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High Osmotic Pressure Chromatography of Poly(ϵ-caprolactone) in Near-Θ Solvent

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ABSTRACT: High osmotic pressure chromatography (HOPC) was applied to preparative separation of poly(ϵ-caprolactone), a biodegradable polymer, by molecular weight (MW). When the solvent was toluene, a near-Θ solvent for the polymer, the MW distribution was narrow in all of the separated fractions except late fractions. In dioxane, which is a good solvent, in contrast, the MW distribution narrowed only in early fractions. The difference is explained by a recent computer simulation study on partitioning in Θ solvent and a concept of self-adjusting pore size by adsorbed polymer.

Introduction

High osmotic pressure chromatography (HOPC) was developed as a preparative-scale technique to separate polymer by molecular weight (MW).[1,2] A viscous, concentrated solution of the polymer is injected into a column packed with porous materials until the first polymer reaches the column outlet. Then, the column is washed with pure solvent, and the eluent is collected in different fractions. Various polymers including polystyrene, poly(methyl methacrylate), poly(ϵ-caprolactone), and poly(vinylpyrrolidone) have been separated.[1−3] Solvents used were always good to the polymer separated. It was partly to avoid clogging of columns. More importantly, though, it was considered that high osmotic pressure of semidilute solutions was needed for HOPC, and therefore a good solvent was better compared with poorer solvent conditions.[1,2]

A recent computer simulation study indicates otherwise, however.[4,5] Partitioning of a bimodal mixture of long and short chains between a slit space with nonadsorbing walls and an unconfined space was studied over a wide range of concentrations from dilute to semidilute. Two solvent conditions, athermal and good, were compared. It was found that the difference in the partition coefficient of the two components, a factor that determines the resolution in HOPC, maximizes at a much higher concentration in the Θ solvent. Furthermore, the latter solvent partitions the short chains to the slit space in a much higher purity over a wide range of concentrations. The difference between the two solvent conditions was ascribed to the missing second virial coefficient and the higher overlap concentration (because of a smaller chain dimension) in the Θ solvent.[4,5] These effects combined make the partitioning of the mixture essentially identical to that of noninteracting chains up to high concentrations well above the overlap concentration of the solution in the good solvent. In addition, formation of dynamic clusters,[4] especially between long chains, in the Θ condition may help partition them in the unconfined space. The simulation result raises a hope that the Θ solvent may offer a better separation in HOPC and allow operation of HOPC at higher concentrations as long as serious adsorption onto the pore surface and concomitant clogging of the column is avoided.

The present article proves that it is the case. Poly(ϵ-caprolactone), a biodegradable polymer, was used as a model polymer. Two samples of the polymer were separated in dioxane (a good solvent) and toluene (near-Θ solvent). We compared separations in the two solvents under different conditions such as surface chemistry, solvent, pore size, and column temperature. The Θ solvent resulted in a far more efficient separation.

There was an attempt of HOPC in a Θ solvent.[6] The polystyrene−cyclohexane system was employed. The preliminary results were promising. Use of Θ solvent was also attempted in analytical size exclusion chromatography.[7] Polystyrene was injected into a styrene−divinylbenzene column with cyclohexane mobile phase. Serious adsorption of the polymer by the cross-linked polymer plagued the separation even at temperatures much higher than the Θ temperature. In contrast, mixing several percent of a good solvent to the mobile phase resulted in a chromatogram close to the one in the good solvent only.

Experimental Section

Materials. Three samples of poly(ϵ-caprolactone) (PCL) were purchased. The weight-average and number-average molecular weights, M_w and M_n (with respect to polystyrene), of the three samples are listed in Table 1. Two grades of controlled pore glass (CPG) were obtained from CPG, Inc. Their properties are listed in Table 2. The surface was modified with chlorotrimethylsilane (CTMS, Acros) and *n*-octyldimethylchlorosilane (C8, Gelest). The C8 surface was end-capped with CTMS. Surface modification method is described elsewhere.[8] Here we use "CTMS-120B" to denote CPG120B modified with CTMS and "C8-120B" for CPG120B modified with C8. The same notation applies to CPG75B. Each modified CPG packed a column of 3.9 mm × 300 mm. Toluene was from Pharmco and dioxane from Fisher.

High Osmotic Pressure Chromatography. The HOPC system is the same as the one used earlier.[1−3] The column temperature was 30 °C unless otherwise specified. Before injection, the column was washed with the same solvent as the one used to dissolve the polymer. The solution was injected at a nominal flow rate of 0.2 mL/min until the first polymer was detected at the outlet. Then the injection was switched to the pure solvent (the same as the one used to dissolve the polymer). Fractions were collected according to the following

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Table 1. Characteristics of Poly(ϵ-caprolactone) Samples

code	$M_w/10^4$ (g/mol)	$M_n/10^4$ (g/mol)	M_w/M_n	source
PCL9K	0.94	0.54	1.75	SP2[a]
PCL22K	2.20	1.33	1.66	Aldrich
PCL72K	7.23	4.23	1.71	Aldrich

[a] Scientific Polymer Products.

Table 2. Characteristics of Packing Materials

code	pore diam (Å)	pore vol (mL/g)	particle size (mesh)
CPG75B	81	0.49	120/200
CPG120B	130	0.68	120/200

schedule: 20 drops each in fractions 1−10, 40 drops each in fractions 11 and 12, 100 drops each in fractions 13 and 14, and 300 drops each in fractions 15 and 16. In separations in toluene with CTMS surface, more fractions were collected after changing the column temperature and/or the solvent. The volume of each fraction was estimated from the measured mass of the solution in the fraction and the density data of solutions at different concentrations. Solvent was evaporated from the solution in each test tube by blowing hot dry nitrogen. The condition of each separation is listed in Table 3 together with the injection amount of the polymer solution.

Size Exclusion Chromatography. The MW distribution was analyzed by using size exclusion chromatography (SEC) with Phenogel columns (Phenomenex; 10^3, 10^4, 10^5 Å) and a refractive index detector. The mobile phase was THF at 1.0 mL/min. A ca. 0.2 wt %, 40 μL solution was injected in each analysis. The columns were calibrated with polystyrene standards of MW from 1.05×10^3 to 9.49×10^5 g/mol.

Results

Phase Diagram. We used a cloud-point method with visual inspection to determine the coexistence curve for a binary mixture of toluene and PCL. Three fractions of PCL (PCL9K, PCL22K, PCL72K) were used. The results are shown in Figure 1 in the temperature−concentration phase diagram. The inset shows the upper critical solution temperature (UCST) T_c as a function of $M_w^{-1/2}$.[9] The intercept of a straight line through the three points, around 15 °C, gives the Θ temperature for the PCL−toluene binary system. We expect that at 30 °C the solvent provides PCL with a near-Θ condition.

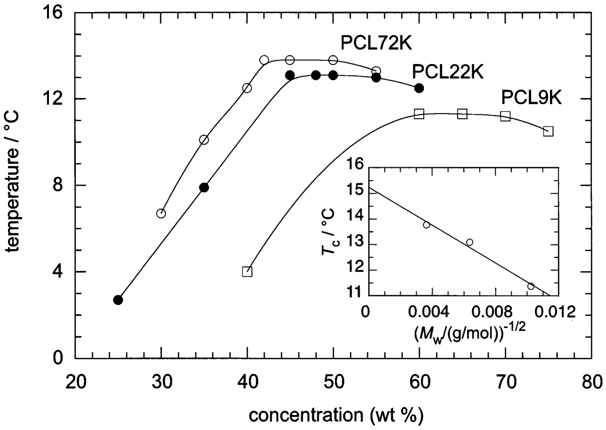

Figure 1. Temperature−concentration phase diagram of toluene−poly(ϵ-caprolactone) binary solutions. Coexistence curves were obtained in the cloud point method for three fractions of the polymer with $M_w = 9.4 \times 10^3$ (PCL9K), 2.20×10^4 (PCL22K), and 7.23×10^4 g/mol (PCL72K). The inset shows the critical temperature T_c as a function of $M_w^{-1/2}$.

HOPC with a Slightly Adsorptive Surface. We separated PCL22K in dioxane and toluene at 30 °C by a column packed with CTMS-120B. The concentrations of the two solutions were 21.9 and 25.0 wt %, respectively. They are nearly the same when expressed in g/mL. In Table 3, the volume of PCL solution injected in the dioxane separation is typical of HOPC in the good solvent condition.[1−3] Nearly all of the injected polymer eluted in a short time. In toluene separation, in contrast, the injection volume was nearly twice as large, and the recovery was lower. These results indicate adsorption of PCL onto the pore surface, although it was not too serious to cause clogging of the column or irreversible damage. In fact, washing the column in dioxane at 80 °C eluted nearly all of the adsorbed polymer, preparing the column for subsequent separation; washing in toluene at 80 °C did not release all of the adsorbed polymer.

Figure 2 compares the plot of polymer concentration in each fraction as a function of the cumulative eluent volume since injection started. The latter would be the elution volume, if the concentration were continuously measured or the eluent were cut into finer fractions. Here we call the plot an HOPC retention curve. In dioxane, the concentration gradually increases in fractions 1−5, followed by a rapid increase in fractions 6−8 and then a decrease in subsequent fractions. In toluene, the concentration climbs rapidly to a plateau in fractions 4−7, followed by a decline similar to the one observed in dioxane. The plateau is almost the same as the concentration of the solution injected. The onset of the

Table 3. HOPC Separation Parameters

column	polymer	solvent	temp (°C)	concentration wt %	concentration g/mL	injection volume (mL)	recovery (%)	layer thickness (Å)
CTMS-120B	PCL22K	toluene	30	25.0	0.228	3.45	84.5,[a] 89.7[b]	20
CTMS-120B	PCL22K	dioxane	30	21.9	0.227	1.88	99.8[a]	
CTMS-120B	PCL22K	toluene	80	25.1	0.229	3.49	89.3,[a] 97.3[c]	14
CTMS-120B	PCL22K	dioxane	80	21.8	0.226	1.91	100.2[a]	
CTMS-120B	PCL72K	toluene	30	20.9	0.189	2.96	70.7,[a] 94.5[c]	32
CTMS-120B	PCL72K	dioxane	30	17.4	0.181	1.86	100.0[a]	
C8-120B	PCL22K	toluene	30	25.0	0.228	2.53	99.1[a]	
C8-120B	PCL22K	toluene	30	20.0	0.180	2.60	98.2[a]	
C8-120B	PCL22K	dioxane	30	21.9	0.228	1.95	99.3[a]	
C8-120B	PCL22K	toluene	80	25.1	0.229	2.31	99.7[a]	
C8-120B	PCL22K	dioxane	80	22.0	0.229	1.90	98.3[a]	
CTMS-75B	PCL22K	toluene	30	24.9	0.227	3.41	75.9,[a] 81.7,[b] 95.4[c]	17
CTMS-75B	PCL22K	dioxane	30	22.2	0.230	2.12	100.4[a]	
C8-75B	PCL22K	toluene	30	25.2	0.229	2.16	85.1[a]	6.6
C8-75B	PCL22K	dioxane	30	22.0	0.229	1.98	98.9[a]	

[a] From the first 16 fractions eluted at indicated temperature. [b] Including later fractions eluted at 80 °C with toluene. [c] Including later fractions eluted at 80 °C with dioxane.

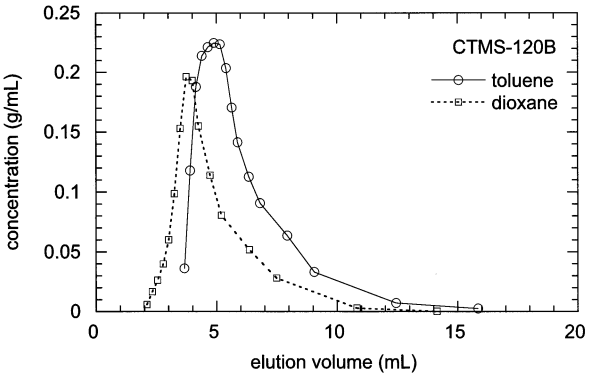

Figure 2. Polymer concentration in each fraction, plotted as a function of the elution volume since injection of the solution in HOPC separation of PCL22K in dioxane and toluene. A 0.228 g/mL solution in toluene and a 0.227 g/mL solution in dioxane were injected into a column packed with CTMS-120B in each separation.

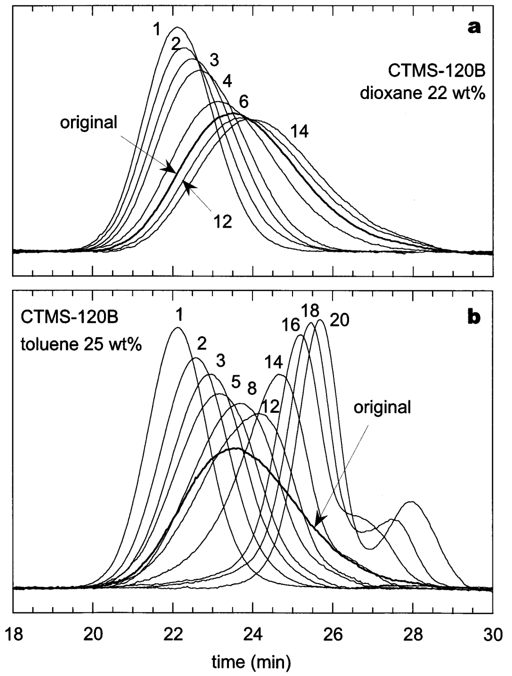

Figure 3. Chromatograms for some of the fractions obtained in HOPC separations of PCL22K in (a) dioxane and (b) toluene by the CTMS-120B column. The fraction number is indicated adjacent to each curve. The chromatogram of the original PCL22K is drawn as a thick line.

chromatogram is nearly identical to the injection volume in each separation, as required.

Two parts of Figure 3 compare SEC chromatograms for some of the fractions obtained in the two separations. Each chromatogram is normalized by the area under the peak. The chromatogram of the original PCL is also shown. The change in chromatogram in the dioxane separation is typical of HOPC in a good solvent:[1,2] Early fractions are enriched with high-MW components. With an increasing fraction number, the peak moves right and broadens. Fraction 8 (not shown) is nearly identical to the original polymer. Fraction 16 recoils to have a chromatogram not much different from that of the original polymer, but its mass is negligible. The trend is different in toluene. Early fractions have peak retention times close to the counterparts in the dioxane separation, but the MW distributions are much narrower. Middle fractions maintain a distribution narrower than that of the original PCL while the peak retention time shifts to a longer time. Apparently, overloading the column did not cause broadening in MW distribution. Fractions 17−20 were collected after raising the column temperature to 80 °C. It is interesting to see a multimodal nature in late fractions. Were it not for the tailing that extends beyond 28 min in the original PCL, low-MW peaks would be absent in these late fractions, and they should claim a much narrower distribution. The multimodal peaks, which may be due to transesterification during polymerization, do not clearly show in the chromatograms of the original PCL or of the fractions separated in dioxane.

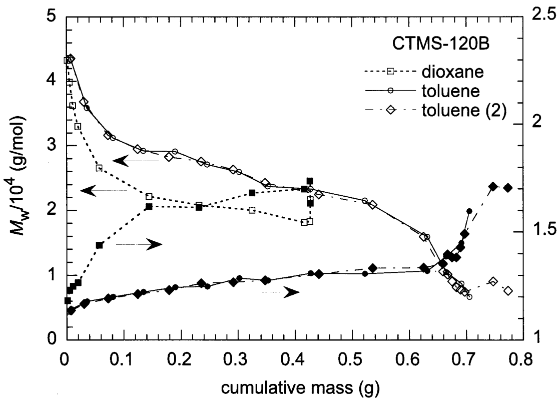

Figure 4. M_w (open symbols) and M_w/M_n (closed symbols) for fractions obtained in HOPC separations of PCL22K by CTMS-120B in dioxane (squares) and toluene (circles), plotted as a function of the cumulative mass of the polymer collected. Results for a second batch of separation in toluene under the same condition are shown by rhombuses.

The performance difference between the two solvents is obvious in Figure 4 which shows plots of M_w and M_w/M_n as a function of the cumulative mass of the polymer collected. Note that not all fractions were analyzed. The span in M_w is broader in toluene. M_w/M_n remains low except for late fractions that have low-MW tails in the chromatograms. No HOPC separations in the past had such small values of M_w/M_n for most of the fractions. The figure shows the plots for another batch of separation in toluene, the other conditions being identical, except that fractions 17−21 (300 drops each) were collected in a 10 deg increment from 40 to 80 °C in toluene and fractions 22 and 23 (300 drops each; the last two points at mass >0.7 g in the plot) were collected at 80 °C in dioxane. The plots for the two toluene separations overlap in each pair, indicating a good reproducibility even in the presence of weak adsorption of the polymer.

We define the narrowing index α by $(M_w/M_n)_1 = [(M_w/M_n)_0]^{\alpha}$, where $(M_w/M_n)_0$ and $(M_w/M_n)_1$ are the values of M_w/M_n of the original PCL and of fraction 1, respectively. Fraction 1 is singled out, because it has usually the smallest M_w/M_n. The index is 0.33 in the dioxane separation, which is one of the best results obtained in the good solvent condition.[2] The toluene separation has $\alpha = 0.26$. Despite the high resolution, the amount of polymer in the first fraction is not small. It is 7.8 mg, as opposed to a mere 1.3 mg in the dioxane separation.

HOPC with a Nonadsorptive Surface. Unlike CTMS-120B, the surface of C8-120B was repulsive to PCL in both dioxane and toluene. In toluene, the injection volume was not as large as that into the CTMS-120B column but still larger than that in dioxane. In the latter solvent, CTMS-120B and C8-120B had

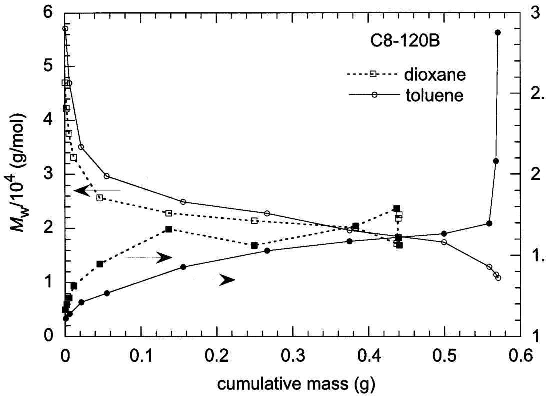

Figure 5. M_w (open symbols) and M_w/M_n (closed symbols) for fractions obtained in HOPC separations of PCL22K in dioxane (squares) and toluene (circles) with the C8-120B column, plotted as a function of the cumulative mass of the polymer collected.

similar injection volumes. The rise in the HOPC retention curve in toluene (not shown) was not as sharp as the one with CTMS-120B. The HOPC retention curves for the C8-120B column in the two solvents have a smaller tailing compared with the respective curves for the CTMS-120B column, indicating either repulsive surface of C8 or attractive surface of CTMS, even in dioxane. Both curves for the C8-120B column reached a plateau close to the concentration of the injected solution. The recovery was nearly 100% in both solvents. The SEC chromatograms obtained in the dioxane separation are similar to those in Figure 3a. There is a recoiling in fractions 15 and 16, but their masses are small. The chromatograms obtained in the toluene separation are between those in the two parts of Figure 3. Middle fractions are not as narrow as in Figure 3b, but multimodal components are visible in late fractions.

The separation performances in the two solvents are compared in Figure 5. Again, the separation is better in toluene with a broader span of M_w in separated fractions and a lower M_w/M_n values, although the difference is not as distinct as that for CTMS-120B in Figure 4. We then compare Figures 4 and 5. It is common to the two solvents that the first fraction has a higher M_w and a smaller M_w/M_n for the C8-120B column, but M_w quickly falls below that obtained with the CTMS-120B column and M_w/M_n becomes greater, compared at the same cumulative mass of polymer collected. The values of α are 0.30 and 0.21 in dioxane and toluene separations, respectively.

Concentration. We separated a 20.0 wt % solution of PCL22K by the C8-120B column. The HOPC elution curve (not shown) was similar to the one obtained for the 25.0 wt % solution except that the overall height was proportionally lower. The plots of M_w as a function of the cumulative mass of the collected polymer relative to the mass of the injected polymer nearly overlap for the two concentrations (not shown). The plot of M_w/M_n for the same abscissa is lower in the 20.0 wt % solution than it is in the 25.0 wt % solution. When plotted as a function of the cumulative mass fraction, the two M_w/M_n plots are nearly identical.

High Temperature. An increase in the temperature in a binary solution that has a UCST-type phase diagram makes the solvent quality better. In cyclohexane and decahydronaphthalane, for instance, polystyrene chains start to swell at temperatures higher than the Θ temperature.[10,11] Increasing the temperature is expected to make the solvent better to the polymer in the PCL–toluene system. The change in the polymer–solvent interaction is rather small, however.[10,11] We separated PCL22K in toluene and dioxane by CTMS-120B and C8-120B columns at 80 °C.

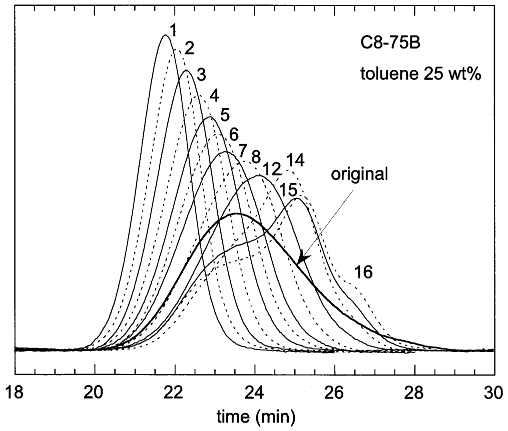

Figure 6. Chromatograms for some of the fractions obtained in HOPC separation of PCL22K in toluene by the C8-75B column. The fraction number is indicated adjacent to each curve. The chromatogram of the original PCL22K is drawn as a thick line.

The injection volume did not change appreciably except for a slight increase in the separation in toluene with the C8-120B column (Table 3). The recovery was greater but still less than 90% in the toluene separation with CTMS-120B. The retention curve has less tailing at 80 °C in each of the four surface–solvent combinations. In the toluene separation with CTMS-120B, the eluent concentration was higher than 0.2 g/mL in fractions 2–8. In the same solvent with C8-120B, the retention curve is slightly shifted to a shorter time. In the plot of M_w/M_n as a function of the cumulative mass, the data obtained at 80 °C are located slightly higher than those at 30 °C in toluene. In dioxane, the two plots are almost the same. Apparently, dioxane is sufficiently good to PCL at 30 °C. An increase in the temperature does not change the interaction any more. In toluene, the increase in the temperature resulted in weaker adsorption but slightly poorer separation.

HOPC by a Small Pore Size. The adsorptive nature of the CTMS surface was more obvious in the smaller pore size. In dioxane, the injection volume was typical of HOPC in a good solvent, and the recovery was nearly 100% with both the CTMS and C8 surfaces (Table 3). In toluene, however, only 76% of the injected polymer eluted from the CTMS-75B column before most of the adsorbed polymer was washed in dioxane at 80 °C. The lower recovery in the smaller pore is ascribed to its greater surface area. Although the injection volume was small, the recovery was 85% with the C8 surface that allowed a full recovery when the pore diameter was 130 Å. The difference will be discussed later. The tailing in the HOPC retention curve in toluene (not shown) is obvious both with the CTMS-75B and C8-75B columns. The peak concentration is close to that of the injected solution in dioxane but slightly lower in toluene. There is no plateau in the HOPC retention curve in any of the four surface–solvent combinations.

Figure 6 shows chromatograms for most of the fractions obtained in the separation of PCL22K in toluene with the C8-75B column. The narrowing index α is 0.18. From fraction 1 to fraction 16, the peak retention time

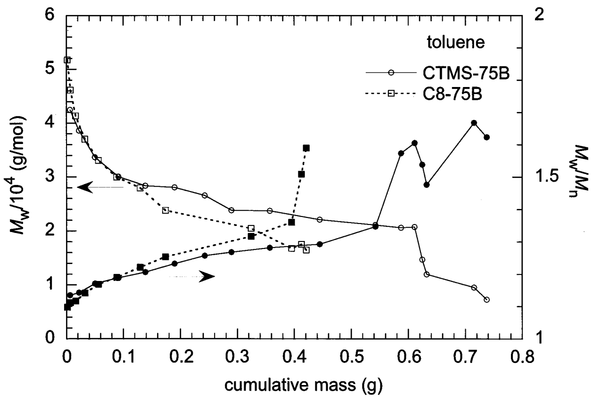

Figure 7. M_w (open symbols) and M_w/M_n (closed symbols) for fractions obtained in HOPC separations of PCL22K in toluene by CTMS-75B (circles) and C8-75B (squares), plotted as a function of the cumulative mass of the polymer collected.

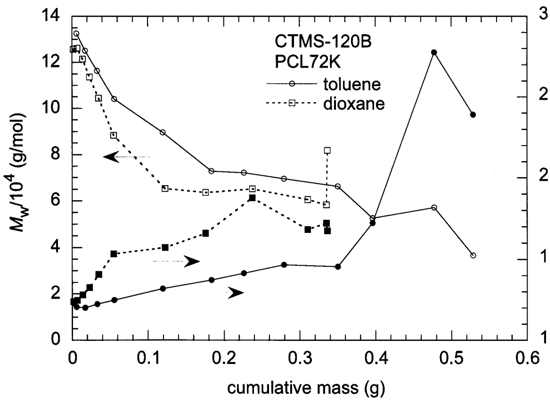

Figure 8. M_w (open symbols) and M_w/M_n (closed symbols) for fractions obtained in HOPC separations of PCL72K by CTMS-120B in toluene (circles) and dioxane (squares), plotted as a function of the cumulative mass of the polymer collected.

moves right and the width increases systematically. In the separation by CTMS-75B in toluene, chromatograms (not shown) of early fractions are similar to the counterparts in Figure 3b, but later fractions are similar to the counterparts in Figure 6. The value of α is 0.25. In the two dioxane separations, chromatograms of the separated fractions (not shown) are similar to those in Figure 3a. Recoiling is observed in the two separations.

The striking difference between the two solvents in the plot of M_w/M_n (Figure 4) was repeated in the CTMS-75B and C8-75B columns. Here we compare the two surfaces in the separation in toluene (Figure 7). The two humps in M_w/M_n in the last six fractions in the CTMS-75B column are due to washing in toluene at 80 °C, followed by dioxane at 80 °C. The less adsorptive C8-75B column has a greater M_w and a smaller M_w/M_n in early fractions. In middle fractions, the C8 surface has a greater M_w/M_n. Then, we compare the two pore sizes for the same surface chemistry and solvent (not shown). The plot of M_w as a function of the cumulative mass for fractions obtained in toluene with CTMS-75B nearly overlaps with the one in toluene with CTMS-120B. So does the plot of M_w/M_n. It appears that adsorption determines the plot of M_w/M_n. In dioxane, the smaller pore resulted in early fractions with a smaller M_w, in agreement with the past results of HOPC in good solvents.[2,3]

PCL72K. The other PCL sample (PCL72K) was separated in dioxane and toluene using the CTMS-120B column. Lower concentrations were enforced in the injected solutions to avoid a high viscosity. The adsorption was absent in dioxane but more serious in toluene compared with PCL22K: Only 70.7% of the injected polymer eluted in toluene at 30 °C. The tailing in the HOPC elution curve was more serious in both solvents compared with PCL22K. Figure 8 shows plots of M_w and M_w/M_n. Again, the resolution is better in toluene. In toluene, early fractions have a greater M_w and a smaller M_w/M_n. The latter increased gradually to 1.4 and then to 1.7 before the adsorbed polymer was released by washing in dioxane at 80 °C. The MW distribution in early fractions did not become as narrow as the one for PCL22K.

Discussion

In toluene, CTMS-75B was the most adsorptive, followed by C8-75B and CTMS-120B; C8-120B was the least adsorptive. None of the columns were too adsorptive in dioxane to decrease the recovery. When the surface was nonadsorptive, the Θ solvent provided the polymer with better separation than the good solvent did, in agreement with the result of the partitioning study by computer simulations.[5] The resolution was even better when the surface was slightly adsorptive. The good resolution persisted through all fractions. None of the fractions broadened the MW distribution to the level of the original polymer. Obviously, a weak adsorption helps HOPC maintain a high resolution throughout the separation. Our speculation is as follows:

When a polymer solution is injected into a weakly adsorbing column, the polymer starts to coat the pore surface. Once the first layer is made, further adsorption is not as easy. Formation of a second layer will be essentially the partitioning to the bonded stationary phase similar to the one occurring in regular normal-phase and reversed-phase liquid chromatography. Adsorption drops the concentration in the front end of the transported solution and delays the onset of the HOPC retention curve. The front end will experience a pore size of single-layer-coated pores. With an increasing concentration in the column for the portion of polymer solution that follows, the adsorbed layer thickens and the effective pore size decreases. The segregation boundary in the partitioning shifts to a lower MW. This mechanism of "self-adjusting pore size" will allow middle and late fractions to claim a narrower MW distribution compared with fractions that would have been obtained in the absence of adsorption. The excess loading in an adsorptive column provides a sufficient amount of polymer to coat the pore surface in layers. The pore size adjustment continues until all of the polymer elutes except the first layer. The first layer is removed when washed in good solvent.

The estimate of the average thickness of the adsorbed PCL layer supports the multilayer adsorption. The estimation uses the measured packing density of 0.55 (CPG particle volume relative to the column volume) and an assumption that the adsorbed layer is a solid with a density of 1.07 g/mL. The last column in Table 3 lists the estimates for the separation that showed significant adsorption. The layer is thinner at 80 °C compared with 30 °C and in the C8-column compared with the CTMS-column. PCL72K formed a thicker layer. The average thickness of 20 Å will be more than sufficient to form a fully coated layer. Furthermore, we find that the pore diameter decreases by adsorption. In

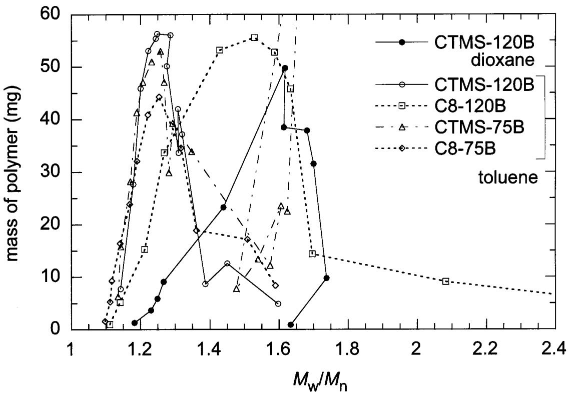

Figure 9. Mass of the polymer in each fraction is plotted as a function of $M_{\mathrm{w}}/M_{\mathrm{n}}$ for separations of PCL22K in toluene by CTMS-120B (open circles), in dioxane by CTMS-120B (closed circles), in toluene by C8-120B (open squares), in toluene by CTMS-75B (open triangles), and in toluene by C8-75B (open rhombuses).

CTMS-75B, the pore diameter decreases nearly to a half of the diameter before injection.

The above mechanism of adsorption is highly sensitive to the interaction between solvent and polymer. As the solvent becomes more attractive (or less repulsive) to the polymer, the second-layer adsorption will become more difficult, but the first-layer adsorption may still exist. The poorer separation at elevated temperatures can be explained by the proposed mechanism.

We also speculate that the narrow pore sizes used in the present study made it difficult for longer chains to be adsorbed into the pore, although they were thermodynamically preferred by the surface. In some separations in toluene, fractions were also collected when the column was washed with dioxane at 80 °C. None of the fractions had high-MW components. Apparently, the small pore opening prevented long polymer chains from being adsorbed. If a sufficiently long time is allowed for equilibration in each plate by employing a slow flow rate, then the landscape of partitioning may be different.

We cannot tell from the present study whether the adsorption alone improves the HOPC separation or not. All the separations in dioxane did not show adsorption.

The narrowing indices obtained in the dioxane separations of PCL22K and PCL72K were in line with those obtained earlier with other amorphous polymers.[2] In the Θ solvent, α was smaller compared with the good solvent, especially in the separation with the C8 surface. The smaller α with the C8 surface compared with the CTMS surface is ascribed to the absence of adsorption or to a weaker adsorption. When adsorbed polymer decreases the pore opening, HOPC loses a resolution toward high-MW components, undermining the narrowness in the early fractions. One step separation was sufficient to decrease $M_{\mathrm{w}}/M_{\mathrm{n}}$ of the first fraction to about $^{1}/_{5}$ power of $M_{\mathrm{w}}/M_{\mathrm{n}}$ of the original polymer.

Figure 9 compares the mass of polymer in each fraction, plotted as a function of $M_{\mathrm{w}}/M_{\mathrm{n}}$, for separations of PCL22K conducted in various conditions. A separation with points located upper left indicates a high efficiency. Starting at the lower left corner, the plot moves up and right then comes down in a typical separation. Note that not all fractions were analyzed, and later fractions collected more drops. In the plot for CTMS-120B in toluene, for instance, the mass jumps twice after $M_{\mathrm{w}}/M_{\mathrm{n}}$ exceeds 1.3. The jump is due to an increase in the number of drops collected. Plots for the other dioxane separations were similar to the one shown in the figure. The amount of polymer with a narrow MW distribution is by far greater in the toluene separations than it is in the dioxane separations. The advantage of HOPC in the Θ solvent is obvious. The weak adsorption improves the efficiency further. The CTMS-120B column is better than other columns in producing a greater amount. The C8-75B (and CTMS-75B, to a lesser extent) column is better in producing fractions in narrower MW distributions.

It is reasonable that C8 is more repulsive to PCL than CTMS is. The difference between the 130 Å pore and the 81 Å pore may be explained through imperfect substitution of surface silanols by the silanization agent. It is known that many surface silanols remain unreacted even after end-capping.[12] They will adsorb PCL, especially in nonpolar solvents such as toluene. It is likely that smaller and more tortured pore structures in the 81 Å pore have left more of its silanols unreacted compared with the 130 Å pore, and therefore its adsorption of PCL was stronger even with the C8 modification. By the same reason, a smaller fraction of surface silanols can react with octyldimethylchlorosilane in the 81 Å pore. The end-capping by CTMS leaves C8-75B with a lower C8 to CTMS ratio on the surface compared with the pore in C8-120B.

The separation of PCL72K was not as good as that of PCL22K. It may be because the pore size was too small or because the flow rate of 0.2 mL/min was too fast for mass transfer of these longer chains between the pore and the unconfined space.

Conclusions

A hallmark of HOPC under the Θ condition, especially with a weakly adsorbing surface, is its capability to churn out fractions with $M_{\mathrm{w}}/M_{\mathrm{n}} \sim 1.2$ from a polydisperse sample with $M_{\mathrm{w}}/M_{\mathrm{n}} \sim 1.7$ in a single step. This resolution was accomplished by using a single thin, short column. Collecting a fewer number of drops in each fraction may have decreased $M_{\mathrm{w}}/M_{\mathrm{n}}$ further. Past studies indicate that use of a longer or thicker column and of a bank of columns improves the resolution.[1,2] An increase in the column cross section does not change the back pressure if a proportionally increased flow rate is adopted, and therefore the separation time is the same. We are currently testing scaled-up HOPC of PCL22K in the Θ condition.

We proposed a mechanism of separation in HOPC in near-Θ condition. For the mechanism to be effective, a solvent that has a Θ temperature slightly below room temperature must be used as a mobile phase and to prepare a solution for injection. Another solvent must exist that is good at accessible temperatures to wash the column. For the surface, it will not be difficult to find surface moieties that are weakly adsorbing from a wide variety of silanization agents. It appears necessary to use theoretical formulation and computer simulations to substantiate the separation mechanism. Chromatographic methods proposed by Berek may be useful to gain insight into the phenomena of adsorption and displacement.[13]

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