Liquid–Liquid Phase Separation in Multicomponent Polymer Solutions. VII. Relations for the Spinodal and Critical Loci

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ABSTRACT: The generalization of the Flory–Huggins model to polydisperse systems with an interaction parameter dependent on over-all polymer concentration, treated in previous papers of the series, is explored further regarding spinodal and critical loci. It is proved mathematically that for this model the critical point is located on the right-hand branch of the cloud-point curve, and this is confirmed experimentally for *n*-hexane–polyethylene. A simple transformation of the equations governing the spinodal and critical loci leads to easier visualization of these loci in terms of certain mappings in the concentration–temperature plane.

Several years ago Tompa[1,2] showed that the maximum (or minimum) precipitation temperature of a partially miscible polymer solution cannot in general be identified with the critical or consolute point. Such an identity exists only in truly binary systems containing a single-component polymer. Actual macromolecular solutions containing a solvent and a polydisperse polymer had better be denoted by the term quasi-binary.

In previous work,[3-6] it was argued that in quasi-binary polymer solutions the critical point is located on the right-hand branch of the cloud-point curve. The reasoning was based on numerical calculations for selected molecular weight distribution functions and on experimental evidence. Conclusive proof has been lacking, however, and it is the purpose of the present note to provide more cogent arguments. At the same time, the visualization of the spinodal and critical loci is improved in terms of mappings in the φ–T plane together with equations connecting them.

We shall use the Flory–Huggins[7-11] expression for the free enthalpy (Gibbs free energy) of mixing ΔG, which is based on the lattice model of the polymer solution

$$\Delta G/RT = \varphi_0 \ln \varphi_0 + \sum_i \varphi_i m_i^{-1} \ln \varphi_i + g\varphi(1 - \varphi)$$

where ΔG = the free enthalpy of mixing per mole of lattice sites, φ_0 = the volume fraction of the solvent, φ_i = the volume fraction of macromolecular species i, $\varphi = \Sigma\varphi_i$ = the volume fraction of the whole polymer, m_i = the chain length of species i, expressed as the number of occupied lattice sites, R = the gas constant, T the absolute temperature, and g = the semiempirical interaction parameter.[3,7,11] The actual thermodynamic behavior of polymer solutions has often been observed to deviate from that predicted by eq 1. Many of these deviations, however, can be quantitatively accounted for by making g dependent not only on the temperature T but also on the polymer concentration φ.

Stockmayer[12] was the first to derive the spinodal and the critical conditions for systems obeying eq 1 with g independent of φ. His equations read

$$\text{spinodal} \qquad 2g = (\varphi m_\text{w})^{-1} + (1 - \varphi)^{-1} \tag{2}$$

$$\text{critical point} \qquad \varphi_\text{c} = 1/[1 + m_\text{w}^{1/2} (m_z/m_\text{w})^{-1/2}] \tag{3}$$

where m_w and m_z are the weight- and z-average chain lengths.

The essential feature of Stockmayer's procedure is a series expansion of the chemical potential of the solvent in the close proximity of the critical point. It follows from eq 2 and 3 that the critical point, which is located on the spinodal (as well as on the cloud-point curve), is at the maximum of the spinodal if the polymer is monodisperse ($m_\text{w} = m_z = m$). It is also obvious that a polymer with a distribution of molecular weights ($m_z/m_\text{w} > 1$) has a higher critical concentration than a monodisperse one ($m = m_\text{w}$). Hence, the critical point for a polydisperse polymer must be located on the right-hand branch of the spinodal and, therefore, also on the right-hand branch of the cloud-point curve. The latter conclusion was also drawn by Šolc,[13] who studied the cloud-point curve itself.

The above considerations apply to a true Flory–Huggins system, in which g is independent of φ. If it is not, the foregoing approach is not practicable and one has to look for an alternative way of reasoning. This can be found by starting from Gibbs' formulation of the spinodal and critical conditions.[14] The equa-

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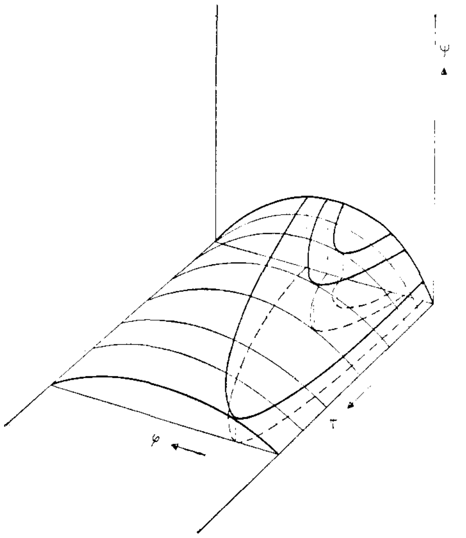

Figure 1. The tunnel-shaped ψ surface. Three spinodals are shown, together with their projections upon the φ–T plane.

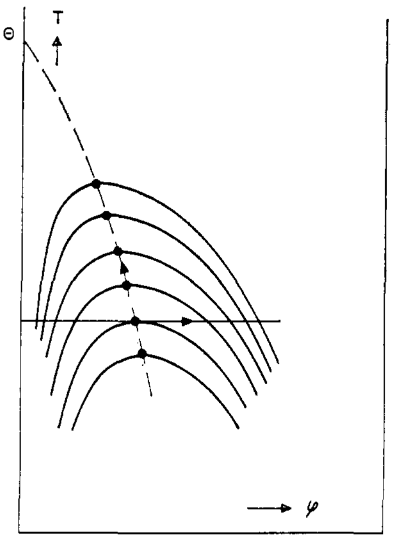

Figure 2. Quasi-binary spinodals for m_w values increasing from bottom to top.

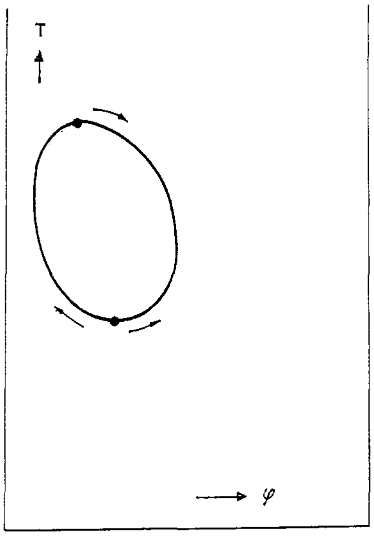

Figure 3. Quasi-binary spinodal for a closed immiscibility region.

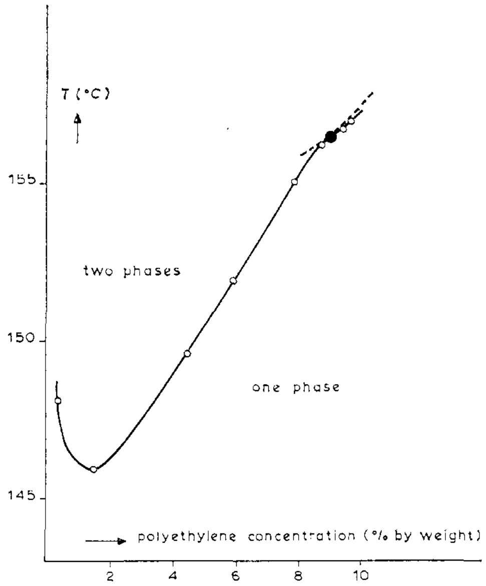

Figure 4. Cloud-point curve for an n-hexane–polyethylene system (Marlex 6009; $M_n = 8 \times 10^3$; $M_w = 1.8 \times 10^5$; $M_z = 1.2 \times 10^6$). The dashed curve indicates the estimated location of the quasi-binary spinodal. The critical point (black dot) was determined by the phase–volume ratio method.

tions thus obtained from eq 1,[3-5] with $g = g(\varphi, T)$, can be written as

spinodal

$$(\partial^2\psi/\partial\varphi^2)_T = -(\varphi m_w)^{-1} - (1 - \varphi)^{-1} \quad (4)$$

critical state

$$(\partial^3\psi/\partial\varphi^3)_T = m_z/m_w^2\varphi_c^2 - (1 - \varphi_c)^{-2} \quad (5)$$

where

$$\psi = g\varphi(1 - \varphi) \quad (6)$$

The typical shape of the function $\psi(\varphi, T)$ is shown in the sketch (Figure 1) in the region below a Flory θ temperature.[8] The function must vanish for $\varphi = 0$ and 1 according to eq 6, and its curvature $\partial^2\psi/\partial\varphi^2$ is everywhere negative according to eq 4. It is readily seen that if g is a continuous and differentiable function of φ and T everywhere, then ψ is a *single-valued* function of φ and T. It follows from eq 4 that for any φ and T, there will generally be a unique value of m_w, which represents the weight average of *any* distribution of the polymer fulfilling the spinodal condition at this (φ, T). We thus have a mapping of families of quasi-binary spinodals in the φ–T plane, of which three are shown in Figure 1, with m_w as the parameter of the family. Every distribution of the same m_w must have the same quasi-binary spinodal curve, which coincides with the binary spinodal of the monodisperse polymer of equal m_w.[3-5] As we change the nature of the distribution at constant m_w, say by increasing m_z (Figure 2) from its lowest possible value m_w, the critical point travels down the right-hand branch of the quasi-binary spinodal. In this way, a second mapping is produced, associating with each suitable (φ, T) a unique value of m_z, being the value of m_z of *any* distribution which fulfils the critical condition at (φ, T). Thus, by differentiating eq 4 with respect to φ at constant T, bearing

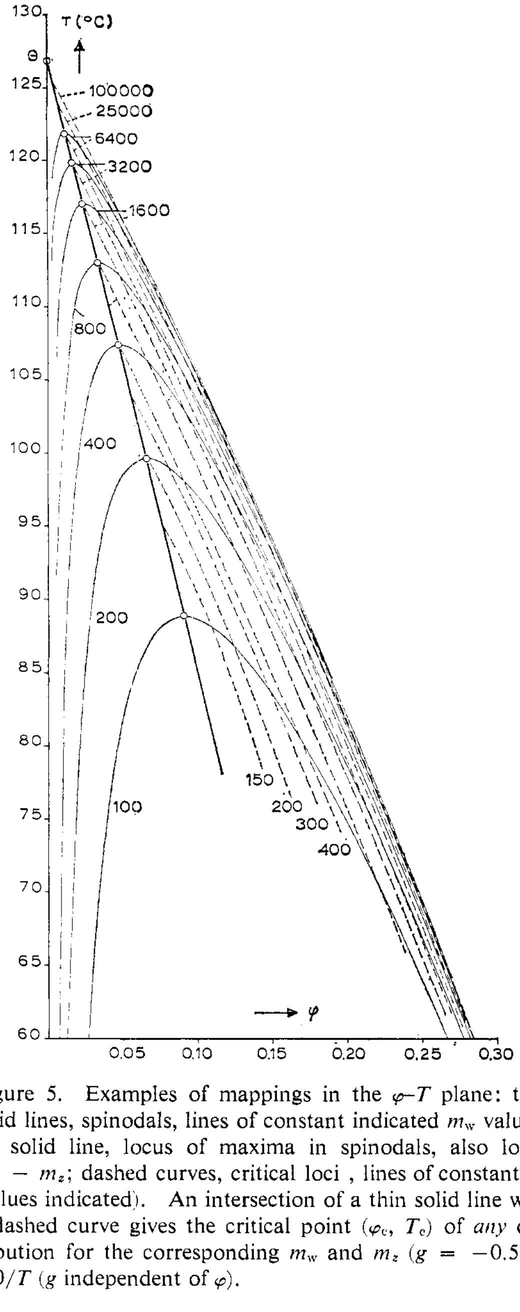

Figure 5. Examples of mappings in the φ–T plane: thin solid lines, spinodals, lines of constant indicated m_w values; fat solid line, locus of maxima in spinodals, also locus $m_w - m_z$; dashed curves, critical loci , lines of constant m_z (values indicated). An intersection of a thin solid line with a dashed curve gives the critical point (φ_c, T_c) of *any* distribution for the corresponding m_w and m_z ($g = -0.5 + 400/T$ (g independent of φ).

in mind that $m_w = m_w(\varphi, T)$ in virtue of the mapping process explained above, and eliminating $\partial^3\psi/\partial\varphi^3$ from the result by means of eq 5, we obtain the important equation

$$m_z - m_w = (\partial m_w/\partial \ln \varphi)_T \tag{7}$$

This equation is valid for the critical condition. From eq 7 it follows that $(\partial m_w/\partial\varphi)_T \geqslant 0$. It follows from eq 2 that for the original Flory–Huggins theory $(\partial m_w/\partial T)_\varphi$ has the opposite sign to $(\partial g/\partial T)_\varphi$. The same conclusion follows for the generalized theory from eq 10. Using the relation

$$\left(\frac{\partial m_w}{\partial\varphi}\right)_T\left(\frac{\partial\varphi}{\partial_T}\right)_{m_w}\left(\frac{\partial_T}{\partial m_w}\right)_\varphi = -1 \tag{8}$$

we find that $(\partial_T/\partial\varphi)_{m_w}$ is negative below the upper critical solution temperature, where $(\partial g/\partial T)_\varphi < 0$ and also $(\partial T/\partial\varphi)_{m_w}$ is positive above the lower critical solution temperature, where $(\partial g/\partial T)_\varphi > 0$ (as is recently found by Rowlinson[15,16] to occur quite often as well[17]). In other words, the critical point must lie on the right-hand branch of the spinodal in all cases.

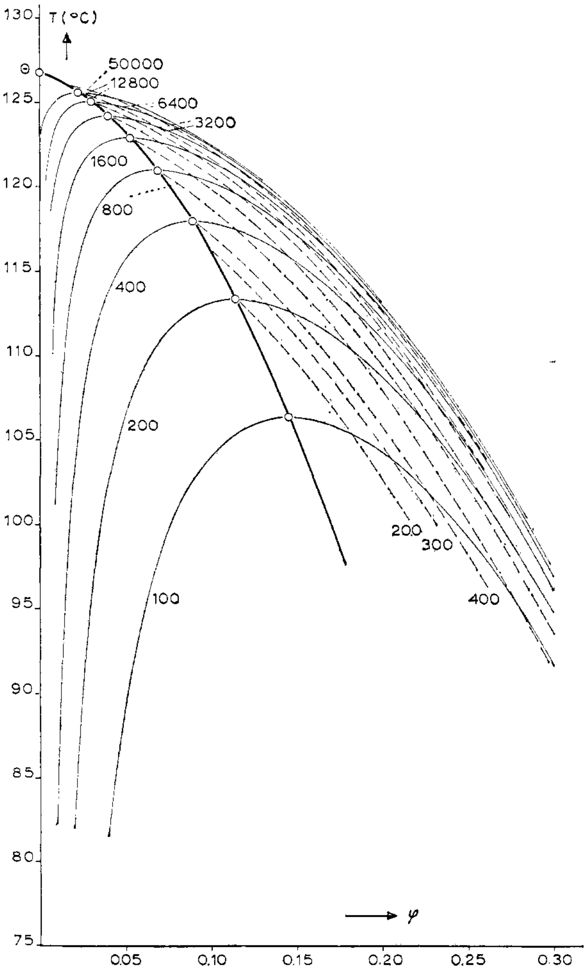

Figure 6. Same as Figure 5 but $g = g_0 + g_1\varphi$; $g_0 = -0.35 + 400/T$; $g_1 = +0.15$.

That the critical point must be located on the same branch of the quasi-binary spinodal in the temperature region above a Rowlinson θ point can also be deduced from physical arguments (Figure 3). Consider a system with a closed immiscibility gap. Such systems have been found experimentally.[18,19] If, upon an increase of the polydispersity, the upper critical point travels down the right-hand branch of the quasi-binary spinodal, while the lower one would ascend the left-hand branch, there would eventually arise a situation where there are two critical points at the same temperature and pressure. This would be in contradiction with the phase rule. Therefore, two critical points must be on the same branch, and, in view of the preceding remarks, this must be the right-hand one.

Experimental evidence for a lower critical solution system is provided by Figure 4, which shows a cloud-point curve for the system *n*-hexane–polyethylene. The

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polyethylene sample used was a Marlex 6009 type whole polymer. The critical concentration was measured by the phase–volume ratio method.[3–5]

Figures 5 and 6 sketch the general behavior of the lines of constant m_w and those of constant m_z. The latter are fully determined by eq 7 in terms of the m_w mapping. Conversely, the m_z mapping (together with its boundary $m_z = m_w$, see Figures 5 and 6) also fully determines the m_w mapping. This follows because, given $m_z = m_z(\varphi)$ at fixed temperature T, we can obtain $m_w = m_w(\varphi)$ by integrating eq 7 in its alternative form

$$m_z = [\partial(m_w\varphi)/\partial\varphi]_T \tag{8}$$

thus

$$m_w = [m_0\varphi_0 + \int_{m_0}^{m_z}(\mathrm{d}\ln m_z^*/\mathrm{d}\varphi)^{-1}\,\mathrm{d}m_z^*]/\varphi \tag{9}$$

The integration starts from any point ($m_0 = m_w = m_z$, $\varphi = \varphi_0$) on the fat lines in Figures 5 and 6, and proceeds horizontally to the right. In principle, the mappings of Figures 5 and 6 can be determined experimentally by finding the critical points of fractions with narrow distributions and known mixtures thereof. Once Figures 5 and 6 are known, a single measurement of the critical point (φ_c, T_c) determines both m_w and m_z of any polymer distribution. Measurements are now being carried out to collect the data needed for constructing graphs like Figures 5 and 6 for actual systems (cyclohexane–polystyrene and diphenyl ether–polyethylene).

Finally, it may be of interest to derive ψ and hence $g(\varphi, T)$ (eq 6) from the mappings in Figures 5 and 6. To this end, we may use the m_w mapping and evaluate ψ from it by integrating twice eq 4, thus

$$\psi = -\int_0^{\phi}\int_0^{y}\frac{1}{xm_w(x, T)}\,\mathrm{d}x\,\mathrm{d}y - (1 - \phi)\ln(1 - \phi) + \phi[g(0, T) - 1] \tag{10}$$

We have used

$$\left(\frac{\partial\varphi}{\partial\psi}\right)_{T,\varphi=0} = g(0, T) \tag{11}$$

which follows from eq 6. We deduce that $m_w(\varphi, T)$ does not fully determine g, except when supplemented by the value of g at infinite dilution ($\varphi = 0$), which arises as an integration constant.

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Carbon-13 Nuclear Magnetic Resonance Analysis of Ethylene Oxide–Maleic Anhydride Copolymers

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ABSTRACT: Natural abundance ^{13}C white noise decoupled nmr spectra of poly(ethylene oxide) and some ethylene oxide–maleic anhydride copolymers have been obtained at 25.1 MHz. The copolymer spectra are interpreted in terms of triads and pentads of monomers in the chain providing both short- and long-range information about chain structure. The relative chemical shifts of the carbons in the central units of these sequences are opposite to and more than an order of magnitude larger than those of the protons in the same units. The ^{13}C shifts correlate with differences in the local π-electron density, while the ^1H shifts correlate with neighbor anisotropic shielding effects of adjacent functional groups.

The ^1H nmr spectra of copolymers can usually be interpreted in terms of triads of monomer units in the chain.[1] The relative chemical shifts of the protons of a unit in the chain depend on the identity of the two nearest neighbor monomer units. (Only rarely are sizable effects of more distant units in the chain observed.[2]) For a given central unit even these triad shifts are generally small, amounting to only a fraction of a part per million. This makes interpretation of the spectra difficult, especially if the resonances show the dipolar broadening characteristic of proton nmr polymer spectra. In addition, the proton nmr spectra of most copolymers are complicated by spin–spin coupling which does not itself contain any sequence information and which often cannot be conveniently removed by homonuclear decoupling techniques.

The extensive range of ^{13}C chemical shifts, the absence of significant dipolar broadening, and the simplicity of spectra in which all spin–spin interactions can be removed by heteronuclear decoupling make the ^{13}C nmr analysis of copolymers attractive enough to overcome the disadvantage of low sensitivity. This paper reports the analysis of the natural abundance ^{13}C nmr spectra of some ethylene oxide–maleic anhydride copolymers.

Experimental Section

Natural abundance ^{13}C nmr spectra were obtained using a Varian HA-100 spectrometer operating at 25.1 MHz. An

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