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# Characterization of Polystyrene-*b*-polyisoprene Diblock Copolymers by Liquid Chromatography at the Chromatographic Critical Condition

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**ABSTRACT:** In the chromatographic separation of macromolecules with a porous stationary phase, the retention is determined by both size exclusion and interaction mechanisms. At the chromatographic critical condition, the effects due to the two separation mechanisms compensate each other, and the retention of homopolymer molecules becomes independent of molecular weight. Liquid chromatography at the critical condition has attracted much interest for the characterization of block copolymers since it might permit the characterization of individual blocks of a block copolymer by making one block chromatographically “invisible”. In this study, we critically examine this method using two sets of styrene–isoprene block copolymers designed to have one block length constant while varying the other block length. For these block copolymer systems we found that a block cannot be made completely “invisible” at the critical condition of its homopolymer, and the retention of block copolymers is affected to some extent by the length of the “invisible” block under its chromatographic critical condition.

## Introduction

In the chromatographic separation of polymers using porous column packing materials, the retention is governed by the size exclusion mechanism, the interaction mechanism, or both.<sup>1</sup> The chromatographic critical condition for a homopolymer is defined as the condition where the entropic size exclusion effect is precisely compensated by the enthalpic interaction effect.<sup>1</sup> At this condition the retention of the homopolymer would become independent of molecular weight. The study on this interesting feature was started in the 1970s,<sup>2,3</sup> which has been supported by a number of experimental studies<sup>1,4–11</sup> although there remains some controversy as to whether such a precise coelution condition indeed exists.<sup>12,13</sup> Furthermore, other anomalies such as limited recovery for high molecular weight polymers as well as peak broadening and/or splitting have been reported at the critical condition.<sup>8,14</sup> Nevertheless, the critical condition has been successfully employed for the chromatographic separation of the components in polymer blends<sup>15,16</sup> and for the separation of polymers with respect to the terminal functional group.<sup>6,11,17–19</sup> This technique is variously termed: liquid chromatography at the critical condition (LCCC), liquid chromatography at the point of exclusion–adsorption transition (LC-PEAT), or liquid chromatography at the critical adsorption point (LC-CAP). Another interesting application of the technique is the characterization of block copolymers.<sup>7,20–25</sup> The application is based on the assumption that a block at the critical condition is chromatographically “invisible”, and the retention of the block copolymer is supposed to be governed solely by the other blocks in the block copolymer. This assumption is only valid if the retention of a

homopolymer is indeed independent of molecular weight and if the retention of the “visible” block is not affected by the presence of the “invisible” block. If these conditions are satisfied, LCCC would undoubtedly become a powerful tool for the characterization of selected blocks within block copolymers.

The applications of LCCC for the characterization of block copolymers made so far can be divided broadly into two categories. One is to elute the block copolymers in the interaction regime (thus eluting after the system peak) in terms of the length of the block(s) to be analyzed. This is realized if the 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 applications are limited to end group analysis or to rather short block lengths, due to the exponential dependence of the retention on the chain length.<sup>6,17,19,26–29</sup> The other separation mode is to elute the block copolymers in the size exclusion regime (eluting before the system peak) in terms of the block length of the block(s) to be analyzed if the “visible” block is less interactive with the stationary phase. Most of the LCCC applications to the characterization of block copolymers have been made in the latter mode, and the determination of the molecular weight distribution of the block of interest has been made using the standard calibration method commonly used in size exclusion chromatography.<sup>7,22–25</sup> For example, Zimina et al. used the standard calibration method to examine the PS fraction of polystyrene/poly(methyl methacrylate) diblock copolymers (PS-*b*-PMMA) under the critical condition of PMMA.<sup>7</sup> In the same paper, they also reported LCCC analysis of diblock copolymers of PS and poly(*tert*-butyl methacrylate) (PtBMA) using various eluent mixtures. Pasch et al. characterized both blocks of PS-*b*-PMMA by LCCC at the respective critical conditions for each

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block.<sup>23,24</sup> Falkenhagen et al. also reported recently that both block lengths in PMMA-*b*-PtBMA were successfully analyzed by the same methodology using a reversed and a normal phase LCCC method.<sup>25</sup> The precision of the method has been reported to be high, but a more critical evaluation of the method may be necessary since there are several reports that even question the precise coelution of homopolymers over a wide molecular weight range at the apparent critical condition.<sup>12–14</sup> Furthermore, it would be important to examine whether there exist differences among particular systems. Mixed solvent systems are commonly used in LCCC in order to achieve the critical condition, and the fact that one component of the mixed solvent system may preferentially adsorb on the polymer chains as well as on the stationary phase complicates the situation.<sup>14, 30–32</sup>

In this study, we employed two sets of polystyrene/polyisoprene diblock copolymers (PS-*b*-PI) keeping one block length constant: an SI series with constant PS block length and an IS series keeping the PI block constant. Using these sets of PS-*b*-PI block copolymers, we examined the individual blocks in the size exclusion regime under the critical condition for the PS block and the PI block.

## Experimental Section

**Anionic Polymerization of Block Copolymers.** Synthesis of the SI series block copolymers began with the polymerization of the polystyrene block. After completion of the polystyrene block polymerization of a fixed molecular weight, polyisoprene blocks of varying lengths were polymerized by adding precalculated amounts of isoprene in sequence. The IS series was synthesized in the reverse order so that it has a constant polyisoprene block and different lengths of polystyrene blocks. Anionic polymerization of the block copolymers was carried out in cyclohexane (Aldrich) at 40 °C under purified Ar atmosphere. Details of the apparatus and the polymerization procedure were described previously.<sup>33</sup>

Styrene and isoprene monomers (Aldrich) were first treated with CaH<sub>2</sub> for a few days to remove dissolved water. Styrene monomer was further purified by stirring with dibutylmagnesium (Aldrich) for 2 h at room temperature. Isoprene monomer was purified by stirring with *n*-butyllithium (Aldrich) for 2 h at 0 °C. An appropriate amount of the initiator, 2-butyllithium in hexane (Aldrich), was added to the solvent in the reaction vessel kept at 45 °C, and the polymerization was initiated by adding purified monomers in sequence. After the polymerization of the first block, a small aliquot of the reaction mixture was transferred to an Ar-filled Erlenmeyer flask through a double-tipped needle. Then an appropriate amount of the second monomer was added and polymerized. After the completion of the polymerization of the second block, an aliquot was taken out, and an additional amount of the second monomer was added to extend the length of the second block. This procedure was repeated to obtain a set of block copolymers having a fixed length first block and second blocks of varying lengths. When the first block was polyisoprene, a small amount of purified THF was added after the polymerization of the PI block in order to expedite the conversion of isoprenyl anion to styryl anion. Two and four hours were allowed for the polymerization of each PS and PI section, respectively. Block copolymers were precipitated from each aliquot in a 1/3 mixture of 2-propanol/methanol with a small amount of antioxidant and dried thoroughly under vacuum.

The molecular weights of the PS and PI precursors were characterized by size exclusion chromatography (SEC). Two PS gel columns (Polymer Lab., PL-mixed C, 80 mm × 300 mm) were used, and tetrahydrofuran (THF, Aldrich, HPLC grade) was the mobile phase. The temperature of the column was kept at 40 °C by use of a column oven (Eppendorf, TC-50). The composition of the block copolymers was determined by <sup>1</sup>H NMR (Bruker, DPX-300). Having the molecular weight (from

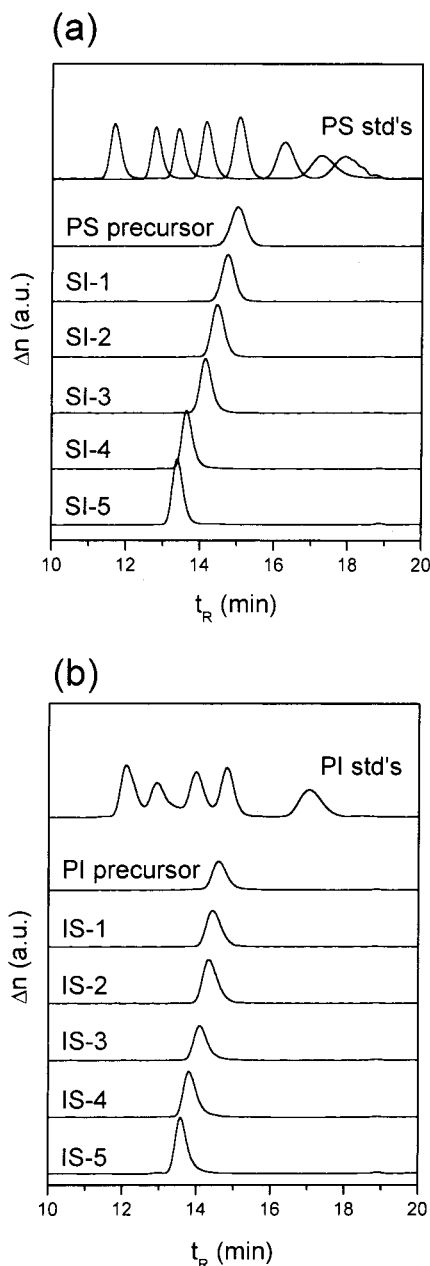
SEC analysis) and the weight fraction (from NMR analysis) of the precursor for each block copolymer, the total molecular weight of each block copolymer was calculated. The weight-average molecular weights of the precursors were obtained by two methods: light scattering detection (LDC, KMX6) and standard calibration. Polydispersities ( $M_w/M_n$ ) of the samples were calculated by the standard calibration method in SEC. To construct the calibration curves, PS standards were used for the SI series and PI standards for the IS series.

**LCCC Analysis of Block Copolymers.** The HPLC apparatus consists of a solvent delivery pump (LDC, CM 3200), a six-port sample injector (Rheodyne, 7125), a variable wavelength UV/vis absorption detector (TSP, Spectra 100), and an evaporative light scattering detector (Polymer Lab. EMD-950). For the characterization of the PS block at the critical condition of the PI block, three reversed phase (RP) columns (Nucleosil C18; 100, 500 and 1000 Å; 250 × 4.6 mm) were serially connected, and a mixture of CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN (78/22, v/v) was used as the eluent. For the characterization of the PI block at the critical condition of the PS block, three normal phase (NP) columns (Nucleosil; 100, 500 and 1000 Å; 250 × 4.6 mm) were serially connected, and a mixture of THF/isooctane (50/50, v/v) was used as the eluent. At these conditions, homopolymers of the "visible" block component are eluted in the size exclusion regime. Three column sets were used to enhance the resolution of the SEC separation of the block copolymers. The temperature of the separation column was controlled by circulating fluid from a programmable bath/circulator (Neslab, RTE-111) through a homemade column jacket. For the calculation of the molecular weight of the block, calibration curves were constructed from five PS standards (in RP mode, for the analysis of the PS block) and six PI standards (in NP mode, for the PI block analysis) by fitting the elution times of the corresponding standards set to a third-order polynomial.

## Results and Discussion

Figure 1 displays SEC chromatograms of the SI (a) and IS (b) series. Chromatograms of standard PS and PI mixtures used for the molecular weight calibration are also shown in the plots. All the block copolymer samples show single peaks without any traces of precursors, and the peak widths are as narrow as the PS and PI standards. The weight-average molecular weights ( $M_w$ ) of the precursors were determined to be 12.0 kg/mol (PS) and 12.5 kg/mol (PI) from SEC analysis. These values were calculated by the calibration method using the standard samples of PS and PI shown in Figure 1 respectively for the PS and PI precursors. These values are a little different from those determined by light scattering detection: 12.4 kg/mol (PS) and 11.9 kg/mol (PI). This much error is reasonable, in particular given the rather low molecular weights. We use the molecular weights determined by the standard calibration method hereafter since the block molecular weights can only be determined by the calibration method in the LCCC analysis. The characterization results for the precursors and the block copolymers are listed in Table 1.

Figure 2 shows the chromatograms of PI (a) and PS (b) standards at various temperatures to establish the critical conditions. Although most LCCC studies have varied the solvent composition to determine the critical condition at a fixed temperature,<sup>22,24,25</sup> we used temperature as a variable to control the retention of polymer solutes at a fixed eluent composition. Temperature variation permits an easier and more reproducible control of the interaction strength between the polymer solutes and the stationary phase.<sup>12,34,35</sup> Five different molecular weight PI and PS standards are used, and their molecular weights span a few thousands to a few hundreds of thousands. As shown in Figure 2, the

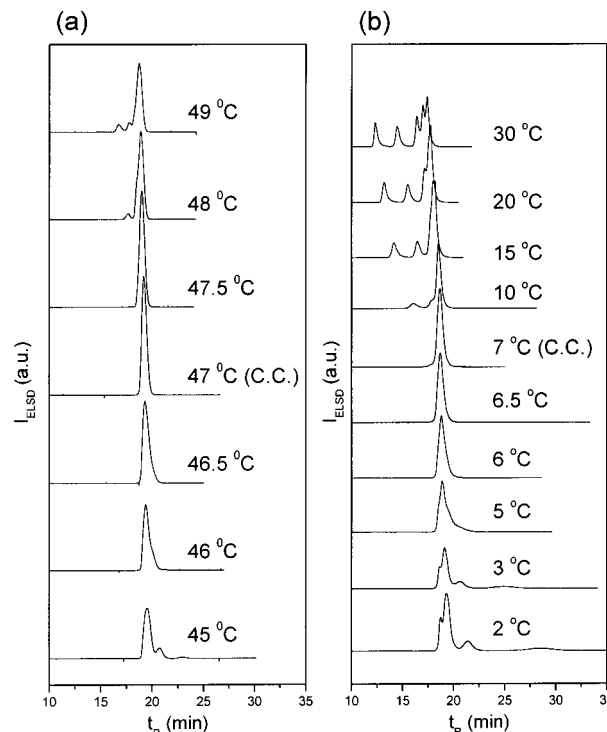


**Figure 1.** SEC chromatograms of block copolymers and their precursors for SI series (a) and IS series (b). Column: two mixed bed columns (Polymer Lab, PL-mixed C, 300 × 8 mm); eluent: THF; temperature: 40 °C. The chromatograms of PS (from left,  $M_w$ : 385, 112, 63.5, 28.9, 11.6, 3.5, 1.3, 0.6 kg/mol) and PI (from left,  $M_w$ : 199, 80.3, 24.5, 10.4, 0.9 kg/mol) standards are also shown at the top of the figures.

**Table 1. Characterization of SI and IS Block Copolymers**

	PS wt % (NMR)	$M_{PS}-M_{PI}$ (kg/mol) ( $M_w/M_n$ )
PS precursor	100	12.0–0 (1.05)
SI-1	80	12.0–3.0 (1.04)
SI-2	67	12.0–6.0 (1.04)
SI-3	52	12.0–11.1 (1.04)
SI-4	36	12.0–21.4 (1.05)
SI-5	26	12.0–34.2 (1.07)
PI precursor	0	0–12.5 (1.09)
IS-1	21	3.3–12.5 (1.06)
IS-2	32	5.9–12.5 (1.06)
IS-3	52	13.5–12.5 (1.08)
IS-4	68	26.6–12.5 (1.07)
IS-5	75	38.1–12.5 (1.08)

critical condition of PI occurs at 47 °C in RP-LC while that of PS occurs at 7 °C in NP-LC. It is clear that the

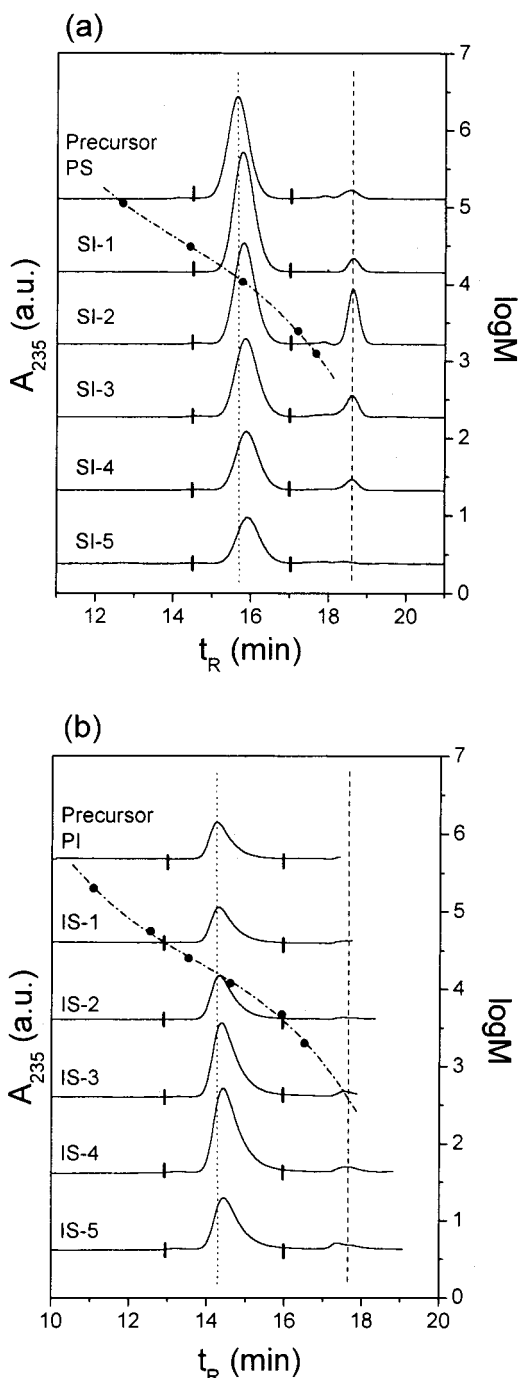


**Figure 2.** (a) Critical condition of PI in RP mode. Column: three reversed phase columns (Nucleosil C18; 100, 500, and 1000 Å; 250 × 4.6 mm); eluent:  $CH_2Cl_2/CH_3CN$  (78/22, v/v); sample: a mixture of five PI standards (2.2, 9.9, 19.8, 53, 148 kg/mol). (b) Critical condition of PS in NP mode. Column: three silica columns (Nucleosil; 100, 500, and 1000 Å; 250 × 4.6 mm); eluent: THF/isooctane (50/50); sample: a mixture of five PSs (2.5, 11.6, 28.9, 112, 385 kg/mol).

critical condition is well established with the retention of the polymers independent of the molecular weight.

The retention of diblock copolymers was examined under the critical condition of a block. First, the blocks of varying chain lengths were subjected to the critical condition. In these experiments all the block copolymers should elute at the same retention time if the blocks under critical condition are “invisible” since the “visible” blocks have the constant chain length of the precursor polymer. Figure 3 shows the chromatograms of this test for the SI series under the critical condition of PI (a) and the IS series at the critical condition of PS (b). The chromatograms were recorded by a UV/vis detector at a wavelength of 235 nm where both PS and PI blocks absorb. Although all the block copolymers elute at the similar retention time, it is clear that as the length of the “invisible” block increases, the retention time becomes progressively larger. Though not shown, the column void volume and the volume of total retention were around 5.0 and 9.3 mL (which correspond to 10.0 and 18.6 min by elution time scale) for the case of LCCC of PI (Figure 3a) and 4.5 and 8.8 mL (9.0 and 17.6 min by elution time scale) for LCCC of PS (Figure 3b), respectively. The molecular weights determined according to the calibration curve shown in the plots are summarized in Table 2. The apparent molecular weight of the “visible” block becomes smaller as the block length of the “invisible” block increases. The systematic discrepancy between the expected block molecular weights in the LCCC analysis reveals that there exists a significant effect of the “invisible” block on the retention of the block copolymers. Although not shown, we tested the elution behavior of the block copolymers at slightly





**Figure 3.** LCCC chromatograms of PS-*b*-PI samples under the critical condition of the block of varying molecular weight: (a) SI series at the critical condition of PI. Column: three reversed phase columns (Nucleosil C18; 100, 500, and 1000 Å; 250 × 4.6 mm); eluent: CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN (78/22, v/v); temperature: 47 °C. (b) IS series at the critical condition of PS. Column: three silica columns (Nucleosil; 100, 500, and 1000 Å; 250 × 4.6 mm); eluent: THF/isooctane (50/50); temperature: 7 °C. The vertical dashed line indicates the elution time of critical component for each case. Calibration curves for the calculation of block molecular weight are shown in the plots, and the integration range for the molecular weight calculation is indicated in each chromatogram. Vertical dotted lines are drawn for visual aid to compare the retention time.

off-critical conditions toward either the SEC or IC regime by either increasing or decreasing the temperature slightly and observed the same trends of decreasing elution order as the “invisible” block size increases. Therefore, we conclude that the block under the critical

**Table 2.** LCCC Characterization Results of the Block of Constant Size in SI and IS Series

	$M_w$ (kg/mol)	
	expected $M_w$	measured $M_w$ by LCCC (error <sup>a</sup> )
PS precursor	12.0	12.0 (0%)
SI-1	12.0	10.6 (12%)
SI-2	12.0	10.3 (14%)
SI-3	12.0	9.9 (18%)
SI-4	12.0	9.7 (19%)
SI-5	12.0	9.3 (23%)
PI precursor	12.5	12.5 (0%)
IS-1	12.5	12.0 (4%)
IS-2	12.5	11.7 (6%)
IS-3	12.5	11.0 (12%)
IS-4	12.5	10.7 (14%)
IS-5	12.5	10.5 (16%)

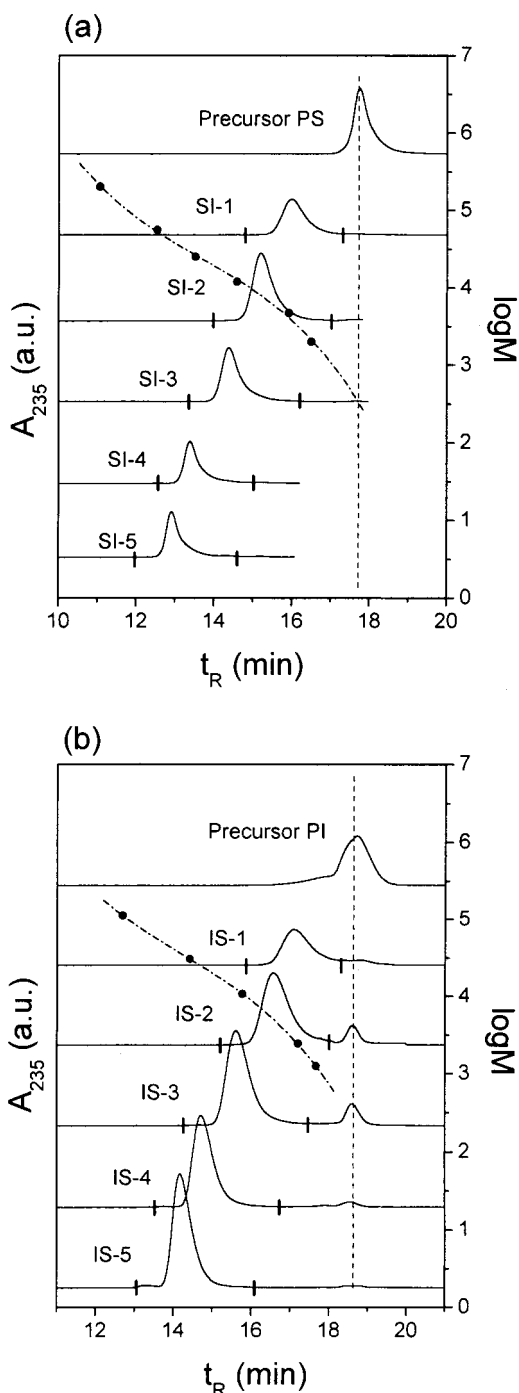
<sup>a</sup> Error:  $100 \times (M_{w, \text{expected}} - M_{w, \text{LCCC}}) / M_{w, \text{expected}}$ .

condition of the corresponding homopolymer is not completely invisible.

We have also examined the IS and SI series block copolymers by LCCC in the opposite way to measure retention of the block of variable lengths while keeping the constant length blocks under the critical condition. Figure 4 shows the chromatograms for the PS blocks in the IS series (a) and the PI blocks in the SI series (b). Molecular weights determined from the standard calibration method are summarized in Table 3, and they confirm the tendency observed in Figure 3 and Table 2. The deviation from the expected value reached more than 20% when the relative size of the “invisible” block is large, as in SI-1 or IS-1.

Our observations conflict with a number of theoretical<sup>36–38</sup> as well as experimental<sup>7,22–25</sup> reports for the LCCC analysis of block copolymers which support the feasibility of the individual block characterization. The origin of the discrepancy remains to be resolved, but it may be due in part to the inevitable uncertainty in the characterization of the block copolymer itself. A 10% error in the accuracy of an individual block molecular weight would not be uncommon in the characterization of block copolymers, and our results show about 10% or less deviation for the molecular weight of the “visible” block except for highly asymmetric block copolymers with large “invisible” blocks. This magnitude of the deviation would have not been regarded significant unless such tailor-made sets of block copolymers are used for the critical comparison. Most of the individual block characterizations by the LCCC technique have not been done in this way, except for the recent work by Falkenhagen et al. in which they reported a successful characterization of individual blocks of PMMA-*b*-PtBMA series.<sup>25</sup>

At the moment we do not have an obvious explanation for the contrast between our results and those of Falkenhagen et al. It might be difficult to compare directly the two different polymer systems, PS-*b*-PI vs PMMA-*b*-PtBMA. However, it is worth noting that they mentioned in their paper that the deviation might occur if the block length of the “invisible block” is much greater (>5 times) than the “visible” block. The mentioned possibility of the deviation is consistent with the observation made in this study, but we observed a deviation at a much lower block length ratio. In addition, the trend of the deviation (longer retention of the block copolymer with a shorter “visible” block length) is in the right direction since it would eventually reach the asymptotic limit of homopolymer of the “invisible



**Figure 4.** LCCC chromatograms of PS-*b*-PIs under the critical condition of the precursor block of the constant molecular weight. (a) SI series at the critical condition of PS. Experimental condition is the same as that of Figure 3b. (b) IS series at the critical condition of PI. Experimental condition is the same as that of Figure 3a. The vertical dashed line indicates the elution time of critical component for each case. Calibration curves for the calculation of block molecular weight are shown in the plots, and the integration range for the molecular weight calculation is indicated in each chromatogram.

block” as the block length of the “visible” block becomes shorter and shorter relative to the “invisible” block. We speculate that the accuracy of the LCCC analysis of block copolymers may depend on the system: polymer, stationary phase, and mobile phase. As mentioned earlier, the use of mixed solvents in LCCC experiments makes the problem more complicated. The mobile phase in LCCC experiments usually consists of a binary

**Table 3.** LCCC Characterization of the Block of Varying Size in SI and IS Series

	$M_w$ (kg/mol)	
	expected $M_w$	measured $M_w$ by LCCC (error <sup>a</sup> )
SI-1	3.0	2.0 (33%)
SI-2	6.0	5.2 (13%)
SI-3	11.1	10.3 (7%)
SI-4	21.4	20.2 (6%)
SI-5	34.2	33.6 (2%)
IS-1	3.3	2.5 (24%)
IS-2	5.9	4.8 (19%)
IS-3	13.5	12.1 (10%)
IS-4	26.6	24.2 (9%)
IS-5	38.1	35.5 (7%)

<sup>a</sup> Error:  $100 \times (M_{w, \text{expected}} - M_{w, \text{LCCC}}) / M_{w, \text{expected}}$ .

mixture of a good solvent and a nonsolvent for the polymer of interest. It is also usually a combination of a polar and a nonpolar solvent. In a mixed solvent, preferential sorption of a component to the polymer chain or on the surface of the stationary phase can occur.<sup>30,31</sup> If one solvent component is preferentially adsorbed either on the surface of stationary phase or to the polymer chain, the retention of the polymer sample will be affected by the adsorbed solvent molecules to result in a complicated LCCC behavior.<sup>9,14</sup> If the preferential sorption depends on the composition of block copolymers, it should affect the critical condition for the “invisible” block. Although we have not varied the mobile phase extensively since it is not easy to find a variety of critical conditions for a given polymer, we examined another critical condition for PS using the same silica columns but with a THF/*n*-hexane mobile phase. We found that the results were not significantly different from this work with the THF/isooctane mixed mobile phase. We are currently extending this approach to other block copolymer systems as well as a wider variety of mobile phases including single solvent systems where the preferential sorption effect can be eliminated. In any event, this study indicates us that it is premature to assume the feasibility of the precise characterization of individual blocks of block copolymers by LCCC analysis. In addition, we emphasize that there exist several papers reporting some practical limitations to the LCCC experiment.<sup>12–14</sup> More careful experimental tests as well as theoretical efforts are called for in order to establish the LCCC method as a general tool for the characterization of block copolymers.

In summary, a rigorous LCCC analysis was made with two sets of PS-*b*-PI block copolymers tailor-made by anionic polymerization. Those sets of block copolymers were prepared from a single batch in order to keep the molecular weight of one block length precisely constant while varying the other block length. Although this study showed that a reasonable estimation of the block molecular weight is possible by the LCCC method, we found that the method does not provide accurate block molecular weights but systematically smaller values. As the chain length of the block under critical condition increases, the deviation becomes larger. We cannot conclude at the moment whether this trend is universal or peculiar to the PS-*b*-PI systems. A more systematic study with variety of block copolymers and chromatographic conditions is required.

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