observed blocking of the column. (The gradualness is due to the simultaneity of transport and distribution. It already causes some fractionation of the polymer during the initial precipitation.)

The higher the THF content of the eluent, the later the precipitating composition is reached. With 40% THF or more in the initial eluent, it is quite impossible to surpass the precipitation threshold. Thus the sample is likely to rush through the column and to show up in the detector signal earlier than the sharp inflection due to the solvent.

The second consequence concerns the mode of separation. The characteristics mentioned above in points i–iii indicate that HPPLC is based on solubility phenomena such as the Baker–Williams fractionated.[15] The distinctness of the peaks suggests a multistage separation mechanism. In Baker–Williams fractionation this is caused by the antiparallel temperature gradient along the column. In HP precipitation chromatography a similar effect can be brought about by differences in the accessibility of the pores. Since the macromolecules are restricted to the interstitial volume of the column, whereas the eluent can enter the pores, any change in solvent properties due to a gradient program moves along the column with only about half the speed of that of a polymer solute. The polymer bypasses the pores and thus overtakes the eluent having sufficient solvent power to keep the polymer in solution. It rushes into the poorer solvent running in front an consequently precipitates. In this way it is transformed into a part of the stationary phase. When precipitated, it is retained at that zone of the column until an eluent of sufficient solvent power reaches this position. Then the polymer is redissolved and transferred back to the mobile phase.

The HP precipitation chromatography described here has advantages and drawbacks. One drawback is that solubility fractionation of copolymers is always linked to a separation by molar mass. The paper gives evidence of the possibility of fitting conditions so well that the sensitivity to composition overrides the sensitivity to molar mass. Nevertheless, it is advantageous to investigate copolymers by the combination of SEC and HPPLC according to the principles of cross fractionation. Fractions obtained by SEC can be nicely analyzed with respect to their composition distribution. Another drawback is the restriction to polymers visible by the detector and to solvents which do not disturb the detector signal.

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Notes

Corresponding States in Polymer Mixtures†

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Recently, it was pointed out by Dayantis[1] that the Flory–Huggins (FH) theory of polymer solutions predicts a corresponding-states behavior for polymer/solvent mixtures that is similar to the scaling predictions of Daoud and Jannink.[2] In this brief note it is shown that the FH model implies that all binary polymer mixtures satisfy a generalized corresponding-states principle. In polymer/solvent mixtures this general corresponding-states principle is similar to that predicted by scaling arguments.

Free Energy Expansion

A Landau-type expansion of the Gibbs free energy, $G(C,T)$, about the critical temperature (T_c) and concentration (C_c) may be used to obtain quantitative relationships for phase equilibria near a critical point. Ignoring gradient terms and retaining only a minimum number of terms, one obtains the expansion[3]

$$G = G(T_c,C_c) + G_C\Delta C + G_T\Delta T + G_{CT}\Delta C\Delta T + \frac{1}{2}G_{TT}(\Delta T)^2 + \frac{1}{2}G_{CCT}\Delta T(\Delta C)^2 + \frac{1}{4!}G_{CCCC}(\Delta C)^4 \quad (1)$$

where the subscripts on G denote partial differentiation, $\Delta C \equiv C - C_c$, and $\Delta T \equiv T - T_c$. All derivatives are evaluated at the critical point. Second and third powers of ΔC are absent from eq 1 because $G_{CC} = G_{CCC} = 0$.

Coexistence Curves

In a two-component, two-phase (α and β) liquid system, equilibrium is characterized by the tangent condition

$$(\partial G/\partial C)|_{C=C_\alpha} = (\partial G/\partial C)|_{C=C_\beta} \quad (2)$$

For the Landau model near the critical point, C_α and C_β are equidistant from C_c; therefore, with $C_\alpha - C_c \equiv \Delta C_e \equiv C_c - C_\beta$, eq 1 and 2 yield

† Dedicated to Professor Walter H. Stockmayer on the occasion of his 70th birthday.

$$G_{CCT}\Delta T\Delta C_e + \tfrac{1}{6}G_{CCCC}(\Delta C_e)^3 = 0 \quad (3a)$$

or

$$\Delta C_e = \pm\left[\frac{6S_{CC}\Delta T}{G_{CCCC}}\right]^{1/2} \quad (3b)$$

where

$$-G_{CCT} = S_{CC} = (\partial^2 S/\partial C^2)|_{T_c,C_c} \quad (4)$$

and S is the entropy. At an upper critical solution temperature (UCST), $S_{CC} < 0$ and $\Delta T < 0$ whereas at a lower critical solution temperature (LCST) $S_{CC} > 0$ and $\Delta T > 0$.[4] Thus, the product $S_{CC}\Delta T$ is always positive. G_{CCCC} is also positive; the first nonzero concentration derivative in the expansion is positive because $G(C,T_c)$ is convex on the critical isotherm everywhere except at $C = C_c$. Thus, ΔC_e as given by eq 3b is always real for either an UCST or a LCST.

According to the well-known Flory–Huggins theory,[5,6] the free energy of a binary mixture of N_1 flexible r_1-mers and N_2 flexible r_2-mers per mer of mixture is (constant terms and linear terms in concentration are omitted since they are unimportant in the analysis)

$$G = kT\left[\frac{1-\phi}{r_1}\ln(1-\phi) + \frac{\phi}{r_2}\ln\phi + \phi(1-\phi)\chi\right] \quad (5)$$

where k is Boltzmann's constant, ϕ is the volume or site fraction of component 2, and χ is a dimensionless interaction parameter.

The spinodal line is defined by the condition

$$\partial^2 G/\partial\phi^2)_T = \{[r_1(1-\phi)]^{-1} + (r_2\phi)^{-1} - 2\chi\}kT = 0 \quad (6)$$

At the critical point, the condition $G_{\phi\phi\phi} = 0$ yields the critical concentration:

$$\phi_c = r_1^{1/2}/(r_1^{1/2} + r_2^{1/2}) \quad (7)$$

Substituting eq 7 into eq 6 yields the critical temperature or, equivalently, the critical χ value, χ_c:

$$2\chi_c = (r_1^{-1/2} + r_2^{-1/2})^2 = \Theta/T_c \quad (8)$$

In the simplest approximation $2\chi = \Theta/T$, where Θ is a characteristic temperature. Thus, from eq 1

$$G_{\phi\phi T} = -S_{\phi\phi} = k(r_1^{-1/2} + r_2^{-1/2})^2 = k\Theta/T_c \quad (9)$$

and

$$G_{\phi\phi\phi\phi} = 2(r_1r_2)^{1/2}(r_1^{-1/2} + r_2^{-1/2})^4 k\Theta \quad (10)$$

Notice that in the FH model $S_{\phi\phi}$ is always negative if, as is customary, χ is proportional to $1/T$ (implies UCST behavior). Other choices for the temperature dependence of χ can result in a positive value for $S_{\phi\phi}$ and a LCST. Substituting eq 9 and 10 into eq 3b yields

$$\Delta\phi_e = \pm\left[\frac{3(T_c - T)/T_c}{(r_1r_2)^{1/2}}\right]^{1/2}(T_c/\Theta) \quad (11a)$$

or in terms of the molecular weights (M_1 and M_2)

$$(\Delta\phi_e)^2 \sim \left[\frac{T_c}{(M_1M_2)^{1/2}}\right]\Delta T \quad (11b)$$

Equation 11 suggests that the set of coexistence or binodal curves for binary mixtures that vary in molecular weight follow the same universal curve if $\Delta\phi_e$ is plotted against $[T_c/(M_1M_2)^{1/2}]\Delta T$. In a polymer/solvent mixture where $M_2 \gg M_1$, $\phi_c \to 0$, $T_c \to \Theta$, and $\Delta\phi_e \to \phi$, eq 11 suggests as an approximation that $M_2^{1/2}\phi$ is a function of $M_2^{1/2}(T - \Theta)/\Theta$ on the polymer-rich branch of the coexistence curve. This is the scaling result which has experimental support.[7] Equation 11 is more specific than scaling because the precise functional relationship among the variables is predicted (parabolic coexistence curve).

Spinodal Curves

The spinodal is defined by the condition $\partial^2 G/\partial^2 C)_T = 0$ and can be determined by differentiating eq 1. Denoting C_s as the spinodal composition and

$$\Delta C_s = C_s - C_c \quad (12)$$

it is easily shown that

$$\Delta C_s = \pm[2S_{CC}\Delta T/G_{CCCC}]^{1/2} \quad (13)$$

Note that the ratio $\Delta C_e/\Delta C_s$ is equal to $3^{1/2}$ as shown by Cook and Hilliard[8] for binary mixtures and by Landau and Lifshiftz[9] for the liquid–vapor transition (the root-three rule). Theoretical estimates based on studies of the three-dimensional Ising model[10] indicate that the spinodal is much closer to the binodal with $\Delta C_e/\Delta C_s \simeq 1.18$ instead of $3^{1/2}$. The "root-three rule" may be useful in establishing a bound for the spinodal in real systems.

Substituting eq 9 and 10 into 13 or using the root-three rule and eq 11a yields

$$(\Delta\phi_s)^2 = (\Delta\phi_e)^3/3 = \frac{\Delta T/T_c}{(r_1r_2)^{1/2}(\Theta/T_c)^2} \quad (14)$$

Thus, both the binodal and spinodal of polymer mixtures are predicated to satisfy a corresponding-states principle. Equation 14 differs slightly from a previous result.[11]

Discussion

Use of a Landau free energy expansion presumes that the free energy is analytical at the critical point. It is well-known from many experiments on nonpolymeric mixtures that the free energy is nonanalytic at the critical point and classical theories such as the general Landau model or the FH model are not rigorously correct. Nevertheless, the classical or mean field picture of critical phase behavior can provide valuable insights. A good example has been provided here. It has long been known that the FH model implicitly suggested a scaling law. Equations 11 and 14 are the explicit scaling laws for the FH model; they suggest a corresponding-states principle for binary polymer mixtures in the critical region. Although the predicted parabolic dependence of the coexistence and spinodal curves is probably inexact, the theory does suggest the appropriate combination of variables for superposing polymer mixture phase diagrams. Daoud[7] has already demonstrated the utility of this procedure in correlating polymer/solvent phase behavior. It may prove to be a more valuable tool in correlating and predicting phase diagrams of oligomeric mixtures and polymer blends. Future experiments will ultimately determine the usefulness of this predicted corresponding-states principle.

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A Simple Explanation of the Polymer Collapse Transition: The (6/5)ths and the (2/3)rds Laws†

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The polymer collapse transition has been the subject of continuing interest since the first work by Flory[1] in 1949. A useful recent review by Williams, Brochard, and Frisch[2] shows the status of the field. The present paper does not contribute new knowledge. What it does is derive the main features of polymer collapse with what I think is the simplest possible treatment. Hopefully, this paper will prove useful to (1) students, (2) others interested in understanding the basic physics with a minimum expenditure of time, and (3) those who cannot follow the more complicated treatments for whatever reason.

Theory

Since the treatment is so simple, we begin with the result.

$$W = [R^2 \exp(-b^2R^2)][\prod_{j=0}^{n-1}(1 - jl^3/R^3)]\left[\exp\left\{n\chi\left(1 - \frac{nl^3}{R^3}\right)\right\}\right] \quad (1)$$

W is the weighting factor (Boltzmann factor) associated with a single polymer molecule of size R, where R is taken to be the end-to-end length. The first term in square brackets is proportional to the total number of configurations of a chain of n segments ($b^2 = 3/2nl^2$, where l^2 is the mean square length of a segment along the contour length of the chain). If there were no interferences between segments, the first term would be all that is needed and $\langle R^2\rangle$ would be proportional to n. This can be verified either by using the definition of $\langle R^2\rangle$, for which case

$$\langle R^2\rangle = \int_0^\infty R^4 \exp(-b^2R^2)\, dR / \int_0^\infty R^2 \exp(-b^2R^2)\, dR = nl^2 \quad (2)$$

or by finding the value of R (R_m) that maximizes the first term

$$R_m{}^2 = {}^2/_3 nl^2 \quad (3)$$

The second term of eq 1 corrects for excluded volume. Let us generate one of the shapes enumerated by the first term by constructing the chain one segment at a time beginning at one end. The construction will be successful only if each of the n contiguous segments shows no overlap. We must therefore estimate the probability that n contiguous sites are all empty. We will use the approximation that the probability that a site is empty given that j segments have already been placed down is $1 - jl^3/R^3$. This "volume fraction of emptiness" term is obtained by assuming that the previously placed segments can occupy the given site with a probability proportional to their volume fraction. The joint probability that the n contiguous sites are all unoccupied is obviously given by the second term of eq 1.

The third factor is the usual energetic term that measures the heat of mixing n polymer segments viewed as being distributed at random with $(R/l)^3 - n$ solvent molecules. The volume fraction of solvent is $V_0 = 1 - nl^3/R^3$ and the χ parameter is $\chi = z(\epsilon^{21} - (\epsilon_{22} + \epsilon_{11})/2)$.

Equation 1 contains all the physics of both the expanded and collapsed states. It remains for us only to extract the information. This is strictly a mathematical question and introduces no new physics. The most straightforward approach would be evaluate various moments $\langle R^d\rangle$

$$\langle R^d\rangle = \int_0^\infty R^d W\, dR / \int_0^\infty W\, dR \quad (4)$$

as a function of the variables n, l, and χ. However, these integrals cannot be done in closed form. The other way is to evaluate the value of R that makes W a maximum (maximum term method). This method results in analytical formulas and has the advantage that it can be compared to previous treatments that also use the maximum term method, but as eq 2 and 3 show, there may be some slight inaccuracies introduced. The value of R that maximizes W is easily shown to be

$$\alpha^5 - {}^2/_3\alpha^3 = -n^{1/2}[n\alpha^6(\ln(1 - n^{-1/2}\alpha^{-3}) + n^{-1/2}\alpha^{-3}) + \chi] \quad (5)$$

where $\alpha = R/(nl)^{1/2}$. In obtaining (5) it was useful to replace the second term by

$$\prod_{j=0}^{n-1}\left(1 - \frac{jl^3}{R^3}\right) = \frac{[(R/l)^3]!}{[(R/l)^3 - n]![(R/l)^3]^n} \quad (6)$$

and to maximize the ln W.

We can compare this to the original Flory result by expaning the ln term.

$$\alpha^5 - {}^2/_3\alpha^3 = n^{1/2}[{}^1/_2 - \chi] + n^{3/2}\alpha^6(\sum_{k=3}^{\infty}(n^{-k/2}\alpha^{-3k}/k)) \quad (7)$$

The right-hand side descends in powers of $n^{1/2}$ so that for $\alpha > 1$ we have for n large

$$\alpha^5 - {}^2/_3\alpha^3 = n^{1/2}[{}^1/_2 - \chi] \quad (8)$$

which is the Flory result except for the unimportant coefficient of ${}^2/_3$ multiplying α^3. There is a simple way to get rid of this coefficient. If we were to have maximized RW rather than W, then eq 3 would read $R_m{}^2 = nl^2$, which is identical with eq 2. This suggests that we maximize RW in the more general problem. The only effect is to change the left-hand side of eq 5, 7, and 8 from $\alpha^5 - {}^2/_3\alpha^3$ to $\alpha^5 - \alpha^3$.

When ${}^1/_2 - \chi > 0$ we have

$$\alpha = [{}^1/_2 - \chi]^{1/5}n^{1/10}$$

$$R^2 = [{}^1/_2 - \chi]^{2/5}n^{6/5}l^2 \quad \text{expanded polymer} \quad (9)$$

which means that R^2 varies as $n^{6/5}$.

As χ becomes greater than ${}^1/_2$, eq 8 gives a nonsensical result, the only real solution for α being negative. To understand the collapse transition one must resort to eq 5. The fact that the bracketed part of the right-hand side is a function of $n^{1/2}\alpha^3$ suggests that we use $\alpha = an^{-1/6}$ as a trial solution. Then we obtain

$$A^5n^{-5/6} - {}^2/_3A^3n^{-3/6} = -n^{1/2}[A^6(\ln(1 - A^{-3}) + A^{-3}) + \chi] \quad (10)$$

† Stockmayer's abilities and efforts as a teacher should be acknowledged in this honorary issue, not only his publications. This paper constitutes a very simple way to derive the properties of expanded and collapsed states in isolated polymers and it should prove useful for the instruction of students.