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Molecular Weight-Sensitive Separation of a Bimodal Polymer Mixture Using Nanoscale Porous Materials

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ABSTRACT: We present a novel scheme for the fractionation of polydisperse polymers in solution. The molecular weight-sensitive separation utilizes nanoscale porous materials. The entropy of a polymer chain that diffuses within the pore is significantly reduced compared with a chain in the free solution. This effect is used in the scheme, in which a semidilute solution of a polymer with a bimodal molecular weight distribution (for illustration) is allowed to equilibrate with the porous material saturated with pure solvent. The high osmotic pressure of the solution and the sharp dependence of the entropy reduction on molecular weight drive the low molar mass fraction preferentially into the pore channels. The high molar mass fraction remains outside. After equilibrium is reached, the external solution is thus enriched in the high molar mass fraction and can be extracted with high yield and in high purity. Concomitantly the solution in the interior of the pores retains the low molar mass fraction also with high purity. When the porous material is allowed to subsequently contact the pure solvent, we can recover the low molar mass fraction from the external solution after the second equilibrium. We estimate the efficiency of this fractionation scheme and propose protocols to be followed for an optimal separation.

Introduction

The totally satisfactory fractionation of polydisperse polymer with respect to molecular weight has been a longstanding problem. Because there is little difference in the chemical properties for polymers of differing molecular weight, effective fractionation has been one of the most difficult tasks in physical chemistry. The most effective route to a monodisperse polymer has been, so far, to synthesize narrow-distribution polymers, thereby circumventing the inefficient physical separation process. Such a synthesis, however, is not always available and is invariably accompanied by increased cost. The number of polymer species available in narrow molecular weight fractions is still very limited.

In this contribution, we present a protocol for the molecular weight-sensitive separation of polydisperse polymers in solution by using porous materials, with pore sizes comparable to the dimensions of the polymer chains. The nanoscale porous materials, provided that their surface is inert, accommodate the chains with a purely geometrical confinement, thus decreasing the configurational entropy of the chain.[1] For illustration, we consider here a bimodal mixture of polymers differing only slightly in molecular weight. Each fraction is regarded as strictly monodisperse; the solvent is considered to be good for both fractions. In a recent contribution, we considered the equilibria in a solution of such a mixture between the interior of a porous medium and the exterior.[2] It was demonstrated theoretically that the low molar mass fraction is constrained in the narrow pore channels while the high molar mass fraction remains outside, provided that the concentration of the latter exceeds its overlap concentration in the exterior solution. The partition coefficient, defined as the ratio of the concentration of the fraction in the interior of the pore to that in the exterior solution, was found to exceed unity for the low molar mass fraction; this inversion in the partitioning, of course, is not possible for a monodisperse polymer solution. In the calculation, we assumed that the volume of the bulk solution in contact with the porous material is much larger than the volume accessible to the solution in the interior of the pore.

The purpose of the present contribution is to apply the results contained in our previous contribution to an example: the separation process of a bimodal polymer mixture in solution into fractions of different molecular weights. After restating the underlying principles for the concentration equilibria for each fraction between the interior of the pore and the exterior, we will show the results of the calculation for the separation process. Two processes, respectively to extract the high and the low molar mass fractions, are carried out consecutively. We will evaluate the efficiency of each process in terms of improvement in the purity of the separated fraction and in terms of the recovery ratio of the fraction. It will be shown that, in the proposed scheme, a bimodal polymer mixture with an initial polydispersity index as low as 1.01 can nevertheless be fractionated in high yield to a material with an index even closer to unity.

Partitioning of a Bimodal Polymer Solution

Before presenting our prescription for the separation process, we first outline principles for the partitioning of each fraction of the polymer mixture between the solution in the interior of the pore and that in the exterior. Details have been given in our previous contribution.[2]

Let N_i be the degree of polymerization and c_i be the number concentration of fraction i in the polymer mixture in the solution (i = H, high molar mass fraction; i = L, low molar mass fraction). The corresponding reduced concentration X_i is defined by $X_i = \alpha_C(c_i/c_i^*)$, with $\alpha_C \cong 3.49$.[3,4] Here c_i^* is the overlap concentration of the fraction i in its unimodal solution and is related to $R_{gi}^{(0)}$, the radius of gyration of the isolated chain by $c_i^*\,(2^{1/2}R_{gi}^{(0)})^3 = 1$.[3] We also use the monomer concentration $w_i = N_i c_i$. In the following, we use these three definitions of concentration interchangeably for quantities with additional subscripts such as c_{i0}, X_{iI}, and w_{iE} (i = H, L), where 0, E, and I denote the original solution, the solution in the interior of the pore, and the solution in the exterior, respectively.

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When a solution of the polymer mixture is added to a vessel containing the porous materials, some of the polymer chains migrate into the pore channels (partitioning). The equilibration of the concentrations $c_{i\mathrm{I}}$ and $c_{i\mathrm{E}}$ of the fraction i in the interior of the pore and in the exterior, respectively, is governed by[2]

$$\ln c_{i\mathrm{E}} + I(X_\mathrm{E};\beta_\mathrm{E}) = \ln c_{i\mathrm{I}} + I(X_\mathrm{I};\beta_\mathrm{I}) + \Delta S_i/k_\mathrm{B} \qquad (i = \mathrm{H, L}) \quad (1)$$

where ΔS_i is the decrease in the configurational entropy of a chain of the fraction i in the pore with respect to the chain in the exterior and k_B is the Boltzmann constant. The interaction $I(X;\beta) \equiv P(X;\beta) - 1 + \int_0^X x^{-1}[P(x;\beta) - 1]\,\mathrm{d}x$ vanishes at $X = 0$, where $P(X;\beta)$ is the reduced osmotic pressure defined by $P(X;\beta) \equiv \Pi/ck_\mathrm{B}T$ with Π the osmotic pressure, c the total number concentration of the polymer, and T the temperature. The total reduced concentrations X_I and X_E in the interior of the pore and in the exterior are related to the reduced concentrations for each fraction by

$$X_j^{1/3}\nu = (1 + c_{\mathrm{L}j}/c_{\mathrm{H}j})^{1/3\nu-1}[X_{\mathrm{H}j}^{1/3\nu} + (c_{\mathrm{L}j}/c_{\mathrm{H}j})^{1-1/3\nu}X_{\mathrm{L}j}^{1/3\nu}] \qquad (j = \mathrm{E, I}) \quad (2)$$

where $\nu \cong 0.588$ and the subscripts E and I again denote the exterior and the interior of the pore. Similarly, the polydispersity index β_j (j = E, I) of the solution defined as $\beta \equiv \langle N^2\rangle/\langle N\rangle^2$, where N is the degree of polymerization, and $\langle ... \rangle$ is the average with respect to its distribution in the solution, is given by

$$\beta_j = \frac{(1 + c_{\mathrm{H}j}/c_{\mathrm{L}j})[1 + (c_{\mathrm{H}j}/c_{\mathrm{L}j})m_N^2]}{[1 + (c_{\mathrm{H}j}/c_{\mathrm{L}j})m_N]^2} \qquad (j = \mathrm{E, I}) \quad (3)$$

in the exterior and in the interior, where $m_N \equiv N_\mathrm{H}/N_\mathrm{L}$.

The partition coefficient p_i of the fraction i is defined by $p_i \equiv c_{i\mathrm{I}}/c_{i\mathrm{E}} = X_{i\mathrm{I}}/X_{i\mathrm{E}}$ (i = H, L). We consider that the pore is of cylindrical shape with radius R_P and that the extension of the polymer chain is not excessively large compared with R_P. Applying the results of a calculation of the confinement entropy ΔS_i for a Gaussian chain to a real chain in a good solvent,[5] ΔS_i is expressed as

$$\Delta S_i/k_\mathrm{B} = -\ln f((R_{\mathrm{g}i}^{(0)}/R_\mathrm{P})R(X_\mathrm{I};\beta_\mathrm{I})) \qquad (i = \mathrm{H, L}) \quad (4)$$

where $R(X;\beta) = R_{\mathrm{g}i}/R_{\mathrm{g}i}^{(0)}$ is the contraction factor of the chain due to the screening of the excluded volume, and

$$f(x) = 4\sum_{m=1}^{\infty} b_m^{-2}\exp(-b_m^2x^2) \quad (5)$$

where b_m (m = 1,2,...) in the mth root of the zeroth-order Bessel function $J_0(b) = 0$.

We employ the expressions for $P(X;\beta)$ and $R(X;\beta)$ obtained by Ohta and Oono,[6] who applied renormalization group theory to a semidilute polymer solution.[7] Functional forms of $P(X;\beta)$ and $R(X;\beta)$ are given in Teraoka et al.[2] By solving eq 1 for differing X_HE and X_LE, concentrations of the fractions in the external solution, p_H and p_L are obtained as a function of these parameters. When the ratio of X_HE to X_LE is fixed, p_L shows a rapid increase as X_HE exceeds about 4.[2] With further increase in X_HE, p_L reaches a value larger than 1 (partitioning inversion). In contrast, p_H remains smaller than one for a monodisperse solution of the high molar mass fraction. The interior concentration is enhanced for the low molar mass fraction, whereas it is suppressed for the high molar mass fraction. When this enhancement and suppression are applied to a system with comparable volumes for the interior and the exterior solutions, we will observe a segregation in the bimodal polymer mixture between the interior of the pore and the exterior. The strong segregation as a function of molecular weight difference originates in the increase of ΔS as the molecular weight increases. The confinement entropy ΔS is approximately given by $\Delta S/k_\mathrm{B} \propto (R_\mathrm{g}/R_\mathrm{P})^2$. In the following two sections, we apply this principle to processes that separate the high and the low molar mass fractions from their mixture.

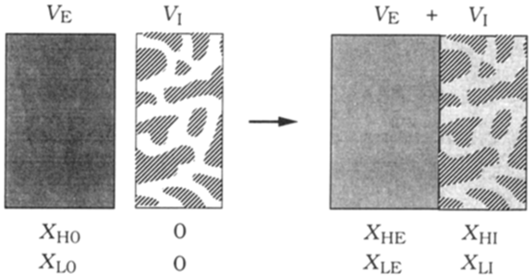

Figure 1. Extraction scheme for the high molar mass fraction from a mixture of low and high molar mass fractions using nanoscale porous material.

Extraction of the High Molar Mass Fraction

As noted, we start with a bimodal polymer solution that contains the high and low molar mass fractions with concentrations X_H0 and X_L0, respectively, and extract first the high molar mass fraction. For illustration, consider a bimodal solution of volume V_E introduced into a vessel that contains porous material with pore volume V_I saturated with pure solvent, the same as used to dissolve the polymer (Figure 1). Note that V_I denotes the volume accessible to the fluid; it does not include the space occupied by the solid phase that supports the pore structure. For simplicity, there is assumed to be no free space other than the pore volume and the solid phase volume. The combined volume then accessible to the fluid becomes $V_\mathrm{E} + V_\mathrm{I}$.

Some of the polymer molecules migrate into the pore. Eventually, equilibrium is reached for each fraction between the interior of the pore and the exterior, yielding reduced concentrations $X_{i\mathrm{I}}$ and $X_{i\mathrm{E}}$, respectively, for the fraction i (i = H, L). The restriction on the number of conformations available to the chain in the pore compared with that of a chain outside is more stringent for the high molar mass fraction than for the low molar mass fraction. Therefore, the high molar mass fraction is enriched in the external solution after concentration equilibrium is reached and can be recovered from the external solution. We examine the enrichment in the recovered fraction in terms of a purity $\rho_\mathrm{H} \equiv w_\mathrm{HE}/(w_\mathrm{HE} + w_\mathrm{LE})$ and a recovery ratio $r_\mathrm{H} \equiv w_\mathrm{HE}/w_\mathrm{H0} = X_\mathrm{HE}/X_\mathrm{H0}$ for the high molar mass fraction.

Self-consistent calculations were performed for varying concentrations of the polymers in the original bulk solution at a given $V_\mathrm{I}/V_\mathrm{E}$, $w_\mathrm{H0}/w_\mathrm{L0}$, m_N, and $p_\mathrm{L}^{(0)}$. Here, $V_\mathrm{I}/V_\mathrm{E}$ is the volume in the interior of the porous material relative to the external volume, $w_\mathrm{H0}/w_\mathrm{L0}$ is the ratio of the monomer concentrations of the two fractions in the original solution, and $m_N = N_\mathrm{H}/N_\mathrm{L}$ is the ratio of the degree of polymerization of the two fractions. When $p_\mathrm{L}^{(0)}$, the dilute solution limit of the partition coefficient for the low molar mass fraction, is specified, it gives the size of the chain from the fraction from $p_\mathrm{L}^{(0)} = f(R_\mathrm{gL}^{(0)}/R_\mathrm{P})$ (see eq 5), which together with m_N determines $R_\mathrm{gH}^{(0)}/R_\mathrm{P}$ and hence $p_\mathrm{H}^{(0)}$. Conservation of mass of each fraction given by $X_{i0}V_\mathrm{E} = X_{i\mathrm{E}}V_\mathrm{E} + X_{i\mathrm{I}}V_\mathrm{I}$ (i = H, L) is assumed.

An example of the results of the calculation is shown in Figure 2 for the conditions $V_\mathrm{E} = V_\mathrm{I}$, $p_\mathrm{L}^{(0)} = 10^{-3}$ (i.e., $R_\mathrm{gL}^{(0)}/$

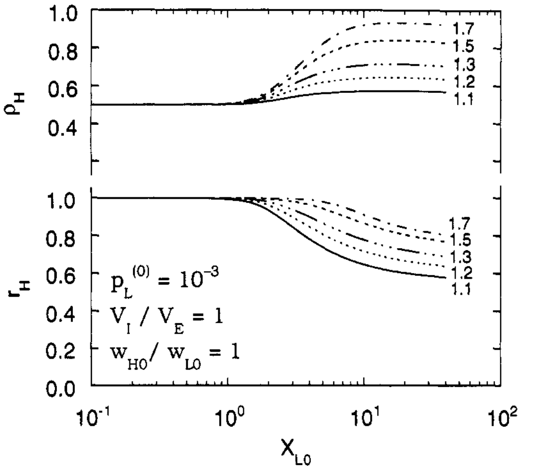

Figure 2. Purity ρ_H and recovery ratio r_H for the extraction of the high molar mass fraction plotted as functions of the reduced concentration X_{L0} of the low molar mass fraction in the original solution of the bimodal mixture. Parameters used are shown in the figure. The respective values of m_N are indicated to the right of the curves. See text for definition of the parameters.

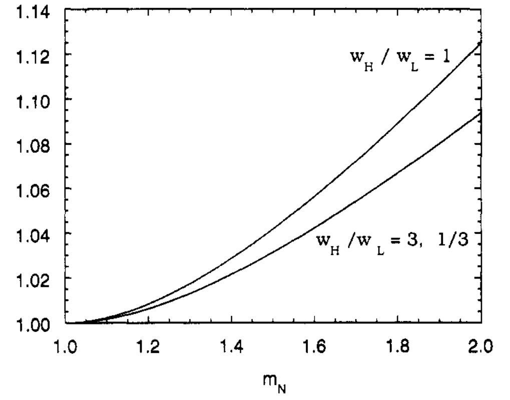

Figure 3. Polydispersity index β of a mixture of two polymer fractions plotted as a function of m_N, the ratio of the two molecular weights. Plots are shown for two values of w_H/w_L, the ratio of the weights of the two fractions in the mixture.

$R_P \cong 1.068$), and $w_{H0}/w_{L0} = 1$ for several values of m_N. Plots of ρ_H and r_H are given as functions of X_{L0}. The high molar mass fraction changes its concentration as $X_{H0} = X_{L0} m_N^{3\nu-1}$ in the original solution for the parameters selected here. For all values of m_N used for the calculation, there is a drastic increase in the purity ρ_H from its original value $^1/_2$ ($w_{H0}/w_{L0} = 1$) as X_{L0} exceeds ca. 2. The increase is larger as m_N becomes larger, indicating a better purification as the difference of the two molecular weights widens. In effect the high osmotic pressure of the external solution pushes the low molar mass fraction preferentially into the pores, leaving the high molar mass fraction separated outside. There is a maximum in the plot of ρ_H vs X_{L0}, which is due to the migration of some of the high molar mass fraction into pore channels at the highest concentrations. We note that the recovery ratio of the high molar mass fraction does not deteriorate significantly as X_{L0} increases and the purity improves. When $m_N = 1.7$, r_H is 0.849 when ρ_H is at a maximum of 0.932 for $X_{L0} \cong 18.4$ ($X_{H0} \cong 27.6$).

To show how sensitive this process of separation is in terms of polydispersity index $\beta = \langle N^2 \rangle / \langle N \rangle^2$, we plot β against m_N for $w_H/w_L = 1$ and 3 in Figure 3 (note that the plot for $w_H/w_L = {}^1/_3$ is identical to that for $w_H/w_L = 3$). Combining the results of Figures 2 and 3, we find that, for example, an original solution with $\beta \cong 1.0417$ ($m_N = 1.5$ and $w_{H0}/w_{L0} = 1$) can enhance its purity to $\beta \cong 1.0225$ with recovery ratio $r_H \cong 0.816$ by starting with the original solution of $X_{L0} \cong 17$ ($X_{H0} \cong 23$). For a solution starting with β as small as 1.00833 ($m_N = 1.2$ and $w_{H0}/w_{L0} = 1$) β decreases to ca. 1.00764 with a recovery ratio 0.741 at $X_{L0} \cong 15$ ($X_{H0} \cong 17$) for the high molar mass fraction.

We also performed equilibrium calculations for other selected conditions. First, we varied V_I/V_E while $p_L^{(0)} = 10^{-3}$ and $w_{H0}/w_{L0} = 1$ were held constant. As V_I/V_E decreases and there is less pore volume available for the low molar mass fraction, the purity of the high molar mass fraction is diminished, but the recovery ratio improves for the values of m_N used in Figure 2. The opposite is seen when V_I/V_E increases.

Secondly, we varied w_{H0}/w_{L0} for fixed $p_L^{(0)} = 10^{-3}$ and $V_I/V_E = 1$. As w_{H0}/w_{L0} decreases, the rapid increase as well as the maximum in ρ_H is seen at a higher concentration X_{L0} (but at similar concentrations in terms of X_0, the total reduced concentration of the original solution). At the same time, the peak height in ρ_H decreases. The trends are the opposite when w_{H0}/w_{L0} increases.

Thirdly, we changed $p_L^{(0)}$ at fixed $V_I/V_E = 1$ and $w_{H0}/w_{L0} = 1$. A decrease in $p_L^{(0)}$ ($p_H^{(0)}$ decreases proportionately for a given m_N) is equivalent to using a smaller pore size or higher molecular weights for both fractions. It was found that decreasing $p_L^{(0)}$ causes the transitions, as represented by an increase in ρ_H and a decrease in r_H, to take place at a higher concentration of X_{L0} but enhances the peak height in ρ_H. The value of r_H at the maximum in ρ_H also becomes larger. The separation characteristics for varying $p_L^{(0)}$ lead to the conclusion that a smaller pore is preferable with the proviso that we can make the solution concentrated enough for the transitions to occur.

The findings above lead us to the following protocol for extracting the high molar mass fraction from a bimodal polymer solution of a given mixture ratio:

(1) Prepare a sufficiently concentrated solution that provides $X_0 \gtrsim 4$.

(2) Introduce the polymer solution into a vessel containing pores that provide sufficient conformational restriction of the low molar mass fraction to give $p_L^{(0)} \lesssim 10^{-3}$.

(3) The ratio of the pore volume to the volume of the original solution can be optimized depending on the ultimate requirement. If high purity is the primary concern, then a larger pore volume should be used. If high yield is preferred, then a smaller pore volume is indicated.

(4) The purity of the high molar mass fraction can be further improved by repetition, with, however, a concomitant decrease in overall yield.

Extraction of the Low Molar Mass Fraction

The low molar mass fraction contained in high concentration in the interior of the pore after equilibrium is reached can be recovered by replacing the external polymer solution with pure solvent of the same type, as shown in Figure 4. The volume of the added pure solvent is assumed to be V_E for simplicity. Most of the polymer molecules in the pores will be driven out. When the second equilibrium is reached for each fraction between the interior of the pore and the exterior, we have concentrations X_{iI}' and X_{iE}', in the interior and the exterior of the pore, respectively, for fraction i (i = H, L). Mass conservation is given by $X_{iI} V_I = X_{iE}' V_E + X_{iI}' V_I$ (i = H, L). We can recover from the external solution a fraction enriched in the low molar mass components. We express the purity of the low-mass component by $\rho_L \equiv w_{LE}'/(w_{HE}' + w_{LE}')$ and the recovery ratio $r_L \equiv X_{LE}'/X_{L0}$. An example of the results after the second concentration equilibrium is

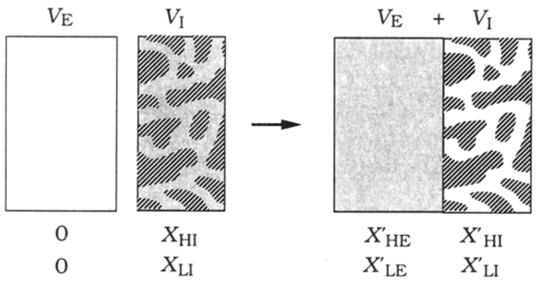

Figure 4. Extraction scheme for the low molar mass fraction from a mixture of low and high molar mass fractions using nanoscale porous material.

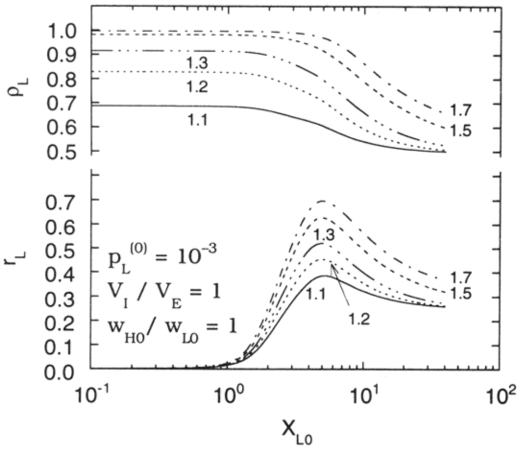

Figure 5. Purity ρ_L and recovery ratio r_L for the extraction of the low molar mass fraction plotted as functions of the reduced concentration X_{L0} of the low molar mass fraction in the original solution of the bimodal mixture. Parameters used are shown in the figure. The respective values of m_N are indicated adjacent to the curves. See text for definition of the parameters.

attained is plotted in Figure 5 for the same parameters as used in Figure 2. The purity is optimized when the starting concentration X_{L0} is low, but the recovery ratio r_L is close to zero, implying that the lower concentrations are of no use for practical purposes. As X_{L0} exceeds ca. 1, r_L increases rapidly. There is a maximum in r_L at $X_{L0} \cong 5$, because, at higher concentrations of X_{L0}, the external solution after the second equilibration also contains higher concentrations and hence provides a high osmotic pressure, thereby confining the polymers in the interior of the pore. The purity ρ_L deteriorates as X_{L0} exceeds ca. 5 due to the influx of the high molar mass fraction into the pore during the first equilibration. However, when r_L is at its maximum, ρ_L is still much larger than the value $^1/_2$ of the original solution. For $m_N = 1.7$, the maximum in r_L ($\cong$0.697) is reached when $X_{L0} \cong 5.0$ with $\rho_L \cong 0.970$ ($\beta \cong 1.0082$; *cf.* $\beta \cong 1.0417$ in the original solution). For $m_N = 1.2$, the peak in r_L ($\cong$0.455) is reached when $X_{L0} \cong 5.0$ with $\rho_L \cong 0.708$ ($\beta \cong 1.0069$; *cf.* $\beta \cong 1.0083$ in the original solution).

Concentration equilibria were calculated for other parameter sets. When V_I/V_E increases while $p_L^{(0)} = 10^{-3}$ and $w_{H0}/w_{L0} = 1$ are held constant, the maximum in r_L increases in intensity and moves to a lower value of X_{L0}. At the X_{L0} that yields the maximum in r_L, the purity ρ_L decreases only slightly. The decreases in ρ_L and r_L at higher concentration, however, become more prominent as V_I/V_E increases. When w_{H0}/w_{L0} increases while $p_L^{(0)} = 10^{-3}$ and $V_I/V_E = 1$ are fixed, the maximum in r_L increases in intensity and moves to a lower X_{L0}. In terms of X_0, however, the peak position does not change appreciably. The purity deteriorates as w_{H0}/w_{L0} increases. When $p_L^{(0)}$ becomes smaller, i.e., the pore size decreases, the maximum in r_L increases in intensity and the peak is observed at a larger X_{L0}; purity also improves.

These trends complement those of ρ_H and r_H. Rules 1–4, above, apply also to the extraction of the low molar mass fraction. With respect to rule 3, the effect of V_I/V_E on the purity is not so large as in the extraction of the high molar mass fraction.

Concluding Remarks

In this contribution, we have demonstrated by considering concentration equilibria that nanoscale pores can be used to fractionate a bimodal mixture of polymers in solution. Fractionation is predicted to be efficient even for a mixture of two fractions differing only slightly in molecular weight. Similar procedures can clearly be applied to the separation of a mixture containing more molecular weight fractions or, in general, to a polydisperse mixture of arbitrary molecular weight distribution. It seems to be of practical importance to estimate the efficiency of the above fractionation scheme for such distributions.

Real porous materials are not free from heterogeneity in pore radius or off-cylindrical pore structure, which will tend to degrade the fractionation resolution and efficiency. The effect of these nonidealities on the sensitivity of our fractionation scheme will be considered in a forthcoming contribution.

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(7) The power dependence of $P(X;\beta)$ on X for $X \gg 1$ is consistent with the result of scaling theory based on a "blob" model. $R(X;\beta)$ has, however, a power law dependence different from the scaling result. See discussion of Teraoka et al.[2]