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Phase Fluctuation Chromatography for Large-Scale Separation of Poly(styrene-*co*-acrylonitrile) by Chemical Composition

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ABSTRACT: We propose phase fluctuation chromatography (PFC) to separate a large amount of random copolymers into fractions with different chemical compositions. PFC is based on the tendency of a concentrated solution of the copolymer to separate into different phases, each of which is enriched with components of a specific composition. When the multiphase solution is injected into a column packed with porous materials that have specific moieties, domains rich in a component with greater affinity to (or less repulsion from) the surface will be retained longer than the domains rich in the other component. Styrene−acrylonitrile copolymers with different acrylonitrile contents were used as model copolymers. The compositions of fractions obtained were determined from IR spectra. A silanol or diphenyl surface retained styrene-rich components longer than the other components, whereas a cyano surface attracted acrylonitrile-rich components. The separation resolution was better when the pore had a large surface area and selective surface moieties and when selective solvents and higher concentrations were used.

Introduction

Statistical copolymers, produced by copolymerizing monomer mixtures, have a molecular weight distribution and a chemical composition distribution (CCD). Compositional heterogeneity can arise from composition fluctuations in the vicinity of a growing chain end and a change in the feed composition with increasing conversion.[1] The latter problem is serious for copolymers away from the azeotropic composition. Mixing problems and changes in reaction conditions by drifting temperature or decreasing initiator concentration may also affect CCD.

Physical properties of a copolymer are determined by the averages of molecular weight (MW) and chemical composition as well as by their distributions. Earlier, high osmotic pressure chromatography (HOPC) was developed[2−4] in our lab and has been used to fractionate various polymers according to MW. In the present paper, we show a novel method to fractionate copolymers by the chemical composition. A narrowed CCD may be required in some applications. In adhesion of a polymer A−polymer B interface by an A−B random copolymer,[5,6] for instance, it was found that there is a narrow range in the monomer ratio where the copolymer is effective in reinforcing the interface. We used here styrene−acrylonitrile (SAN) copolymer as a model copolymer. Thermodynamic properties of SAN blends have been studied intensively. It was found that, when SAN copolymers with different acrylonitrile (AN) contents are mixed, the blend forms a homogeneous phase until the difference in the AN content reaches about 5%.[7] Formation of uniform blends of a SAN copolymer with another polymer requires a narrow CCD for the SAN copolymer. As seen in these properties, the two monomers of the SAN copolymer have a strong incompatibility, which makes it an ideal copolymer for exploring a separation method with respect to the chemical composition.

There have been attempts to prepare a chromatographic calibration curve for composition analysis of SAN copolymers. They include column elution,[8] gradient high-performance liquid chromatography (HPLC),[9] and thin-layer chromatography (TLC).[10] These methods used, for analytical separation, either a SAN sample with an artificially broad CCD or a mixture of several SAN fractions with different AN contents. It is difficult, however, to isolate CCD from the effect of MW. Cross fractionation[11] by the size exclusion column and the HPLC column was developed to avoid the MW effect, but the inherent band broadening makes it difficult to evaluate the CCD accurately. Preparative separation was also attempted for a mixture of two SAN fractions with average AN contents of 21 and 23 wt % by using successive precipitation.[12] Note that closeness of the AN contents precludes separation by demixing of the solution. All of these separation methods employ low concentrations of the polymer. Therefore, these methods have a low processing capacity and consume a large amount of solvent. The chromatographic separation method we introduce here is based on the tendency of a concentrated solution of copolymer to separate into different microphases.[13] Each phase is enriched with components of a specific composition. We therefore term the method as phase fluctuation chromatography (PFC). Unlike other separation techniques, PFC has a large processing capacity.

Principle of Separation

The separation principle and operation of PFC are analogous to those of HOPC.[2−4] PFC involves partitioning of a nondilute solution of copolymer with CCD between a confined space in the porous materials and the surrounding solution. Strong repulsions between polymer chains at high concentrations, especially between those of different chemical compositions, will force components with greater affinity to (or less repulsion from) the pore surface to enter the pore at a greater proportion than at low concentrations. When the concentration is sufficiently high and the total pore volume is comparable to the volume of the exterior solution, then the pore will be crowded with those components to make the exterior solution deficient in

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Table 1. Characteristics of SAN Copolymers

polymer	source	wt % of AN	x_{AN}	M_w/1000	h_{Ph}/h_{CN}
SAN20	Asahi Chemical	20	0.33	198	1.288 ± 0.022
SAN25	Aldrich	25	0.39	184	0.948 ± 0.006
SAN29	Asahi Chemical	29	0.44	195	0.772 ± 0.011
SAN30	Aldrich	30	0.46	211	0.741 ± 0.012
SAN40	Asahi Chemical	40	0.57	137	0.484 ± 0.004

Table 2. Characteristics of Controlled Pore Glasses

code	source	pore diameter (Å)	particle size (mesh)	surface area (m^2/g)	pore volume (mL/g)
CPG350C	CPG, Inc.	364	200/400	48.9	0.77
CPG500B	CPG, Inc.	500	120/200	39.7	0.97
CPG1000B	Haller	1073	100/200	31.2	1.32
CPG3000C	CPG, Inc.	2860	200/400	6.3	0.71

them. In effect, there will be a segregation between the pore space and the surrounding solution with respect to the chemical composition. It is easy to expect that the segregation will be more effective if the solution is phase-separated or, in the single phase, the correlation length is greater than the pore size. We can also expect that accommodation of the surface-preferred components will be more effective if the solvent is poorer for those components than for the other components. PFC will therefore benefit from the dependence of the solubility on the chemical composition.

When the phase-separated solution is injected into a column packed with porous materials that have specific surface moieties, domains rich in a component with greater affinity to the surface will be retained longer by the pore than the domains rich in the other component. The separation at high concentrations is repeated as the mobile phase is transferred along the column. The front end of the transported mobile phase repeatedly sheds surface-preferred components as it approaches the column outlet and thus becomes purer in the other components. The concentration of the front end will drop in the process, but it will not degrade its purity; the partitioning at low concentrations also contributes to separation, although it may not be as efficient as the one at high concentrations. The following portion of the mobile phase has to drive the components into the stationary phase that already has some of them, and it becomes less easy to remove the components from the mobile phase. As a result, later fractions will decrease the purity. Toward the end of the processing, components initially retained by the stationary phase will be eluted. The injected solution has to be sufficiently concentrated, and the injection volume has to be sufficiently large to maintain the high-concentration condition throughout the processing. As in HOPC, the advantage of PFC will be its ability to produce a sizable amount of purified copolymer in early fractions.

Earlier, a solution of two homopolymers in a common solvent—polystyrene (PS) and poly(vinyl chloride) (PVC) dissolved in THF at 23 wt % (total)—was separated by a similar method.[14] Unmodified porous glass with pore size 286 nm was used. The early eluent was close to pure PVC, and the late eluent was close to pure PS. The change of the composition in the eluent was gradual. PS was apparently retained longer by the silanol-rich surface. However, a systematic study of the PFC under various conditions such as the surface chemistry, pore size, solvent, and concentration was not conducted. Here, we will show results of fractionation for SAN copolymers under the different separation conditions.

Experimental Section

Materials. Three fractions of SAN copolymer, SAN20, SAN29, and SAN40, were received from Asahi Chemical. Lubricant on the surface was removed by washing in methanol. Two fractions, SAN25 and SAN30, were purchased from Aldrich and used as received. Table 1 shows characteristics of the five SAN samples. Data for the weight percentage of acrylonitrile (AN) were supplied by the manufacturer or supplier. The molar fraction of the AN content, x_{AN}, was calculated from the weight percentage. The weight-average molecular weight, M_w, with respect to polystyrene standards was measured in size exclusion chromatography. Data in the last column will be explained below. These copolymer fractions are expected to have a narrow CCD. Assuming a statistical copolymer, the standard deviation in x_{AN} is estimated to be around 0.010. Then it will be difficult to characterize CCD for these fractions in conventional chromatographic analysis.

Silanization agents, diphenylmethylchlorosilane and (3-cyanopropyl)dimethylchlorosilane, were purchased from Gelest. Tetrahydrofuran (THF, HPLC grade) and dioxane were from EM Science; methyl ethyl ketone (MEK) was from J. T. Baker. Methanol, from EM Science, was filtered before use. Controlled pore glasses (CPG)[15] are gifts from CPG, Inc. or Dr. Haller at NIST. Table 2 shows characteristics of the CPG used. The data were supplied from the manufacturers.

Surface Treatment of CPG. The CPG samples were first soaked in concentrated nitric acid at 50−60 °C overnight and rinsed thoroughly with deionized water. Then they were dried in a convection oven and in a vacuum oven. These CPG samples have a surface rich in silanols and therefore are coded as CPGxxxx-OH. We also prepared surface-derivatized CPG. Diphenylmethylsilane-substituted CPG, coded as CPGxxxx-Ph, was prepared by reacting the acid-washed, dried CPG in a solution of diphenylmethylchlorosilane in toluene (2 M) at 50−60 °C under nitrogen for 72 h. Unreacted silanols were end-capped with chlorotrimethylsilane. The silanation reaction was quenched by adding methanol. Subsequently, the CPG beads were washed with methanol. The beads were then dried in the convection oven at 50 °C overnight and at 210 °C in a vacuum oven for 1 h. (3-Cyanopropyl)dimethylsilane-substituted CPG, coded as CPGxxxx-CN, was prepared in the same way except that (3-cyanopropyl)dimethylchlorosilane was used as a silanation agent.

The surface modification was verified by FT-IR (4000−2000 cm^{-1}) using a packed bed of the modified CPG immersed in carbon tetrachloride in an IR-grade silica cell of path length 1 mm. CPGxxxx-Ph showed multiple bands at 3100−3000 cm^{-1} indicative of aromatic C−H stretching. CPGxxxx-CN absorbed around 2260 cm^{-1}, ascribed to the C≡N vibration. In comparison, CPGxxxx-OH showed a strong adsorption only at around 3500 cm^{-1}.

Column Packing. Stainless steel columns (Isolation Technologies) of dimension 300 mm (length) × 3.9 mm (interior diameter) were packed with various grades of CPG with different surface functional groups and different pore sizes. The packing procedure is described elsewhere.[2]

Solvent Quality. SAN copolymers of different AN contents were dissolved in dioxane or MEK at different concentrations. Solutions in MEK were clear for all of the copolymers up to 25 wt %. A solution of SAN40 in dioxane was cloudy even at a concentration as low as 5 wt %. SAN copolymers with the lower AN contents, however, formed clear solutions in dioxane up to 16 wt %. These observations indicate that MEK is nonselective but dioxane is selective (poorer to AN-rich components). These solutions of single SAN fractions do not macroscopically phase separate for at least several months.

Model Copolymer. Mixtures of two copolymer fractions were used here as a model copolymer that has a bimodal CCD to study the PFC performance. For these mixtures, PFC may not be the optimal separation method. A SAN20/SAN40 mixture and a SAN29/SAN40 mixture in MEK at a total

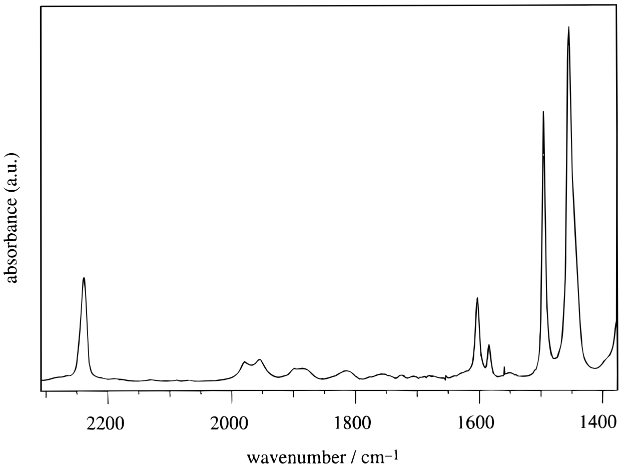

Figure 1. IR absorption spectra of SAN29.

concentration of 21 wt % phase separated macroscopically over time. Then, demixing is certainly the optimal method. The method cannot be used, however, for a SAN25/SAN30 mixture at a total concentration of 16 wt % in dioxane, which remained in single phase at least for several months.

Instrumentation. A standard system of HOPC, comprising a high-pressure liquid pump (SSI, AcuFlow series II), a packed column, a fraction collector (Eldex, model 1243) with a drop counter, and a differential refractometer (Waters, model R401), was used for PFC. Prior to injection of the polymer solution in each batch, the column was washed with the same solvent as the one used to dissolve the polymer. A concentrated solution of SAN was injected from a vial through the pump into the column at a nominal rate of 0.3 mL/min (the actual rate was lower). Because a mixture of two SAN samples with different AN contents tended to separate macroscopically, the vial was shaken vigorously to prevent the separation while injecting. When the polymer was detected at the outlet, the injection was switched to the pure solvent (same solvent as used to dissolve the copolymers). Typically around 3 g of the solution was injected, about 60% more than the amount injected in HOPC. The eluent was collected into different test tubes. The solvent injection was continued at 0.3 mL/min until no more polymer eluted. 15 drops were collected in each test tube in fractions 1 to 5. Fractions 6 to 8 collected 30 drops each, fractions 9 to 14 collected 50 drops each, and fraction 15 collected 150 drops. In most of the separations, the viscosity was the highest in fractions 3 to 5. Middle to late fractions were always cloudy. Early fractions were clear or cloudy, depending on the solvent and the composition of copolymer in them. It took less than 2 h to complete the whole process.

Analysis of Molecular Weight. The molecular weight distribution was analyzed for some of the fractions by using a Waters analytical size exclusion chromatography (SEC) system with a Model 510 HPLC pump and a Model 410 differential refractometer. Columns (Phenomenex) packed with Phenogel (5 μm) of pore sizes 10^3, 10^4, and 10^5Å were used. The columns were housed in a column heater thermostated at 35.0 °C. The mobile phase was THF, and the flow rate was 1.0 mL/min. The columns were calibrated with polystyrene standards purchased from Pressure Chemical.

Measurement of Average AN Content. The average AN contents of fractions collected as well as the original SAN samples were determined from FT-IR spectra. SAN solutions were cast into films on polished KBr disks (25 mm × 5 mm, Wilmad) and then dried in a vacuum at 50 °C for more than 45 min. The IR spectra were measured by using a Mattson Cygnus-100 FT-IR spectrometer. Figure 1 shows an example of the IR spectra (SAN29). The isolated peak around 2239 cm^{-1}, due to C≡N stretching, was selected to estimate the AN content in the sample. Sharp bands near 1605, 1584, 1495, and 1454 cm^{-1} are characteristic of phenylene rings. The peak around 1605 cm^{-1}, free from absorption of methylene groups in the chain backbone, was selected to represent the styrene content. The ratio h_{Ph}/h_{CN}, where h_{Ph} and h_{CN} are the peak heights at 1605 and 2239 cm^{-1}, is expected to be proportional to the molar ratio x_{ST}/x_{AN}, where $x_{ST} = 1 - x_{AN}$.

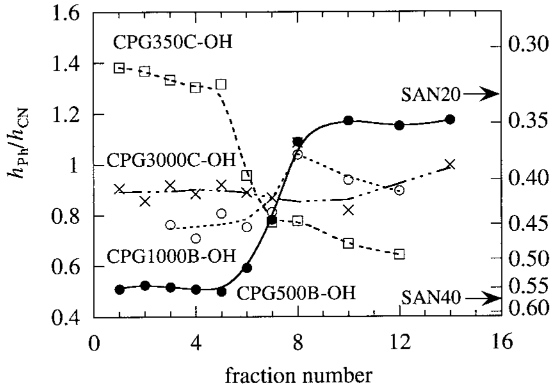

Figure 2. Pore size and surface area dependence of PFC. A 16 wt % (total) solution of a mixture of SAN20 and SAN40 (1:1, w/w) in dioxane was separated. The peak height ratio h_{Ph}/h_{CN} is plotted as a function of the fraction number. The lines are shown for convenience. The column packing materials are CPG350C-OH (open squares), CPG500B-OH (closed circles), CPG1000B-OH (open circles), and CPG3000C-OH (crosses). The right ordinate shows the corresponding x_{AN}. The arrows indicate the values of x_{AN} measured for SAN20 and SAN40.

Calibration. To verify the proportionality between h_{Ph}/h_{CN} and x_{ST}/x_{AN}, we measured the IR spectra for SAN20, SAN25, SAN29, SAN30, and SAN40. The results are listed in Table 1. When h_{Ph}/h_{CN} is plotted as a function of x_{ST}/x_{AN}, the data points are on a straight line through the origin, given by $h_{Ph}/h_{CN} = 0.625 \times x_{ST}/x_{AN}$. The root-mean-square deviation (relative) is 0.0104. The proportionality allows us to estimate x_{AN} from the h_{Ph}/h_{CN} reading for each separated fraction.

Results and Discussion

Pore Size and Surface Area. PFC needs porous materials with surface moieties that have a sufficiently strong influence on the solution in the entire pore volume. The larger the surface area, the higher the number of surface moieties and the stronger the interaction between the pore wall and the polymer. It is also necessary to avoid the size exclusion effect by the pores. These two requirements are inconsistent, because porous materials with a smaller pore diameter have a greater surface area-to-volume ratio. There will be an optimal pore size for separation of a given copolymer. To find the optimal pore size, four columns packed with CPG350C-OH, CPG500B-OH, CPG1000B-OH, and CPG3000C-OH were prepared. The surface area of these grades of CPG ranges between 6.3 and 48.9 m^2/g. A 16 wt % (total) solution of a mixture of SAN20 and SAN40 (1:1 w/w) in dioxane was used for injection.

Figure 2 compares the results by the four columns. The peak height ratio h_{Ph}/h_{CN} is plotted as a function of the fraction number for fractions analyzed. Some early fractions are missing because of premature collection of the eluent. In the separation with CPG1000B-OH, for example, fraction 3 is in practice the first fraction with polymer. The right ordinate shows the corresponding x_{AN}. The arrows indicate the values of x_{AN} measured for original SAN20 and SAN40. For the separation with CPG 500B-OH, h_{Ph}/h_{CN} increased stepwise from a near SAN40 value to a near SAN20 value. Apparently, early fractions mainly contain SAN40, and late fractions contain SAN20. Silanol groups on the surface of CPG retained domains rich in styrene longer than those rich in acrylonitrile.

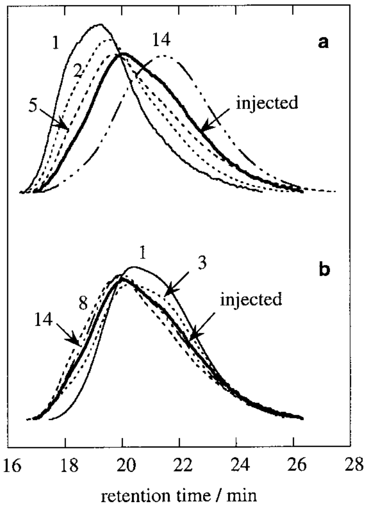

Figure 3. SEC chromatograms for some of the fractions obtained in PFC. A 16 wt % (total) solution of a mixture of SAN20 and SAN40 (1:1, w/w) in dioxane was separated by (a) CPG350C-OH and (b) CPG500B-OH. The fraction numbers are indicated adjacent to the curves. The elution curve of the injected sample is also shown.

The separation with CPG1000B-OH is poorer, although h_{Ph}/h_{CN} tends to increase with fraction number. There is almost no separation with CPG3000C-OH. The larger the surface area, the better the separation performance, except for CPG350C-OH. It has the largest surface area, but its separation trend is opposite to the others. Components of SAN20 ($M_w = 1.98 \times 10^5$) eluted earlier than those of SAN40 ($M_w = 1.37 \times 10^5$). To see the effect of size exclusion with CPG350C-OH, we characterized some of the fractions by SEC. The chromatograms in Figure 3a show that the average MW decreased as the fraction number increased, although the resolution was worse than is typical in separation by HOPC. Apparently, the size exclusion superseded the segregation by the chemical composition in the separation with CPG350C-OH.

In the separation with CPG500B-OH (Figure 3b), in contrast, fractions collected showed only a slight difference in the MW distribution. Early fractions had a lower peak MW, whereas late fractions had a higher MW compared with the injected sample. The size exclusion was suppressed in this separation. Since SAN40 that eluted earlier has a lower average MW than SAN20 does, it is reasonable that early fractions have a lower peak MW. We expect that there would be little size exclusion effect in the separations with CPG1000B-OH and CPG3000C-OH. We thus find that CPG500B provides the optimal pore size for the SAN fractions used. Other studies shown below were therefore conducted by using CPG500B.

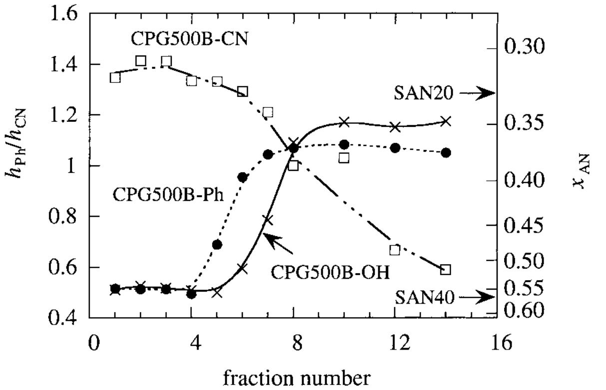

Figure 4. Surface chemistry dependence of PFC. The same solution as used in Figure 2 was separated by three columns packed with CPG500B-CN (open squares), CPG500B-OH (crosses), and CPG500B-Ph (closed circles).

Surface Chemistry. Surface chemistry is key to successful separation by PFC. The resolution depends critically on the interactions between polymers of different chemical compositions and between polymer and the surface moieties. Here we compare separations by CPG500B-Ph, CPG500B-CN, and CPG500B-OH. A 16 wt % solution of a mixture of SAN20 and SAN40 (1:1 w/w) in dioxane was injected into the three columns. Figure 4 shows h_{Ph}/h_{CN} as a function of the fraction number. The pattern is different between CPG500B-CN and the other columns. Surface phenyl moieties and hydroxyl moieties retained components rich in styrene longer than those rich in AN. The peak height ratio is almost constant for early fractions and increases to another plateau for late fractions. The shift takes place later with CPG500B-OH compared with CPG500B-Ph, and the second plateau level is higher. In contrast, the surface cyano groups provided less repulsion to components rich in AN than to the other components, leading to segregation of the AN-rich phase to the pore space and the styrene-rich phase to the mobile phase. Although the change in x_{AN} is more gradual compared with other surfaces, the span in x_{AN} in the separated fractions is greater. Early fractions contained less AN compared with SAN20. The gradual change in x_{AN} in the early fractions resulted because CPG500B-CN separated not only SAN20 from SAN40 but also AN-rich components of SAN20 from the other components of SAN20.

The pattern of a change in h_{Ph}/h_{CN} with increasing fraction number was repeated in the separation of a SAN29 and SAN40 mixture (1:1, w/w) as a 16 wt % solution in dioxane (not shown). When the CPG500B-CN column was used, the values of h_{Ph}/h_{CN} for initial fractions were larger than the value for SAN29. In separation with the CPG500B-Ph column, the increase in h_{Ph}/h_{CN} was stepwise. In the separation of a SAN20/SAN29 mixture (1:1, w/w) in dioxane at 16 wt % by the CPG500B-Ph column, h_{Ph}/h_{CN} increased gradually from 0.80 to 1.10 with an increasing fraction number. In the separation of a SAN25/SAN30 mixture in dioxane at 16 wt % with the CPG500B-Ph column, h_{Ph}/h_{CN} increased from 0.71 to 0.91. In contrast to the separation of SAN20/SAN40 by the same column, the increase in h_{Ph}/h_{CN} was not stepwise in the last two separations, indicating a weaker segregation between two copolymers of closer compositions.

The three columns packed with CPG500B-Ph, CPG500B-CN, and CPG500B-OH were used to separate a 16 wt % solution of SAN20 in dioxane. The results of separation are shown in Figure 5. The ratio h_{Ph}/h_{CN} increased with an increasing fraction number when CPG500B-Ph was used, whereas the ratio decreased for CPG500B-CN. CPG500B-OH showed no discernible trend. The span in x_{AN} was the greatest with the cyano surface, a result similar to the one for a mixture of SAN20 and SAN40. We cannot evaluate the distribution in x_{AN} for each separated fraction, however. We are therefore unable to say that PFC narrowed CCD, although it appears likely.

When the same three columns were used to separate SAN40 dissolved in dioxane at 16 wt %, it was only with

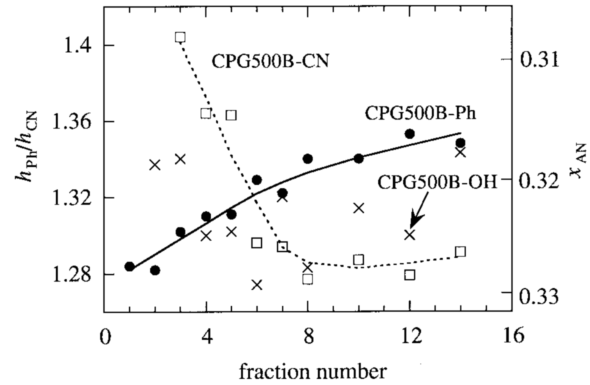

Figure 5. Surface chemistry dependence of PFC. A 16 wt % solution of SAN20 in dioxane was separated by three columns packed with CPG500B-CN (open squares), CPG500B-OH (crosses), and CPG500B-Ph (closed circles).

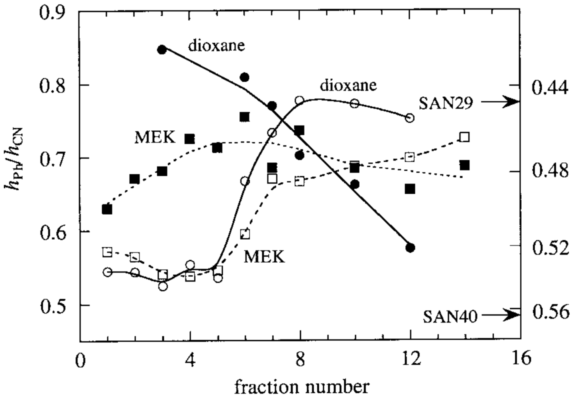

Figure 6. Solvent dependence of PFC. A mixture of SAN29 and SAN40 (1:1, w/w), dissolved in dioxane (closed circles) and in MEK (closed squares), was separated with CPG500B-CN. The same mixture, dissolved in dioxane (open circles) and in MEK (open squares), was separated with CPG500B-Ph.

CPG500B-CN that a systematic trend in h_{Ph}/h_{CN} was shown for the separated fractions. The ratio h_{Ph}/h_{CN} decreased from 0.533 to 0.487 (x_{AN} increased from 0.540 to 0.562) with an increasing fraction number (not shown).

In the above two separations of individual SAN fractions, the span in x_{AN} in the fractions separated with CPG500B-CN is about twice as large as the standard deviation expected for a statistical copolymer of the given degree of polymerization. The agreement may lead to a possible application of PFC for the analysis of CCD.

As mentioned in the section for the separation principle, use of a column with a surface less repulsive to and of a solvent poorer for one component of the copolymer mixture makes a better separation. This is the case with the cyano surface and dioxane, not with the phenyl surface and dioxane.

Solvent. A selective solvent may segregate SAN copolymers of different compositions more sharply compared with a nonselective solvent. Here we compare MEK and dioxane. Dioxane is not as good a solvent as MEK, especially to SAN copolymers with a high AN content. A mixture of SAN29 and SAN40 (1:1 w/w) was dissolved in each of the two solvents. The concentration was 16 wt % in dioxane and 21 wt % in MEK. The two concentrations are almost equal in mass/volume (about 0.167 mg/mL). Figure 6 compares the two sets of separations using dioxane and MEK when CPG500B-CN and CPG500B-Ph were used as separation media. When the CPG500B-CN column was used, h_{Ph}/h_{CN} for the separation in dioxane decreased with fraction number, whereas it was scattered in the separation with MEK. When the CPG500B-Ph column was used, both dioxane and MEK separations showed a stepwise increase in h_{Ph}/h_{CN} with an increasing fraction number, but the span in the ratio was larger for dioxane than it was for MEK. Thus a selective solvent was found to result in a better separation than a nonselective solvent in both cyano and phenyl surfaces. We also find that the good separations obtained with CPG500B-CN in dioxane (Figures 4 and 5) were helped more by a poor quality of the solvent to AN-rich components than by a difference in the pore wall–monomer interaction between copolymers of different AN contents.

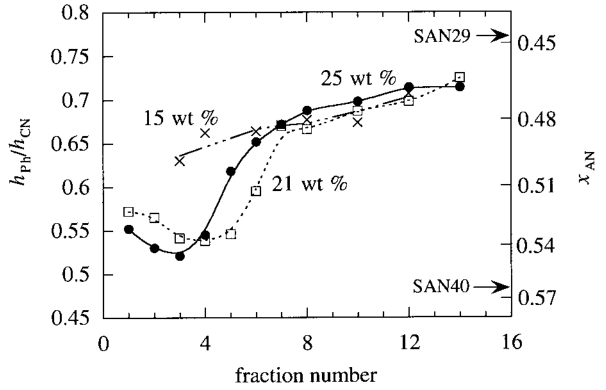

Figure 7. Concentration dependence of PFC. A mixture of SAN29 and SAN40 (1:1, w/w) was dissolved in MEK at total concentrations of 25 wt % (closed circles), 21 wt % (open squares), and 15 wt % (crosses). CPG500B-Ph was used as a separation medium.

Concentration. A higher concentration will result in a stronger segregation. Figure 7 demonstrates the concentration effect on the separation in MEK. A mixture of SAN29 and SAN40 (1:1 w/w) was dissolved in MEK at total concentrations of 25, 21, and 15 wt %. When left overnight, the first two solutions separated into two phases, but the 15 wt % solution remained in a single phase. The 25 wt % concentration resulted in the best separation with the largest span in h_{Ph}/h_{CN}, followed by the 21 wt % solution. Separation at 15 wt % was poor. Injection of the two-phase solution resulted in a much better separation compared with the injection of the single-phase solution. We also compared separations with CPG500B-Ph for an equal mass mixture of SAN20 and SAN40 in dioxane at 16 and 10 wt % (total). At 16 wt %, h_{Ph}/h_{CN} showed a stepwise increase from 0.51 for the initial fractions to about 1.08 for the late fractions (see Figure 2). The 10 wt % solution resulted in a poorer resolution (not shown). h_{Ph}/h_{CN} showed only a gradual increase from 0.76 to 0.90. These results indicate that the higher the concentration, the better the separation, as long as the pump and column can withstand the high back-pressure that increases with increasing concentration.

There is a decreasing trend in h_{Ph}/h_{CN} in early fractions before it increases for separations in MEK at 21 and 25 wt %. This trend is absent or weak in the separations in dioxane. We consider that the decreasing trend was caused by dilution of the front end of the polymer solution transported in the column. For the portion of the solution that follows, the concentration did not decrease as much. As shown in the separation principle, the segregation is sharper at higher concentrations. When the solvent does not help in differentiating copolymers of different compositions, the concentration will be a dominant factor to determine the sharpness of segregation.

Conclusions

We have shown that PFC can separate SAN copolymers according to the chemical composition. We applied here PFC to a mixture of two copolymer fractions and to a single copolymer. It will be interesting to see the results of PFC when the mixture consists of three or more fractions. For PFC to become a universal separation method, it is necessary to show that other random copolymers and block copolymers can be separated as well.

In the present study, we did not carry out a systematic study to optimize the resolution. Use of other surface modifications and other solvents may further improve the resolution. The large surface area (but the pore size should be sufficiently large to avoid size exclusion effect), selective surface moieties, selective solvents, and high concentrations are favored for a better separation resolution. The results would be explained within the proposed separation mechanism. To examine the mechanism more closely, it is necessary to study the partitioning itself in experiments.

As mentioned earlier, we may be able to use PFC also for analytical purposes, for instance, to characterize CCD and to estimate interactions between polymer and various surfaces. For these purposes, injection of a concentrated solution in a narrow band and a uniform transport of the solution band along the column will be necessary.

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