Effect of Block Copolymer Chain Architecture on Chromatographic Retention

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ABSTRACT: The chain architecture dependence of the retention behavior of block copolymers in the temperature gradient interaction chromatography (TGIC) and liquid chromatography at the critical condition (LCCC) was investigated. For the purpose, polystyrene (PS)/polybutadiene (PB) diblock (SB), SBS triblock, and BSB triblock copolymers were prepared by sequential anionic polymerization and further fractionated by reversed-phase TGIC to obtain a set of the block copolymers with high purity, narrow distribution, and matched block length. In the TGIC separation with C18 bonded silica stationary phase and a mixture of CH_2Cl_2/CH_3CN mobile phase, retention of the three block copolymers with matched molecular weight and composition shows a significant architecture effect: SBS elutes significantly earlier while BSB or SB elute later at similar retention volume. It indicates that the polymer−stationary phase interaction is less effective for the PB block located at the middle of the chain than the blocks located at the chain end. In LCCC separation at the critical condition for PB block, SBS is eluted early while SB and BSB were eluted later at the same retention time. Therefore, triblock copolymer with an *invisible* middle block behaves differently from those having *invisible* end block(s). This behavior is consistent with the theoretical prediction by Guttman et al. [*Macromolecules* **1996**, *29*, 5723].

Introduction

Block copolymers gain increasing attention recently in both fundamental and technological points of view. The physical property of block copolymers is affected by the molecular characteristics such as molecular weight, composition, and chain architecture.[1−3] Therefore, precise information on these molecular parameters of block copolymers is necessary to establish the relationship between the molecular characteristics and their physical properties. However, the rigorous characterization of copolymers is in general much more complicated than homopolymer because they have distributions not only in molecular weight but also in other molecular parameters.

HPLC is the most widely used method to characterize various distributions in molecular characteristics of synthetic polymers. A good example is size exclusion chromatography (SEC), which is an HPLC technique to separate polymer molecules according to the hydrodynamic volume of polymer chains. Since there is a simple relationship between hydrodynamic volume and molecular weight for linear homopolymers, SEC has been the most popular method to measure molecular weight distribution of synthetic polymers. For the analysis of the other molecular characteristics that are not simply correlated with the hydrodynamic volume, however, SEC is not an efficient method. There have been continued efforts to develop other HPLC techniques to complement the limitation of SEC. Interaction chromatography (IC) is an HPLC method to separate analytes according to the interaction energy between the analytes and the stationary phase of the HPLC column. IC has been successfully employed to separate synthetic polymers according to the various molecular characteristics such as molecular weight, composition, tacticity, architecture, and so on.[4−6]

To fully characterize a diblock copolymer, one needs to obtain information on molecular weight distribution (MWD) as well as on chemical composition distribution (CCD). SEC cannot provide information on the distributions since the hydrodynamic volume of a diblock copolymer chain is affected by both molecular weight and composition. IC retention is also affected by the two molecular characteristics, but it is possible to separate diblock copolymers mainly according to individual block lengths. With this method, we have recently shown that IC can fractionate diblock copolymers into fractions having narrower distributions both in chemical composition and in molecular weight.[7,8]

Another HPLC method that has been widely used for the characterization of polymers is liquid chromatography at the critical condition (LCCC). At the critical condition, enthalpic interaction of polymeric solutes is exactly compensated by the entropic size exclusion effect, and the polymers elute at near the total column void volume independent of molecular weight.[9] At this condition the polymers can be regarded chromatographi-

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cally *invisible,* and this interesting feature has been widely utilized in the characterization of block copolymers and functionality.[10,11] At the critical condition of one block, the block is chromatographically *invisible*, and the retention of the diblock copolymer is solely determined by the other *visible* block.[10–12] Despite the controversy as to the precision of the method, there is a consensus that LCCC can estimate individual block length of diblock copolymers reasonably.[13–15]

For two component triblock copolymers, there can exist another variation in chain architecture, i.e., ABA or BAB type. If they have similar molecular weight and composition, can we distinguish them by chromatography? Guttman et al. reported a theoretical result about the influence of polymer architecture on the LCCC retention behavior of AB, ABA, and BAB type block copolymers.[12] They predicted that, under the critical condition of B block, retention of AB and BAB follows the normal LCCC behavior, and one can measure the molecular weight of A block by LCCC while the elution behavior of ABA depends on the relative size of B block. If B block length were long, LCCC analysis would not provide the correct molecular weight of 2A.

In this study, we would like to report on how LCCC retentions of block copolymers depend on chain architecture: AB, ABA, and BAB types. In addition, we were also interested in how IC retention would change with the chain architecture of block copolymers. The interaction efficiency of polymer segments with the stationary phase would depend on the location in a polymer chain. It would be expected that the segments near the chain end have more freedom to interact with the stationary phase. For the purpose, we prepared a set of polystyrene (PS)/polybutadiene (PB) block copolymers of similar MWD and CCD but different chain architecture by sequential anionic polymerization: PS-*b*-PB (SB), PS-*b*-PB-*b*-PS (SBS), and PB-*b*-PS-*b*-PB (BSB). We further fractionated them by HPLC to acquire the fractions having a near identical PS block lengths. Using the three types of block copolymers, we examined the effect of the chain architecture on the HPLC retentions.

Experimental Section

Block Copolymers. Three block copolymers, SBS, SB, and BSB, were synthesized at room temperature by sequential anionic polymerization of styrene and butadiene in cyclohexane with 0.01 wt % THF. The relative amount of the two monomers was adjusted to make 30 wt % PS, and the target molecular weight was 100 kg/mol. Irganox (Ciba Geigy, 0.3%) and tris-(*p*-nonylphenyl) phosphite (0.5%) were added as antioxidants. The block copolymers were characterized by SEC at 40 °C. Two PS gel columns (Polymer Lab., PL mixed C × 2) were used, and the eluent was tetrahydrofuran (THF, Duksan, HPLC grade). Chromatograms were recorded with a multiangle laser light scattering detector (Wyatt, mini-DAWN), a refractive index detector (Wyatt, Opti-Lab), and a UV/vis absorption detector (SpectraSeries, UV 100) operating at a wavelength of 260 nm. The composition of the block copolymers was determined by ^{1}H NMR spectroscopy (Bruker, DPX-300), and the molecular weight was determined by extrapolation of the light scattering intensities measured at three different angles (45°, 90°, 135°) to zero angle.

TGIC Fractionation. For the fractionation of block copolymers using temperature gradient interaction chromatography (TGIC), a C18 bonded silica column (Zorbax, 100 Å pore, 250 × 9.4 mm) and a mixture of CH_2Cl_2/CH_3CN (74/26, v/v) were used as the stationary and mobile phase, respectively. The HPLC apparatus consists of a solvent delivery pump (SpectraSeries P100), a six-port sample injector (Rheodyne, 7125) equipped with a 200 μL injection loop, and a variable
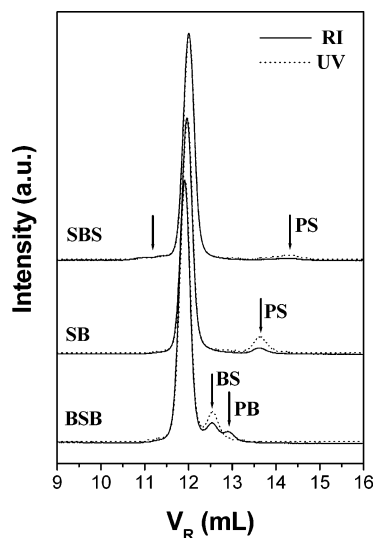

Figure 1. SEC chromatograms of block copolymers with different architectures. Column: two mixed bed columns (Polymer Lab, PL mixed C, 300 × 8 mm); eluent: THF, column temperature 40 °C.

wavelength UV/vis absorption detector (SpectraSeries, UV 100) operated at a wavelength of 260 nm. The injection sample concentration was about 40 mg/mL, and the flow rate of the mobile phase was 0.80 mL/min. The temperature of the column was controlled by circulating fluid from a programmable bath/circulator (Haake, C25P) through a column jacket.

LCCC Analysis. The HPLC instrument for the LCCC analysis is the same as that for the TGIC fractionation except for the use of an evaporative light scattering detector (Polymer Lab, EMD-950). Three reversed phase (RP) columns (Nucleosil C18; 100, 500, and 1000 Å; 250 × 4.6 mm each) were serially connected to enhance the SEC resolution for the PS block at the critical condition of the PB block. The critical condition for the PB block was established at 29.2 °C under the eluent of 1,4-dioxane (Junsei, HPLC grade). The critical condition changes with moisture uptake of the solvent, and a fresh bottle of 1,4-dioxane was used for a set of experiments prior to significant moisture uptake.

Results and Discussion

SEC Analysis of Block Copolymers. Figure 1 displays the SEC chromatograms of SB, SBS, and BSB recorded by RI (solid line) and UV (dotted line) detector, in which all three block copolymers show similar SEC retention volumes as expected. The hydrodynamic volumes should be alike for the three block copolymers with different architectures but with similar molecular weight and composition. All the block copolymers show byproduct peaks corresponding to the precursors in the sequential polymerization process. The RI detector is able to detect both PS and PB blocks while the UV detector operating at a wavelength of 260 nm detects the PS block only. The intensity of the two chromatograms recorded by two detectors was adjusted to match the height of the major peak. Therefore, a peak showing a larger UV signal intensity than the RI signal intensity represents a polymer species with higher PS content than the major product, vice versa.

The SBS triblock copolymer shows a PS homopolymer peak near $V_R \approx 14.3$ mL, whose MW of 17 kg/mol is in reasonable agreement with the target MW. It also shows a small amount of high molecular weight species that seems to be the coupling products of the styryl anions. The SB diblock copolymer also contains a peak of PS precursor at $V_R \approx 13.6$ mL, of which MW is about
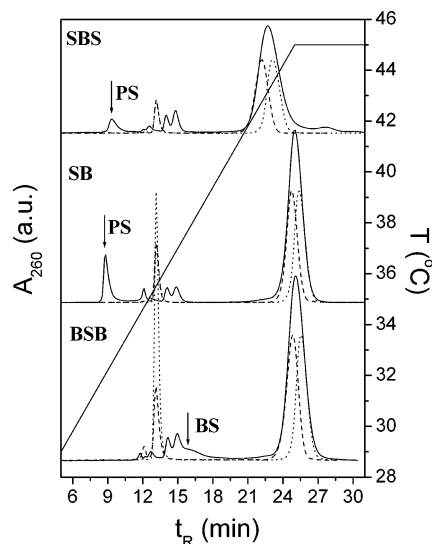
Figure 2. TGIC chromatograms of SBS, SB, and BSB (solid lines) and their fractions (dashed and dotted lines). Temperature program is shown in the plot. Column: C18 bonded silica (Zorbax, 100 Å pore, 250 × 9.4 mm); eluent: a mixture of CH_2Cl_2/CH_3CN (74/26, v/v), flow rate 0.80 mL/min.

Table 1. Characterization of Fractionated SBS, SB, and BSB Block Copolymers

fraction	M_w (total, kg/mol)	f_{PS} (wt %)	PS/PB (kg/mol)
SBS F1	104.4	34.25 ± 0.12	35.8/68.6
SBS F2	106.4	29.83 ± 0.01	31.8/74.6
SB F1	107.6	38.44 ± 0.06	41.4/66.2
SB F2	110.3	28.56 ± 0.05	31.5/78.8
BSB F1	117.0	30.28 ± 0.01	35.4/81.6
BSB F2	115.7	27.42 ± 0.02	31.7/84.0

byproduct elutes later than BSB. It is not detected with UV_{260} detection but confirmed by UV_{235} detection.

Two narrow TGIC fractions were collected from each mother block copolymer sample by cutting the major peak by half. The dashed and dotted lines in Figure 2 are the chromatograms of the TGIC fractions from each block copolymer. All six fractions obtained from the TGIC fractionation were characterized by ^{1}H NMR for composition and SEC-MALLS for total molecular weight. The characterization results are summarized in Table 1. Two fractions of each block copolymers, F1 and F2, were collected at low and high retention, respectively. The uncertainty in the composition was estimated from two ^{1}H NMR measurements, and the block molecular weights are calculated from the composition and the total molecular weight.

In the reversed phase TGIC separation condition, PB interacts more strongly than PS and a block copolymer with higher PS content elutes earlier than a block copolymer with lower PS content.[7] Therefore, F1 fractions always contain higher PS and lower PB content than F2. The variation of the composition between F1 and F2 varies most for SB (~10%) and least for BSB (~3%). In other words, the dispersion of the major elution peak of SB diblock copolymer is larger than triblock copolymers, which makes the fractionation according to the composition more effective for the diblock copolymer. On the other hand, the total molecular weights of F1 and F2 are not much different. In SBS and SB, the total molecular weight of F2 is slightly larger than that of F1 while BSB shows an opposite trend, which clearly indicates that the TGIC retention of the block copolymers is a result of complicated contribution of PS and PB blocks depending on chain architecture rather than PB block length only.

Although a more systematic study is called for to shed light on the detailed effect of chain architecture on the IC separation mechanism, we can get some idea from the available data. The F2 fractions of the three block copolymers have almost an identical PS block length, and we can compare their elution behavior rigorously according to PB block length. If there is no architecture effect, block copolymers with higher PB block length should show longer t_R. As shown in Figure 2, the retention times for BSB–F2 and SB–F2 are very similar. BSB–F2 is eluted slightly later than SB–F2 likely due to the higher molecular weight of PB blocks in BSB–F2 for ~5 kg/mol. On the other hand, SBS–F2 elutes much earlier than SB or BSB as shown in Figure 2. The significant retention difference cannot be explained by the small difference in PB block length, and it clearly indicates the presence of the architecture effect on the IC retention. As mentioned earlier, PB block shows a stronger interaction than PS block, and the retention of the polymers with high PB content is generally large. In addition, the presence of PS block decreases the retention, which can be understood considering the contribution of several effects from the

34 kg/mol, twice as large as the PS precursor of SBS. The BSB triblock copolymer shows two conspicuous peaks in addition to the major peak. The peak at $V_R \approx$ 12.9 mL does not show any UV detection intensity, indicating that it is the homo-PB precursor, while the peak eluted at $V_R \approx$ 12.5 mL corresponds to the BS diblock precursor. To examine the architecture dependence of the HPLC retention behavior of the block copolymers, it is desirable to remove the byproducts and to prepare a set of the block copolymers having identical MW as well as composition. Therefore, TGIC fractionation of the block copolymers was carried out.

TGIC Separation of Block Copolymers. Unlike SEC, IC utilizes mainly the enthalpic interaction of the solutes with the stationary phase, and the interaction strength between the solutes and the stationary phase is controlled by varying the column temperature in TGIC.[16] TGIC has shown much higher resolution than SEC in the separation according to the molecular weight.[17,18] Figure 2 displays TGIC chromatograms of the three block copolymers SBS, SB, and BSB recorded by a UV detector at 260 nm. The solid lines are the chromatograms of the block copolymers before fractionation. In this reversed phase TGIC separation condition, polydiene block interacts more strongly with the C18 stationary phase than PS block.[19,20] Therefore, PB homopolymer or block copolymers with a relatively high PB content elute in the interaction regime (after the injection solvent peak) while PS homopolymer elutes in SEC regime (before the injection solvent peak).

In the TGIC chromatograms of SBS and SB, the elution peaks of PS precursors show up in the SEC regime at $t_R \approx$ 9.4 and 8.8 min as indicated with arrows, respectively. The multiple peaks eluted at $t_R \approx$ 12−15 min are due to the added antioxidant. A broad peak appearing just after the major peak in SBS corresponds to the high molecular weight impurity observed in the SEC chromatogram in Figure 1. In the case of BSB, BS precursor appeared at $t_R \approx$ 16 min. Since BS diblock precursor has a lower B content than BSB triblock copolymer, it elutes earlier than the BSB major peak. Although the PB homopolymer has a lower molecular weight than the total B content of BSB, the homo-PB

increasing amount of PS content: (1) solubility increase of block copolymers to the mobile phase (the eluent is a good solvent for PS and a marginal solvent for PB), (2) screening PB block from the effective interaction with the stationary phase, and (3) increase of size exclusion effect due to the larger chain size. Considering the near identical molecular weight and composition of the three F2 fractions, the low retention of SBS relative to SB and BSB appears to be mainly due to the difference in the screening effect of PS block. With PB block located in the middle and the two PS blocks at both ends of the PB block, the interaction of PB block would be screened most effectively for the SBS type chain architecture.

LCCC Analysis of Block Copolymers. The applications of LCCC for the characterization of block copolymers made so far can be categorized into two separation modes. One is to elute the block copolymers in the IC elution regime (thus eluting after the injection solvent peak) in terms of the length of the block to be analyzed. This is realized if the *visible* block is more interactive with the stationary phase than the *invisible* block. Since the elution condition needs to be fixed at the critical condition for the block made *invisible*, the application is limited to rather short *visible* block lengths (or end-group analysis) due to the exponential dependence of the retention on the chain length (Martin's rule).[21-26] The other method is to elute the block copolymers in the size exclusion regime (eluting before the injection solvent peak) if the *visible* block is less interactive with the stationary phase. The majority of the LCCC applications to the characterization of block copolymers have been made in this mode, and the molecular weight distribution of the block of interest is determined by the standard calibration method commonly used in SEC.[14,27-30]

In the present study, we used the latter separation mode to investigate the effect of architecture on the chromatographic retention. The three F2 fractions were used for the LCCC analysis because their total PS block lengths are almost identical. The LCCC condition for homo-PB is established using a single solvent, 1,4-dioxane, as an eluent, and the block copolymers elute in the SEC regime. The use of a single solvent provides an excellent reproducibility in chromatographic retention, which is very sensitive to the solvent composition when a mixed eluent system is employed. The single solvent LCCC condition was reported previously by Lee et al. for polyisoprene (PI), and it was not much different for PB.[15] The critical condition of PB was established at 29.2 °C, whereas the critical condition of PI was at 47.7 °C.

Figure 3 displays the LCCC chromatograms of the three F2 fractions. At the critical condition for PB, the PB block is *invisible* and their retentions are supposed to be determined by the PS block length. In other words, if there is no architecture effect, three block copolymers are supposed to be eluted at the same t_R. However, the SBS−F2 is eluted much earlier than SB−F2 and BSB−F2, while SB−F2 and BSB−F2 show an identical retention volume. Therefore, there clearly exists an architecture effect. The SEC and LCCC characterization results of the three F2 fractions are summarized in Table 2. The LCCC molecular weights were determined by calibration with homo-PS standards. The LCCC molecular weight of SBS−F2 is about 30% as large as that of the SEC value while SB and BSB are about 8.5% smaller than that of SEC. Lee et al. observed the same
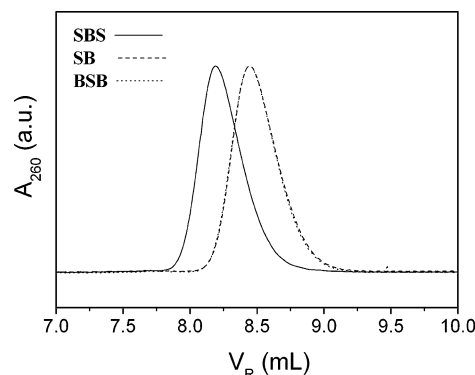

Figure 3. LCCC chromatograms of SBS (solid line) SB (dashed line) BSB (dotted line) at the critical condition of PB block. Column: C18 bonded column (Nucleosil C18, 100, 500, and 1000 Å pores, 250 × 4.6 mm); eluent: 1,4-dioxane.

Table 2. LCCC Characterization of Block Copolymer F2 Fractions and Comparison with SEC Results

	SEC		LCCC
	M_w (total, kg/mol)	PS/PB (kg/mol)	PS (kg/mol)
SBS F2	106.4	31.8/74.6	41.3 (+29.9%)
SB F2	110.3	31.5/78.8	28.8 (−8.6%)
BSB F2	115.7	31.7/84.0	29.0 (−8.5%)

phenomena for PS-*b*-PI diblock copolymers that the molecular weight of the *visible* block was somewhat underestimated by LCCC compared to the true values.[14] SB and BSB follow the same trend as observed in PS-*b*-PI, while SBS shows a significant deviation from the other architectures in the LCCC analysis at the critical condition of PB block.

There are not many LCCC analysis results for triblock copolymers. Braun et al. reported on PS/PB block copolymers that for triblock copolymers with sharp composition transitions between the blocks, the block lengths of the outer and the center blocks can be determined with high accuracy by LCCC.[31] Falkenhagen et al. characterized di- and triblock copolymers of poly-(methyl methacrylate) and poly(*tert*-butyl methacrylate) by LCCC.[30,32] They reported that LCCC could yield correct molecular weight of the *visible* block regardless of the chain architecture. The existing results are in conflict with the prediction of Guttman et al. on the LCCC retention behavior of AB, ABA, and BAB type block copolymers.[12] They predicted that the retention of AB and BAB would follow the normal LCCC behavior under the LCCC condition of B block, while the elution behavior of ABA would be influenced by the relative size of the B block. If the B block length is long, the LCCC retention of ABA would differ from AB or BAB and does not provide the correct molecular weight of 2A. The LCCC retention behavior observed in this work is in good agreement with their prediction.

It remains to be investigated more critically whether this discrepancy depends on block copolymer systems. Lee et al. reported for SI diblock copolymer that LCCC analysis yields apparent molecular weights somewhat smaller than the true value, and the deviation becomes larger as the invisible block length increases.[14,15] Again in this work, we found that SBS behaves quite differently from SB or BSB. Therefore, we again conclude that LCCC analysis is certainly not able to provide accurate molecular weights of individual blocks but a reasonable estimate for the block copolymers of styrene and dienes.

In summary, a rigorous HPLC analysis was made with SBS, SB, and BSB block copolymers. The block

copolymer fractions of high purity and matched block lengths were obtained by TGIC fractionation. The TGIC retention of SBS was conspicuously smaller than SB or BSB, indicating that the interaction of middle PB block of SBS with the stationary phase is not as effective as the end block(s). At the critical condition for PB, LCCC elution behavior of the block copolymers also showed significant architecture dependence. Again, SBS showed a lower retention than BSB or SB while the retention of SB and BSB was indistinguishable. This architectural dependence of LCCC retention is in good agreement with the theoretical prediction.

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