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Critical Properties of Incompatible Polymer Blends Dissolved in a Good Solvent

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ABSTRACT: A theory of phase separation transition in polymer blends dissolved in a good solvent is presented. We show that due to excluded volume interactions the critical behavior is not of the mean field type, except for very long and slightly incompatible polymer chains. Critical behavior of polymer–polymer–good solvent systems is, however, different from that of low molecular weight ternary mixtures, and singularities are characterized by unrenormalized Ising exponents. We give scaling laws for the molecular weight dependence of the critical amplitudes of the coexistence curve, the correlation length of composition fluctuations, the osmotic compressibility, and the interfacial tension.

I. Introduction

In recent years a considerable experimental[1–6] and theoretical[7–11] effort has been devoted to the study of ternary polymer–polymer–solvent systems. An important motivation for studying incompatible polymer blends dissolved in a common solvent is to get an insight into interactions between unlike polymer species. Hence, experiments have focused on the determination of conditions under which phase separation occurs (phase diagrams) and on light scattering from the homogeneous systems. More recently the interfacial properties of demixed phases have been investigated.[12]

The simplest interpretation of the experiments is based on a Flory–Huggins theory.[7–9] The adequacy of this approach has been questioned very recently both by comparison with experiments[12–17] and by renormalization group theories.[18–20] Excluded volume interactions induce important correlation effects not accounted for in the Flory–Huggins model and which must be included in the description of the conformation of polymer molecules and of the thermodynamic properties of ternary solutions.

These renormalization group theories[18–20] lead to a qualitatively new picture of both dilute and semidilute solutions of polymer blends. In dilute solutions in good solvents the interpenetration of unlike polymer chains is prevented by excluded volume effects. Interactions between unlike monomers do not play an important role and manifest themselves only through corrections to scaling laws. The corrections tend to zero when the molecular weight of the chains increases. This may explain experimental observations of the apparent molecular weight dependence of the Flory interactions parameters.[13,14,17] Since in the dilute regime the excluded volume effects dominate the effective repulsive interactions between unlike species, the demixing transition may occur only in semidilute solutions where the chains overlap strongly. Schäfer and Kappeler[20] have calculated the spinodal and the critical concentration of demixing using a mean field (tree) approximation. The results for critical point differ substantially from those obtained with the Flory–Huggins model and seem to be in good agreement with experimental observations.[15,17]

The purpose of this article is to extend the renormalization theories to describe the demixing transition of incompatible polymer blends dissolved in a common good solvent. In particular we study the critical properties of demixing, namely, the shape of the coexistence curve, the monomer concentration fluctuations, the scattering spectra, and the interfacial properties. We find that near the demixing transition the composition fluctuations are important, the mean field (tree) approximation fails and the critical exponents are expected to be nonclassical, except when the polymer chains are extremely long. However, the predicted exponents for polymeric blends in solution are expected to be those of the Ising model and thus to differ slightly from those of ternary mixtures of small molecules for which exponents are renormalized Ising exponents (Fischer renormalization).[31–33] We find that excluded volume effects and composition fluctuations yield a rather specific molecular weight dependence of all critical properties.

The article is organized as follows. We first recall the main results of renormalization group theories and show how they can be interpreted in terms of a simple blob picture convenient for a further discussion of the demixing transition (section II). In section III we examine the role of monomer concentration fluctuations in the vicinity of the critical line of demixing and we find that the mean field theory is not an adequate approximation for most experimental situations. We therefore study in more detail the nonclassical aspects of the demixing transition and discuss both the critical exponents and the molecular weight dependence of critical amplitudes (section IV).

II. Excluded Volume Effects and a Blob Picture

According to renormalization theories the excluded volume interactions play a dominant role in thermodynamic properties of polymer blends dissolved in a common good solvent.[18–20] The most precise information about the excluded volume effects in ternary systems often comes from experiments on dilute solutions. It seems therefore desirable to recall briefly predictions of renormalization theories for dilute systems and to show that they fit well experimental observations. Such a discussion may be a useful starting point for understanding the properties of more concentrated systems for which in most cases phase separation is expected to occur.

A. Dilute Solutions of Polymer Blends (in a Good Solvent). In dilute solutions in a good solvent the interpenetration of chains is limited by excluded volume interactions, and in the asymptotic limit of high molecular weights M the chains behave as hard spheres. Actually it has been demonstrated, both experimentally[22] and theoretically,[21] that the interpenetration function

$$\psi = BM^2/(4\pi^{3/2}R_g^{\,3}N_A) \qquad (1)$$

rapidly tends when the molecular weight of chains increases to a universal asymptotic limit $\psi^* \simeq 0.24$ independent of the chemical nature of the polymer and of the solvent. Here, B and R_g denote respectively the second virial coefficient and the radius of gyration and N_A is the Avogadro number. For a solution of two chemically different polymers A and B in a common good solvent, excluded volume interactions are still dominant and mask the specific A–B interactions.

According to renormalization theory,[18-20] the mutual virial coefficient B_{AB} has the same scaling behavior as the virial coefficient of identical chains B_{AA} (or B_{BB}), and moreover the interpenetration function

$$\psi_{AB} = B_{AB}M_AM_B/(4\pi^{3/2}{R_{gB}}^{3/2}{R_{gA}}^{3/2}N_A) \qquad (2)$$

also tends to the same asymptotic limit ψ^* as the self-interpenetration function ψ_{AA} (or ψ_{BB}). It is remarkable, however, that due to interactions between unlike chemical species, ψ_{AB} reaches the asymptotic limit much more slowly. In fact for chains of similar molecular weight M the difference

$$\Delta\psi = \psi_{AB} - (\psi_{AA} + \psi_{BB})/2$$

which directly characterizes the interactions between unlike chains, tends to zero according to a power law

$$\Delta\psi/\psi^* \simeq AM^{-\chi} \qquad (3)$$

The crossover exponent χ has been calculated in ref 18 using a direct renormalization method up to the second order in ϵ-expansion. A better estimation, $\chi \simeq 0.22$, may be obtained with the magnetic analogy and the Pade–Borel approximation.[23] A is a prefactor giving a measure of the degree of incompatibility of polymers A and B.

For virial coefficients, which are directly measurable quantities, eq 2 and 3 yield

$$\Delta B = B_{AB} - \frac{1}{2}(B_{AA} + B_{BB}) = \frac{\Delta\psi}{\psi^*}B \simeq A'M^{-a} \qquad (4)$$

where the characteristic exponent a is equal to

$$a = 2 + \chi - 3\nu \simeq 0.45 \qquad (5)$$

with ν being the swelling exponent for chains in a good solvent, approximately equal to the Flory exponent 3/5 ($\nu \simeq 0.588$).

The prefactors A' and A depend essentially on interactions between unlike chemical species and should be approximately proportional to the Flory interaction parameter χ_{AB} characterizing these interactions in the absence of the solvent (χ_{AB} should not be confused with the crossover exponent χ). However for the same polymer pair A' may differ from one solvent to another. It may be thus more convenient to use the prefactor $A = \Delta B\ M^{-a}/B$ defined in (3), which should depend much less on the solvent quality.

This renormalization picture seems to be in excellent agreement with very recent light scattering experiments,[13,14-17] in which ΔB has been measured quite precisely for several polymer pairs using the so-called optical Θ-solvent method.[24] It is in fact observed that ΔB is not constant as would be predicted by a Flory–Huggins model but tends to zero when the molecular weight of the polymers increases. Moreover ΔB does not scale with molecular weight like B but decreases with a characteristic exponent a very close to the thoretically predicted one (eq 5). This seems to be the case for weakly incompatible systems like polystyrene (PS)/poly(methyl methacrylate) (PMMA),[13-17] where $a \simeq 0.4 \pm 0.04$,[17] and for strongly incompatible pairs like PS/PDMS (poly(dimethylsiloxane)) for which $a = 0.45 \pm 0.02$.[17] Experiments show that the prefactor A increases with incompatibility degree[17] and even that it is negative for solutions of compatible blends (e.g., poly(styrene)–poly(vinylmethylene) blends).[14]

The precise determination of the prefactor A should be very important for the interpretation of thermodynamic properties of the corresponding more concentrated system (see Appendix A, eq A.10).

Hence, except for very short chains, the non-excluded volume interactions between unlike polymer chains play only a marginal role in dilute solutions. We thus expect demixing to occur well in the semidilute regime where chains overlap strongly.

B. Semidilute Solutions of Polymer Blends (in a Good Solvent). The situation is quite different in the semidilute regime where the overall monomer concentration, $c = c_A + c_B$, is much higher than the overlap concentration c^*. Here chains are forced to interpenetrate to some extent, and the excluded volume interactions are partially screened out.[25] They are only effective over distances smaller than a certain characteristic distance ξ where the chain is swollen (as in the dilute regime) and prevent contacts between monomers (in particular between unlike monomers). At larger distances contacts between different chains cannot be avoided. This correlation length ξ measures in fact the decay of overall monomer concentration fluctuations. We define it through the structure factor

$$S_{cc}(q) = \int d^3r\ e^{i\mathbf{q}\cdot\mathbf{r}}[\langle c(0)c(\mathbf{r})\rangle - c^2] \qquad (6)$$

which at low scattering vectors q may be approximated by the Ornstein–Zernike form

$$S_{cc}(q) = \frac{4c^2\xi}{q^2 + \xi^{-2}} \qquad (7)$$

When the monomer concentration c increases, the screening becomes more efficient and the correlation length ξ decreases as $c^{-\nu/(3\nu-1)} \simeq c^{-3/4}$. The dominant term, the osmotic pressure ω, is then

$$\frac{\omega_0}{kT} = K'\xi^{-3} \simeq c^{3\nu/(3\nu-1)}\ (\simeq c^{9/4}) \qquad (8)$$

K' being a universal constant: $K' \simeq 0.03$ (see Appendix A, eq A.8). Because of excluded volume correlation effects, the probability of contact between two monomers is no longer proportional to c^2 (or c_Ac_B for unlike monomers), but it is reduced by a factor proportional to $c^{(2\nu-1)/(3\nu-1)} \simeq c^{1/4}$. The probability of contacts between unlike monomers is even more reduced, which is reflected by a correction term ω_i to the osmotic pressure

$$\frac{\omega_i}{kTK'\xi^{-3}} = K_i'x(1 - x)c^{\chi_{SD}} \qquad (9)$$

with $x = c_A/c$ being the fraction of monomers A.

The prefactor K_i' should be roughly proportional to the effective interactions between unlike monomers. The exponent χ_{SD} characterizes the corrections to scaling behavior. It has been calculated up to first order in ϵ-expansion in ref 18 and has been found to be consistent with the general expression

$$\chi_{SD} = \chi/(3\nu - 1) \qquad (10)$$

This latter result can be easily obtained with a continuity requirement. Namely, at the crossover concentration that is expected to scale with molecular weight like $M^{1-3\nu}$, the expression (9) for the contribution due to interactions between unlike monomers ω_i should have the same molecular weight dependence as the correction term ΔBc_Ac_B in the dilute regime.

Hence the osmotic pressure of a semidulute solution of two chemically distinct polymers in a good solvent is[18]

$$\frac{\omega}{kT} = \frac{c_A}{M_A} + \frac{c_B}{M_B} + K'\xi^{-3}(1 + K_i' x(1 - x)c^{\chi_{SD}}) \quad (11)$$

The first two terms represent the translational entropy contribution to the osmotic pressure (corresponding to a zero-loop contribution in the diagrammatic expansion of ω). In the semidilute regime these terms are small compared to the dominant excluded volume term $K'\xi^{-3} \simeq c^{9/4}$ but not to the correction to scaling term ω_i/kT arising from the interaction between unlike monomers. It is the competition between these translational entropy and A–B interactions that determines when the phase separation occurs. At the demixing transition these two contributions are comparable.

The free energy density (per unit volume) $F(c,x)$ can be simply obtained by integrating the expression for the osmotic pressure $\omega = c(\partial F/\partial c) - F$. The result reads

$$\left.\frac{F}{kT}\right|_{\text{cm}^3} = \frac{cx}{M_A} \ln x + \frac{c(1 - x)}{M_B} \ln (1 - x) + K\xi^{-3}[1 + K_i x(1 - x)c^{\chi_{SD}}] \quad (12)$$

with $K = K'(3\nu - 1)$ and $K_i = K_i'/(1 + \chi)$. The first two terms represent the standard translational entropy of chains. Equation 12 can be used as a starting point for a general study of the phase equilibria of ternary systems by analyzing the equality of the chemical potentials of species in coexisting phases.

We limit our considerations to a symmetrical case of a good solvent of equal quality for both polymers A and B. Then it is convenient to introduce a blob picture that yields a useful physical interpretation of the ternary system properties. In the symmetric solvent case the blob picture is strictly equivalent to the full thermodynamic analysis based on (12). Because the screening effects the chains may be viewed as a succession of uncorrelated subunits, blobs, of type A or B. Each blob occupies the correlation volume ξ^3, i.e.

$$c\xi^3 = M_b \quad (13)$$

and as far as the demixing properties or composition (x) fluctuations are concerned the system behaves as a binary mixture of Gaussian chains of blobs. The end-to-end distance R_i of chains of type i (i = A, B) is then given by

$$R_i^2\,(c) = K_\rho Z_i \xi^2 = K_\rho M_i / c\xi \quad (14)$$

where $Z_i = M_i/M_b$ represents the number of blobs per chain of type i and the universal prefactor K_ρ is of order unity (see Appendix A, eq A.9).

The free energy density per site (of volume ξ^3) may be then simply written as

$$\left.\frac{F}{kT}\right|_{\text{site}} = \frac{x}{Z_A} \ln x + \frac{1 - x}{Z_B} \ln (1 - x) + ux(1 - x) \quad (15)$$

where u denotes the effectives interaction parameter between unlike blobs

$$u = K_i K c^{\chi_{SD}} \quad (16)$$

Expression 15 shows an obvious analogy with that for the free energy density of a polymer molten mixture in the Flory–Huggins model. The presence of the solvent introduces excluded volume interactions (and non-mean field correlations of total monomer concentration c) that manifest themselves through a nontrivial[26] concentration dependence of the interaction parameter u. Typical values of the interaction parameter near the demixing concentration are 10^{-2}–10^{-3} for slightly incompatible pairs such as PS–PMMA of molecular weight around 10^6,[15] and 10^{-2}–10^{-1} for the more incompatible pair PS–PDMS of similar molecular weight.[17]

As clearly shown by (9) we have assumed that monomers (blobs) A and B are randomly distributed and that the number of contacts between unlike monomers (blobs) is proportional to $x(1 - x)$. Hence we neglect the composition x fluctuations and eq 12 (or 15) represents only a mean-field approximation for studying the phase separation. We will see in the following section that very often this may be a nonadequate approximation near the critical point.

III. Mean Field Theory of Demixing and Its Validity

We limit our considerations to the case when the solvent is equally good for both polymers. Then it may be easily checked from the conditions of phase equilibria (equality of chemical potentials of polymer A, polymer B, and solvent in two phases) that when the phase separation occurs the total monomer concentration in both phases is identical and equal to c. The two phases differ only by their composition $x = c_A/c$; i.e., in the triangular phase diagram the tie lines are parallel to the A–B basis. We discuss in particular detail the totally symmetric case of chains A and B of equal radias of gyration (equal molecular weights).

A. Phase Diagrams. Critical Line. The critical line $c_K(T)$ is the line at which the spinodal surface $x_S(c,T)$ giving the limit of the metastability of the homogeneous solution and the binodal surface giving the composition of two coexisting phases are tangent. For the symmetric situation considered here, the analogy with polymer mixtures (eq 15) readily yields the following conditions for the critical concentration c_K and the critical composition x_K:

$$u(c_K,T) = (Z_A^{1/2} + Z_B^{1/2})^2/(2Z_A Z_B)$$
$$x_K = M_B^{1/2}/(M_A^{1/2} + M_B^{1/2}) \quad (17)$$

The critical point is located at the top of the coexistence curve. For concentrations $c < c_K$ the system is always homogeneous, whereas for $c > c_K$ phase separation occurs. From eq 13 and 17 we find that at a given temperature T (and thus for a given interaction parameter K_i) the critical concentration c_K obeys the equation

$$K_i(T) \left(\frac{c_K}{c_B^*}\right)^{1/(3\nu-1)} c_K^{\chi/(3\nu-1)} = \frac{3}{8\pi} K_\xi^3 K^{-1}[1 + (M_B/M_A)^{1/2}] \quad (18)$$

where $c_B^* = M_B/(4/3\pi R_{gB}^3)$ scales like $M_B^{1-3\nu}$ and

$$\frac{2\pi}{3} K K_\xi^{-3} K_i(T) \left(\frac{c_K}{c^*}\right)^{1/(3\nu-1)} c_K^{\chi/(3\nu-1)} = 1 \quad (19)$$

for the symmetric case $M_A = M_B$, for which $x_K = {}^1/_2$.

Hence, we find that the critical concentration decreases when the incompatibility degree and/or molecular weights of chains increase. Neglecting the temperature dependence of c^*, we get for c_K the scaling law

$$c_K \simeq [K_i(T) M_B]^{-b} \quad (20)$$

with

$$b = \frac{3\nu - 1}{1 + \chi} \simeq 0.62 \quad (21)$$

a result first found for the symmetric case by Schäfer and Kappeler.[20] As expected c_K is greater than the overlap concentration for long chains. Let us note that for very short incompatible chains we might expect that demixing occurs in the dilute regime and use the virial expression for the osmotic pressure. We would find that c_K varies like $M^{a-1} \simeq M^{-0.55}$, i.e., c_K even bigger than predicted by the semidilute result. This is because of the partial screening of excluded volume interactions in semidilute solutions. If the screening were total as supposed in the Flory–Huggins approximation, the critical concentration would be even much more smaller ($c_K \simeq 1/M$).[7] In any case for long chains demixing occurs at $c_K > c^*$ and the scaling law eq 20 derived for the semidilute regime is expected to be valid. For experiments at a fixed concentration c, the critical temperature of demixing is given by

$$K_i(T_K) \simeq c^{-1/b}\, M^{-1} \tag{22}$$

and T_K should be roughly proportional to the molecular weight M.

Spinodal Surface. As for binary polymer mixture the spinodal $x_S(c,T)$ is given by the conditions $\partial^2F/\partial x^2 = 0$ or from (15) by

$$u(c,T) = \frac{1}{2}\left[\frac{1}{Z_A x_S} + \frac{1}{Z_B(1 - x_S)}\right] \tag{23}$$

Using eq 18 and 19, we get

$$[1 + (M_B/M_A)^{1/2}]\left(\frac{c}{c_K}\right)^{(1+\chi)/(3\nu-1)} = \frac{M_B}{M_A}\left[\frac{1}{x_S} + \frac{1}{1 - x_S}\right] \tag{24}$$

For the symmetric case also considered in ref 20 we find a very simple equation for the spinodal

$$x_s(c,T) = \frac{1}{2}\left\{1 \pm \left(1 - \left(\frac{c_K}{c}\right)^{(1+\chi)/(3\nu-1)}\right)^{1/2}\right\} \tag{25}$$

This result is to be compared with the result of the Flory–Huggins theory

$$\frac{1}{2}[1 \pm (1 - c_K/c)^{1/2}]$$

Coexistence (Binodal) Surface. From analogy with binary polymer mixtures it is easy to get the coexistence surface in the general case $M_A \neq M_B$ by solving the equilibrium conditions

$$\left(\frac{\partial F}{\partial x}\right)_{x_-} = \left(\frac{\partial F}{\partial x}\right)_{x_+}$$

$$x\frac{\partial F}{\partial x} - F|_{x_-} = x\frac{\partial F}{\partial x} - F|_{x_+} \tag{26}$$

with x_- and x_+ being the A monomer fraction in B-rich and A-rich phases, respectively. For the symmetric case we simply have $x_+ = 1 - x_-$ given by the condition

$$\frac{1}{Z(c)} \ln \frac{1 - x_-}{x_-} = u(c,T)(1 - 2x_-) \tag{27}$$

More explicitely by defining the order parameter

$$\eta = x_+ - x_- = 1 - 2x_- \tag{28}$$

equal to the difference of compositions in two phases, we get from eq 16, 19, 27, and 28 the following equations for the binodal surface:

$$\frac{1}{\eta} \ln \frac{1 + \eta}{1 - \eta} = 2\left(\frac{c}{c_K(T)}\right)^{(1+\chi)/(3\nu-1)} \tag{29a}$$

or equivalently

$$\frac{1}{\eta} \ln \frac{1 + \eta}{1 - \eta} = 2\frac{K_i(T)}{K_i(T_K)} \tag{29b}$$

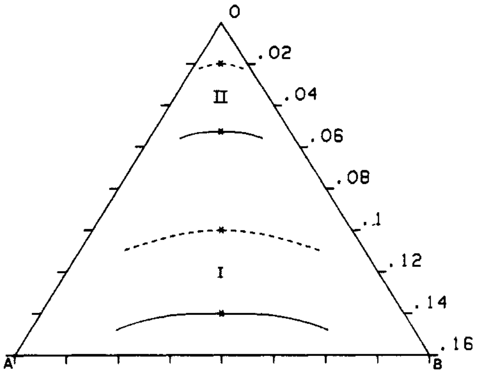

Figure 1. Typical diagrams at constant temperature for the symmetric case of chains with polymerization index $N_A = N_B = 2 \times 10^3$ (I) and $N_A = N_B = 10^4$ (II). The dotted lines correspond to the mean field predictions for a system characterized by a Flory interaction parameter $\chi_{AB} = 10^{-2}$ (this value corresponds for example to estimations for PS/PMMA blends in a molten state). Crosses denote critical points. The full lines illustrate the predictions of the present theory. The critical concentrations have been calculated according to expression 20 with the prefactor found for the PS/PMMA/benzene system.[17]

These equations correspond to two kinds of experiments corresponding to two different sections of the coexistence surface. The first one (eq 29a) is a section at constant temperature T: only total concentration c varies (the standard triangular phase diagram) (see Figure 1). The second one (eq 29b) is a section at fixed total monomer concentration c: only the temperature T varies.

In the vicinity of the critical point eq 29 leads to a classical mean field behavior. For a fixed temperature experiment we get

$$\eta \simeq \left(3\,\frac{1 + \chi}{3\nu - 1}\,\frac{\Delta}{c_K}\right)^{1/2} \tag{30a}$$

with $\Delta = c - c_K$. The critical amplitude within the mean field approximation varies like $c_K^{-1/2} \simeq M^{(3\nu-1)/2(1+\chi)}$, which naturally means for higher molecular weights of the polymers the composition difference of two coexisting phases for the same distance $\Delta = c - c_K$ from the critical point is bigger. For fixed total concentration c we get

$$\eta = \left(3\frac{\Delta T}{T_K}\right)^{1/2} \tag{30b}$$

where $\Delta T = T_K - T$ and we have assumed that $K_i(T)$ varies as the incompatibility degree, i.e., like $1/T$. We note that we find the same mean field exponent $\beta = {}^1/_2$ for both sections of the coexistence surface, which is in fact a more general result.[27]

B. Correlation Functions. In order to discuss the validity of the mean field theory of phase separation, we study the composition fluctuations in the vicinity of the critical point. We calculate correlation functions for a homogeneous solution slightly above the critical point with an average composition $x = x_K = {}^1/_2$ in the symmetric case ($M_A = M_B$) using the random phase approximation of de Gennes.[28] It is straightforward to show that for the symmetric system with the composition $x = x_K$ the fluctuations of the total monomer concentration c and of the composition x are not coupled. Therefore, when we consider the long-range (as compared to the solution correlation length ξ) fluctuations we can readily use our analogy with binary mixtures of chains of blobs. The composition correlation functions $\Gamma(q)$ for $q > 1/\xi$ is simply given by[11,28]

$$\Gamma^{-1}(q) = \Gamma_{A0}^{-1}(q) + \Gamma_{B0}^{-1}(q) - 2u \tag{31}$$

where Γ_{AO} and Γ_{BO} are correlation functions of independent ideal chains of blobs A and B, respectively, e.g.

$$\Gamma_{AO}(q) = xZ_Af(q^2R_A{}^2/6) \tag{32}$$

where $f(y) = 2[y - 1 + \exp(-y)]/y^2$ (with $y = q^2R_A{}^2/6$) is the Debye function and R_A is the end-to-end distance of chains A. The blob–blob correlation function $\Gamma(q)$ is simply related to the composition correlation function $S_{xx}(q)$, which is of interest here

$$S_{xx}(q) = \int d^3r\, e^{iq\cdot r}(\langle x(0)x(r)\rangle - x^2) = \xi^3\Gamma(q) \tag{33}$$

we recall that the correlation length ξ characterizes the decay of fluctuations of the total monomer concentration and the respective correlation function is given by eq 7.

For long-range fluctuation $q < 1/R$ we get from eq 31–33

$$S_{xx}^{-1}(q) \simeq \frac{4c}{M}\left\{1 + \frac{q^2R^2(c)}{18} - \left(\frac{c}{c_K}\right)^{(1+\chi)/(3\nu-1)}\right\} \tag{34a}$$

for experiments at fixed temperature T and

$$S_{xx}^{-1}(q) = \frac{4c}{M}\left\{1 + \frac{q^2R^2(c)}{18} - \frac{K_i(T)}{K_i(T_K)}\right\} \tag{34b}$$

for experiments at fixed concentration c. In the vicinity of the critical line the composition fluctuations become very important and correlated over long distances. The correlation functions (34) may be represented in a standard Ornstein–Zernicke form

$$S_{xx}^{-1}(q) = \frac{4c}{M}\frac{1+\chi}{3\nu - 1}\frac{\Delta}{c_K}\{1 + q^2\xi_t{}^2\} \tag{35a}$$

$$S_{xx}^{-1}(q) = \frac{4c}{M}\frac{\Delta K_i}{K_i(T_K)}\{1 + q^2\xi_t{}^2\} \tag{35b}$$

where we have introduced the thermal correlation length ξ_t which describes the decay of composition fluctuations

$$\xi_t = \frac{R_g(c)}{3^{1/2}}\left(\frac{1+\chi}{3\nu-1}\right)^{-1/2}\left(\frac{\Delta}{c_K}\right)^{-1/2} \tag{36a}$$

and

$$\xi_t = \frac{R_g(c)}{3^{1/2}}\left[\frac{\Delta K_i}{K_i(T_K)}\right]^{-1/2} \simeq \frac{R_g(c)}{3^{1/2}}\left(\frac{\Delta T}{T_K}\right)^{-1/2} \tag{36b}$$

with $\Delta = c - c_K$, $\Delta T = T_K - T$, and $\Delta K_i = K_i(T) - K_i(T_K)$. $R_g(c)$ denotes the radius of gyration of chains in the semidilute solution, that scales like $M^{1/2}c^{-(2\nu-1)/2(3\nu-1)}$ (see also Appendix eq A.3).

Hence we find that the correlation length ξ_t diverges with the characteristic mean field exponent $\nu_t = {}^1/_2$ when Δ or ΔT tends to 0. The divergence of the forward scattered intensity (or of the osmotic compressibility) proportional to $S_{xx}(0)$ is characterized by the classical exponent $\gamma = 1$.

C. Ginzburg Criterion and the Breakdown of the Mean Field Theory. Ginzburg criterion enables one to estimate the range of concentrations Δ^* and temperatures ΔT^* for which the composition fluctuations are important and the mean field approximation fails.[10,11,36] The importance of fluctuations is estimated by comparison of the composition fluctuations above the critical point averaged over the correlation volume $\xi_t{}^3$ with the composition difference η of two phases at the same distance below the critical point. When the ratio

$$\Sigma = \frac{\langle\delta\eta^2\rangle}{\eta^2} = \frac{4S_{xx}(q{=}0)}{\xi_t{}^3\eta^2} \tag{37}$$

is (much) smaller than 1 the composition fluctuations are not dangerous. Hence, the critical regions Δ^* and ΔT^* are determined by the condition $\Sigma \simeq 1$ or from eq 30, 35–37, and A.2–A.6 by

$$\Delta^*/c_K = \frac{16\pi^2}{3K_R{}^3}\frac{3\nu - 1}{1 + \chi}(c_K/c^*)^{-1/(3\nu-1)} \simeq 12(c_K/c^*)^{-1/(3\nu-1)} \simeq M^{-\chi/(1+\chi)} \tag{38a}$$

or equivalently

$$\Delta^*/c_K = \frac{16\pi^2}{3K_R{}^3K_\xi{}^2}\left(\frac{3\nu-1}{1+\chi}\right)(\xi(c_K)/R_g(c_K))^2 = 70(\xi(c_K)/R_g(c_K))^2 \tag{39a}$$

and for fluctuations at constant concentration c

$$\Delta K^*/K_i(T_K) = \Delta T^*/T_K = \frac{16\pi^2}{3K_R{}^3}(c_K/c^*)^{-1/(3\nu-1)} \simeq 20(c_K/c^*)^{-1/(3\nu-1)} \tag{38b}$$

or equivalently

$$\Delta T^*/T_K = \frac{16\pi^2}{3K_R{}^2K_\xi{}^2}\left(\frac{\xi(c_K)}{R_g(c_K)}\right)^2 \simeq 100\left(\frac{\xi(c_K)}{R_g(c_K)}\right)^2 \tag{39b}$$

It is interesting to point out that the law (38b) for instance is a very general law for polymer systems.[10] For example, for mixtures of two polymers (without solvent) we have $\nu = {}^1/_2$, $c_K = {}^1/_2$, and $c^* \simeq M^{-1/2}$ since chains are Gaussian and (38b) gives $\Delta T^* \simeq T_KM^{-1}$; i.e., the nonclassical region is very small and the mean field theory should be valid. Similarly for the demixing of a polymer in a Θ-solvent we have $\Delta K_i^* \simeq \Delta T^*$, $K_i(T_K) \simeq \Theta - T_K$ (Θ being the Θ-temperature), and $c_K \simeq M^{-1/2} \simeq c^*$ so that $\Delta T^* \simeq \Theta - T_K$ and the critical behavior is expected to be not of the mean field type. As remarked by de Gennes[10] c_K/c^* is proportional to the number of chains interpenetrating with a given chain at the critical concentration. If this number is high the mean field approximation is valid except in an extremely narrow region near the critical point.

For our ternary system eq 38 suggests that for extremely long chains the critical behavior may be of the mean field type over almost the whole temperature range. In practice, however, for most cases the ratio c_K/c^* will be not high enough and the nonclassical region will be quite wide. For instance even for the nearly compatible pair PS–PMMA of very high molecular weight $M \simeq 2.2 \times 10^6$. Fukuda et al.[13] found that $c_K/c^* \simeq 10$, and we except that the critical region should be quite wide. The solutions of polymer blends are thus interesting systems in which the crossover from nonclassical to classical behavior could be in principle observed by increasing the molecular weight of the chains.

IV. Scaling Picture

The molecular weight dependence of the position of the critical line may be expected to be only weakly affected by composition fluctuations, and we assume that eq 20 for critical concentration c_K and $K_i(T_K)$ is valid even beyond the mean field approximation.[29] On the other hand for most experimental situations the overlap ratio c_K/c^* is not very high and we expect the critical properties not to be of the mean field type but to be nonclassical.

The expansion of the mean field expression for the free energy density eq 12 in powers of composition fluctuations $\delta x = x - {}^1/_2$

$$\frac{F(c,T)}{kT} = K\xi^{-3}(c) + \xi^{-3}(c)\left[\frac{\delta x^2}{2}\left[\frac{4}{Z(c)} - 2u(c,T)\right] + \frac{4}{3Z(c)}\delta x^4\right] \tag{40}$$

suggests that the phase separation in solutions of polymer blends in a good solvent should belong to the same universality class as the Ising model (or phase separation in binary mixtures). Hence, for experiments at a fixed exchange chemical potential $\mu = \partial F/\partial c$ (the field conjugated to the total monomer concentration c), the properties in the vicinity of the critical point $T_K(\mu)$ are described by Ising exponents (e.g., $\alpha \simeq 0.11$ for specific heat divergence, $\beta \simeq 0.325$ for the coexistence curve, $\nu_t \simeq 0.63$ for the correlation length, and $\gamma \simeq 1.24$ for osmotic compressibility).[30] The same exponents are expected to occur for the temperature T fixed and the exchange potential approaching the critical value $\mu_K(T)$.

In practice the situation may be more complex because experiments are not performed at fixed μ but rather at fixed total monomer concentration c. As shown by eq 22 the critical temperature depends on the concentration c. The local fluctuations of the total monomer concentration c in principle shift the critical temperature and modify the critical exponents (Fisher renormalization).[31] For instance for fixed concentration c, the divergences when T tends to $T_K(c)$ are characterized by renormalized exponents $\tilde{\alpha} = -\alpha/(1-\alpha)$, $\tilde{\beta} = \beta/(1-\alpha)$, $\tilde{\gamma} = \gamma/(1-\alpha)$, and $\tilde{\nu}_t = \nu_t/(1-\alpha)$. The same renormalized exponents may be expected at a fixed temperature T and c aproaching the critical concentration $c_K(T)$. Such renormalized critical exponents have been found for ternary mixtures of small molecular weight liquids.[32,33] We discuss now whether fluctuations of c play an important role for solutions of polymer blends.

A. Critical Exponents. We consider a homogeneous system with a total monomer concentration c at temperature T. The exchange chemical potential is $\mu = \mu(c,T)$. If we consider a critical singularity in term of $\epsilon_\mu = [T - T_K(\mu)]/T$, Ising exponents are expected.

For instance the singular part of the grand potential should scale like

$$A_s(T,\mu,\mu_x) \simeq kT\xi_t^{-3} \simeq A_0\epsilon_\mu^{2-\alpha} \tag{41}$$

where μ_x is the field conjugated to composition x and ξ_t is the composition fluctuation correlation length, which should scale like[42]

$$\xi_t \simeq R_g(c)\epsilon_\mu^{-\nu_t} \tag{42}$$

with $3\nu_t = 2 - \alpha$. On the other hand at fixed total concentration c the demixing transition is observed at the temperature $T_0(c) = T_K(\mu(c,T_0))$ different from $T_K(\mu) = T_K(\mu(c,T))$. In order to examine when this shift in critical temperature affects the critical exponents we have to compare ϵ_μ with the experimental distance from the critical point $\epsilon = (T - T_0)/T$

$$\epsilon_\mu = \epsilon - \frac{d\epsilon_\mu}{d\mu}\left[\frac{dc}{d\mu}\right]^{-1}(c - c_K(\mu)) \tag{43}$$

where

$$c_K(\mu) = -\left(\frac{\partial A}{\partial\mu}\right)_{T_K(\mu)} = -\left(\frac{\partial G}{\partial\mu}\right)_{T_K(\mu)} \tag{44}$$

is the concentration at the critical point $T_K(\mu)$. $A = A_S + G$ denotes the grand potential containing both the singular and regular parts. Then from eq 43 and 44 we get

$$c - c_K(\mu) \simeq -\left(\frac{\partial A_S}{\partial\mu}\right)_{T,\mu} = A_0\epsilon_\mu^{1-\alpha}\frac{d\epsilon_\mu}{d\mu} \tag{45}$$

In (45) the contribution of the regular term $\partial^2 G/\partial\mu\partial\epsilon_\mu$ has been neglected. Therefore we find from eq 43 and 45

$$\frac{T_0 - T_K(\mu)}{T} = \frac{\epsilon - \epsilon_\mu}{\epsilon_\mu} = B\epsilon_\mu^{-\alpha} \tag{46}$$

with

$$B = A_0\left(\frac{d\epsilon_\mu}{d\mu}\right)^2\frac{d\mu}{dc} \simeq \frac{A_0}{\mu c} \simeq \left[\frac{\xi(c)}{R_g(c)}\right]^3 \tag{47}$$

In writing eq 47 we have kept only the dominant contribution to $\mu(c) = \partial F/\partial c$ namely $kT\xi^{-3}/c$ and we have omitted all numerical factors.

Thus the temperature range ΔT^{**} around the critical temperature T_K for which renormalized exponents may be observed is given by the condition

$$\frac{\Delta T^{**}}{T_K} \simeq \left(\frac{\xi_K}{R_{gK}}\right)^{3/\alpha} \tag{48}$$

For a temperature between T_K and $T_K \pm \Delta T^{**}$, ϵ is very different than ϵ_μ. The range ΔT^{**} seems to be very narrow because of the huge exponent ($\simeq 30$) in the right-hand side of (48). We note that ΔT^{**} is much smaller than ΔT^*, the critical region evaluated by Ginzburg criterion (eq 39). Physically this result shows that the critical behavior is not affected by the overall monomer concentration fluctuations whose range ξ is small compared to the range of composition fluctuations $R_g(c)$. Within a wide range of molecular weights for which ΔT^{**} is negligible but not ΔT^*, unrenormalized Ising critical exponents should be observed near the critical temperature.

B. Critical Amplitudes. In the following, we modify the mean field equations for the coexistence curve (eq 30), the correlation length of the composition fluctuations (eq 35) and the inversed osmotic compressibility (eq 34 at $q = 0$) which are not valid near the critical demixing point, i.e., for $\epsilon Z_K < 1$ (here $\epsilon = \Delta T/T_K$ or Δ/c_K and $Z_K = (c_K/c^*)^{1/(3\nu-1)} \simeq M^{\chi/(1+\chi)}$ is the number of "blobs" per chain at demixing); cf. eq 38 where the critical behavior is of the Ising type. Following the method of Sariban and Binder[38] the singular behavior of these quantities may be described near the demising point ($\epsilon \to 0$) by a crossover scaling law:

$$p(\epsilon) = A_c\epsilon^c f_p(\epsilon Z_K) \tag{49}$$

where A_c is the classical critical amplitudes and c the classical critical exponent of the quantity p (see eq 30, 35, and 34, respectively). f_p is a scaling function having the properties $f_p(\infty) = 1$ and $f_p(x \ll 1) \simeq x^{s-c}$, where s is the (scaling) Ising critical exponent corresponding to the quantity p and $\beta = 0.325$, $\nu_t = 0.63$, and $\gamma = 1.24$. The critical amplitude is thus $A = A_c Z_K^{s-c} = A_c M^{\chi(s-c)/(1+\chi)}$. We generalize scaling laws in the molecular weight of chains M for critical amplitudes. Finally, we show that the amplitudes should be connected by universal relationships, (i.e., independent of mass and concentration).

B.1. Coexistence Curve. The mean field equation for the coexistence curve eq 30 is changed into

$$\eta \simeq \epsilon^{1/2}(\epsilon Z_K)^{\beta-(1/2)} \simeq Z_K^{\beta-(1/2)}\epsilon^\beta \tag{50}$$

Hence the critical amplitude for the coexistence curve η_0

(defined as $\eta = \eta_0\epsilon^{\beta}$) should scale with the molecular weight of chains M as

$$\eta_0 \simeq M^{\chi(\beta-(1/2))/(1+\chi)} \simeq M^{-0.032} \tag{51}$$

and should decrease very weakly as M increases. Figure 1 illustrates an appreciable difference between the present and classical theories for typical experimental situations.

B.2. Correlation Length. In the same way, eq 36 should be replaced by

$$\xi_t/R_g \simeq \epsilon^{-(1/2)}(\epsilon Z_K)^{(1/2)-\nu_t} \tag{52}$$

The critical amplitude is thus

$$\xi_{t0} \simeq R_{gK}M^{\chi((1/2)-\nu_t)/(1+\chi)} \simeq R_g(c_k)M^{-0.024} \tag{53}$$

where, from eq A.3 and 20, R_{gK} scales like

$$R_{gK} \simeq M^{(2\nu+\chi)/2(1+\chi)} \tag{54}$$

B.3. Osmotic Compressibility. According to the fluctuation–dissipation theorem the osmotic compressibility κ is proportional to the reduced intensity at zero scattering angle: $kT\kappa \simeq I(q{=}0)/c$. Near the critical point where the composition fluctuations dominate, $kT\kappa \simeq cS_{xx}(q{=}0)$. The composition fluctuates by a quantity $\delta x \simeq x_+ - x_- = \eta$ over (large) distances of the range of ξ_t. Then from eq 33 we find a scaling relation

$$S_{xx}(q{=}0) \simeq \xi_t^{\,3}\eta^2 \tag{55}$$

Then, using the scale relation $2\beta - 3\nu_t + \gamma = 0$ and eq 50–55, we get

$$kT\kappa \simeq c_K R_{gK}^{\,3} M^{\chi((1/2)-\gamma)/(1+\chi)}\epsilon^{-\gamma} \tag{56}$$

Using eq 20 and 54, we obtain the critical amplitude for the osmotic compressibility:

$$\kappa_0 \simeq M^{1+\chi(1-\gamma)/(1+\chi)} \simeq M^{0.956} \tag{57}$$

Such a result could have been derived directly by writing the scaling relation eq 49 for the osmotic compressibility.

B.4. Interfacial Tension. The thickness of the interface between the A-rich and B-rich phases of the demixed solution is (near the critical conditions) comparable to the correlation length ξ_t. The energy of the interface is (per surface unit) $\sigma\xi_t^{\,2} \simeq kT_c$, σ being the interfacial tension. The critical exponent is $2\nu_t$ and, from eq 53 the critical amplitude reads

$$\sigma_0 = \xi_{t0}^{\,-2} \simeq R_{gK}^{\,-2}M^{\chi(2\nu_t-1)/(1+\chi)} \tag{58}$$

or, by using eq 54,

$$\sigma_0 \simeq M^{-d} \tag{59}$$

where the exponent d is equal to

$$d = (2\nu + 2\chi - 2\chi\nu_t)/(1 + \chi) \simeq 1.10 \tag{60}$$

B.5. Universal Relationships between the Amplitudes. Critical amplitudes (as well as critical exponents) should thus be typical of binary mixtures of simple liquids. For such systems it has been shown, both theoretically[39] and experimentally,[40] that universal relationships exist between these amplitudes. For example, the ratios $(4S_{xx}^{\,0})/(\xi_{to}^{\,3}\eta_0^{\,2}) = \sum_0$ and $(\sigma_0\xi_{to}^{\,2})/(kT_c)$ are universal numbers in binary mixtures[40] (the subscript 0 designates the amplitudes). (The first number appears in fact in the Ginzburg criterion and is close to one[41].) The measurement of such ratios on polymer–polymer–good solvent systems should allow us to test whether the critical behavior of solutions of polymer blends is analogous to that of binary mixtures, contrary to the ternary mixtures of small molecular weight liquids.

V. Conclusions

The essential conclusion of the present analysis is that the critical behavior of most incompatible polymer pairs is nonclassical and cannot be described by mean field approximation. Nevertheless it seems that the composition fluctuations should not affect the molecular weight and temperature dependence of the critical line eq 20. Actually, recent measurements for both strongly incompatible (PS/PDMS)[17] and weakly incompatible (PS/PMMA)[34] pairs seem to confirm well the scaling law $c_K \simeq M^{-(3\nu-1)/(1+\chi)}$. The prefactor depends on the interactions between unlike monomers and on the solvent quality.

In most practical situation demixing occurs well in the semidilute regime, but still the overlap ratio c_K/c^* at the demixing transition rarely exceeds 10 or 20. Thus the composition fluctuations are important and the Ginzburg criterion (eq 18) shows that the critical region in which nonclassical behavior is expected should be quite large (Δ^*/c_K or $\Delta T^*/T_K$ of about a few percent). The behavior of the system is strongly affected by composition fluctuations that are not taken into account in mean field type theories. Figure 1 for example shows the phase diagrams predicted by these different approaches for typical experimental situations. Similar important differences are also expected for scattering and interfacial properties. The critical exponents should be of the Ising type as for demixing transition in binary mixtures because the total monomer concentration fluctuations is small compared to the composition fluctuations (eq 48). In this respect the critical properties of such polymer systems are very original since ternary mixtures of small molecular weight liquids exhibit singularities described by renormalized Ising exponents.[32,33] The nonclassical behavior due to composition fluctuations also manifests itself in the scaling laws for molecular weight dependence of critical amplitudes.

Few experimental studies of critical properties are available. Shinozaki et al.[12] studied the solutions in propylbenzene of PS and PDMS of relatively low molecular weight ($M_w < 10^5$) and found that the coexistence curve exponent β is close to the Ising value. The corresponding amplitude seems to be compatible with 51 the scaling law. Their measurements of the interfacial tension are less conductive but still are compatible with the theoretical predictions for the exponent and the amplitude.[35]

Radiation scattering gives a direct method of measuring the correlation length and the osmotic compressibility. In particular, the "optical Θ" method, recently introduced by Tanaka et al.[24] is of great interest, because it allows a direct determination of the interactions between unlike chains. We give in Appendix B formulas for the scattered intensity $I(c,q)$ at low scattering vector q and nondilute concentration ($c > c^*$) under "optical Θ" conditions. Recent light scattering measurements on PS/PMMA blends under "Θ optical" conditions[15] in the semidilute regime far from the critical concentration yield $c/I(c,q{=}0)$, in reasonable agreement with eq B.9. Further experiments near the critical line allowing us to observe the crossover between critical and semidilute behavior will be of great interest.

Note Added in Proof. We are deeply indebted to Professor K. Binder for sending a preprint of his work with A. Sariban[38] on Monte Carlo simulations of solutions of polymer blends. Their method of analyzing the crossover from Ising to mean field behavior helped us to correct our predictions for molecular weight dependence of critical amplitudes. We find an excellent agreement with the results of simulations of ref 38 both for the coexistence curve and the osmotic compressibility (our eq 51 and 57). This seems to indicate the importance of excluded volume effects in the critical behavior of solutions of polymer blends.

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Appendix A

We recall some results concerning universal constants appearing as prefactors in the scaling laws for the reduced osmotic pressure, the correlation length, and the radius of gyration of polymer chains in semidilute solutions, respectively[37]

$$\frac{M_\omega}{RTc} = K_\omega(c/c^*)^{1/(3\nu-1)} \tag{A.1}$$

$$\frac{\xi(c)}{R_g} = K_\xi(c/c^*)^{-\nu/(3\nu-1)} \tag{A.2}$$

$$\frac{R_g{}^2(c)}{R_g{}^2} = K_R(c/c^*)^{-(2\nu-1)/(3\nu-1)} \tag{A.3}$$

The experimental values of these constants have been determined and are closed to the calculated values[37]

$$K_\omega = 1.5 \tag{A.4}$$

$$K_\xi = 0.5 \tag{A.5}$$

$$K_R = 1.4 \tag{A.6}$$

From (A.1) and (A.2) we can deduce the value of the constant K' appearing in the scaling law relating the osmotic pressure to the correlation length

$$\frac{\omega}{kT} = K'\xi^{-3} \tag{A.7}$$

$$K' = \frac{3}{4\pi}K_\omega K_\xi{}^3 \simeq 0.03 \tag{A.8}$$

The constant K' could be directly measured by making osmotic pressure and (light or neutron) scattering measurements on the same samples. Similarly the constant K_ρ defined by eq 14 is related to K_R and K_ξ through

$$K_\rho = 9K_RK_\xi/2\pi \simeq 1 \tag*{(A9)}$$

Whether there exists universal relations between the interaction prefactors A (dilute regions) and K_i (semidilute regions) is a delicate question. Such a relation could allow us to simply relate dilute properties (virial coefficients) to semidilute properties (critical concentration of demixing c_K)

$$\Delta B/B = AM^{-\chi} = C^{te}(c_K/c^*)^{-(1+\chi)/(3\nu-1)} \tag{A.10}$$

(one has to assume in fact that the correction term to osmotic pressure induced by chemical mismatch is continuous at about the overlap concentration c^*).

Appendix B: Radiation Scattering Spectra

Many properties of polymer blends in solution (e.g., second virial coefficients, radia of gyration, correlation lengths, osmotic compressibility, or critical concentration of demixing) can be extracted from radiation scattering measurements. For example the spinodal surface $c_S(x,T)$ is usually obtained by extrapolating to zero the inverse reduced intensity at zero scattering angle $c/I(c,q{=}0)$. The general expression for the scattered intensity is

$$I(q) = r_A{}^2S_{AA}(q) + r_B{}^2S_{BB}(q) + 2r_Ar_BS_{AB}(q) \tag{B.1}$$

where r_i is the contrast factor (the refractive index increment in light scattering experiments) of polymer i in the solvent and

$$S_{ij}(q) = \int \mathrm{d}^3r\, e^{iq\cdot r}[\langle c_i(0)c_j(r)\rangle - c_ic_j] \tag{B.2}$$

is the structure factor associated to i and j monomer concentration fluctuations (i, j = A, B). In the symetric case considered here $R_{g_A}{}^2 = R_{g_B}{}^2$ and hence $S_{AA} = S_{BB}$ at low q. Then one can write $I(q)$ in terms of $S_{CC}(q)$ (see eq 6) and of $S_{xx}(q)$ (eq 33)

$$I(q) = \tfrac{1}{2}(r_A + r_B)^2S_{cc}(q) + (r_A - r_B)^2c^2S_{xx}(q) \tag{B.3}$$

Two particular cases are important from an experimental point of view. The first consists in matching the refractive indexes of the solvent and one polymer (e.g., $r_B = 0$). One only "sees" the other polymer

$$I(q) = \tfrac{1}{4}r_A{}^2S_{cc}(q) + r_A{}^2c^2S_{xx}(q) \tag{B.4}$$

We analyze below the scattered intensity in the case of an "optical Θ" system,[24] where (here) $r_A + r_B = 0$ (the solvent has a refractive index between those of the polymers). Composition fluctuations are directly measured

$$I(q) = (r_A - r_B)^2c^2S_{xx}(q) \tag{B.5}$$

In the *critical regime* near the critical concentration of demixing ($c < c_K$) I is dominated by the composition fluctuations part. At small q ($qR < 1$)

$$I(q) \simeq (r_A - r_B)^2c^2S_{xx}(q) = I(q{=}0)(1 + q^2\xi_t{}^2) \tag{B.6}$$

where $I(q{=}0) \simeq c\kappa$, κ being the osmotic compressibility determined in section IV.3 and ξ_t the correlation length of composition fluctuations (B.2).

In the *semidilute regime* far from both the overlap and the demixing concentrations ($c^* < c < c_K$) the mean field results of section III.B are valid. In an optical Θ solvent the inverse reduced scattered intensity takes the simple form at small q ($qR < 1$)

$$\frac{Kc}{I(q,c)} = \frac{1}{M}\left[1 - \left(\frac{c}{c_K}\right)^{(1+\chi)/(3\nu-1)}\right]\left(1 + \frac{1}{3}q^2R^2_{\text{gapp}}\right) \tag{B.7}$$

with K being the optical constant where the apparent radius of gyration is

$$R^2_{\text{gapp}}(c) = R_g{}^2(c)/[1 - (c/c_K)^{(1+\chi)/(3\nu-1)}] \tag{B.8}$$

At zero scattering angle eq B.7 becomes

$$\frac{Kc}{I(q{=}0,c)} - \frac{1}{M} = -\frac{1}{M}(c/c_K)^{(1+\chi)/(3\nu-1)} \simeq -c^{(1+\chi)/(3\nu-1)} \tag{B.9}$$

In the *dilute regime* scattering experiments under optical Θ conditions allow the direct determination of the second virial coefficients B_{ij} and have been amply discussed[24] and performed.[13,14,17] In particular, the optical Θ method allows the direct determination of the difference of the virial coefficient ΔB.

References and Notes

(1) Stockmayer, W. H.; Stanley, H. E. *J. Chem. Phys.* **1950**, *18*, 153.

(2) Hyde, A. J.; Tanner, A. G. *J. Colloid Interface Sci.* **1968**, *28*, 179.

Macromolecules 1987, *20*, 1943–1947

(3) Kuhn, R.; Cantow, H. J.; Burchard, W. *Angew. Makromol. Chem.* **1968**, *2*, 146.

(4) Van der Esker, M. W. J.; Vrij, A. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, 2, 146.

(5) Kratochvil, P.; Strakova, D.; Tuzar, Z. *Br. Polym. J.* **1977**, *9*, 217.

(6) Kratochvil, P.; Vorlicek, J. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 1561.

(7) Scott, R. L. *J. Chem. Phys.* **1949**, *17*, 279.

(8) Tompa, H. *Trans. Faraday Soc.* **1949**, *45*, 1142.

(9) Koningsveld, T.; Chermin, R.; Gordon, M. *Proc. R. Soc., London A* **1970**, *319*, 331.

(10) de Gennes, P.-G. *J. Phys. Lett.* **1977**, *38*, L-441.

(11) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979; Chapter 4.

(12) Shinozaki, K.; Saito, Y.; Nose, T. *Polymer* **1982**, *23*, 1937.

(13) Fukuda, T.; Nagata, M.; Inagaki, H. *Macromolecules* **1984**, *17*, 548.

(14) Klotz, S.; Cantow, H. J.; Kogler, G. *Polym. Bull.* (*Berlin*) **1985**, *13*, 393.

(15) Fukuda, T.; Nagato, M.; Inagaki, H. *Macromolecules* **1986**, *19*, 1411.

(16) Ould Kaddour, L.; Strazielle, C. *Polymer* **1987**, *28*, 459.

(17) Ould Kaddour, L.; Soleda Anasagasti, M.; Strazielle, C. *Makromol. Chem.*, in press.

(18) Joanny, J. F.; Leibler, L.; Ball, R. *J. Chem. Phys.* **1984**, *81*, 4640.

(19) Kosmas, M. K. *J. Phys. Lett.* **1984**, *45*, L-889.

(20) Schäfer, L.; Kappeler, Ch. *J. Phys.* (*Les Ulis, Fr.*) **1985**, *46*, 1853.

(21) Witten, T. A., Jr.; Schäfer, L. *J. Phys. A* **1978**, *11*, 1843.

(22) See, for example: Lapp, A.; Herz, J.; Strazielle, C. *Makromol. Chem.* **1985**, *186*, 1919 and references therein.

(23) In terms of analogy with magnetic phase transitions, the problem of ternary solutions corresponds to the limit $n = 0$ of the quadratic anisotropy n-vector model rather than the cubic anisotropy model as has been erronously remarked in ref 18. χ is in fact the crossover exponent of the good solvent isotropic fixed point considered here which in the limit $n = 0$ is identical with the corresponding crossover exponent of the cubic anisotropy model, calculated at third order in $\epsilon = 4 - d$ (d being the space dimension) by: Keitley, I. J.; Wallace, D. J. *J. Phys. A: Math. Gen. Phys.* **1973**, *6*, 1667. Using a Pade Borel approximation, we obtain $\chi \simeq 0.225 \pm 0.005$.

(24) Tanaka, T.; Inagaki, H. *Macromolecules* **1979**, *12*, 1229.

(25) See ref 12, Chapter 3, for a description of semidilute (homo)-polymer solutions. Equation 8 has been derived first by: des Cloizeaux, J. *J. Phys.* (*Les Ulis, Fr.*) **1975**, *36*, 281.

(26) For polymers in solution this parameter is thus neither a constant, as assumed in the first Flory–Huggins models[7,8] nor analytic in c, as assumed in more recent modifications of the Flory–Huggins theory.[9]

(27) In an experiment of type (a) (at constant $T = T_K$ temperature) $\eta \simeq (c - c_K(T_K))^\beta$ $c > c_K$ is in fact the critical concentration of demixing at a lower temperature T_K': $c = c_K(T_K')$. c_K being a derivable function of T_K, we get $\eta \simeq (\mathrm{d}c_K/\mathrm{d}T)^\beta (T_K' - T_K)^\beta \simeq (\mathrm{d}c_K/\mathrm{d}T)^\beta (\Delta T/T_K)^\beta$.

(28) See ref 11, Chapter 10.

(29) It is in fact assumed that the thermodynamical potentials may be split into a singular part whose first derivatives are all zero and a regular part (such as eq 12 for the free energy) which yields the critical line (eq 20). The singular part is only responsible for the (nonclassical) critical divergencies near the critical line. Such an assumption is usually made in the study of ternary systems. See, for example: Leung, S. S.; Griffiths, R. G. *Phys. Rev. A* **1973**, *8*, 2670.

(30) Le Guillou, J. C.; Zinn-Justin, J. *Phys. Rev. Lett.* **1977**, *39*, 95.

(31) Fisher, M. E. *Phys. Rev.* **1968**, *176*, 1.

(32) Widom, B. *J. Chem. Phys.* **1967**, *46*, 3324. Clark, K. K. *Ibid.* **1968**, *48*, 741. Neece, G. *Ibid.* **1967**, *47*, 4112. Clark, R. K.; Neece, G. A. *Ibid.* **1968**, *48*, 2575. Wheeler, J. C.; Widom, B. *J. Am. Chem. Soc.* **1968**, *90*, 3064; *J. Chem. Phys.* **1970**, *52*, 5334.

(33) Zollweg, J. A. *J. Chem. Phys.* **1971**, *55*, 3. Wold, L. E., Jr.; Pruitt, G. L.; Morrison, G. *J. Chem. Phys.* **1973**, *77*, 1572. Ohbayashi, K.; Chu, B. *J. Chem. Phys.* **1978**, *68*, 5066.

(34) From the data of ref 15 (Table III) one can extract $c_K \simeq M^{-0.58}$ (Fukuda, T., personal communication).

(35) The values found for $2\nu_t$ in ref 12 range from 1.18 to 1.50 (theory predicts 1.26) and the value for d that one can extract from ref 12 is $d \simeq 1.26$. It seems that, because of the low molecular weight of the chains ($M_w < 10^5$), the asymptotic règime is not reached for the system (PS/PDMS) of ref 12. For example c_K does not scale like $M^{-0.62}$, except for the two longer chains.

(36) Ginzburg, V. L. *Sov. Phys. Solid State* **1960**, *2*, 1824.

(37) For a discussion on these constants (K_ω, K_ξ, K_R) see, for example: des Cloizeaux, J.; Noda, L. *Macromolecules* **1982**, *15*, 1505. Broseta, D.; Leibler, L.; Lapp, A.; Strazielle, C. *Europhys. Lett.* **1986**, *2*, 733.

(38) Sariban, A.; Binder, K. *J. Chem. Phys.*, in press.

(39) Stauffer, D.; Ferrer, M.; Wortis, M. *Phys. Rev. Lett.* **1972**, *29*, 345. Hohenberg, P. C.; Aharony, B. I.; Halperin, B. I.; Siggia, E. D. *Phys. Rev. B: Solid State* **1976**, *13*, 2986.

(40) Beysens, D.; Bourgou, A.; Calmettes, P. *Phys. Rev. A* **1982**, *26*, 3589. Chaar, H.; Moldover, M.; Schmidt, J. *J. Chem. Phys.* **1986**, *85*, 418.

(41) In the notation of ref 40, this ratio is $^1/_4[R_\xi{}^+ R_c{}^{-1/3}]^{-3} \simeq 0.85$. As a consequence the prefactors in eq 38 and 39 should be reduced by one-third.

(42) Strictly speaking the proportionality factor in eq 42 may depend very weakly on molecular weight (cf. eq 53). We neglect this dependence which does not change the qualitative conclusion of this section.

On the Cooccurrence of Demixing and Thermoreversible Gelation of Polymer Solutions. 1. Experimental Observations

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ABSTRACT: The phase diagram of the system 2-propanol/poly(n-butyl methacrylate) (2-POH/PBMA) was determined for two narrowly distributed polymer samples of M_w ca. 500 000. Demixing curves were measured viscometrically and visually and gelation curves by means of the velocity of a falling body. A third curve (situated within the two-phase region and also resulting from viscosity measurements), which can be related to the aggregation of droplets of the segregated phase upon cooling, is also presented. The evaluation of the gelation conditions for homogeneous solutions according to Eldridge and Ferry yields 37 kJ/mol of cross-links for the heat of gelation. Measurements with lower molecular weight PBMA (M_w 8900) confirm the cooccurrence of phase separation and gelation, although the stability of the gels against shear is rather low in this case. The exchange of the Θ-solvent 2-POH against ethanol, 1-propanol, 1-butanol, or n-decane does not reveal principal differences.

Introduction

Thermoreversible gelation has been described for biological systems[1-3] and a variety of synthetic polymers in solutions, such as PVC,[4,5] polystyrene,[6-11] and polyethylene.[12,13] In many cases gelation occurs together with phase separation[3,6,14,15] where the two phenomena have been suggested to be closely associated. For example, in concentrated aqueous solutions of barium poly(styrene-

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