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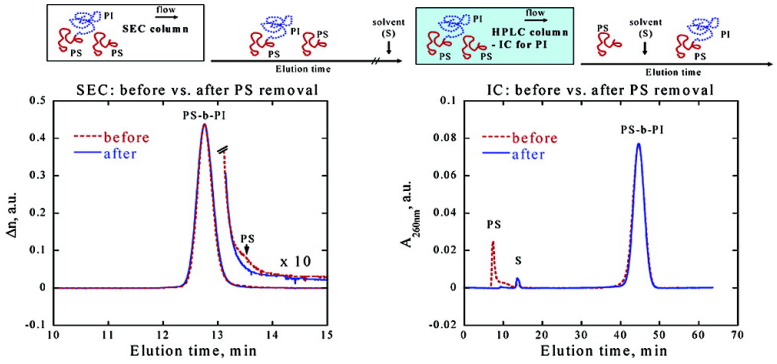

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Interaction-Controlled HPLC for Block Copolymer Analysis and Separation

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In complex polymer systems such as polymer blends, functionalized polymers, and block copolymers, the development of analysis and purification techniques to separate polymers in terms of chemical heterogeneity is imperative.[1] Interaction chromatography (IC), wherein chromatographic separation depends on the enthalpic adsorption of polymers instead of entropic exclusion, is an effective tool for this purpose and offers chromatographic separation with respect to the chemical entity difference. Because the prevalent size exclusion chromatography (SEC) technique[2] hinges on hydrodynamic volume differences for its chromatographic separation, it is inherently insensitive to polymer separations based on differences in chemical composition and functionality. In this study, we report that the IC technique is complementary and even superior to SEC for rigorous *analysis* of chemically heterogeneous copolymers such as block copolymers.

Another advantage of the IC technique is that it enables *semiprep-scale separation* of block copolymers. Because it is very challenging to synthesize block copolymers free of homopolymer precursor, and because compositional broadening can also occur during a sequential living polymerization, a chromatographic posttreatment technique is desirable for obtaining well-defined block copolymer samples that are homopolymer-free and compositionally narrower than the as-synthesized ones. For semiprep-scale separation, we have developed a chromatographic "filtering" technique, instead of solely relying on the retention time difference for the HPLC separation. By adapting the affinity chromatography technique,[3] we developed a total adsorption−desorption interaction chromatography (TADIC) strategy, in which the HPLC columns are essentially utilized as chromatographic filters. We employed a multiple-injection scheme during TADIC to monitor polymer accumulation in the HPLC column. TADIC is very similar to affinity chromatography; the only difference could be the adsorption specificity.[4] Because affinity chromatography utilizes specific binding between bioanalytes and immobilized ligands, specialized columns have to be used for specific separations. On the contrary, our TADIC technique for block copolymer separation simply utilizes "conventional" HPLC columns such as bare silica or C18-modified silica columns. Because TADIC employs readily available HPLC columns, it could rapidly and broadly affect the separation efforts of chemically heterogeneous copolymers.

We chose the AB diblock copolymer system to demonstrate the unique capability of IC analysis (Figure 1) and TADIC separation (Figure 2). Though many synthetic efforts have been developed to minimize homopolymer A "contamination" and polydispersity in block copolymers, precursor contamination, in particular, is almost inevitable during the synthesis of block copolymers with complex chain architectures.[5] Figure 1 highlights the superior analytical sensitivity of the IC mode over SEC in the analysis of chemically heterogeneous copolymers such as block copolymers. It contrasts

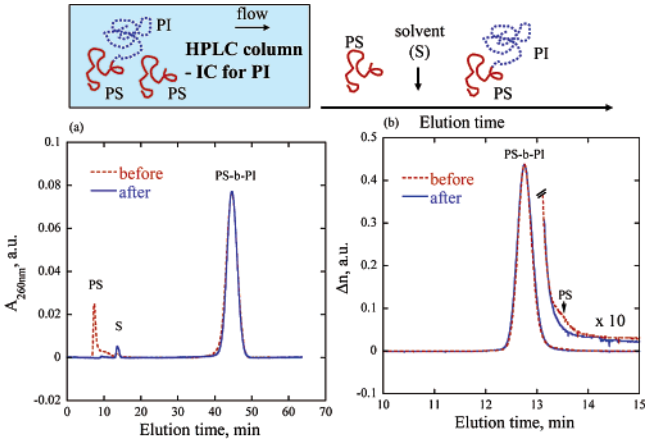

Figure 1. (a) TGIC and (b) SEC profiles of PS-*b*-PI diblock copolymers before and after the homopolymer PS removal. A fraction of the SEC signals was increased 10-fold ("x 10") in (b) to highlight the SEC profile change before and after the PS removal.

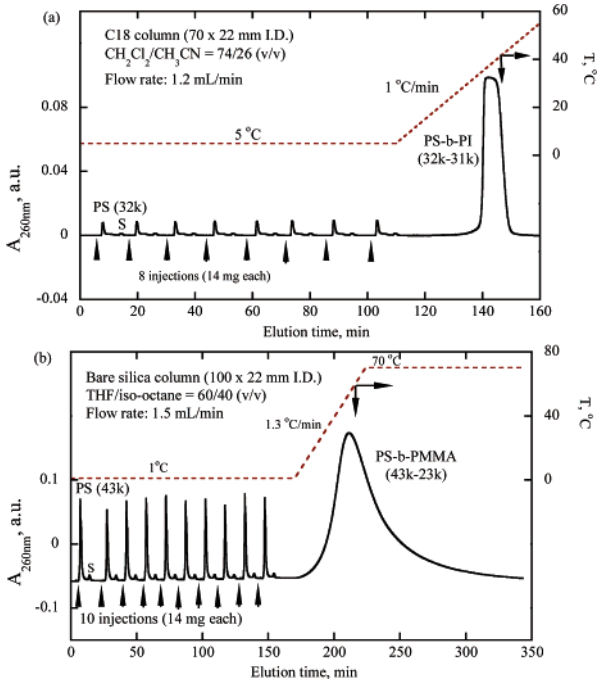

Figure 2. TADIC profiles with multiple injections showing the separation of PS precursors from as-synthesized (a) PS-*b*-PI (32k−31k) and (b) PS-*b*-PMMA (43k−23k) diblock copolymers.

the IC and SEC profiles before and after the PS homopolymer removal for an as-synthesized PS-*b*-PI (32k−31k) diblock copolymer, which contains 6 wt % PS (32k). The homopolymer PS was removed by the TADIC technique (Figure 2a). A C18 HPLC column with CH_2Cl_2/CH_3CN = 74/26 (v/v) was employed[6] for

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temperature gradient IC (TGIC) experiments, where the column was maintained at 5 °C for 20 min and then heated to 60 °C at 1 °C/min. Distinctive chromatographic separation of the homo-PS and the PS-*b*-PI was possible, because the PI-adsorbing IC conditions caused the elution of PS before the solvent peak, whereas PS-*b*-PI elution occurred after the solvent peak (Figure 1a). On the contrary, SEC analysis in THF before and after PS removal gave the same polydispersity index (PDI) of 1.02 and the homopolymer removal effect only appeared as a slight decrease in the lower molecular weight shoulders of the SEC profile (Figure 1b). Thus, SEC is a poor choice for block copolymer analysis, since it separates polymer chains only according to their hydrodynamic size.

TADIC was employed for separating the PS homopolymer precursors from as-synthesized (a) PS-*b*-PI and (b) PS-*b*-PMMA diblock copolymers, and their profiles with multiple injections are shown in Figure 2. With a semiprep column (ID = 22 mm), viscous solutions (140 mg/mL) could be injected (injection volume = 100 μL) without developing a significant pressure increase in the column, and we were able to achieve ~100 mg-scale separation within a few hours. Selective accumulation of the diblock copolymers was achieved by keeping the column temperature low to induce the total adsorption of the "second" block (PI or PMMA) during multiple injections. As the PS homopolymers have little enthalpic affinity with the column surface for the given HPLC conditions, they will be eluted from the column and appear as multiple peaks during succesive injections. In fact, the PS elution follows the chromatographic elution by SEC mechanism, because the PS homopolymers are eluted from the column before the solvent in the injected solution ("S" in Figures 1 and 2). The multiple-injection scheme was particularly useful in monitoring the block copolymer accumulation in situ. If more samples were injected than the column could accommodate, we observed an upward drift in the baseline of the HPLC profile. Therefore, we limited the numbers of our injections, so that the baseline remained flat, and collected the separated PS homopolymers. When the column temperature was increased, the adsorbed blocks started to lose their strong binding in the column and a large peak was observed, indicating the elution of homopolymer-free diblock copolymers. These results demonstrate that TADIC with a multiple-injection scheme can easily be scaled up with a semiprep column for efficient and high-purity recovery of diblock copolymers. This technique could be also applied in general to remove remnants of polymer precursors in any chemically heterogeneous copolymer.

An unique capability of the IC technique is that we can obtain block copolymer samples that have much narrower compositional distributions than as-synthesized ones. Figure 3a shows an isothermal HPLC profile of an as-synthesized PS-*b*-PMMA (43k−23k) diblock copolymer that contains 10 wt % PS (43k) precursors. Figure 3b shows HPLC profiles of five fractions of PS-*b*-PMMA diblock copolymers (F1, F2, ..., and F5), collected in the PMMA IC region shown in Figure 3a. From NMR analysis,[7] we find that the average PMMA composition of the fractions ranges from 29 to 38 wt %, whereas the homopolymer-free mother PS-*b*-PMMA diblock copolymer has 34 wt % PMMA. When the fractionated PS-*b*-PMMA diblock copolymers were reinjected, we observed narrower peaks in the PMMA IC region than the mother diblock sample. Because of the small degree of band broadening in the IC analysis,[8] the narrower peak means a narrower PMMA compositional distribution in the fractions. The increase in the average

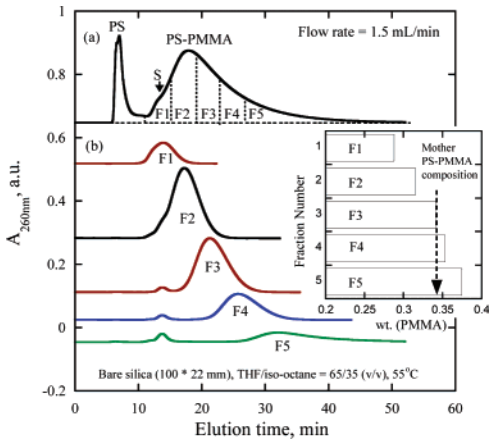

Figure 3. Isothermal HPLC profiles of (a) as-synthesized diblock copolymers and (b) five fractions of PS-*b*-PMMA diblock copolymers, which were taken from the isothermal elution shown in a. Figure inset displays the PMMA composition of each fraction from NMR.

retention time in the fractions also correlates with an increase in the PMMA content of the PS-*b*-PMMA fractions.

In conclusion, we find that the IC technique can be (i) superior to the prevalent SEC method for analyzing chemically heterogeneous copolymers such as block copolymers and (ii) useful for obtaining block copolymers that are homopolymer-free and compositionally narrower than the as-synthesized ones. We showed that homopolymer precursors in block copolymer systems are not easily identified by SEC, and IC should be employed for rigorous analysis of block copolymers. The HPLC fractionation technique also demonstrated that several diblock copolymers of narrow compositions could be obtained without extra synthetic efforts.

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Supporting Information Available: Experimental descriptions on synthesis and HPLC of the block copolymers and NMR data of fractionated PS-*b*-PMMA diblock copolymers (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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