Enhanced Partitioning Fractionation of a Bimodal Mixture of Polystyrene Using Porous Glass Beads

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Introduction. There are a number of methods for separation of polydisperse polymer samples into fractions with a narrow molar mass distribution. Physical separation techniques such as fractional precipitation, ultracentrifugation, gel permeation chromatography (GPC), and field-flow fractionation[1-3] are in use at present.[4] These methods, however, work only for dilute solutions and are suitable primarily for analytical purposes. The huge solvent requirement also raises environmental safety concerns and adds to the cost of processing.

Recently, a novel technique of fractionation that uses porous materials and a semidilute polymer solution was proposed.[5,6] We call it enhanced partitioning fractionation (EPF). The solvent requirement is minimal, and therefore the technique can be applied on a processing scale. EPF is based on a segregation effect of a polydisperse polymer in semidilute solution with respect to molar mass between a pore volume and the surrounding solution. The two volumes are assumed to be comparable. When porous materials with a pore size comparable to the polymer chain dimension are immersed into the semidilute solution, a high osmotic pressure in the external solution drives lower molar mass components (LMMC) preferentially into the pore channels, leaving the external solution enriched with high molar mass components (HMMC). When the polymer solution is dilute, in contrast, a reduction in the conformational entropy due to geometrical restriction partitions most polymer molecules in the exterior solution.[1,7-9] Thus a larger proportion of polymer molecules are partitioned in the exterior as the chain dimension increases.

The scheme of EPF involves two steps.[6] The first and second steps produce fractions enriched in the HMMC and LMMC, respectively. In step 1, the porous materials soaked in the pure solvent are added to a semidilute solution of the original polymer fraction. The external solution enriched with HMMC is separated from the porous materials for extraction. In step 2, an excess pure solvent is added to the porous materials to drive the polymer out of the pores. The external solution enriched with LMMC is separated from the porous materials.

EPF involves equilibration of the chemical potential of a polymer molecule between the exterior solution and the pore volume. Unlike GPC, there is no mobile or stationary phase in EPF. The optimal separation can be achieved by adjusting conditions such as the polymer concentration in the original solution, the pore size, and the ratio of the total pore volume to the volume of the exterior solution.[6]

This paper is the first to report the application of EPF. To demonstrate and analyze its effectiveness, we applied EPF to a bimodal mixture of polystyrene (PS) standards. As porous materials we used highly porous silica glass beads. Among other conditions we focus here on the pore size and the processing time for step 1.

Table 1. Characterization of Polystyrene Standards

code	peak molar mass	polydispersity	R_{g0}, nm	c^*, mg/mL
PS30K	30 300	1.06	5.8	91.2
PS90K	89 300	1.04	11.1	39.4
PS290K	293 000	1.06	22.2	15.3
PS942K	949 000	1.06	44.8	6.12
PS1.9M	2,161 000	1.26	68.5	3.20

Experimental Section. Two grades of porous beads, Shell Silica Spheres S980A and S980G (Shell Development), were used. They are manufactured in spinodal decomposition of sodium borosilicate glass into a bicontinuous structure. The boron-rich phase is subsequently acid leached. The skeletal solid phase is nearly pure silica. The spheres have a well-defined pore size and a highly interconnected pore network. Over short distances the pores are cylindrical with radius R_p. The bead diameters of S980A and S980G are 2.3 and 2.2 mm, R_p's are 7.5 and 25 nm, and the surface areas are 267 and 80 m^2/g, respectively. The pore volume is 1.0 cm^3/g for both of them (manufacturer supplied).[10] Surface hydroxyl groups were replaced with trimethylsilanyl groups to prevent polymer adsorption. The surface treatment was done in an excess of a 2 M chlorotrimethylsilane solution in toluene at 90 °C under nitrogen for a week.[11] PS standards were purchased from Pressure Chemical Inc. Manufacturer-supplied characterization data of the five standards, PS30K, PS90K, PS290K, PS942K, and PS1.9M, are shown in Table 1. The radii of gyration, R_{g0}, in the dilute solution limit were calculated from the literature.[12] The overlap concentration c^* is defined by $c^*(2^{1/2}R_{g0})^3 = M/N_A$,[13] where M is the molar mass and N_A is Avogadro's number.

An original bimodal PS solution was made by dissolving an equal mass mixture of two PS standards in toluene. The concentration of the original PS solution ranged from 2 to 15 wt %. In step 1 of EPF, the glass beads were first soaked in pure toluene for at least 30 min. They were then transferred into the original solution contained in a vial. The volume of the original solution was adjusted to be nearly equal to the total pore volume of the glass beads. Typically 1–3 mL of a PS solution and 1–3 g of porous beads were used. Seven to ten days were allowed to pass for equilibration unless otherwise mentioned. Step 1 was concluded by separating the external solution from the glass beads, followed by precipitation of polymer in methanol. Subsequently, in step 2, an excess pure toluene was added to the glass beads. After at least a week the external solution was again separated for recovery of the polymer by precipitation. The glass beads were washed a few times in excess solvent for the next batch of processing. All processings were carried out at room temperature. Molar mass distributions of the recovered polymer fractions and the original mixtures were analyzed in tetrahydrofuran (0.05 wt %), using a Waters GPC system with a Model 410 differential refractometer.

Results and Discussion. An example of the GPC elution curves is shown in Figure 1 for the two fractions obtained in steps 1 and 2 of EPF (Δn is the output of the differential refractometer). Here, 3.1 g of a 9.8 wt % solution of an equal mass mixture of PS30K (LMMC) and PS290K (HMMC) in toluene and 3.2 g of S980A glass beads were used. The glass beads–solution

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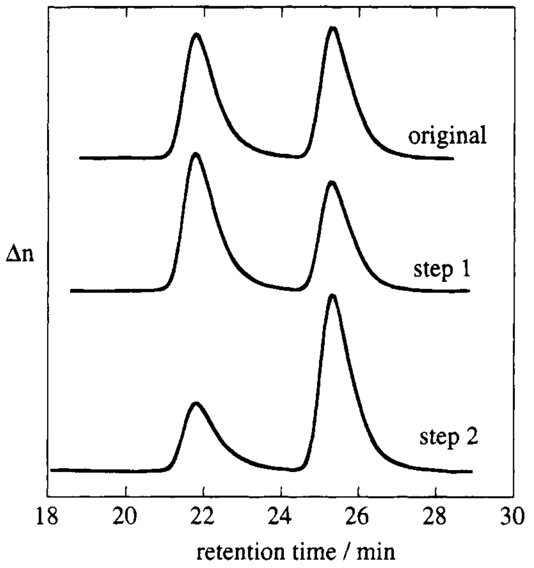

Figure 1. GPC elution chromatograms for the original sample and the two fractions obtained in steps 1 and 2 of enhanced partitioning fractionation. See the text for the conditions.

Table 2. Effect of Pore Size on EPF

porous glass bead	R_p, nm	mixture composition	conc, wt %	% of the desired component step 1	step 2
S980A	7.5	PS290K/PS30K	9.7	58	72
S980G	25	PS290K/PS30K	9.7	53	51
S980G	25	PS900K/PS90K	4.1	57	61
S980G	25	PS1.9M/PS290K	2.0	58	72

system was equilibrated for 11 and 10 days for steps 1 and 2, respectively. The EPF conditions are not optimized. A GPC chromatogram of the original mixture is included in Figure 1. The fraction obtained in step 1 exhibits an enrichment of HMMC in 58% by mass. The enrichment effect is more evident in step 2. The step 2 fraction contained LMMC in 72% by mass. Apparently EPF works. All the results presented below, of a mass percentage of the desired component in the recovered fraction, were obtained by analyzing GPC elution chromatograms.

We first examine the effect of the pore size. The first and second rows of Table 2 compare the performance of two EPF processings that employ the porous glass beads of different pore size, S980A ($R_p = 7.5$ nm) and S980G ($R_p = 25$ nm). For the same mixture of PS290K and PS30K in the original solution at the same concentration, S980A spheres ($R_{g0}/R_p \cong 3.0$ and 0.8, for the two components) exhibited a better performance than S980G spheres ($R_{g0}/R_p \cong 0.9$ and 0.2) did. The difference is ascribed to a less discriminatory accommodation of HMMC along with LMMC by the S980G. We thus find that it is necessary to use porous materials that provide sufficient geometrical restriction on HMMC. It then may be reasonable to expect that even the S980G spheres will show a better performance for a mixture of higher molar mass PS standards. We therefore applied EPF to two additional sets of mixtures using S980G spheres. One contained an equal weight mixture of PS942K and PS90K ($R_{g0}/R_p \cong 1.8$ and 0.4), and the other was an equal weight mixture of PS1.9M and PS290K ($R_{g0}/R_p \cong 2.7$ and 0.9). The total concentration of the original solution was adjusted so that the reduced concentration, defined as the ratio of the concentration to the overlap concentration c^*, of HMMC did not change. As shown in Table 2, the performance improved as the chain size increased. It is to be noted that the performance of PS1.9M/PS290K with S980G is comparable to that of PS290K/PS30K with S980A. For a given reduced concentration, the separation by EPF depends on the chain size relative to the pore size.

Table 3. Effect of Processing Time on EPF

porous glass bead	mixture composition	conc, wt %	duration of step 1, days	% of the desired component step 1	step 2
S980A	PS942K/PS90K	14.8	15	53	61
S980A	PS942K/PS90K	14.8	30	58	65

The theoretical estimation[6] of EPF performance assumes that chemical potential equilibrium is attained between a polymer molecule in the pore and the one in the external solution. We were not sure whether 7−10 days was sufficient in step 1, because the center of mass diffusion of polymer molecules is slow at high concentrations in the pore, especially for high molar mass components.[14] The performance is expected to change as the time for step 1 increases until equilibrium is reached. We therefore carried out two sets of fractionations for an equal weight mixture of PS942K and PS90K using S980A spheres. The processing times for step 1 were 15 and 30 days. The other conditions were identical. We intentionally employed a high concentration in the original solution to reduce the diffusion coefficient of the polymer. The results are shown in Table 3. The percentages of the desired components in the recovered fractions were greater for the set processed for 30 days. Apparently, a longer processing time improved the EPF performance. We do not know at this stage how long the equilibration takes.

The time t necessary for equilibration is determined by a self-diffusion coefficient D of the polymer molecule in the porous medium at a given interior concentration and bead diameter d_b as $t \sim d_b^2/D$. Therefore, a higher processing temperature, use of a less viscous solvent, and mechanical agitation will decrease the processing time. More significantly, use of smaller porous materials can reduce the processing time, especially of step 1. Preliminary experiments, carried out using controlled pore glass with a bead size of about 0.15 mm, indicate a comparable EPF performance in only 2 days.

The performance of EPF observed so far using Shell spheres falls short of theoretical predictions. There are several reasons. First, the theoretical calculations assume cylindrical pores of uniform size throughout the medium.[5,6] The spheres used have a nonuniform pore size and a highly interconnected pore structure. Larger cavities can accommodate HMMC with less restriction. We are currently studying the effect of the pore size distribution on EPF. Second, some polymer can remain on the bead surface (not on the pore walls), especially when the spheres are separated from the external solution in step 1. Third, our processing time may have been too short.

We demonstrated in this paper that EPF using Shell spheres works. We expect that EPF can be scaled up without sacrificing efficiency or resolution. There are yet a number of studies to be carried out to optimize the EPF performance. Future work will be carried out using smaller beads. We will compare EPF performance under different conditions that include the pore size, the concentration of the original solution, and the interior to exterior volume ratio. We will also seek to improve the resolution by using geometrically controlled pores and apply EPF to polydisperse polymers.

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References and Notes

(1) Giddings, J. C. *Unified Separation Science*; John Wiley: New York, 1991.
(2) *Chromatography of Polymers*; Provder, T.; Ed.; American Chemical Society: Washington, DC, 1991; Vol. 521.
(3) *Particle Size Distribution II*; Provder, T., Ed.; American Chemical Society: Washington, DC, 1991; Vol. 472.
(4) Bello, A.; Barrales-Rienda, J. M.; Guzman, G. M. In *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; John Wiley: New York, 1989.
(5) Teraoka, I.; Zhou, Z.; Langley, K. H. Karasz, F. E. *Macromolecules* **1993**, *26*, 3223.
(6) Teraoka, I.; Zhou, Z.; Langley, K. H.; Karasz, F. E. *Macromolecules* **1993**, *26*, 6081.
(7) Casassa, E. F. *J. Polym. Sci., Polym. Lett. Ed.* **1967**, *5*, 773.
(8) Casassa, E. F.; Tagami, Y. *Macromolecules* **1969**, *2*, 14.
(9) Giddings, J. C.; Kucera, E.; Russell, C. P.; Myers, M. N. *J. Phys. Chem.* **1968**, *72*, 4397.
(10) "Shell silica spheres", Shell Chemical Co.
(11) Bishop, M. T.; Langley, K. H.; Karasz, F. E. *Macromoleucles* **1989**, *22*, 1220.
(12) Huber, K.; Bantle, S.; Lutz, P.; Burchard, W. *Macromolecules* **1985**, *18*, 1461.
(13) des Cloizeaux, J.; Jannink, G. *Polymers in Solution: Their Modelling and Structure*; Clarendon Press: Oxford, U.K., 1990.
(14) Teraoka, I.; Zhou, Z.; Langley, K. H.; Karasz, F. E., submitted to *Macromolecules*.

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