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TGIC Separation of PS-*b*-P2VP Diblock and P2VP-*b*-PS-*b*-P2VP Triblock Copolymers According to Chemical Composition

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Introduction

Block copolymer systems have received continuing attention in both fundamental and technological points of view. The physical properties of block copolymers are affected by several molecular characteristics such as molecular weight, chemical composition, and chain architecture.[1−3] Precise characterization on these molecular parameters of block copolymers is thus highly required; however, rigorous characterization of copolymers is in general much more complicated than the analysis of homopolymers due to composition distribution in addition to molecular weight distribution.

HPLC is the most widely used technique to characterize various distributions in molecular characteristics of polymers. In general, HPLC techniques used in polymer characterization can be divided into two groups, namely size exclusion chromatography (SEC) and interaction chromatography (IC). SEC has been the most popular method to measure molecular weight distribution of polymers;[4,5] however, this method is not an efficient tool to separate polymers in terms of chemical heterogeneity, such as difference in microstructure and end group of homopolymers and difference in chemical composition of copolymers because SEC separates polymer molecules in terms of hydrodynamic volume only. In contrast to SEC, interaction chromatography (IC) utilizes the enthalpic interaction, adsorption, or partition of polymer chains to the stationary phase. Therefore, IC has been employed frequently to separate polymers in terms of their molecular weight,[6−8]chemical composition,[9] tacticity,[10] and functionality[11] since its separation mechanism is sensitive to the chemical nature of the polymer chains.

For block copolymer systems, we need to obtain information on chemical composition distribution (CCD) as well as molecular weight distribution (MWD). For this purpose, two-dimensional liquid chromatography (2DLC)[12−15] and liquid chromatography at the critical condition (LCCC)[16,17] methods have been successfully applied for the characterization of various block copolymer systems.

Several block copolymers containing poly(2-vinylpyridine) have been widely used as polymer samples for a variety of studies since this polar polymer exhibits strong incompatibility against commonly used polymer species such as polystyrene and polyisoprene so that the copolymers show interesting structures and properties.[18−20] However, there are no reports on the chromatographic characterization of block and graft copolymers containing poly(2-vinylpyridine) as one component because it is very difficult to find out separation condition of these copolymers in IC regime. Until now, the SEC method has been successfully applied for the characterization of block copolymers composed of P2VP block only under the condition with small amount of quaternary amine or salt.[21]

In this paper, we report on the separation condition of SP diblock and PSP triblock copolymers having various compositions using an amine-bonded silica gel column and a mixture of THF/ACN with LiCl salt as stationary phase and mobile phase, respectively. Both diblock and triblock copolymers can be separated clearly in terms of chemical composition by temperature gradient interaction chromatography (TGIC). The TGIC method utilizes mainly the interaction between the polymer chains and the stationary phase, where the interaction strength is controlled by varying the column temperature.[22]

In general, the solvent gradient method has been employed for the separation of various copolymers according to chemical composition. In this study, however, we have successfully separated SP diblock and PSP triblock copolymers according to chemical composition by TGIC in isocratic elution conditions for the first time.

Experimental Section

Materials. *SP Diblock and PSP Triblock Copolymers*. Nine PS-*b*-P2VP (SP) diblock and nine P2VP-*b*-PS-*b*-P2VP (PSP) triblock copolymers with similar molecular weight but different chemical composition were prepared by sequential anionic polymerizations in tetrahydrofuran (THF) at −78 °C with cumyl−potassium and naphthalene−potassium as initiators, respectively. The details of the polymerization procedure were reported previously.[21,23] A small amount of PS solutions for all block copolymers was separated as precursors to check the molecular weight of PS blocks in the course of polymerization reactions.

The absolute weight-average molecular weights of SP diblock and PSP triblock copolymers were measured by a multiangle laser light scattering of the type DAWN EOS of Wyatt Technology at 35 °C in THF. The refractive index increment, dn/dc, of PS and P2VP in THF is 0.185 and 0.180, respectively. These values are very close to each other; therefore, the difference was ignored in evaluating M_w. The molecular weight distribution of PS precursors and block copolymers was estimated by size exclusion chromatography (SEC) with three TSK-gel G4000H columns (TOSOH, 300 × 7.8 mm i.d.). The SEC chromatograms were recorded with a refractive index detector of TOSOH with THF as an eluent at 40 °C. About 2 vol % of tetramethylethylenediamine was added to THF to avoid adsorption phenomena of P2VP block chains on polystyrene gel. Volume fractions of SP diblock and PSP triblock copolymers were measured by pyrolysis−gas chromatography using a gas chromatograph GC-2010 of Shimadzu equipped with a microfurnace pyrolyzer PY-2020s of Frontier Lab. having an ultra alloy column and a flame ionization detector.[24] The molecular characteristics of SP diblock and PSP triblock copolymers thus obtained are listed in Tables 1 and 2.[25,26]

HPLC Measurement. The TGIC experiments were carried out on a typical isocratic HPLC system equipped with a NH_2-bonded silica gel column (Hypersil APS-1, 100 Å pore, 150 × 4.6 mm, 3 μm particle size). The mobile phase is a mixture of THF and CH_3CN (Kishida Chemical, HPLC grade, 53/47 in volume) with 0.005 M LiCl, and the flow rate was 0.5 mL/min. Each block copolymer sample was dissolved in the mobile

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Table 1. Molecular Characteristics of PS-*b*-P2VP Diblock Copolymers

samples	$M_w{}^a/10^3$	$M_w/M_n{}^b$	$\phi_s{}^c$
SP 91	160	1.05	0.896
SP 82	151	1.04	0.792
SP 73	130	1.05	0.687
SP 64	136	1.06	0.591
SP 55	135	1.04	0.462
SP 46	136	1.05	0.399
SP 37	114	1.05	0.302
SP 28	114	1.03	0.193
SP 19	105	1.03	0.100

[a] Weight-average molecular weights measured by multiangle laser light scattering. [b] Apparent molecular weight distribution determined by size exclusion chromatography. [c] Volume fractions of polystyrene blocks measured by pyrolysis−gas chromatography.

Table 2. Molecular Characteristics of P2VP-*b*-PS-*b*-P2VP Triblock Copolymers

samples	$M_w{}^a/10^3$	$M_w/M_n{}^b$	$\phi_s{}^c$
PSP 91	148	1.06	0.922
PSP 82	135	1.05	0.820
PSP 73	165	1.05	0.687
PSP 64	164	1.04	0.578
PSP 55	156	1.05	0.496
PSP 46	139	1.03	0.422
PSP 37	144	1.07	0.328
PSP 28	158	1.07	0.224
PSP 19	161	1.08	0.112

[a] Weight-average molecular weights measured by multiangle laser light scattering. [b] Apparent molecular weight distribution determined by size exclusion chromatography. [c] Volume fractions of polystyrene blocks measured by pyrolysis−gas chromatography.

phase (0.3 mg/mL) and injected through a Rheodyne 7125 injector equipped with a 100 μL sample loop. The column temperature was varied in a preprogrammed manner by circulating a fluid through a column jacket from a bath/circulator (HAAKE, P2, Germany). The TGIC chromatograms were recorded with a UV absorption detector, UV-8020, of Tosoh operating at a wavelength of 254 nm.

Results and Discussion

Figure 1 displays the SEC chromatograms of nine SP diblock (a) and nine PSP triblock (b) copolymers recorded by a refractive index detector, where SEC chromatograms from SP 19 to SP 91 (a) and from PSP 19 to PSP 91 (b) are arranged from bottom to top. From these chromatograms, all SP diblock and PSP triblock copolymers show single peaks only, and nine copolymers are eluted within 2 min. This indicates that all SP diblock and PSP triblock copolymers have similar molecular weights and narrow molecular weight distribution, respectively. From Tables 1 and 2, we could confirm that SP diblock and PSP triblock copolymers have similar molecular weights but different chemical composition. It is apparent that ϕ_s of these copolymers is covering the range $0.1 < \phi_s < 0.9$ with its constant step width of about 0.1.

In general, however, block copolymers are contaminated with some amount of precursor polymers produced as byproducts in the course of polymerizations. Therefore, it is very important to check the contents of precursor polymers in block copolymers for the further study. Although the SEC method has been widely used on the separation of various copolymer systems, it is not an efficient method to characterize copolymers in detail, especially in terms of chemical heterogeneity. In this work, we employed the TGIC technique to separate homopolymers from the SP diblock and PSP triblock copolymers according to chemical composition. In TGIC analysis, the stationary and mobile phases have to be properly chosen for individual polymer system of interest to achieve a reproducible and high-resolution separation.

In the case of SP and PSP block copolymers, unfortunately, it is very difficult to find out the separation condition due to the strong adsorption phenomenon of P2VP block on various stationary phases. As a matter of fact, even for the SEC analysis of P2VP, we have to add a small amount of quaternary amine or salt to avoid adsorption on polystyrene gel. To find out the elution condition of SP and PSP block copolymers in IC regime, first, we chose an amine-bonded silica gel column and a mixture of THF/ACN (53/47, v/v) as a stationary phase and a mobile phase, respectively. In reality, because of the strong adsorption of P2VP block on stationary phase, we found that it was impossible to elute SP diblock copolymers with several different chemical composition in this experimental condition. Therefore, to reduce the adsorption effect of P2VP block, a small amount of LiCl salt (0.005 M) was added to mobile phase; the procedure was already used in SEC analysis of P2VP polymers.[27−29]

Figure 2 shows the TGIC chromatograms of nine SP diblock copolymers (top) and PS 100K homopolymer (bottom) in amine-bonded silica gel stationary phase and THF/ACN (53/47, v/v) with 0.005 M LiCl as a mobile phase. In this experimental condition, the eluent is a good solvent for PS chains, and the PS block shows no essential interaction with the polar stationary phase. Therefore, PS homopolymer was eluted in the SEC regime while P2VP block has a sufficient interaction with polar stationary phase. In the top chromatograms, TGIC was able to separate the seven SP diblock copolymers, from SP 73 to SP 19, showing the increase in retention time in the order of increasing P2VP chemical composition, while SP 91 and SP 82 samples were mostly eluted in SEC regime in this eluent condition due to the high contents of PS.

Additionally, we were not able to separate the seven SP diblock copolymers completely due to the effect of both molecular weight distribution and chemical composition distribution. Although SP diblock copolymers were prepared by anionic polymerizations, the finite distributions of the synthetic polymers in molecular weight and in chemical composition lead to the finite peak width, which would result in the peak overlap. Furthermore, it seems the adsorption phenomenon of P2VP block could not be removed completely in this experimental condition, and the broad peaks of copolymers with high amounts of PS content result from the low starting temperature in this TGIC experiment. In this study, the peak broadness of copolymers can be controlled by experimental conditions such as mobile phase composition, temperature, and salt concentration. Nevertheless, we successfully separated seven SP diblock copolymers in terms of chemical composition in isocratic elution condition for the first time. This result is highly interesting considering that the solvent gradient method has been exclusively employed in the separation of copolymers having wide different chemical composition distribution.[9,30,31] It has been also confirmed that all SP diblock copolymers contain very small amounts of PS precursors, less than 1%.

As for the PSP triblock copolymers, TGIC was also able to separate the seven PSP triblock copolymers

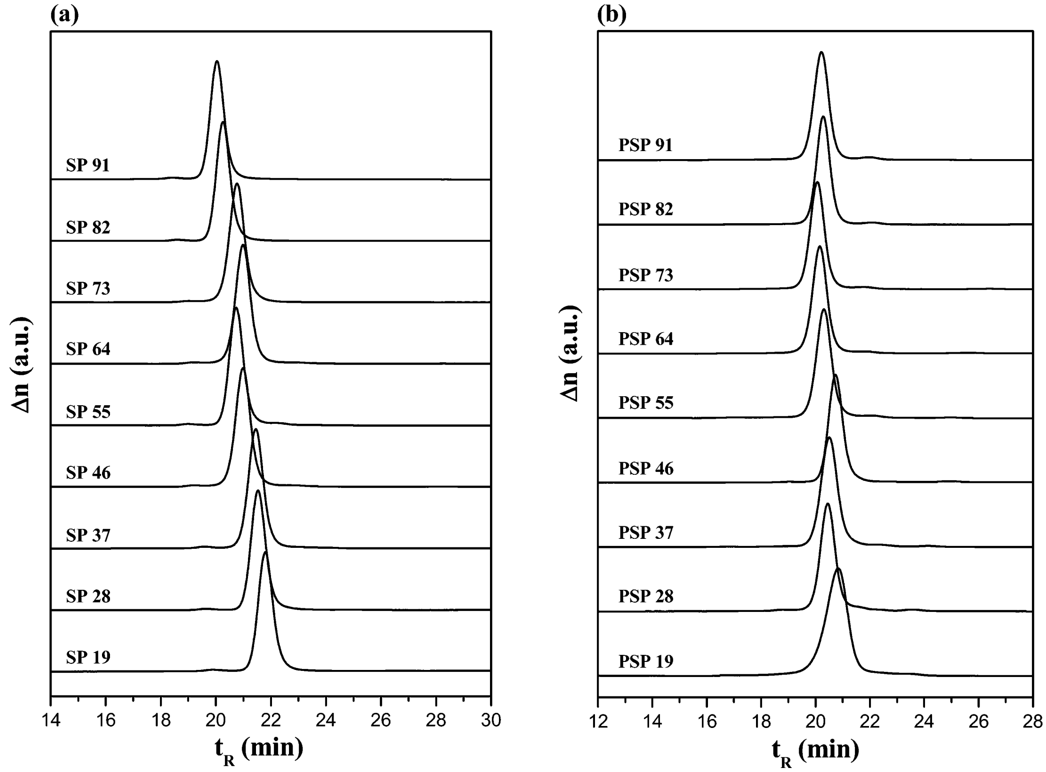

Figure 1. SEC chromatograms of nine PS-*b*-P2VP (SP) diblock copolymers (a) and nine P2VP-*b*-PS-*b*-P2VP (PSP) triblock copolymers (b). All SP diblock and PSP triblock copolymers show similar molecular weights and narrow molecular weight distribution.

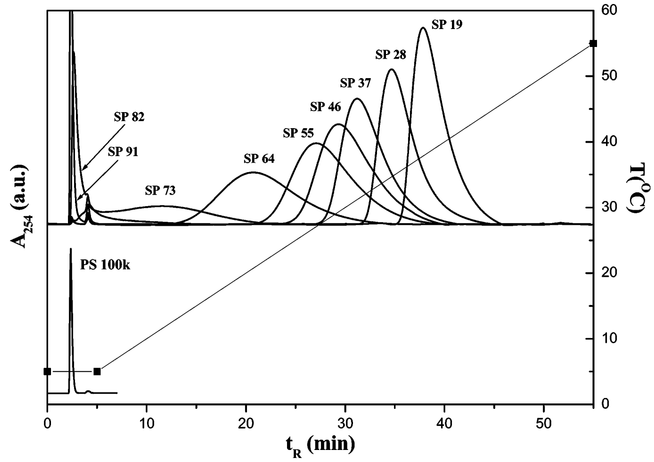

Figure 2. TGIC chromatograms of nine PS-*b*-P2VP (SP) diblock copolymers (top) and PS homopolymer with molecular weight of 100K (bottom). Seven SP diblock copolymers, i.e., the samples from SP 73 to SP 19, were eluted in the interaction chromatography regime, and they were separated in terms of chemical composition of P2VP, while, SP 91 and SP 82 samples were eluted in the size exclusion regime. Column: Hypersil ASP-1 amine-bonded silica gel, 100 Å, 150 × 4.6 mm. Eluent: THF/ACN (53/47, v/v) with 0.005 M LiCl at a flow rate of 0.5 mL/min.

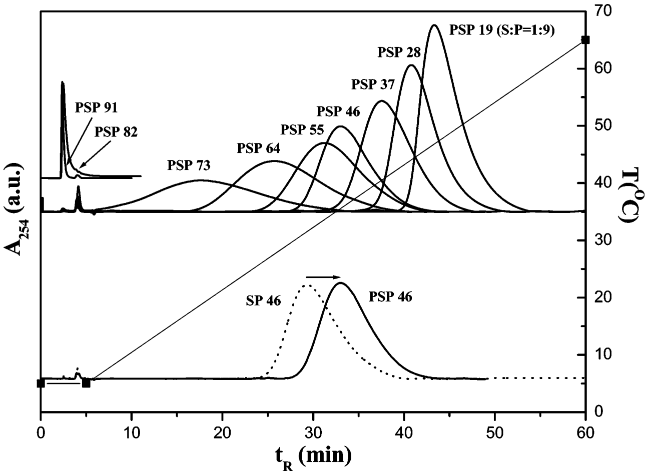

Figure 3. TGIC chromatograms of nine P2VP-*b*-PS-*b*-P2VP (PSP) triblock copolymers (top) and comparable two SP 46 and PSP 46 block copolymers (bottom). Column: Hypersil ASP-1 amine-bonded silica gel, 100 Å, 150 × 4.6 mm. Eluent: THF/ACN (53/47, v/v) with 0.005 M LiCl at a flow rate of 0.5 mL/min.

according to chemical composition of P2VP in the same experimental conditions for SP diblock copolymers. Figure 3 displays the TGIC chromatograms of the nine PSP triblock copolymers at the top and two SP 46 and PSP 46 copolymers at the bottom.

The seven PSP triblock copolymers, from PSP 73 to PSP 19, were separated in terms of chemical composition of P2VP, whereas PSP 91 and PSP 82 were eluted in SEC region due to the same reason for SP 91 and 82 samples. From the TGIC chromatograms, we also have found that the amount of PS precursors is estimated to be all below 1%; this value is very small compared with usual block copolymer systems.[32]

In the TGIC chromatograms at the bottom, we are able to compare the retention time for SP 46 and PSP 46 copolymers with similar molecular weight and chemical composition. The molecular weight and PS volume fraction ϕ_S of SP 46/PSP 46 are 136K/139K and 0.399/0.422, respectively. Although ϕ_S for PSP 46 triblock copolymer is slightly larger than that for SP 46, the TGIC retention time for PSP 46 is longer than that for SP 46 beyond the difference in volume fraction. Namely, in these experimental conditions, if we have block copolymers with exactly the same molecular weights but with different compositions, the TGIC retention time should be decreased as the PS volume fraction increases, as is clearly shown in Figures 2 and 3. From this small difference in retention behavior between SP diblock and PSP triblock copolymers, we are convinced that both end P2VP blocks in a PSP molecule have more effective interaction with the stationary phase than one end P2VP block of a SP molecule. Thus, the TGIC retention of block copolymers evidently could be affected by chain architecture.[33]

For the salt effect, it can be thought that the Li cation could interact strongly with lone-pair electrons in nitrogen atoms of P2VP, which reduced the adsorption strength of P2VP block on stationary phase since the adsorption phenomenon of P2VP comes from the strong interaction of lone-pair electrons on a nitrogen atom of P2VP with various HPLC stationary phases. It was confirmed that the TGIC retention of SP and PSP block copolymers was affected by the concentration of LiCl salt: as the concentration of LiCl salt increases, the TGIC retention time of SP and PSP block copolymers decreases. However, it is necessary to study more about the effect of salt concentration on IC retention of P2VP polymers in detail.

In conclusion, by adding a tiny amount of LiCl salt to mobile phase, we have found out the separation condition of SP diblock and PSP triblock copolymers from styrene homopolymers. We have successfully separated the SP and PSP block copolymers with high P2VP content in terms of chemical composition in isocratic elution conditions by the TGIC method.

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