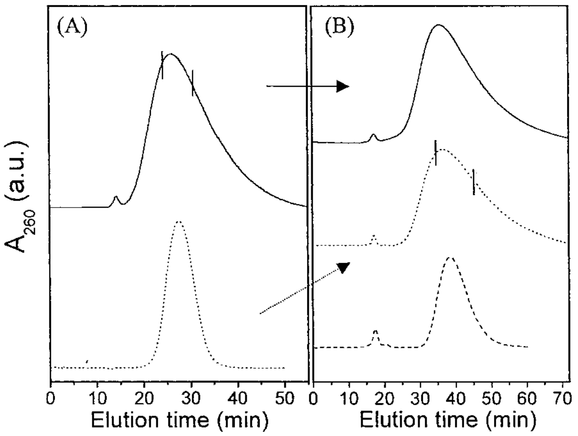

Figure 4. RPLC and NPLC fractionation of the high molecular weight PS-*b*-PI (24 kg/mol, 34.8 wt % PI content): (A) RPLC chromatogram of the mother PS-*b*-PI (top, solid line) and the middle fraction taken between the small vertical bars shown in the top chromatogram (bottom, dotted line); (B) NPLC chromatogram of the mother PS-*b*-PI (top, solid line) and the RPLC middle fraction (middle, dotted line). The two chromatograms are almost identical since they differ in MWD of the PI block only and NPLC separates PS-*b*-PI according to the PS block length. The bottom chromatogram (dashed line) of part B shows the NPLC fraction between the small vertical bars of the RPLC fractionated PS-*b*-PI, which has a narrower MWD for both blocks.

C18 bonded silica and a mixture of CH_2Cl_2/CH_3CN (75/25,v/v) as stationary and mobile phase, respectively. Figure 4A shows a RPLC chromatogram of PS-*b*-PI whose molecular weight is 24 kg/mol and PI composition is 34.8 wt %. Because of the high molecular weight, resolution of each *mer* was impossible and a continuous elution curve was observed as shown in Figure 4A (top). The middle fraction was collected as indicated with small vertical bars and the bottom chromatogram of Figure 4A was obtained from the middle fraction at the same RPLC condition. A small broadening of the collected fraction is observed, but it is apparent that the peak width of the fraction is much narrower than the mother PS-*b*-PI, indicative of the narrower MWD of the PI block.

Figure 4B displays NPLC chromatograms obtained at 32 °C that separate the PS-*b*-PI according to the PS block length using a diol-bonded silica and isooctane/THF (70/30, v/v) as a stationary and mobile phase, respectively. The top (solid line) and middle (dotted line) chromatograms correspond to the mother PS-*b*-PI and the RPLC middle fraction (the bottom chromatogram in Figure 4A), respectively. The two chromatograms are almost identical indicating that the two polymers have almost the same MWD in the PS block, which confirms that the first RPLC separation fractionated the polymer in terms of PI block length only. Although it is impossible to confirm it directly like the MALDI−TOF MS analysis for low molecular weight PS-*b*-PI, the identical NPLC chromatograms of the mother and the RPLC fraction indicate quite convincingly that the 2D-LC separation is carried out as expected. The bottom chromatogram (dashed line) of Figure 4B shows the NPLC fraction of the RPLC fractionated PS-*b*-PI between the small vertical bars of the middle chromatogram, which has narrower MWD for both blocks.

To find how the fractionation would affect the properties of PS-*b*-PI block copolymers, the mother block copolymer was fractionated into nine fractions, three fractions each by NPLC and RPLC. Figure 5A displays the RPLC chromatograms of the mother copolymer (solid line) and its low, middle and high molecular weight fractions in the PI block (dash−dot line) separated by RPLC. Figure 5B shows the NPLC chromatograms of the RPLC middle fraction in Figure 5A (solid line) and its three fractions (dash−dot line) that have different PS content. Small vertical bars on the solid line chromatogram indicate the portions collected. In this way, nine fractions of the mother PS-*b*-PI with different molecular weights and weight fractions were obtained.

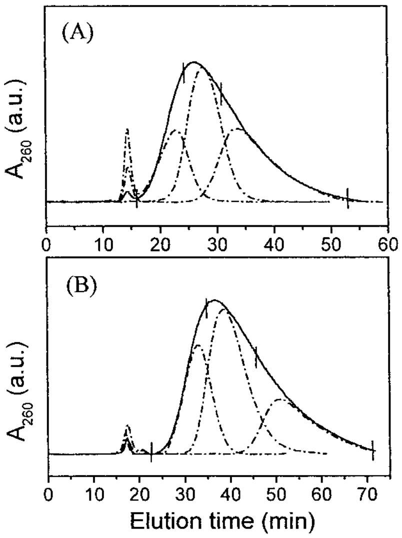

Figure 5. 2D-LC fractionation of high molecular weight PS-*b*-PI (24 kg/mol, 34.8 wt % PI content): (A) RPLC chromatograms of the mother PS-*b*-PI (solid line) and its three fractions (dash−dot line); (B) NPLC chromatograms of the middle fraction of RPLC separation (solid line) and its three fractions. RPLC fractionates the PI block while NPLC fractionates the PS block. The range of the fraction collected is indicated with small vertical bars.

Table 1. Characteristics of the PS-*b*-PI Block Copolymers

mother PS-*b*-PI
(M_n = 23.4 kg/mol, 34.8 PI wt %, gyroid morphology)

sample code[a]		NPLC		
		S_L	S_M	S_H
RPLC	I_H	21.8 kg/mol[b] 39.0 wt %[c] lamellar[d]	23.5 kg/mol 37.6 wt % lamellar	25.2 kg/mol 35.3 wt % lamellar
	I_M	21.4 kg/mol 37.2 wt % -	23.0 kg/mol 34.8 wt % gyroid	24.5 kg/mol 31.9 wt % gyroid
	I_L	21.0 kg/mol 32.3 wt %	22.5 kg/mol 32.1 wt % hexagonal cylinder	24.0 kg/mol 30.4 wt % hexagonal cylinder

[a] S and I stand for PS and PI block fractionated by NPLC and RPLC, respectively. Subscripts L, M, and H stand for low, medium, and high molecular weight fractions, respectively. [b] Number-average molecular weights determined by SEC. [c] Weight fraction of PI block determined by ^{1}H NMR spectroscopy. [d] Morphology determined by SAXS.

The fractionated PS-*b*-PI was characterized by SEC−light-scattering detection for the average molecular weight and ^{1}H NMR for the composition and the results are summarized in Table 1. Specific refractive index increments (d*n*/d*c*) of the PS-*b*-PI samples were calculated by the following equation.[36]

$$(\mathrm{d}n/\mathrm{d}c)_{\mathrm{PS}-b-\mathrm{PI}} = (\mathrm{wt})_{\mathrm{PS}}(\mathrm{d}n/\mathrm{d}c)_{\mathrm{PS}} + (\mathrm{wt})_{\mathrm{PI}}(\mathrm{d}n/\mathrm{d}c)_{\mathrm{PI}} \quad (1)$$

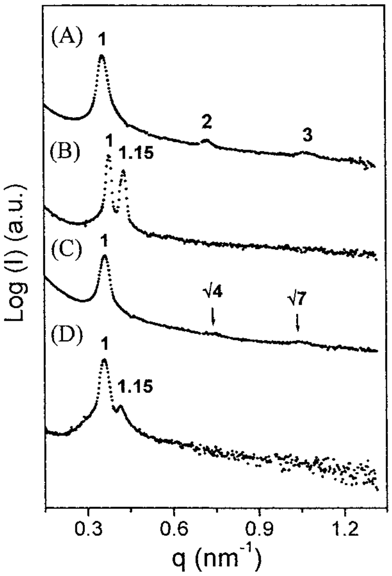

Figure 6. SAXS profiles of the mother and three fractionated PS-*b*-PI: (A) S_LI_H fraction showing lamellar morphology; (B) S_MI_M fraction showing gyroid morphology; (C) S_HI_L fraction showing hexagonal cylinder morphology; (D) mother PS-*b*-PI showing gyroid morphology. The number on the peak positions represents the scattering vector of the peak position relative to the first-order scattering maximum.

The d*n*/d*c* values of homopolymers were determined (Wyatt, Opti-Lab) as PS = 0.185 mL/g and PI = 0.120 mL/g in THF, and the weight fraction (wt) was determined by ^{1}H NMR measurement. The subscripts L, M, and H in the sample code stand for low, middle, and high molecular weight fraction of each block. In Table 1, the variation in molecular weight as well as in composition shows a reasonable trend. The magnitude of the variation is significant, almost 15% difference in average molecular weight and close to 10 % difference in composition between the extreme cases. This result clearly tells us that the mother block copolymer is far from a “monodisperse” chemical species. So far, block copolymers prepared by anionic polymerization have never been examined for their detailed molecular characteristics to this extent.

Next we have examined how such differences in molecular weight and composition would affect the morphological behavior of the block copolymers. Under appropriate conditions, diblock copolymers undergo microphase separation to form characteristic self-assembled structures, in which domains consisting primarily of one block are locally separated from domains consisting primarily of the other block. The phase behavior is governed by molecular weight, the interaction parameter between the block species and the composition.[37−39] The morphologies of the microphase-segregated block copolymers were studied by SAXS, and the determined morphology of each fraction is listed in Table 1. We observed various morphologies of the fractions different from that of the mother PS-*b*-PI. In the cases of S_LI_L and S_LI_M samples, we could not identify their morphologies, likely due to their low molecular weights.

Figure 6 shows the plots of SAXS intensity vs scattering vector of the mother and three fractionated PS-*b*-PI moieties spanning the largest composition variation among the fractionated samples, S_LI_H, S_MI_M, and S_HI_L. The SAXS profile of S_LI_H in Figure 6A shows scattering maxima at the scattering vectors of integer multiples of the first-order scattering maximum, which indicates that this block copolymer has lamellar morphology.[2] The scattering profile is clearly different from the mother polymer shown in Figure 6D, which shows gyroid morphology as evidenced from the shoulder appearing at the scattering vector of 1.15 times the first-order peak position.[2] The S_MI_M sample also shows gyroid morphology as expected from the similar molecular weight and composition to that of the mother PS-*b*-PI. However, the scattering profile is very distinct from that of the mother polymer; the S_MI_M fraction shows remarkably sharp peaks. It is likely due to the larger grain size in the fractionated sample. The quantitative analyses of the grain size and other morphological features relative to the MWD and CCD of PS-*b*-PI are in progress. The SAXS profile of S_HI_L fraction in Figure 6C shows another different morphology. The higher order scattering peaks appearing at the scattering vectors of $\sqrt{4}$ and $\sqrt{7}$ times relative to the position of the first-order scattering maximum are weak but discernible enough to confirm hexagonal cylinder morphology.[2]

In conclusion, it is apparent that the PS-*b*-PI diblock copolymer made by anionic polymerization has wide MWD and CCD enough for its fractions to exhibit various morphologies from lamellar, to gyroid, to cylinder. It remains to be investigated further how the finite MWD and CCD would affect our current knowledge on various properties of block copolymers and what benefit in the application side would be expected from the time-consuming fractionation.

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Note Added after ASAP Posting

This article was released ASAP on 5/25/2002 with an error in the title and the first line of the abstract. The corrected version was posted on 6/11/2002.

References and Notes

(1) Bates, F. S.; Fredrickson, G. H. *Annu. Rev. Phys. Chem.* **1990**, *41*, 525.
(2) Hamley, I. W. *The Physics of Block Copolymers*; Oxford University Press: New York, 1998.
(3) Park, M.; Harrison, C.; Chaikin, P. M.; Register, R. A.; Adamson, D. H. *Science* **1997**, *276*, 1401−1404.
(4) Black, C. T.; Guarini, K. W.; Milkove, K. R.; Baker, S. M.; Russell, T. P.; Tuominen, M. T. *Appl. Phys. Lett.* **2001**, *79*, 409−411.
(5) Kim, H. C.; Jia, X. Q.; Stafford, C. M.; Kim, D. H.; McCarthy, T. J.; Tuominen, M.; Hawker, C. J.; Russell, T. P. *Adv. Mater.* **2001**, *13*, 795−797.
(6) Thurn-Albrecht, T.; Schotter, J.; Kastle, C. A.; Emley, N.; Shibauchi, T.; Krusin-Elbaum, L.; Guarini, K.; Black, C. T.; Tuominen, M. T.; Russell, T. P. *Science* **2000**, *290*, 2126−2129.
(7) Urbas, A.; Sharp, R.; Fink, Y.; Thomas, E. L.; Xenidou, M.; Fetters, L. J. *Adv. Mater.* **2000**, *12*, 812−814.
(8) Szwarc, M. *Nature (London)* **1956**, *178*, 1168−1169.
(9) Hsieh, H. L.; Quirk, R. P. *Anionic Polymerization: Principles and Practical Applications*; Marcel-Dekker: New York, 1996.
(10) Yau, W. W.; Kirkland, J. J.; Bly, D. D. *Modern Size-Exclusion Liquid Chromatography, Practice of Gel Permeation and Gel Filtration Chromatograph*; John Wiley & Sons: New York, 1979.

(11) Mori, S.; Barth, H. G. *Size Exclusion Chromatography*; Springer-Verlag: New York 1999.
(12) Johnson, A. F.; Mohsin, M. A.; Meszena, Z. G.; Graves-Morris, P. *J. Macromol. Sci.*—*Rev. Macromol. Chem. Phys.* **1999**, *C39*, 527−560.
(13) Chang, T.; Lee, H. C.; Lee, W.; Park, S.; Ko, C. *Macromol. Chem. Phys.* **1999**, *200*, 2188−2204.
(14) Lee, W.; Lee, H.; Cha, J.; Chang, T.; Hanley, K. J.; Lodge, T. P. *Macromolecules* **2000**, *33*, 5111−5115.
(15) Flory, P. J. *J. Am. Chem. Soc.* **1940**, *62*, 2, 1561−1565.
(16) Glöckner, G. *Gradient HPLC of Copolymers and Chromatographic Cross-Fractionation*; Springer-Verlag: Berlin, 1992.
(17) Berek, D. *Prog. Polym. Sci.* **2000**, *25*, 873−908.
(18) Pasch, H.; Trathnigg, B. *HPLC of Polymers*; Springer-Verlag: Berlin, 1997.
(19) Trathnigg, B. *Prog. Polym. Sci.* **1995**, *20*, 615−650.
(20) Belenkii, B. G.; Valchikhina, M. D.; Vakhtina, I. A.; Gankina, E. S.; Tarakanov, O. G. *J. Chromatogr.* **1976**, *129*, 115−124.
(21) Skvortsov, A. M.; Gorbunov, A. A. *Polym. Sci. USSR* **1979**, *21*, 371−380.
(22) Lee, H.; Lee, W.; Chang, T.; Choi, S.; Lee, D.; Ji, H.; Nonidez, W. K.; Mays, J. W. *Macromolecules* **1999**, *32*, 4143−4146.
(23) Lee, H.; Chang, T.; Lee, D.; Shim, M. S.; Ji, H.; Nonidez, W. K.; Mays, J. W. *Anal. Chem.* **2001**, *73*, 1726−1732.
(24) Falkenhagen, J.; Much, H.; Stauf, W.; Muller, A. H. E. *Macromolecules* **2000**, *33*, 3687−3693.
(25) Stadalius, M. A.; Quarry, M. A.; Mourey, T. H.; Snyder, L. R. *J. Chromatogr.* **1986**, *358*, 17−37.
(26) Lee, W.; Park, S.; Chang, T. *Anal. Chem.* **2001**, *73*, 3884−3889.
(27) Lee, W.; Cho, D.; Chang, T.; Hanley, K. J.; Lodge, T. P. *Macromolecules* **2001**, *34*, 2353−2358.
(28) Murphy, R. E.; Schure, M. R.; Foley, J. P. *Anal. Chem.* **1998**, *70*, 4353−4360.
(29) Jandera, P.; Holcapek, M.; Kolarova, L. *J. Chromatogr. A* **2000**, *869*, 65−84.
(30) Kwon, K.; Lee, W.; Cho, D.; Chang, T. *Korea Polym. J.* **1999**, *7*, 321−324.
(31) Bolze, J.; Kim, J.; Huang, J. Y.; Rah, S.; Youn, H. S. *Macromol. Res.* **2002**, *10*, 2−12.
(32) Lee, W.; Cho, D.; Chun, B. O.; Chang, T.; Ree, M. *J. Chromatogr. A* **2001**, *910*, 51−60.
(33) Lee, H. C.; Chang, T. *Polymer* **1996**, *37*, 5747−5749.
(34) Lee, W.; Lee, H. C.; Park, T.; Chang, T.; Chae, K. H. *Macromol. Chem. Phys.* **2000**, *201*, 320−325.
(35) Cho, D.; Park, S.; Chang, T.; Ute, K.; Fukuda, I.; Kitayama, T. *Anal. Chem.* **2002**, *74*, 1928−1931.
(36) Huglin, M. B., Ed. *Light scattering from polymer solutions, Specific refractive index increments*; Academic press: New York, 1972.
(37) Leibler, L. *Marcromolecules* **1980**, *13*, 1602−1617.
(38) Bates, F. S.; Schulz, M. F.; Khandpur, A. K.; Forster, S.; Rosedale, J. H.; Almdal, K.; Mortensen, K. *Faraday Discuss.* **1994**, *98*, 7−18.
(39) Khandpur, A. K.; Forster, S.; Bates, F. S.; Hamley, I. W.; Ryan, A. J.; Bras, W.; Almdal, K.; Mortensen, K. *Macromolecules* **1995**, *28*, 8, 8796−8806.

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