Notes

Characterization of Poly(2-vinylpyridine) by Temperature Gradient Interaction Chromatography

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Introduction

Recently, the polymers containing a pyridine moiety have attracted increasing attention for various applications in nanotechnology.[1−5] Because of the strong affinity of the amines to various ions and polar groups, the polymers containing a pyridine moiety can make strong bonds with various metal ions or nanoparticles. Therefore, nanopatterned polymers containing a pyridyl group can be converted to the nanostructure of various materials. To obtain a nanostructure of polymers with a long-range order, it is necessary to acquire a well-defined polymer of homogeneous molecular characteristics such as molecular weight and chemical composition. Poly(2-vinylpyridine) (P2VP) meets this requirement since 2-vinylpyridine can be polymerized by anionic polymerization which is able to yield polymers with narrow molecular weight distribution (MWD) and various block copolymers.

Synthetic polymers are inherently heterogeneous in molecular weight (MW), and the precise characterization is a prerequisite for such applications requiring well-defined polymers. Size exclusion chromatography (SEC) coupled with various detection methods has been the most widely used tool for the MWD analyses of polymers.[6,7] However, SEC is sensitive to the polymer chain size only and suffers from the relatively low resolution due to the band broadening.[8] Interaction chromatography (IC) shows a much higher resolution than SEC.[9−12] IC has an additional advantage over SEC by its sensitivity to the chemical nature of the molecules.[11,12] A number of successful IC separation according to MW have been reported for high-MW homopolymers of polystyrene,[9,10] poly(methyl methacrylate),[13] polyisoprene,[14] and poly(ethylene oxide).[15]

The LC characterization of poly(vinylpyridine) is difficult due to the strong adsorption of the amine group to the packing materials. In the SEC separations, additives such as LiCl or amines need to be added to the eluent to reduce the strong affinity of the pyridine moiety to the stationary phase. Schmitz et al. reported on the separation of poly(vinylpyridine) oligomers by gradient elution LC and supercritical fluid chromatography.[16,17] However, the separation condition cannot be applied to high-MW poly(vinylpyridine) since the polymer is insoluble in the eluent. Recently, Cho et al. successfully separated polystyrene-*b*-poly(2-vinylpyridine) (PS-*b*-P2VP) diblock copolymers and PS-*b*-P2VP-*b*-PS triblock copolymers according to the chemical composition at the IC regime by using an amine-bonded silica column.[18] The separation was done according to the composition only for the block copolymers of similar molecular weight. This separation condition works for the block copolymers containing P2VP blocks, but it cannot be extended to separation of high-MW P2VP homopolymers due to the strong adsorption to the stationary phase.

In this study, we employed temperature gradient interaction chromatography (TGIC) to characterize high-MW homo-P2VP using a bare silica column. In TGIC, the column temperature is varied during the elution to control the solute retention.[19] Anionic polymerized homo-P2VP samples were successfully separated by TGIC with much higher resolution than SEC.

Table 1. Molecular Characteristics of Five P2VP Samples

	SEC			TGIC	
samples	M_p[a] (kg/mol)	M_w[b] (kg/mol)	M_w/M_n[b]	M_w[b] (kg/mol)	M_w/M_n[b]
PVP 10	9.5				
PVP 38	38.3	39.8	1.06	41.2	1.009
PVP 99	98.9	100	1.06	100	1.007
PVP 230	230	235	1.05	233	1.007
PVP 488	488				

[a] Measured by SEC-MALLS. [b] Calculated by the calibration curve constructed from the M_p of five P2VPs.

Experimental Section

The TGIC 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, a multiangle laser light scattering detector (MALLS, Wyatt, miniDawn), a refractive index detector (Wyatt, Optilab), and a variable wavelength UV/vis absorption detector (TSP, Spectra 100) operating at a wavelength of 260 nm. TGIC separation of P2VP homopolymer was carried out with three different columns: an amine-bonded silica column (Lunasil, 150 × 4.6 mm i.d., 100 Å pore, 3 μm particle size), a diol-bonded silica column (Nucleosil, 100 × 4.6 mm i.d., 100 Å pore, 7 μm particle size), and a bare silica column (Nucleosil, 100 × 4.6 mm i.d., 500 Å pore, 5 μm particle size). The mobile phase was either a mixture of THF/CH_3CN (Samchun, HPLC grade) or CH_3OH/THF (Samchun, HPLC grade) depending on the column used. A small amount of LiCl (Sigma-Aldrich) or *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMED, Aldrich) was added to the mobile phases to reduce the peak tailing. Temperature of the separation column was controlled by circulating fluid from a programmable bath/circulator (Neslab, RTE-111) through a home-made column jacket.

For the SEC separation, two mixed bed columns (PL-Gel Mixed C, 300 × 7.5 mm i.d.) were used. The eluent was THF containing 2 vol % TMED at a flow rate of 0.8 mL/min.[20,21] The absolute molecular weight of P2VP samples were measured by light scattering detection using a MALLS detector. The d*n*/d*c* value of P2VP sample in the eluent was measured as 0.181 L/g.

Anionic polymerized P2VP homopolymers were purchased from the Scientific Polymer Products. The molecular characteristics determined by SEC are summarized in Table 1.

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10.1021/ma060326d CCC: $33.50

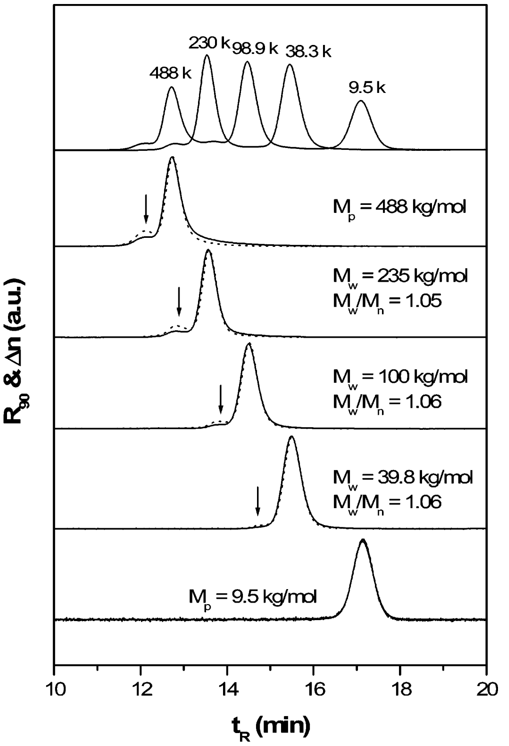

Figure 1. SEC chromatograms of five P2VPs recorded with a light scattering detector (dotted line) and a refractive index detector (solid line). All P2VP samples show small peaks (marked with arrows), of which MW is exactly twice the MW of the main peak. The peak molecular weight (M_p) is an absolute MW obtained from the light scattering detection, while M_w and M_w/M_n were determined from the calibration curve constructed from the peak positions and M_p of five P2VPs.

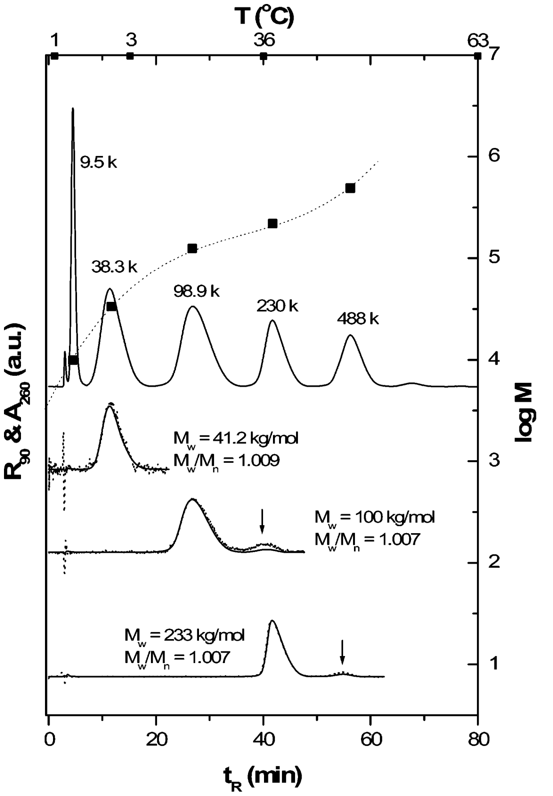

Figure 2. TGIC chromatograms of five P2VP samples (top) and three separately injected samples. The calibration curve constructed from the peak position of five P2VP samples (log M_p vs t_R) is shown in the plot. The temperature program is shown in the top abscissa. The molecular characteristics of three samples are shown in each TGIC chromatogram of individual samples. Column: bare silica, 100 × 4.6 mm i.d., 500 Å pore, 5 μm particle size. Eluent: CH_3OH/THF (86/14, v/v, TMED 1 vol %) at a flow rate of 0.5 mL/min.

Results and Discussion

Figure 1 displays the SEC chromatograms of five P2VP samples. The solid line and dotted line are the chromatograms recorded by a refractive index detector and a MALLS detector, respectively. The top chromatogram is the overlap of the individual chromatograms. All P2VP samples show no noticeable peak tailing, and the peak shapes are symmetric, indicating that the adsorption of P2VP was suppressed well by addition of TMED to the mobile phase. For most of the samples, a small peak (marked with an arrow) shows up earlier than the main peak, of which MW is exactly twice the MW of the main peak. They are likely the coupled products formed in the anionic polymerization of the P2VP samples.[22] The absolute molecular weights at the elution peak position (M_p) are determined from the light scattering intensity and the refractive index detector intensity. Weight-average molecular weight (M_w) and MWD (M_w/M_n) of three P2VPs in the middle are calculated according to the calibration curve constructed from the peak positions and M_p of five P2VPs. The molecular characteristics of the P2VP samples are summarized in Table 1.

For the IC separation of polymers, a proper set of the stationary and mobile phase has to be found. Previously, Cho et al. successfully separated block copolymers of PS and P2VP by TGIC using an amine-bonded silica column and THF/CH_3CN (53/47, v/v) eluent containing 5 mM LiCl.[18] Therefore, the separation of homo-P2VP was attempted first using the same column. All P2VP samples elute at the separation condition; however, the elution peaks show tailing which gets more serious for high-MW P2VP, and the elution peaks of the high-MW P2VP samples are not resolved.[23] To find a better IC separation of P2VP, a diol-bonded silica column was also employed, and an elution condition was found as CH_3OH/THF (92/8, v/v) containing LiCl (20 mM). The resolution of the P2VP samples is better than the case of the amine column, but elution peaks still show tailing and two high-MW samples are not fully resolved.[23]

Such peak tailing problems of amine-containing materials are commonly observed in the chromatographic separation using bonded stationary phase, and it is generally accepted due to the strong interaction of the amine with the free silanol groups in the stationary phase.[24,25] To prevent the peak tailing in the separation of poly(vinylpyridine), either soluble salts such as LiCl or amine compounds are added to the eluent. TMED is a commonly used additive and works well in the SEC separation using a styrene-based column.[20,21] When 0.3 vol % TMED was added in place of LiCl for the TGIC separations described above, all P2VP samples were eluted in the SEC regime. Apparently, the TMED reduces the interaction of P2VP too much for the amine- or diol-bonded column. Since the retention is too sensitive to the TMED content, no serious attempt was made to adjust the retention with the TMED content. Instead, we employed a more strongly interacting stationary phase, a bare silica column. The TGIC separation condition was found at the mobile phase composition of CH_3OH/THF (86/14, v/v) containing 1 vol % TMED.

Figure 2 displays TGIC chromatograms of the five P2VP samples (top) and the separate runs of three P2VP samples (bottom three). The column temperature was varied in three linear ramps as shown in the upper abscissa of the plot. No serious peak tailing was observed, and all P2VP samples are separated down to the baseline as shown in the top chromatogram. In the TGIC chromatograms of individual P2VP samples, the small peaks seemingly due to the coupling of the P2VP anions are clearly seen as indicated with arrows for the bottom two chromatograms. It is evident that the TGIC resolution is far superior to the SEC resolution when the separations of the adjacent elution peaks in SEC (Figure 1) and TGIC (Figure 2) chromatograms are compared.

From the elution peak positions of five P2VP samples, a calibration curve (log M_p vs t_R) was constructed by fitting the peak positions to a third-order polynomial as shown in the plot. For the M_p, the values measured by SEC-MALLS were used. The weight-average MW (M_w) and MWD (M_w/M_n) of three P2VP samples were calculated according to the calibration curve and listed in Table 1 in comparison with the SEC characterization results. The M_w and M_w/M_n values from both SEC and TGIC analysis are calculated for the main peaks, only neglecting the small side-product peaks since the coupling reaction usually occurs in the termination process that can be avoided.[22] While the M_w obtained by TGIC analysis are in good agreement with the values determined by SEC, the M_w/M_n values are considerably smaller than the SEC values. The same phenomena were found in various polymers prepared by anionic polymerization.[9,10,13−15] It is due to the band broadening in SEC, and the M_w/M_n values calculated by the calibration method always overestimate the MWD of the narrowly dispersed polymers.[9,10,12] The molecular weight of P2VP in a SEC elution peak shown in Figure 1 is in fact quite homogeneous as can be read from the nearly identical light scattering and concentration detector traces. Therefore, the M_w/M_n values of narrowly dispersed polymers measured by light scattering detection are lower than that measured by the calibration method.[26] However, the calibration method is much more widely used due to the convenience and no extra cost for a light scattering detector.

In summary, an efficient IC separation condition was established for the P2VP characterization using a bare silica column, and the molecular characteristics of P2VP obtained from the temperature gradient IC analysis were compared to SEC. The MWD of anionic polymerized P2VP was found much narrower than the values commonly measured by SEC like other polymers prepared by anionic polymerization. This result demonstrates that amine-containing polymers can be separated with high-resolution by IC.

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Supporting Information Available: Results of TGIC separation when different columns and mobile phases are used. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Lin, Y.; Boeker, A.; He, J.; Sill, K.; Xiang, H.; Abetz, C.; Li, X.; Wang, J.; Emrick, T.; Long, S.; Wang, Q.; Balazs, A.; Russell, T. P. *Nature (London)* **2005**, *434*, 55−59.

(2) Li, X.; Lau, K. H. A.; Kim, D. H.; Knoll, W. *Langmuir* **2005**, *21*, 5212−5217.

(3) Sfika, V.; Tsitsilianis, C.; Kiriy, A.; Gorodyska, G.; Stamm, M. *Macromolecules* **2004**, *37*, 9551−9560.

(4) Lei, L.; Gohy, J.-F.; Willet, N.; Zhang, J.-X.; Varshney, S.; Jerome, R. *Macromolecules* **2004**, *37*, 1089−1094.

(5) Malynych, S.; Luzinov, I.; Chumanov, G. *J. Phys. Chem. B* **2002**, *106*, 1280−1285.

(6) Mori, S.; Barth, H. G. *Size Exclusion Chromatography*; Springer-Verlag: New York, 1999.

(7) Yau, W. W.; Kirkland, J. J.; Bly, D. D. *Modern Size Exclusion Liquid Chromatography, Practice of Gel Permeation and Gel Filtration Chromatography*; John Wiley & Sons: New York, 1979.

(8) Popovici, S. T.; Kok, W. T.; Schoenmakers, P. J. *J. Chromatogr. A* **2004**, *1060*, 237−252.

(9) Lee, H. C.; Chang, T. *Polymer* **1996**, *37*, 5747−5749.

(10) Lee, W.; Lee, H.; Cha, J.; Chang, T.; Hanley, K. J.; Lodge, T. P. *Macromolecules* **2000**, *33*, 5111−5115.

(11) Chang, T. *Adv. Polym. Sci.* **2003**, *163*, 1−60.

(12) Chang, T. *J. Polym. Sci., Polym. Phys. Ed.* **2005**, *43*, 1591−1607.

(13) Lee, W.; Lee, H. C.; Chang, T.; Kim, S. B. *Macromolecules* **1998**, *31*, 344−348.

(14) Lee, W.; Lee, H. C.; Park, T.; Chang, T.; Chae, K. H. *Macromol. Chem. Phys.* **2000**, *201*, 320−326.

(15) Cho, D.; Park, S.; Hong, J.; Chang, T. *J. Chromatogr. A* **2003**, *986*, 191−198.

(16) Schmitz, F. P.; Hilgers, H.; Gemmel, B. *J. Chromatogr.* **1986**, *371*, 135−144.

(17) Schmitz, F. P.; Hilgers, H.; Lorenschat, B.; Klesper, E. *J. Chromatogr.* **1985**, *346*, 69−79.

(18) Cho, D.; Noro, A.; Takano, A.; Matsushita, Y. *Macromolecules* **2005**, *38*, 3033−3036.

(19) Chang, T.; Lee, H. C.; Lee, W.; Park, S.; Ko, C. *Macromol. Chem. Phys.* **1999**, *200*, 2188−2204.

(20) Lee, J.; Hogen-Esch, T. E. *Macromolecules* **2001**, *34*, 2805−2811.

(21) Ohtani, H.; Kotsuji, H.; Momose, H.; Matsushita, Y.; Noda, I.; Tsuge, S. *Macromolecules* **1999**, *32*, 6541−6544.

(22) Park, S.; Cho, D.; Ryu, J.; Kwon, K.; Chang, T.; Park, J. *J. Chromatogr. A* **2002**, *958*, 183−189.

(23) See Supporting Information.

(24) Scholten, A. B.; Claessens, H. A.; de Haan, J. W.; Cramers, C. A. *J. Chromatogr. A* **1997**, *759*, 37−46.

(25) Berek, D.; Tarbajovska, J. *J. Chromatogr. A* **2002**, *976*, 27−37.

(26) Netopilik, M.; Podzimek, S.; Kratochvil, P. *J. Chromatogr. A* **2001**, *922*, 25−36.

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