

Liquid-Liquid Phase Separation in Multicomponent Polymer Systems. XI. Dilute and Concentrated Polymer Solutions in Equilibrium*1

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ABSTRACT: A simple free enthalpy function is proposed for interpolating between the extremes of dilute and concentrated polymer solution behavior. This permits thermodynamic discussions of liquid-liquid equilibria in systems involving both concentrated and dilute phases. The function does not require introduction of new arbitrary parameters, and affords improved agreement with observed stability limits in practically binary polystyrene-cyclohexane systems.

In almost all previous discussions of liquid-liquid phase equilibria in multicomponent polymer systems, the dependence of the thermodynamic properties on chain length has been confined to the classical Flory-Huggins entropy terms.^{2a,b} That is, in the expression for the free enthalpy (Gibbs free energy) of mixing of a quasibinary system (single solvent plus multicomponent homologous polymer)

$$\Delta G/RT = n_1 \ln \phi_1 + \sum_i n_i \ln \phi_i + g n_1 \phi_2 \quad (1)$$

the dimensionless interaction function g is allowed to depend on temperature, pressure, and concentration, but not on the molecular weights of any of the species. In the above equation, n_1, n_i are the numbers of moles and ϕ_1, ϕ_i the volume fractions of solvent and polymer species i , respectively; $\phi_2 = \sum_i \phi_i$ is the whole polymer volume fraction, and RT has its usual meaning.

A treatment of the above type has been quite successful in explaining the principal aspects of liquid-liquid equilibrium in polymer systems,^{2,3} but quantitative discrepancies have been noted.

(a) Spinodals (i.e., the loci of metastability limits) calculated for polystyrene-cyclohexane systems with g independent of chain length, when compared with experimental curves derived from extrapolation of light-scattering measurements,⁴ show significant differences which increase with decreasing molecular weight and with decreasing polymer concentration.⁵

(b) Direct measurements of distribution ratios for the partition of polymeric species between the two liquid phases of the polystyrene-cyclohexane system⁶ disagree with the predictions of eq 1 for a molecular weight independent g parameter. This equation leads to a distribution coefficient of the form

$$\phi_i''/\phi_i' = \exp(\sigma m_i) \quad (2)$$

in which single and double primes are used to denote the

dilute and concentrated phases, respectively, m_i is the ratio of molar volumes of polymer species i to solvent, and σ is a function of temperature, pressure and concentration obtainable from eq 1. After introduction of the masses w_i' and w_i'' of the polymer species in the two phases, the above distribution law can be rewritten in the form

$$\ln (w_i'/w_i'') = -\sigma m_i + \ln r \quad (2')$$

where r is the ratio V'/V'' of the total volumes of the phases. Breitenbach and Wolf found that although a plot of $\log (w_i'/w_i'')$ vs. m_i indeed appears to be linear in the range of their data the apparent value of r as found from their intercept is of the order of only 10% of the directly measured value.

End-group contributions offer a possible explanation for anomalies of the type described, and are predicted theoretically for both enthalpy and entropy of mixing.^{2a,7,8} For example, Case, Gibbs, and Ghosh⁹ found that special interactions involving terminal hydroxyl groups could explain the observed distribution ratios of poly(propylene glycols) between water and organic solvents. For nonpolar systems, end groups can reasonably produce a contribution of not much more than RT per mole to the free enthalpy of mixing, corresponding to a contribution of about $1/m_n$ in the parameter g , where m_n represents the number-average value of m_i . A term of about this magnitude, however, cannot be made to account for the aforementioned spinodal data without an unreasonably large temperature coefficient; i.e., the separate enthalpy and entropy effects required are much too large.¹⁰ A modest end-group effect, however, must clearly be recognized by any general theory of polymer solutions, as for example in the treatment of n -alkane mixtures.¹¹

A second molecular weight dependent contribution to g is due to the well-known inherent nonuniformity of local polymer segment concentration at high dilutions.¹² It has long been recognized that an interaction function g independent of chain length cannot describe the thermodynamic properties of dilute polymer solutions; e.g., the second and third osmotic virial coefficients are known to depend on molecular weight. The calculations to be described below indicate that the accompanying effect on liquid-liquid phase equilibrium can be far from negligible when one

* The authors dedicate this paper to Professor Oto Wichterle of Prague on the occasion of his 60th birthday, in recognition of his inspiration to polymer scientists and his own significant contributions to the field.

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of the phases is dilute. To treat this problem, we require a tractable free-enthalpy function applicable continuously to solutions of all polymer concentrations from high to low. Although the basic problem has been recognized and discussed in some detail by Fixman,^{13,14} and by Edwards,¹⁵ their results are not convenient in the sense desired; nor have we found any published alternatives. Here we offer a simple formula for interpolation between the dilute and concentrated regimes which can be crudely justified in physical terms, which essentially invokes no new arbitrary parameters, and which gives an improved account of spinodal behavior in the polystyrene-cyclohexane system.

Interpolation between Dilute and Concentrated Polymer Solutions

The two extremes of polymer solution behavior are well known. At sufficiently high concentrations, we have an enmeshed, intertwined and entangled assembly of chains. Under these conditions, an essentially uniform polymer segment concentration may be assumed throughout the solution, and the familiar theoretical treatments^{2a,8,12} lead to eq 1 with an interaction coefficient g that is independent of chain length save for the specific end-group effects noted above. At high dilutions, however, the macromolecules are more or less isolated from each other, only occasionally interacting in small clusters. The natural theoretical development of this situation is a virial expansion of the osmotic pressure

$$\pi/c_2RT = (1/M_n) + A_2c_2 + A_3c_2^2 + \dots \quad (3)$$

where c_2 is the concentration in mass of whole polymer per unit volume, M_n is the number-average molecular weight, and the virial coefficients A_2, A_3, \dots , correspond to the interactions of pairs, triplets, \dots , etc., of macromolecules in the solvent medium. Both theoretical and experimental study of the virial coefficients shows that in general they depend on the chain lengths of the molecules involved, in contradiction to the predictions based on a g independent of molecular weight.

According to eq 1, the chemical potential of the solvent, referred to its value in the pure liquid, is given by

$$\Delta\mu_1/RT = \ln(1 - \phi_2) + (1 - m_n^{-1})\phi_2 + \chi\phi_2^2 \quad (4)$$

where $\chi = g - \phi_1\partial g/\partial\phi_2$. Expressing the concentration dependence of χ in series form

$$\chi = \chi(\phi_2) = \chi_1 + \chi_2\phi_2 + \dots \quad (5)$$

and expanding the logarithmic term in eq 4, we have

$$-\Delta\mu_1/RT = (\phi_2/m_n) + [(1/2) - \chi_1]\phi_2^2 + [(1/3) - \chi_2]\phi_2^3 + \dots \quad (6)$$

Thus, when g is independent of molecular weight, the various coefficients in the above expansion are also independent of molecular weight, save for the leading infinite-dilution term. In highly dilute solutions, on the other hand, eq 3 corresponds to

$$-\Delta\mu_1/RT = (\phi_2/m_n) + (A_2V_1/\bar{v}_2^2)\phi_2^2 + (A_3V_1/\bar{v}_2^3)\phi_2^3 + \dots \quad (7)$$

where V_1 is the molar volume of the solvent and \bar{v}_2 the specific volume of the polymer in solution. For a strictly

monodisperse polymer solute, the second virial coefficient is customarily written in the form

$$A_2V_1/\bar{v}_2^2 = [(1/2) - \chi_1]h(z) \quad (8)$$

where χ_1 , the coefficient appearing in eq 5 and 6, is independent of molecular weight and concentration but in general dependent on solvent, temperature, and pressure. The factor $h(z)$ is always less than unity above the θ temperature, and is theoretically related¹⁶⁻¹⁸ to the average number of nearest-neighbor segment-segment contacts between the two polymer chains of a binary cluster. Its argument z (see below) is proportional to $m^{1/2}$, and thus in dilute solution the coefficient g defined by eq 1 must necessarily be a function of chain length.

We now propose to express g for a polymer solution of arbitrary concentration as a simple linear combination of the two extreme cases described above

$$g = g_{\text{dil}}P + g_{\text{conc}}(1 - P) \quad (9)$$

with a suitable choice for the fraction P . The spirit of this maneuver is similar to that of the approximate "significant structure theory" of liquids due to Eyring and Ree;¹⁹ they describe a liquid as possessing both solid-like and gas-like degrees of freedom. We similarly regard a polymer solution of arbitrary concentration as an appropriate hybrid of the highly non-uniform dilute-solution limit and the much more regular concentrated-solution state. In this physical context, it is natural to take the fraction P as equal to the probability that a small volume element in the solution is not pervaded by any polymer segments. This quantity can be readily estimated.¹²

Consider a solution of total volume V , containing N_i polymer molecules of species i , etc. Let the volume of solution effectively occupied by a randomly coiling molecule of this species be v_i . To a rough but perhaps adequate approximation, we take

$$v_i = 4\pi a S_i^3/3 \quad (10)$$

where S_i^2 is the mean-square polar radius of gyration of the coil in its unperturbed state, and a is a geometric factor, of the order of unity. This factor takes account of the various uncertainties associated with the concept of the effective volume v_i ; these include deviations from spherical shape,²⁰ interstitial volume among the coils, and others. At high dilution in good solvents the macromolecules are of course expanded by excluded-volume effects, and in sufficiently poor solvents they must be somewhat contracted. However, as the concentration is increased, mutual interaction among the coils forces their dimensions toward the unperturbed values,^{12,14} and so we are content to use the latter in our obviously crude model. Now if the chains in the solution were completely independent of each other, the probability that no polymer segment from any dissolved macromolecule is found within a chosen volume element in the solution would be

$$P = \prod_i [1 - (v_i/V)]^{N_i} = \exp\left(-\sum_i N_i v_i/V\right) \quad (11)$$

where the second equality holds for the limit of large N_i

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and V . This result may also be written as

$$P = \exp(-\sum \lambda_i \phi_i) = \exp(-\lambda_0 \sum \phi_i m_i^{1/2}) = \exp(-\lambda_w \phi_2) \quad (12)$$

where

$$\lambda_0 = \lambda_i m_i^{-1/2} = 4\pi a N_A b^3 V_1^{1/2} / 3\bar{v}_2^{3/2} \quad (13)$$

In the last expression, we have used the parameter $b = S_L M_i^{-1/2}$, and N_A is Avogadro's number. The number $1/\lambda_w$ corresponds to the volume fraction of solute at which the sum of the coil volumes as estimated by eq 10 equals the volume V of the entire solution. Just this concentration has very often been taken as a sort of watershed between the extremes of dilute and concentrated solution behavior described earlier. The "transition" between these two extremes is, according to eq 9 and 12, quite gradual, and by no means as sharp as has sometimes (erroneously, we think) been supposed. It is also perhaps interesting to remark that $1/\lambda_i$ corresponds to the concentration at which the root-mean-square fluctuation of the solute concentration in a volume of size v_i just matches the mean concentration itself.

At this point we make a further simplification for practical purposes. If eq 9 is rewritten as

$$g = g_{\text{conc}} + P(g_{\text{dil}} - g_{\text{conc}}) \quad (9')$$

it is clear that the last term will make its greatest contribution at very low concentrations and will be damped out exponentially by the factor P as the concentration is increased. We therefore replace the coefficient of P in eq 9' by its limiting value, writing

$$g = g_{\text{conc}} + g^* P \quad (9'')$$

$$g^* \equiv \lim_{\phi_2 \rightarrow 0} (g_{\text{dil}} - g_{\text{conc}})$$

Putting eq 9'' and 12 into eq 1, we may now write the free enthalpy of mixing as

$$\Delta G / N_\phi RT = \phi_1 \ln \phi_1 + \sum_i m_i^{-1} \phi_i \ln \phi_i + \Gamma \quad (14)$$

where $N_\phi = n_1 + \sum_i n_i m_i$ and

$$\Gamma \equiv \phi_1 \phi_2 [g_{\text{conc}} + g^* \exp(-\lambda_w \phi_2)] \quad (15)$$

It should be noted that these equations define a free enthalpy function into which no new adjustable parameters have been introduced to cope specifically with the transition from dilute-solution to concentrated-solution behavior. The term g_{conc} can be evaluated from measurements of various kinds on concentrated solutions, and (as shown below) the coefficient g^* in the perturbation term is simply related to the second virial coefficient A_2 which may be evaluated from osmotic or light-scattering measurements on very dilute solutions. Further, λ_w is also predictable from independently measurable quantities, save for a possible small adjustment in the factor a . The function bears no evident relation to those appearing in the more fundamental theoretical treatments of Fixman^{13,14} or Edwards,¹⁵ but essentially the same physical variables are involved.

The quantity g^* , as stated above, can in principle be obtained from the osmotic second virial coefficient. In the case of a multicomponent polymer, however, the detail of information required places great strain on existing data since the dependence of A_2 on the entire molecular weight distribution of the solute is required. In this paper we

shall be content to give explicit results only for a strictly binary system. For that case, λ_w reduces to $\lambda_0 m^{1/2}$. Since g^* is defined to be independent of ϕ_2 , eq 14 and 15 give

$$A_2 V_1 / \bar{v}_2^2 = (1/2) [1 + (\partial^2 \Gamma / \partial \phi_2^2)_{\phi_2=0}] = (1/2) - \chi_1 - (1 + \lambda_0 m^{1/2}) g^* \quad (16)$$

where we have used the series representation of g_{conc} from eq 4 and 5. Direct comparison of eq 16 with eq 8 yields

$$(1 + \lambda_0 m^{1/2}) g^* = [(1/2) - \chi_1] [1 - h(z)] \quad (17)$$

In applications to a given binary system, we have the choice of evaluating g^* either (a) by eq 16 directly from measured values of A_2 or (b) by eq 17 from one of the several available theoretical expressions for the function $h(z)$. The χ_1 needed in both cases is based on data for concentrated solutions. The former route needs no further comment. As to the latter, we may remark that at temperatures not too far from $T = \Theta$, theory gives¹⁶⁻¹⁸

$$h(z) = 1 - 2.865z + \dots \quad (18)$$

and the variable z is defined by

$$z = (\bar{v}_2 / 4\pi b^2)^{3/2} (m / V_1)^{1/2} (1 - 2\chi_1) / N_A \quad (19)$$

If these relations are used in eq 17, the result is

$$(1 + \lambda_0 m^{1/2}) g^* = 5.73 (m / V_1)^{1/2} (\bar{v}_2 / 4\pi b^2)^{3/2} [(1/2) - \chi_1]^2 / N_A \quad (20)$$

which indicates that g^* is positive both above and below the Θ temperature, vanishing quadratically at $T = \Theta$.

According to eq 14 and 15, the third virial coefficient is given by

$$A_3 V_1 / \bar{v}_2^3 = \frac{1}{3} \left[1 + \left(\frac{\partial^3 \Gamma}{\partial \phi_2^3} \right)_{\phi_2=0} \right] = \frac{1}{3} - \chi_2 + \lambda_0 m^{1/2} (1 + 2\lambda_0 m^{1/2}) g^* \quad (21)$$

This expression does not bear comparison with any existing theoretical relation¹⁷ for A_3 , but it agrees with theory insofar as the contribution from binary segment-segment interactions, here proportional to g^* , vanishes at $T = \Theta$.

Binary Stability Limit and Miscibility Gap

In a strictly binary polymer solution, the previous results reduce to

$$Z = \Delta G / N_\phi RT = \phi_1 \ln \phi_1 + m^{-1} \phi_2 \ln \phi_2 + g \phi_1 \phi_2 \quad (22)$$

where

$$g = g_{\text{conc}} + [(1/2) - \chi_1] [1 - h(z)] (1 + \lambda)^{-1} \exp(-\lambda \phi_2) \quad (23)$$

$$\lambda = \lambda_0 m^{1/2}$$

We now apply this expression to the calculation of some spinodal and binodal curves for the binary polystyrene-cyclohexane system. In an earlier paper it was shown⁵ that for sufficiently concentrated solutions the experimental data for this system are well represented by the function

$$g_{\text{conc}} = \alpha + \beta (1 - \gamma \phi_2)^{-1} \quad (24)$$

$$\beta = \beta_0 + \beta_1 T^{-1}$$

with $\alpha = -0.1597$, $\gamma = 0.2365$, $\beta_0 = 0.4987$, and $\beta_1 =$

111.74K. From standard literature sources²¹ we have $\bar{v}_2 = 0.925 \text{ cm}^3 \text{ g}^{-1}$, $V_1 = 108 \text{ cm}^3 \text{ mol}^{-1}$ and $b^2 = 7.6 \times 10^{-18} \text{ cm}^2 \text{ mol g}^{-1}$, so that from eq 13 and 19 we find $\lambda_0 = 0.57a$, and

$$z = 0.305[(1/2) - \chi_1]m^{1/2} \quad (25)$$

According to eq 24, $\chi_1 = \alpha + \beta(1 - \gamma)$. For the function $h(z)$ we have a choice of approximate theoretical expressions¹⁷ from which we use the familiar ones of Flory, Krigbaum, and Orofino (FKO (m)), Stockmayer (S), Kurata and Yamakawa (KY), and Casassa and Markovitz (CM)

$$\text{FKO}(m) \quad h(z) = (1/5.73z) \ln(1 + 5.73z) \quad (26a)$$

$$\text{S} \quad h(z) = 1/(1 + 2.865z) \quad (26b)$$

$$\text{KY} \quad h(z) = 1 - (1 + 3.903z)^{-0.4683}/1.828z \quad (26c)$$

$$\text{CM} \quad h(z) = [1 - \exp(-5.73z)]/5.73z \quad (26d)$$

All these forms agree with eq 18 in the neighborhood of the Θ temperature, and all give more or less adequate representations of second virial coefficients for temperatures above Θ . The first three expressions all lead to infinite values of $h(z)$ at some temperature below Θ , but this catastrophe is too far from the range of existing data to cause serious inconvenience. Alternatively, as mentioned earlier, we might avoid use of an explicit $h(z)$ function and instead resort to direct extrapolation of observed second virial coefficients for substitution in eq 16. For this purpose, the simple empirical expression presented by Ueberreiter and Sotobayashi²² is convenient.

The stability limit or spinodal is defined by the condition

$$(\partial^2 Z / \partial \phi_2^2)_{T,P} = 0 \quad (27)$$

which, from eq 22, 23, and 24 yields

$$\begin{aligned} (1/\phi_1) + (1/m\phi_2) &= 2\alpha + 2\beta(1 - \gamma)(1 - \gamma\phi_2)^{-3} + \\ &[(1/2) - \alpha - \beta(1 - \gamma)][1 - h(z)](1 + \lambda)^{-1} \times \\ &(2 + 2\lambda - 4\lambda\phi_2 - \lambda^2\phi_1\phi_2) \exp(-\lambda\phi_2) \end{aligned} \quad (28)$$

This expression displays the concentrated-solution terms reported earlier,⁵ but is now amended for dilute-solution effects by addition of the last term. This term is attenuated by its exponential factor, becoming insignificant at sufficiently high concentrations.

The loci of the stable two-phase region are specified by the equilibrium conditions

$$\begin{aligned} \Delta\mu_1' &= \Delta\mu_1'' \\ \Delta\mu_2' &= \Delta\mu_2'' \end{aligned} \quad (29)$$

where as before the single prime is for the more dilute phase. From eq 22-24 we have

$$\Delta\mu_1/RT = \ln \phi_1 + (1 - m^{-1})\phi_2 + \xi_1\phi_2^2 \quad (30)$$

$$m^{-1}\Delta\mu_2/RT = m^{-1} \ln \phi_2 - (1 - m^{-1})\phi_1 + \xi_2\phi_1^2 \quad (31)$$

where

$$\begin{aligned} \xi_1 &= g - \phi_1 \partial g / \partial \phi_2 = \alpha + \beta(1 - \gamma)(1 - \gamma\phi_2)^{-2} + \\ &[(1/2) - \alpha - (1 - \gamma)\beta][1 - h(z)](1 + \lambda)^{-1} \times \\ &(1 + \lambda\phi_1) \exp(-\lambda\phi_2) \end{aligned} \quad (32)$$

$$\begin{aligned} \xi_2 &= g + \phi_2 \partial g / \partial \phi_2 = \alpha + \beta(1 - \gamma\phi_2)^{-2} + \\ &[(1/2) - \alpha - (1 - \gamma)\beta][1 - h(z)](1 + \lambda)^{-1} \times \\ &(1 - \lambda\phi_2) \exp(-\lambda\phi_2) \end{aligned} \quad (33)$$

Spinodal curves calculated for various $h(z)$ functions, by the procedure described in the Appendix, are shown in Figure 1, together with available experimental data. It is seen that the extended free enthalpy function gives a better description of the spinodal data, especially at lower molecular weights, than a standard function which omits the dilute-solution term. The choice of $h(z)$ makes some difference. The CM expression appears to underestimate the effect, the S and KY expressions are quite useful, but the FKO(m) function seems to afford the best fit. If the alternative treatment based on eq 16 and the Ueberreiter-Sotobayashi²² parameters is used, then the calculated spinodals (not shown in Figure 1) almost coincide with those for the CM function.

The value of λ_0 is of some importance, as indicated by Figure 2. With the KY expression for $h(z)$ the best fit is attained with $\lambda_0 \approx (1/2)$. With the FKO(m) function this figure could be somewhat higher, though still well below $\lambda_0 = 1$. These results are in comforting accord with eq 13 for a near unity, and thus support the assertion that the added dilute-solution perturbation term does not involve new adjustable parameters. Addition of the new term produces changes of the correct sign and order of magnitude in the spinodal which, involving the second derivative of the free enthalpy, provides a sensitive test for its validity.

Miscibility gaps (binodals) calculated as described in the Appendix are displayed in Figure 3 for $m = 800$ and the CM function for $h(z)$. These results show that a value of λ_0 much in excess of unity would give negligible effects on the boundary of the two-phase region, while a figure much less than $1/2$ would produce an unpalatably large change on the high concentration side of the diagram.

Discussion

Over the concentration range so far studied for the polystyrene-cyclohexane system, the dilute-solution effect appears to become negligible as M_w increases beyond about 5×10^5 . At higher molecular weights, dilute-solution effects would be observed only at lower concentrations. This is because the "yardstick" λ in the exponential damping function of eq 12 does not depend on molecular weight in the same way as, for instance, the maximum point of the spinodal curve.

By virtue of eq 13, λ also depends on the unperturbed dimensions of the polymer. Thus, if all the other parameters remain fixed the dilute-solution effect would be less visible for polymers with larger unperturbed dimensions than polystyrene. However, as is seen in eq 19, the unperturbed dimensions also affect the parameter z , and it is therefore not possible to make any detailed statement without knowledge of the temperature and concentration dependence of g_{conc} . That the unperturbed dimensions should exert *some* effect may be qualitatively argued from the circumstance that the "overlap concentration" $1/\lambda_w$ does depend on the unperturbed dimensions whereas the critical concentration, according to present theories of concentrated polymer solutions, does not. In general, the magnitudes found for the polystyrene-cyclohexane system are thought to be typical, but it would be very valuable to have data for at least one rather different polymer-solvent system.

Extension of the present treatment to a general quasibinary system is perfectly feasible in principle, but for its practical implementation a precise specification of the de-

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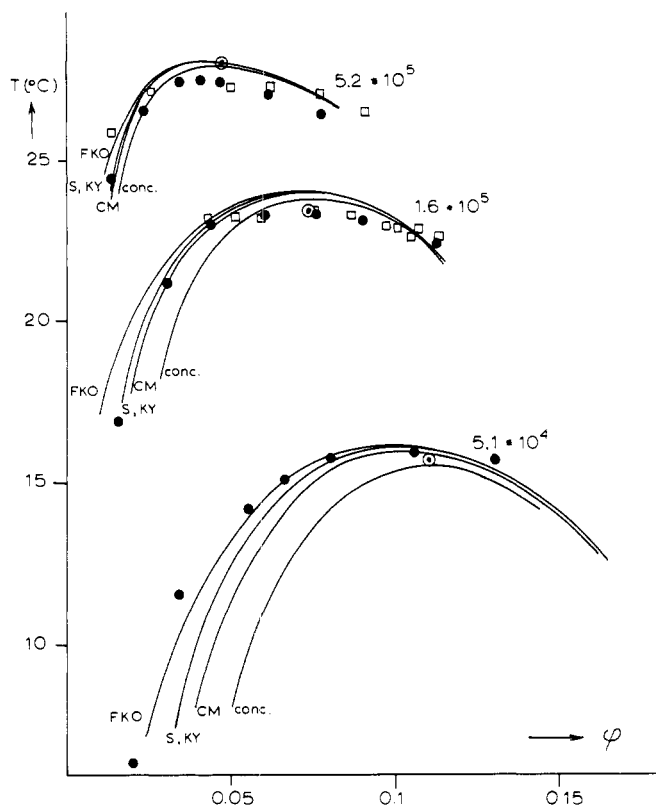


Figure 1. Spinodals for three samples of narrow-distribution polystyrene in cyclohexane. Weight-average molecular weights M_w are indicated. Experimental data by light scattering: filled circles, Scholte;⁴ open squares, Gordon *et al.*²³ The experimental critical points (dotted circles) are from Koningsveld, Kleintjens, and Shultz.²⁴ Calculated curves, for $\lambda_0 = (1/2)$, are from eq 28 with the various $h(z)$ functions of eq 26. The curve marked "conc" corresponds to $h(z) = 1$; i.e., to complete omission of the dilute-solution effect.

pendence of A_2 on molecular weight and molecular weight distribution is required. Present experimental and theoretical knowledge of this dependence is quite limited. Ueberreiter and Sotobayashi,²² for example, suggest that A_2 simply depends linearly on $m_n^{-1/2}$ or $m_w^{-1/2}$ but these forms cannot be correct for arbitrary chain lengths or distributions, even though they appear to offer a satisfactory correlation of many existing experimental data. A more fundamental theoretical attack on the problem is unfortunately still at a relatively early stage of development.^{17,18}

We are thus at present not in a strong position to discuss critically the distribution-ratio problem raised by the observations of Breitenbach and Wolf.⁶ It is difficult to separate effects due to approximations in our interpolation function from those due to uncertainties in the basic thermodynamic treatment of dilute multicomponent polymer solutions. An account of our attempts to deal with these difficulties is deferred to a later paper.

A brief comment must also be offered on the effects of long-range correlations in the critical region.²⁵ It is well known that all treatments based on a continuously differentiable free enthalpy function lead to a parabolic coexistence curve in the immediate vicinity of the critical point, in contradiction to both experiment and modern theory,

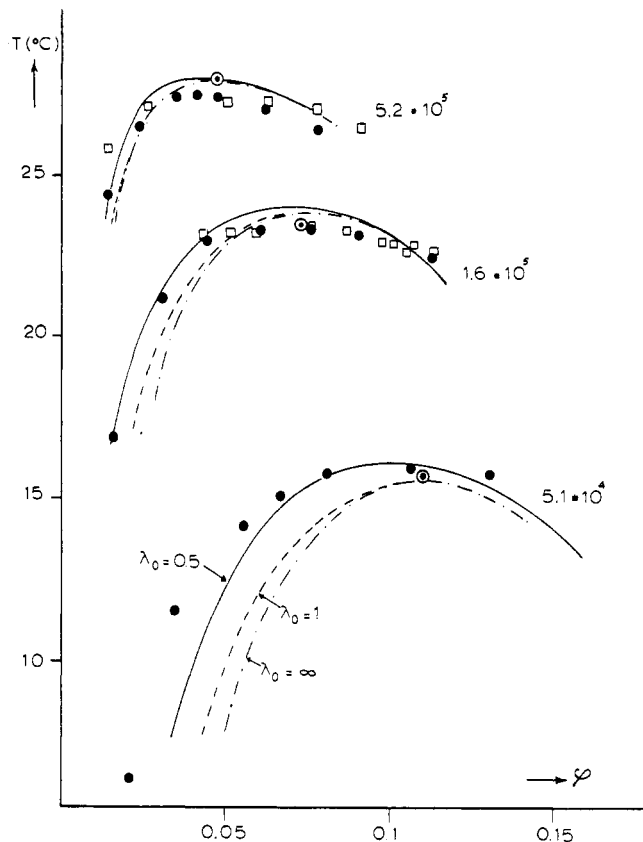


Figure 2. Spinodals calculated for the same three samples as in Figure 1, with the KY expression for $h(z)$ and various values of λ_0 . Full curve, $\lambda_0 = (1/2)$; dashed curve, $\lambda_0 = 1$; dash-dot curve, $\lambda_0 \rightarrow \infty$ (conc).

which show the true curve to be flatter. Chu and his co-workers²⁶ have offered evidence of such nonclassical behavior in the polystyrene-cyclohexane system, and it is possible that the slightly flatter appearance of the experimental spinodals of Figures 1 and 2 as compared to the calculated curves can be attributed to this cause. We believe, however, that the temperature and concentration range of the nonclassical region is much narrower for polymeric systems than for solutions of small molecules, and that such effects cannot be large enough to account for the entire "dilute-solution" contribution that we have treated. We hope to discuss this question more extensively elsewhere.

Finally, it is interesting historically to recall that Benedict, Webb and Rubin²⁷ long ago found that insertion of a Gaussian function of density into their well-known equation of state afforded an economical representation of vapor-liquid equilibrium in hydrocarbons and their mixtures, in superficial resemblance to the present concoction for polymer solutions.

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Appendix

Because z is a function of $\beta(T)$ (eq 25; $\chi_1 = \alpha + (1 -$

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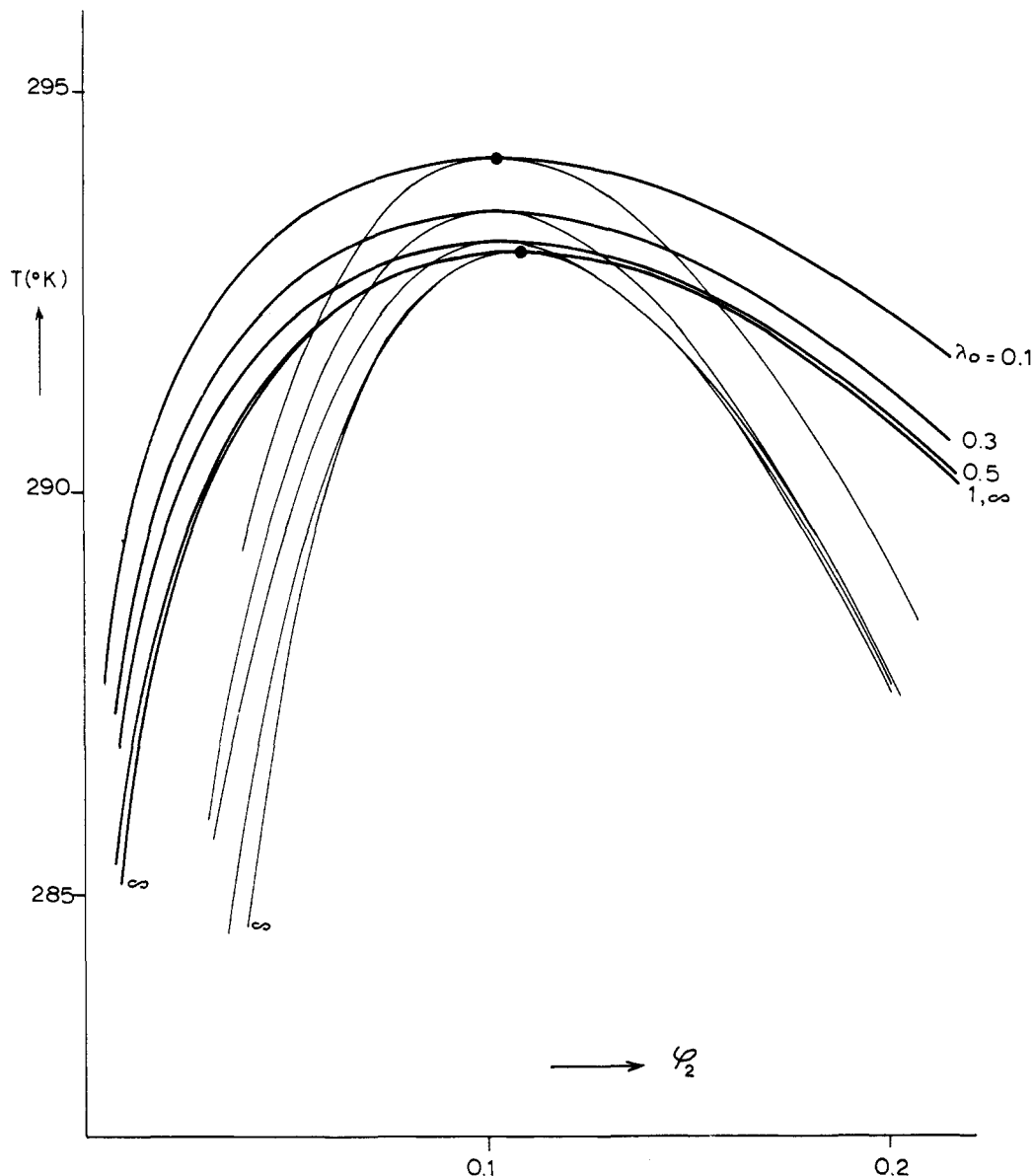


Figure 3. Calculated miscibility gaps and spinodals in a strictly binary polystyrene-cyclohexane system with $m = 800$, the CM expression for $h(z)$, and various indicated values of λ_0 . Outer (heavy) curves are binodals; inner (light) curves are spinodals; filled circles are critical points (only two indicated).

$\gamma\beta$), the spinodal expression (28) is implicitly defined in $\beta(T)$. Its value, β_ϕ , at some fixed $\phi_2 (= 1 - \phi_1)$ along the binary spinodal is nevertheless easily found by rewriting eq 28; thus

$$\beta = F_1/F_2 \quad (\text{A1})$$

where

$$\begin{aligned} F_1 &= (1/\phi_1) + (1/m\phi_2) - 2\alpha - [(1/2) - \alpha] \times \\ &\quad (1 - h)(1 + \lambda)^{-1} F_3 \exp(-\lambda\phi_2) \\ F_2 &= (1 - \gamma)[2(1 - \gamma\phi_2)^{-3} - \\ &\quad (1 - h)(1 + \lambda)^{-1} F_3 \exp(-\lambda\phi_2)] \\ F_3 &= 2 + 2\lambda - 4\lambda\phi_2 + \lambda^2\phi_1\phi_2 \\ h &= h(z) \end{aligned}$$

On setting $h(z) = 1$ in eq A1 all dilute solution terms vanish and we obtain the exact solution $\beta(T)_{\text{conc}}$ corresponding to the usual concentrated theory spinodal. This affords a good first approximation to β_ϕ from which z and hence $h(z)$ may be calculated by means of eq 25 and 26,

respectively. Substituting for $h(z)$ in eq A1 obtains an improved approximation to β_ϕ . This recursive procedure may be continued to yield successively closer approximations to β_ϕ and the spinodal temperature (corresponding to the value ϕ_2) computed therefrom with eq 24; viz. $T = \beta_1/(\beta_\phi - \beta_0)$. In practice only four or five iterations are required to determine the spinodal temperature to within 0.001° .

To calculate binodals; consider the chemical potential of each component in the dilute (') and concentrated (') phases. From eq 30 and 31 it is convenient to define the functions

$$f_1 \equiv \Delta\mu_1'' - \Delta\mu_1' = \ln(\phi_1''/\phi_1') + (1 - m^{-1})(\phi_2'' - \phi_2') + (\xi_1''\phi_2''^2 - \xi_1'\phi_2'^2) \quad (\text{A2})$$

$$f_2 \equiv \Delta\mu_2'' - \Delta\mu_2' = m^{-1} \ln(\phi_2''/\phi_2') - (1 - m^{-1})(\phi_1'' - \phi_1') + (\xi_2''\phi_1''^2 - \xi_2'\phi_1'^2) \quad (\text{A3})$$

For each fixed m and $\phi_2'' (= 1 - \phi_1'')$, we seek the corresponding values of T and $\phi_2' (= 1 - \phi_1')$ which complete

the definition of two points at the ends of a tie line in a binodal. To this end we regard $f_1 \equiv f_1(\phi_2', T)$ and $f_2 \equiv f_2(\phi_2', T)$ and note that the solution is found when the equilibrium conditions, $f_1(\phi_2', T) = 0$ and $f_2(\phi_2', T) = 0$ (eq 29), are met.

Combining Newton-Raphson and Gauss-Seidel methods; if T_i and $\phi_{2,i}'$ represent approximations to T and ϕ_2' , then closer approximations T_{i+1} and $\phi_{2,i+1}'$ are given by

$$T_{i+1} = T_i - f_1(T_i, \phi_{2,i}')/f_1'(T_i, \phi_{2,i}')$$

and

$$\phi_{2,i+1}' = \phi_{2,i}' - f_2(T_{i+1}, \phi_{2,i}')/f_2'(T_{i+1}, \phi_{2,i}')$$

where

$$f_1' \equiv \partial f_1 / \partial T \quad f_2' \equiv \partial f_2 / \partial \phi_2'$$

From the rather arbitrary starting values, $T_0 = 300$, and $\phi_{2,0}' = 0.005$, the values of T and ϕ_2' were determined to sufficient accuracy (0.002 in T and 0.001 in ϕ_2') at step $i \approx 6$ in this recursive routine.

All of the calculations above were performed on a programmed Hewlett-Packard desk calculator, Model 9810A.

Entanglement Networks of 1,2-Polybutadiene Cross-Linked in States of Strain. I. Cross-Linking at 0°

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ABSTRACT: Linear 1,2-polybutadiene is cross-linked at 0° (12° above T_g) by γ -irradiation while strained in simple extension, with extension ratios (λ_0) from 1.2 to 2.0. After release, the sample retracts to a state of ease (λ_s) at room temperature. From λ_0 , λ_s , and Young's modulus in the state of ease (E_s), the molar concentrations of network strands terminated by cross-links (ν_x) and by trapped entanglements (ν_N) are calculated by composite network theories of Flory and others. With increasing irradiation time t , ν_x (corrected for free ends) is directly proportional to t and ν_N attains a constant value. With increasing λ_0 , ν_x is constant and ν_N diminishes somewhat. Extrapolated to $\lambda_0 = 1$, ν_N is somewhat smaller (1.2×10^{-4} mol cm $^{-3}$) than the concentration of entanglement strands estimated from viscoelastic measurements on uncross-linked polymer in the plateau zone ($\nu_e = 2.5 \times 10^{-4}$). Young's modulus was also calculated indirectly from equilibrium swelling in *n*-heptane. The swelling is slightly anisotropic, being larger in the direction of extension.

In certain ranges of frequency (or time) and temperature, the viscoelastic properties of amorphous polymers of high molecular weight resemble those of cross-linked polymers, as though a temporary network existed, usually attributed to coupling by entanglements.¹ The concentration of network strands terminated by entanglements has been estimated from viscoelastic measurements in the plateau zone,² but these are not measurements at elastic equilibrium. To measure the effect of entanglements at equilibrium, they must be trapped between chemical cross-links to prevent eventual disentanglement. Concentrations of trapped entanglements have been estimated in several ways,³⁻⁶ involving additive contributions from strands terminated by chemical cross-links and by entanglements.

The present work treats systems in which the elastic effects of strands terminated by chemical cross-links and by trapped entanglements, instead of being additive, are in opposition. Their concentrations can in principle be determined without any assumptions of stoichiometric cross-linking, and the effectiveness of entanglements as a function of strain and other variables can be investigated. A preliminary report of such experiments has appeared elsewhere.⁷

Theory

When a rubber containing ν_1 (mol cm $^{-3}$) of elastically effective strands between cross-links which were introduced in the isotropic state is subjected to a substantial deformation and then a new set of cross-links is introduced to give an additional ν_2 (mol cm $^{-3}$) of elastically effective strands, the equilibrium elastic properties can be described as the sum of two independent networks. The most general treatment of such composite networks has been presented by Flory,⁸ who gave the following expression for the elastic free energy ΔF_{el} of the composite network, assuming Gaussian chains

$$\Delta F_{el}/RT = (\nu_1/2)(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) + (\nu_2/2) \times (\lambda_{x,2}^2 + \lambda_{y,2}^2 + \lambda_{z,2}^2 - 3) - (1/2)(\nu_1 + \nu_2) \ln V/V_0 \quad (1)$$

where λ_x , λ_y , and λ_z represent the extension ratios relative to the initial isotropic state; $\lambda_{x,2}$, $\lambda_{y,2}$, and $\lambda_{z,2}$ represent the extension ratios relative to the state in which the second set of cross-linkages was introduced; V is the actual volume; V_0 is a reference volume. After release of the stress, the sample assumes a state of ease in which the free energy is at a minimum and the force due to the network introduced in the isotropic state is equal to and opposes the force due to the network introduced in the strained state. From the strain in the state of ease the relative concentrations of elastically effective strands introduced in the strained and isotropic states, i.e., ν_2/ν_1 , can be calculated. The ideal composite network is isotropic in its elastic properties, taken relative to the state of ease.

If an uncross-linked polymer of high molecular weight

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