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$$R(\bar{q}) = I_s(\bar{q})d^2/I_0V_s$$

where d is the sample-to-detector distance, $I_s(\bar{q})$ is the scattered intensity, I_0 is the incident beam intensity, and V_s is the scattering volume. The $R(\bar{q})$ used in light scattering is equivalent to the differential scattering cross section $d\Sigma/d\Omega$ used in neutron scattering.

Multiphase Equilibria in Solutions of Polydisperse Homopolymers. 3. Multiple Critical Points[†,‡]

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ABSTRACT: The cloud-point curve equation is derived for a solution of a polydisperse polymer with a concentration-dependent interaction parameter $g(T,\phi)$, and a method for its numerical solution is devised. Also, a classification scheme is proposed for critical points based on their multiplicity, and the relationship between our and the previously devised categories is probed (particularly between our triple critical point and the tricritical point). Criteria for the existence of critical points of multiplicity $m = 2$–6 are given in terms of chain-length averages, concentration derivatives of $g(T,\phi)$, and the overall polymer concentration ϕ. The significance of multiple critical points lies in their close association with multiphase equilibria. Such points may arise because of the asymmetry of the chain-length distribution and/or because of a strong concentration dependence of $g(T,\phi)$. Two specific cases are analyzed: a polydisperse polymer solution with a concentration-independent parameter $g(T)$, and a monodisperse polymer solution with a concentration-dependent parameter $g(T,\phi)$. In the first instance, multiple critical points may appear even in systems with only a few components if their characteristics are properly chosen. At most, an s-component system at constant pressure may display a critical point of multiplicity $2s - 3$, and it may separate into s phases. In the latter case, double and triple critical points may appear if the concentration dependence of $g(T,\phi)$ is at least quadratic. The pattern of cloud-point curves for the two analyzed cases is distinctly different.

1. Introduction

The first to introduce the concept of a critical point of multiplicity higher than one was probably Korteweg.[2] Without much reference to any physical situation, he studied the characteristics of certain singular points (critical points, or plait points, among others) on a three-dimensional surface, as well as their behavior during a continuous transformation of this surface. His classification of critical points into points of the first and second kind (located on convex–convex and convex–concave parts of the surface, respectively) has been shown[3,4] to have a thermodynamic significance, as the phases around such points on the free energy ternary surface are (meta)stable and unstable, respectively. Furthermore, Korteweg noticed that upon transformation of the surface, two real critical points may approach each other, merge, forming a double plait point, and become imaginary (i.e., disappear from the surface). A homogeneous double critical point was defined as a confluence of two critical points of the first kind, while a heterogeneous double critical point designated merging of critical points of the first and second kind.

Extensive thermodynamic interpretation of the above singular points was given by van der Waals[3] and Schreinemakers,[4] although only in terms of mathematical criteria and general patterns of resulting phase diagrams. Meijering[5] with Hardy[6] then analyzed in detail the phase behavior of ternary and quaternary regular solutions and concluded that these systems may contain only homogeneous double critical points since all critical points in such solutions have to be stable or metastable. Tompa,[7] on the other hand, studied three-phase separation in solvent–polymer (1)–polymer (2) ternary systems where the two polymers differed merely by their chain lengths but did not interact with each other. Assuming simple Flory–Huggins thermodynamics (with a concentration-independent parameter χ),[8] he discovered that the phase separation proceeded via a heterogeneous double plait point mechanism. The validity of this claim was later proven conclusively by applying Korteweg's instability criterion to this case.[9] The same mechanism is in effect for three-phase separations in some solutions of ternary polymer mixtures[10] and of polydisperse polymers in general. The types of double critical points encountered and the manner in which multiphase separations proceed in

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[†] We take pleasure in dedicating this paper to our friend, Professor Walter H. Stockmayer, on the occasion of his 70th birthday.

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low molecular weight regular solutions thus seem to be diametrically different from the behavior of polydisperse polymer solutions.

There are very few references in the older literature to critical points of higher multiplicities. Kohnstamm[11] foresaw possible existence of critical points where three (rather than the usual two) stable phases would become critically identical. Unfortunately, he did not realize that, in terms of multiplicity, such points represent simply *triple* critical points (although he was aware of the existence of double ones) and chose to refer to them as the critical points of the *second order*. His prediction was indeed experimentally confirmed by Soviet authors in a series of papers on ternary and quaternary systems (for an extensive listing, see ref 12). In the area of ternary polymer solutions, Tompa[7] actually derived a criterion for such a triple critical point where two heterogeneous double critical points merge and the size of the three-phase region just becomes infinitesimal; however, he never used this or any other term to designate this significant point.

In the modern era the term *tricritical* point[13] or, more specifically, *symmetrical tricritical* point[12,14] was coined by Griffiths for the point where a first-order transition turns into a λ transition, a phenomenon predicted by Landau almost 50 years ago[15] and observed in metamagnets, mixtures of ^{3}He and ^{4}He, etc. The chosen term signified the fact that, after adding a (nonphysical) "field" coupling to the order parameter, the tricritical point became a terminus of three critical lines drawn in the thus augmented space of thermodynamic variables. Alternatively, such a point could be viewed as a terminus of a three-phase line[16] where the three coexisting phases become critically identical.[12] Obviously, it is the latter interpretation which makes such points directly analogous to Kohnstamm's[11] second-order critical points, and the term tricritical point has been recently used widely in papers dealing with phase behavior of some ternary and quaternary systems.[17] The list of synonyms unfortunately does not end with the above-mentioned triplet; as compiled in ref 12, it also includes a *three-phase* critical point and, somewhat at odds with Kohnstamm's suggestion (but more logically), a *third-order* critical point.[12,18] The confusion is augmented by some of these synonyms having been used as homonyms in a different sense by other authors; for instance, contrary to Kohnstamm,[11] Meijering[5] defines his second-order critical point as Korteweg's double critical point,[2] i.e., as an extremum of the critical line in coordinates temperature vs. composition.

Clearly, this situation calls for standardization of terminology. It is our suggestion to adhere to the original term of "multiple critical points" advanced by Korteweg[2] (i.e., we shall employ the term triple critical point for the above-discussed case). There are several reasons for our choice: (i) It has a historical precedence. (ii) It is more general, compared to order-based notation, as explained in section 4. (iii) It is mathematically justified since such critical points arise as multiple (nontrivial) roots of phase equilibrium equations that happen to coincide with the critical composition. (iv) Full realization of the latter circumstance makes obvious some other points. For instance, it is then natural to view such m-multiple critical points as termini of critical lines of lower multiplicities and to immediately see, e.g., for $m = 3$, the equivalence of such points with Griffiths' tricritical points in respects not obvious before. Furthermore, generalization to critical points of higher multiplicities becomes straightforward; criteria for their existence are derived simply by taking successively higher derivatives of phase equilibrium equation(s) with respect to some conveniently chosen parameter(s). This is important since the simple geometrical insight helpful earlier for double[2] and triple[7] critical points necessarily fails for reasons of complexity when attempted for critical points of higher multiplicities existing in spaces of higher dimensions.[10]

The significance of multiple critical points is in their association with multiphase equilibria, where they act as sources of new developing phases. Polymer solutions turn out to be particularly suitable for studying this phenomenon. Even in solutions of polydisperse homopolymers alone (the subject of this paper), the various polymer homologues may display (i) enough distinction to tend to phase separate (e.g., a solution of two homologues differing in chain length by a factor of ≈10 can separate into three phases[7]) yet also (ii) enough likeness to have similar critical temperatures and thus to eventually form a homogeneous solution upon change in temperature. (iii) Importantly, there is also enough latitude in the range of available molecular weights to accommodate a series of such homologues successively differing by an order of magnitude in their chain lengths and thus to hopefully enter the realm of m-phase equilibria where $m > 3$. The list of available options grows even longer when the molecular composition is included as a variable (as, e.g., in statistical copolymers[19]). Other multicomponent systems are often too soluble (i.e., they will not separate into more than a few phases), or they are too incompatible (such as the classical example of a seven-phase system in Hildebrand's monograph[20] that will not dissolve to a homogeneous solution within reasonable limits of state variables).

Section 2 contains the derivation of the cloud-point curve equation for a solution of a polydisperse homopolymer with a concentration-dependent interaction parameter. Criteria for multiple critical points in terms of molecular weight averages and derivatives of the interaction term are then developed in section 3 and discussed for two specific examples in sections 3.1 and 3.2.

2. Cloud-Point Curve Equation

We start with the common form of the Flory–Huggins free enthalpy of mixing per mole of lattice sites

$$\Delta G/RT = \phi_0 \ln \phi_0 + \sum_{i=1}^{n} \frac{\phi_i}{r_i} \ln \phi_i + \Gamma(T,\phi) \qquad (1)$$

where ϕ_i and r_i are the volume fraction and the relative chain length of the species i, with $i = 0$ denoting the solvent ($r_0 = 1$) and $i = 1, 2, ..., n$ the polymer homologues of various chain lengths but identical repeat units. The interaction term Γ is usually given as[21]

$$\Gamma(T,\phi) = g(T,\phi)\phi\phi_0 \qquad (2)$$

where the interaction parameter g is an arbitrary function of temperature T and total volume fraction of the polymer ϕ $(=\sum\phi_i)$.

The phase equilibrium equations, obtained from the condition of equality of chemical potentials of the solvent and all polymeric species in the two phases, are then

$$\ln \frac{\phi_0''}{\phi_0'} + \phi'' - \phi' - \left(\frac{\phi''}{r_n''} - \frac{\phi'}{r_n'}\right) + \phi''^2[g'' - (1 - \phi'')g_1''] - \phi'^2[g' - (1 - \phi')g_1'] = 0 \qquad (3)$$

$$\ln (\phi_i''/\phi_i') = \sigma r_i \qquad (4)$$

$$\sigma = \ln \frac{\phi_0''}{\phi_0'} - (g'' - g') + \phi''(2g'' - \phi_0''g_1'') - \phi'(2g' - \phi_0'g_1') \qquad (5)$$

where r_n is the number-average chain length, σ is the separation factor, and g_k is the kth concentration derivative of g, $(\partial^k g/\partial\phi^k)_T$. The single and double primes refer to the two coexisting phases, with the former traditionally used for the less concentrated phase and σ of eq 4 thus restricted to nonnegative values.[8] (This definition was used in our previous work.) It is apparent, however, that for a discussion of cloud-point curve equilibria, it is more convenient to speak in terms of the incipient and principal (or bulk) phases rather than more and less concentrated ones. Hence, we interpret the single and double primes as referring to the principal and incipient phases, respectively, with the parameter σ now allowed to take any real value. For the sake of brevity, hereafter the superscript will be omitted for quantities referring to the principal phase, and an asterisk will be used to designate parameters of the incipient phase.

The cloud-point curve is the locus of points representing limiting equilibria where, in general, the phase volume ratio approaches zero or infinity.[21] Thanks to the simple form (4), the chain-length distribution in the incipient phase $w^*(r)$ and its moments ν_k can be expressed in terms of σ and the original normalized distribution $w(r)$ or its moments μ_k as[9,22]

$$w^*(r) = w(r)e^{\sigma r} \qquad (6)$$

$$\nu_k = \int_0^\infty w^*(r) r^k \,\mathrm{d}r = \int_0^\infty w(r) r^k e^{\sigma r} \,\mathrm{d}r = \sum_{j=0}^{\infty} \mu_{k+j}\sigma^j/j! \qquad (7)$$

Note that the chain-length distribution in the incipient phase, $w^*(r)$, is not normalized, and its zeroth moment ν_0 defines the concentration ratio of the incipient and principal phases, $\nu_0 = \phi^*/\phi$. It follows from eq 7 that the moments ν_k depend only on the separation factor σ, with a simple derivative

$$\mathrm{d}\nu_k/\mathrm{d}\sigma = \nu_{k+1} \qquad (7a)$$

Equation 3 can now be modified by using eq 5, with the result cast in terms of moments as

$$F_1(\sigma,\phi,T) \equiv \tfrac{1}{2}\sigma(\nu_0 + 1) + \nu_0 - 1 - (\nu_{-1} - \mu_{-1}) + \left(\phi^{-1} - \frac{\nu_0 + 1}{2}\right) \ln \frac{1 - \phi\nu_0}{1 - \phi} - (g^* - g)[\phi\nu_0 - \tfrac{1}{2}(\nu_0 + 1)] - \tfrac{1}{2}(\nu_0 - 1)\phi[g_1^*\nu_0(1 - \phi\nu_0) + g_1(1 - \phi)] = 0 \qquad (8)$$

while eq 5 yields

$$F_2(\sigma,\phi,T) \equiv 2g\phi(\nu_0 - 1) + \ln \frac{1 - \phi\nu_0}{1 - \phi} - \sigma - (g^* - g)(1 - 2\phi\nu_0) - \phi[g_1^*\nu_0(1 - \phi\nu_0) - g_1(1 - \phi)] = 0 \qquad (9)$$

The advantage of the form (8) is apparent: if g is independent of polymer concentration ϕ, the last two terms disappear, and the function F_1 becomes independent of temperature and enables one to directly compute the volume fraction ϕ for any chosen value of σ. The temperature T is then calculated from the simplified form of eq 9. The simultaneous iteration of two or more equations, a lengthy procedure even for a computer, can thus be avoided as was shown in our previous work.[22] In fact, the applicability of this straightforward method is wider than indicated above. Also covered are systems where the interaction parameter can be split into temperature- and concentration-dependent parts like

$$g(T,\phi) = g^T(T) + g^\phi(\phi) \qquad (10)$$

It is obvious that neither the difference $g^* - g$ nor the concentration derivatives g_1 and g_1^* are then temperature dependent, and F_1 stays a function of only σ and ϕ. Only in the most general case is double-iteration solution of eq 8 and 9 necessary.

3. Multiple Critical Points

At a critical point the coexisting phases become identical; consequently, $\sigma \rightarrow 0$, $\nu_k \rightarrow \mu_k$, $g_k \rightarrow g_k^*$, etc. In the neighborhood of a critical point, the interaction parameter and its concentration derivatives can thus be expanded in terms of a concentration series

$$g_k^* = g_k + \sum_{i=1} g_{k+i}\phi^i(\nu_0 - 1)^i/i!, \qquad k = 0, 1, 2, \ldots \qquad (11)$$

and, with the aid of series (7) and expansion of logarithmic terms, eq 8 and 9 become

$$F_1 \equiv \sum_{n=3} \frac{(n-2)\sigma^n\mu_{n-1}}{2n!} - \frac{x^2(\nu_0 - 1)}{2} \sum_{n=0} \frac{n+1}{(n+2)(n+3)} x^n + \tfrac{1}{2}\phi^2(\nu_0 - 1)^3[g_1 + g_2(\phi\nu_0 - \tfrac{1}{2})] + \tfrac{1}{2}[1 + \nu_0(1 - 2\phi)] \sum_{n=3} \frac{g_n y^n}{n!} - \tfrac{1}{2}\nu_0(1 - \phi\nu_0) \sum_{n=3} \frac{g_n y^n}{(n-1)!} = 0 \qquad (12)$$

$$F_2 \equiv y[2g - (1 - \phi)^{-1} - 2g_1(1 - 2\phi) - g_2\phi(1 - \phi)] - \sigma - \sum_{n=2} x^n/n + y^2[3g_1 + g_2(\phi\nu_0 + \phi - 1)] - (1 - 2\phi\nu_0) \sum_{n=2} \frac{g_n y^n}{n!} - \phi\nu_0(1 - \phi\nu_0) \sum_{n=3} \frac{g_n y^{n-1}}{(n-1)!} = 0 \qquad (13)$$

where $y = \phi(\nu_0 - 1)$ and $x = y/(1 - \phi)$. If g is independent of concentration, only the first two sums remain in eq 12, and the expanded F_1 reduces to the previously reported relations.[22]

Note that as $\sigma \rightarrow 0$, F_1 converges like σ^3 while F_2 becomes proportional to σ

$$\lim_{\sigma\rightarrow 0} F_1 = \frac{(\sigma\mu_1)^3}{12} \left\{ \frac{\mu_2}{\mu_1{}^3} - \left(\frac{\phi}{1 - \phi}\right)^2 + \phi^2[6g_1 - 3(1 - 2\phi)g_2 - \phi(1 - \phi)g_3] \right\} + \mathcal{O}(\sigma^4) \qquad (14)$$

$$\lim_{\sigma\rightarrow 0} F_2 = \sigma\phi\mu_1[2g - (1 - \phi)^{-1} - 2g_1(1 - 2\phi) - g_2\phi(1 - \phi) - (\phi\mu_1)^{-1}] + \mathcal{O}(\sigma^2) \qquad (15)$$

Thus, at a critical point itself, the equilibrium conditions, $F_1 = F_2 = 0$, are always trivially satisfied. The criteria for the critical point and spinodal contained in the braces and brackets of eq 14 and 15, respectively, can be formally recovered in several equivalent ways: (i) by insisting that the conditions $F_1 = F_2 = 0$ are met also in the neighborhood of a critical point where $\sigma \neq 0$; (ii) by defining the critical point as

$$\lim_{\sigma\rightarrow 0} \left(\frac{\partial^3 F_1}{\partial\sigma^3}\right)_{T,\phi} = \lim_{\sigma\rightarrow 0} \left(\frac{\partial F_2}{\partial\sigma}\right)_{T,\phi} = 0 \qquad (16)$$

(iii) by working with modified functions $\bar{F}_1 \equiv F_1/\sigma^3$ and $\bar{F}_2 \equiv F_2/\sigma$, where the trivial roots have been removed. The critical conditions are then simply

$$\lim_{\sigma\rightarrow 0} \bar{F}_1 = \lim_{\sigma\rightarrow 0} \bar{F}_2 = 0 \qquad (17)$$

In order to simplify further algebraic operations, we employ the last definition, eq 17.

The critical point conditions contained in eq 14 and 15 were derived earlier in a different manner (method of Gibbs critical determinants).[21] It may be recalled that the present series method was used in the past by Stockmayer to analyze the special case with concentration-independent parameter g.[23]

Multiple critical points arise as multiple roots of phase equilibrium equations, located at the critical point of the system. Since the phase equilibrium exists under isothermal conditions, multiple roots in turn can be discovered by analyzing partial derivatives of any of the functions F_1, F_2, $\bar{F}_1$, or $\bar{F}_2$, with respect to σ at constant T and ϕ. For instance, the criterion $\lim_{\sigma\to 0} \bar{F}_1 = 0$ alone (with the spinodal condition) guarantees only a single nontrivial root, as apparent from eq 14, and thus represents a single critical point. If also the first partial derivative equals zero, $\lim_{\sigma\to 0} (\partial \bar{F}_1/\partial\sigma)_{T,\phi} = 0$, the function $\bar{F}_1(\sigma)$ at constant T and ϕ exhibits an extremum at $\sigma = 0$ and has a double root there, and the critical point is qualified as a double critical point. In general, the condition for a critical point of multiplicity m in terms of $\bar{F}_1$ is

$$\lim_{\sigma\to 0}\left(\frac{\partial^n \bar{F}_1}{\partial\sigma^n}\right)_{T,\phi} = 0, \qquad n = 0, 1, 2, ..., m - 1 \quad (18)$$

in addition to the spinodal condition. The analogous condition in terms of partial derivatives of the original function F_1 was given in note 12 of ref 10.

Listed below are the explicit conditions (18) for n = 1–5. For completeness, the list also includes the previously reported conditions for the spinodal ($n = -1$) and the critical point ($n = 0$). An m-multiple critical point is thus determined by $m + 1$ independent relations with $n = -1$, 0, 1, ..., $m - 1$, where

$$n = -1:\ -1 + r_{\mathrm{w}}\phi[(1 - \phi)^{-1} - 2g + 2(1 - 2\phi)g_1 + \phi(1 - \phi)g_2] = 0 \quad (19)$$

$$n = 0:\ r_z - r_{\mathrm{w}}^2\phi^2[(1 - \phi)^{-2} - 6g_1 + 3(1 - 2\phi)g_2 + \phi(1 - \phi)g_3] = 0 \quad (20)$$

$$n = 1:\ r_z(r_{z+1} - 3r_z) - r_{\mathrm{w}}^3\phi^3[2(1 - \phi)^{-3} - 12g_2 + 4(1 - 2\phi)g_3 + \phi(1 - \phi)g_4] = 0 \quad (21)$$

$$n = 2:\ r_z(r_{z+2}r_{z+1} - 10r_{z+1}r_z + 15r_z^2) - r_{\mathrm{w}}^4\phi^4[6(1 - \phi)^{-4} - 20g_3 + 5(1 - 2\phi)g_4 + \phi(1 - \phi)g_5] = 0 \quad (22)$$

$$n = 3:\ r_z[r_{z+2}r_{z+1}(r_{z+3} - 15r_z) - 5r_{z+1}r_z(2r_{z+1} - 21r_z) - 105r_z^3] - r_{\mathrm{w}}^5\phi^5[24(1 - \phi)^{-5} - 30g_4 + 6(1 - 2\phi)g_5 + \phi(1 - \phi)g_6] = 0 \quad (23)$$

$$n = 4:\ r_z[r_{z+3}r_{z+2}r_{z+1}(r_{z+4} - 21r_z) - 35r_{z+2}r_{z+1}r_z(r_{z+1} - 6r_z) + 140r_{z+1}r_z^2(2r_{z+1} - 9r_z) + 945r_z^4] - r_{\mathrm{w}}^6\phi^6[120(1 - \phi)^{-6} - 42g_5 + 7(1 - 2\phi)g_6 + \phi(1 - \phi)g_7] = 0 \quad (24)$$

$$n = 5:\ r_z[r_{z+4}r_{z+3}r_{z+2}r_{z+1}(r_{z+5} - 28r_z) - 14r_{z+3}r_{z+2}r_{z+1}r_z(4r_{z+1} - 27r_z) - 35r_{z+2}r_{z+1}r_z(r_{z+2}r_{z+1} - 36r_{z+1}r_z + 90r_z^2) + 140r_{z+1}^2r_z^2(2r_{z+1} - 45r_z) + 3465r_z^4(5r_{z+1} - 3r_z)] - r_{\mathrm{w}}^7\phi^7[720(1 - \phi)^{-7} - 56g_6 + 8(1 - 2\phi)g_7 + \phi(1 - \phi)g_8] = 0 \quad (25)$$

The symbols r_t stand for chain-length averages of the polymer defined as usual:

$$r_{\mathrm{w}} = \mu_1, \qquad r_{z+i} = \mu_{i+2}/\mu_{i+1}$$

Several observations concerning the above equations are here in place:

(1) At first sight, it might seem surprising why the criteria can be derived from a single function $\bar{F}_1$ when, on the other hand, computation of a general point of a cloud-point curve may require simultaneous solution of eq 8 and 9. The explanation is simple: the above discussion concerns a critical point, where, by definition, equilibrium conditions are met and eq 8 and 9 simultaneously satisfied. Any multiple critical roots found from $\bar{F}_1(\sigma)$ have to be also reflected in the behavior of $\bar{F}_2(\sigma)$. Indeed, this is confirmed by examining partial derivatives of $\bar{F}_2$ with respect to σ. As expected from eq 14 and 15, they are trailing the derivatives of $\bar{F}_1$: the first derivative of $\bar{F}_2$ yields the critical state condition (20), the second derivative gives the condition for a double critical point, (21), etc. Thus, the criterion (18) stays the same even if expressed in terms of $\bar{F}_2$; only the index n runs up to m rather than $m - 1$.

(2) Although the set of formulas determines uniquely a multiple critical point, each separate formula can be recast in many different forms. For instance, for systems with concentration-independent g, the concentration terms $\phi^k/(1 - \phi)^k$ for $n \geq 1$ can be substituted from eq 20, yielding criteria conveniently in terms of the average chain lengths only.

(3) The derivation of criteria as described is rather unwieldy. With the benefit of hindsight there appears to be an easier way, amounting to separate treatment of the interaction and combinatorial contributions. Since the interactions in eq 1 are insensitive to the chain-length distribution and depend only on the total polymer concentration ϕ, their contribution to the critical equations can be derived simply by taking concentration derivatives of ΔG as in binary systems. Indeed, the three interaction terms in brackets of each equation are identical with partial derivatives of $\Gamma(T,\phi)$ of eq 1

$$\left(\frac{\partial^{n+3}\Gamma}{\partial\phi^{n+3}}\right)_T = (n + 3)[-(n + 2)g_{n+1} + (1 - 2\phi)g_{n+2}] + \phi(1 - \phi)g_{n+3} \quad (26)$$

The remaining terms can be obtained "normally" as partial derivatives with respect to σ of the first two (combinatorial) terms $F_{1,\mathrm{c}}$ of function F_1, eq 12

$$\lim_{\sigma\to 0} r_w^{-1}\left(\frac{\partial^{n+3}F_{1,\mathrm{c}}}{\partial\sigma^{n+3}}\right)_{T,\phi} \quad (26a)$$

albeit with some precautions. Each such derivative contains concentration terms $[\phi/(1 - \phi)]^k$, $k = 1, 2, ..., n + 2$. It is imperative that only the last term, the $(n + 2)$nd power, be left as a concentration term while all the lower powers have to be recast in terms of chain-length averages, using previously derived expressions of the type (26a) without any additional operations. For instance, the fourth power appearing in equations for $n \geq 3$ has to be expressed from the simplified eq 22 for $n = 2$, but it cannot be substituted as a square of the second power from eq 20 for $n = 0$. The normally valid equivalence of these two options is lost when the combinatorial and interaction terms, derived separately, are combined.

(4) As a matter of practical importance for those wishing to extend the list of criteria, note that the sum of numerical coefficients in the r_z term should be $(-1)^n(n + 1)!$

The criteria given above reduce to previously reported relations for some special cases. Thus, for g independent of concentration, eq 21 and 22 for double and triple critical points become equivalent to relations derived earlier.[7,9,22] Also, it is shown in Appendix 1 that for a ternary system solvent–two polymer homologues with a linear dependence of g on concentration, our general relations for a triple critical point reduce to the form obtained recently by Fujita and Einaga.[24]

The best way to comprehend the behavior of multiple critical points and multiphase regions around them is to

Table I
Relations between Various Characteristics of Previously Studied Multicomponent Systems with g Independent of Concentration

no. of components s	no. of independent variables	critical point: multiplicity m	no. of relations	degrees of freedom[a] f
2	3	1	2	r_1
3	5	1	2	r_1, r_2, w_2
		2	3	r_1, r_2
		3	4	r_1
4	7	1	2	r_1, r_2, r_3, w_2, w_3
		2	3	r_1, r_2, r_3, w_3
		3	4	r_1, r_2, r_3
		4	5	r_1, r_2
		5	6	r_1

[a] The listed degrees of freedom serve as convenient examples only. Other combinations are conceivable.

analyze the simplest possible cases where these phenomena originate from a single cause. In the next two sections we shall consider separately the effects of polymer polydispersity and of the concentration dependence of the interaction parameter g.

3.1. Polydispersity Effect. Assume that g is independent of concentration; then multiple critical points occur, even in systems with only a few components, strictly because of the polydispersity of the polymer. We shall be particularly interested in relations between the multiplicity m and the number of degrees of freedom f of a critical point, the number of components s, and the number of phases p. Characteristics of systems that were analyzed in the past are summarized in Table I; w_i here indicates normalized weight fraction of species i in the polymer mixture. It will be apparent that our line of reasoning is consistent with these past results and can be generalized. It should be noted that the formalism used in Table I differs from the usual phase-rule terminology (see Appendix 2); in particular, degrees of freedom also include chain lengths r_i that characterize the solute.

Unless stated otherwise, the term "s-component system" will refer henceforth to the entire $(s - 1)$-dimensional composition space rather than to just an s-component mixture of a particular composition. Simpler yet, an equivalent $(s - 2)$-dimensional *polymer* composition space (**w** space) may be used for discussion since the polymer concentration ϕ at a critical point is always fixed by eq 20.

A system is classified as a p-phase system if, for a given choice of polymeric components r_i, the maximum number of stable liquid coexisting phases displayed is p. It is apparent that in certain composition ranges, such a system also exhibits equilibria with fewer phases.

The polymeric components are ordered so that $r_1 < r_2 < ... < r_{s-1}$, and their chain lengths will be sometimes expressed in relative terms, $\rho_j \equiv r_j/r_{j-1}$, $j = 2, 3, ..., s - 1$. Note that $\rho_j > 1$. For a given number of components some multiple critical points can be developed only upon variation of the set of ρ_j's that can be visualized as occurring in ρ space.

In a binary solution at a fixed pressure, there are three variables characterizing its state (T, ϕ, and r_1) and two equations specifying the (single) critical point (eq 19 and 20); hence, the number of variables that are free to be varied, f, equals one. Indeed, the critical point is here fully determined by choosing, for instance, the chain length r_1.[25] Before proceeding further, note that an increase in the number of components s by one brings two more independent variables, r_i and w_i, whereas an increase in the multiplicity m of a critical point by one augments the number of equations to be satisfied just by one (cf. eq 19–25).

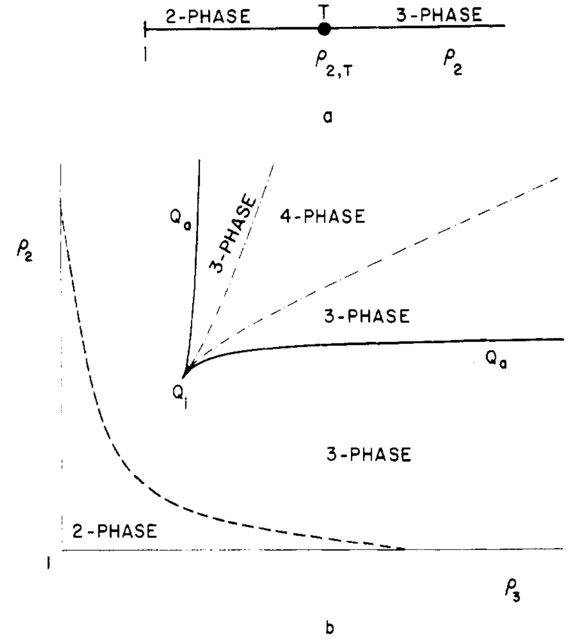

Figure 1. Multiple critical point diagrams in ρ space ($\rho_j \equiv r_j/r_{j-1}$): (a) ternary system; (b) quaternary system. Multiple critical points: T, triple; Q_a, quadruple; Q_i, quintuple. Positions of the point T and of both quadruple lines depend on the value of r_1.

Every ternary system contains an entire line of single critical points defined for the whole spectrum of polymer mixtures, ranging in composition from polymer 1 to polymer 2; thus r_1, r_2, and w_2 are all free to vary. Heterogeneous double critical points appear only in ternary systems undergoing three-phase separation as extrema of the critical line, i.e., as points of fixed polymer composition w_2. Hence, only two variables (r_1 and r_2) can be varied (within certain limits) if the double character of the critical point is to be preserved. Finally, it is well-known that a ternary system with a triple critical point has to satisfy a predetermined ratio r_2/r_1, and the only variable allowed to be chosen is r_1.[7,9] The above considerations can be succinctly represented in a critical point diagram that maps the regions of existence of multiple critical points and multiphase behavior in the ρ space. For a ternary system the graph is one-dimensional, with the triple critical point T marking the onset of systems with double critical points and three-phase separation (see Figure 1a). The position of T, $\rho_{2,T} \equiv \rho^*(r_1)$, depends on r_1, varying from $\rho^* \simeq 15.645$ for $r_1 = 1$ to $\rho^* \simeq 9.899$ for $r_1 \to \infty$.

The behavior of quaternary systems is consistent with the content of Table I as well. Three-phase quaternary systems are known to contain an infinite number (a continuous line) of heterogeneous double critical points, and at least one triple critical point of a fixed composition w_2,w_3, which may or may not be physically real.[10] Quadruple critical points are found only in systems where the ratio ρ_3 satisfies a prescribed value that is a function of r_1 and r_2. Finally, a quintuple critical point requires both ratios ρ_3 and ρ_2 fixed at certain values, and only r_1 is free to move.[26] The critical point diagram is displayed in Figure 1b. The condition for three-phase separation and for the existence of a line of double critical points and of isolated triple critical point(s) is now $r_3/r_1 = \rho_2\rho_3 \geq \rho^*(r_1)$; i.e., in the coordinates of Figure 1b, the boundary appears as a hyperbolic function (dashed line). The locus of quadruple critical points Q_a consists of two asymptotic branches meeting at a cusp that defines the quintuple critical point Q_i. These asymptotes also form the boundary between systems with a single three-phase region and systems with a more complex behavior (two distinct three-phase regions, one of which may not be stable, and a four-phase region).[26]

For an s-component system, the above considerations can be generalized as follows:

(i) The maximum multiplicity of a critical point possible is $2s - 3$. This situation is very rare since for a given r_1, it occurs at just a single set of ratios ρ_j, $j = 2, 3, ..., s - 1$, and at a particular composition of polymer mixture, solvent concentration, and temperature. Although the resulting s-phase equilibrium is in this case restricted to infinitesimal ranges of concentration, temperature, and composition space, such a system is significant as it marks the onset of well-developed s-phase equilibria, generally in the direction of increasing ratios ρ_j.

(ii) Existence of critical points of the next $s - 3$ lower multiplicities, with $m = 2s - 4, 2s - 5, ..., s$, still requires certain relations between r_j's of the system to be satisfied, but the extent of restrictions gradually decreases: for $m = 2s - 4$, only one ratio ρ_j can be freely chosen, producing line(s) of such critical points in ρ space; for $m = 2s - 5$ two ratios are free to be selected, generating surface(s) in ρ space, until at $m = s$ all but one ratio can freely move within certain ranges of values. It is apparent that none of the above critical points, $s \leq m \leq 2s - 3$, is a permanent feature of the composition space, since a small perturbation of a single ratio ρ_j may let them vanish. In a way, they are illusory: by being restricted to a subspace of the ρ space, it is very difficult to pinpoint them experimentally, and systems containing them primarily serve as boundaries separating distinct types of phase behavior. In Griffiths' terminology[12] their occurrence in a particular system is a "lucky accident", although perhaps one requiring less luck than in a typical low molecular weight system; note that in the limit of high molecular weights, r becomes virtually a continuous variable that can be tuned to a great degree of accuracy.

(iii) Critical points of multiplicity $m = s - 1$ assume a special role. Although they still occur only sporadically throughout the composition space, i.e., as isolated points rather than as a continuum, they are permanent in the sense of surviving within an entire region of ρ space, with the mixture composition predetermined as follows from Table I. They are the invariant critical points of the highest "order" (or, strictly speaking, multiplicity) that can be achieved without a "lucky accident" in an s-component all-liquid system.[11,12,18]

(iv) Critical points of multiplicity $m = s - 2$ are the first to appear continuously in **w** space, as one or more one-dimensional arrays (lines) passing through it. All of the critical points with higher multiplicities mentioned above, if present, are positioned on this line, and each higher one can be viewed as a confluence of two or more of the lower ones. A quaternary system which was analyzed in detail recently[10,26] can serve as an example. If, for a given r_1, the ratios ρ_2 and ρ_3 are selected from a certain range of values, the triangle of polymer compositions contains a continuous line of heterogeneous double critical points (HDPP line). In Figure 2 it is schematically plotted in coordinates critical temperature vs. the value of $r_{z,D}$ at the double critical point, assuming $dg/dT < 0$. (The choice of the r_z average is convenient since this quantity was proven to change monotonously along the HDPP line and thus can serve as a yardstick.) Since the slope of the HDPP line starts as positive and ends as negative, the line has to possess at least one maximum (Figure 2a). At this point, two double critical points (12 and 23) merge to form a triple critical point T_1 (123). If the ratio ρ_3 happens to equal a certain predetermined value that is a function of r_2 and r_1, the HDPP line develops a point of inflection with a horizontal slope (Figure 2b). This is a quadruple critical point Q_a where four nontrivial roots of phase equilibrium equations (1, 2, 3, and 4) coincide with the critical point. From Figure 2b it can be interpreted as a triple point of the displayed line, i.e., as a confluence of three double critical points (pairs 12, 23, and 34). A slight increase of one of the ratios then develops a local minimum and maximum around the original point of inflection Q_a, forming a pair of new triple critical points: an unstable T_2 and a stable T_3 (Figure 2c). Hence, the quadruple point can be also regarded as a confluence of two triple critical points (123 and 234). Finally, at a particular value of ratios ρ_3 and ρ_2, a flat maximum is formed by merging of three triple critical points T_1, T_2, and T_3 (123, 234, and 345) into a quintuple critical point Q_i (12345). Again, other equivalent interpretations of this particular point are possible, such as confluence of four double points (12, 23, 34 and 45) directly tied to the flat maximum of Figure 2d, etc. It is apparent that cases b and d of Figure 2 represent unique boundary situations ("lucky accidents") virtually impossible to pinpoint experimentally (cf. Figure 1b), while cases a and c

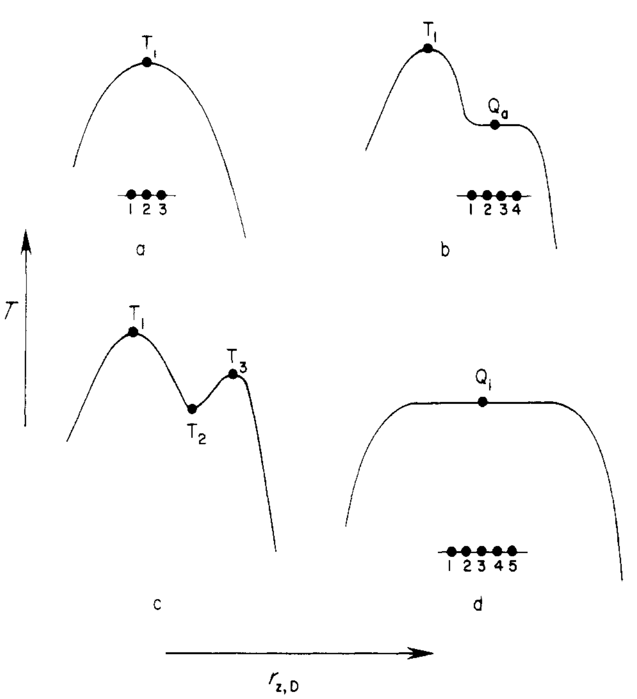

Figure 2. Multiple critical points appearing in **w** space as special points of the HDPP line for a quaternary system. Coordinates: T, critical temperature; $r_{z,D}$, z-average molecular weight at a point of the HDPP line. Critical point notation explained in the legend for Figure 1. Dots represent single critical points whose overlapping collection defines a multiple critical point.

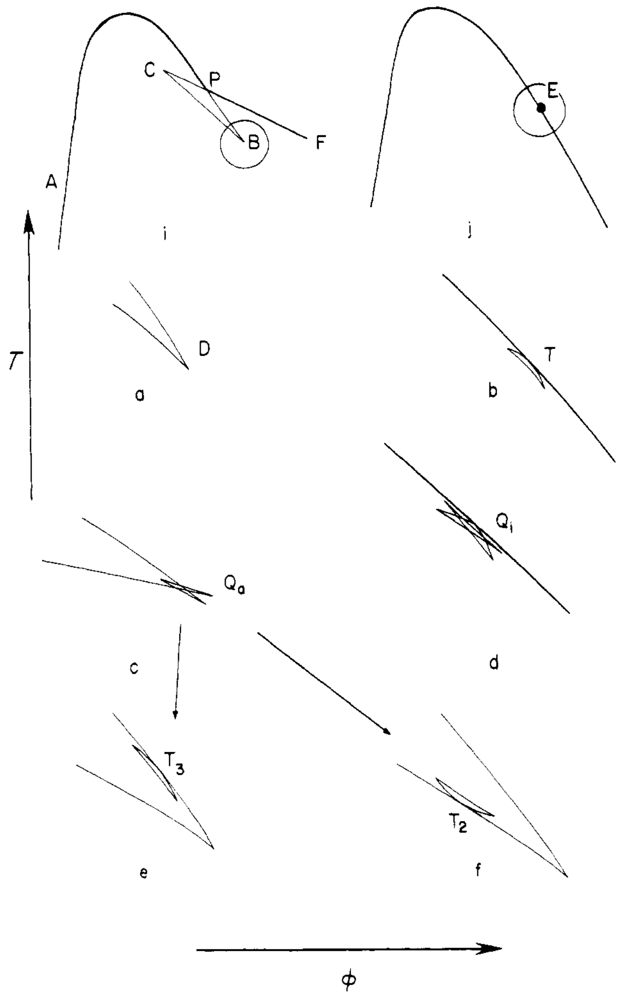

Figure 3. Projection of multiple critical points onto the plane of the cloud-point curve. (i) and (j) Two most common types of CPC; P, three-phase point. Infinitesimal neighborhoods of points B and E are magnified in sketches (a), (c), (e), and (f) and (b) and (d), respectively. D, double critical point; the rest of the notation is identical with that of Figure 1.

are typical for this kind of system.

(v) Critical points of even lower multiplicities occur in the composition space as subspaces higher than a line: for $m = s - 3$ they exist as surfaces, for $m = s - 4$ as three-dimensional regions, etc. It should be stressed that none of the multiple critical points discussed above is guaranteed to exist in every s-component system; their presence is restricted to systems whose ratios ρ_j, for a given r_1, satisfy certain relations or at least fall within certain intervals of values. Only the single critical points have a guaranteed existence at every point of the polymer composition space.

The only practical (albeit vastly incomplete) representation of phase equilibrium data on solutions of polydisperse polymers is in the form of cloud-point curves (CPC). Thus it is important to recognize how the critical points of various multiplicities are projected onto this simplified phase diagram. While the behavior of double and triple critical points in ternary and quaternary systems is well understood, more general information on critical points of higher multiplicity is lacking.

For polydisperse polymers whose solutions in the entire concentration range separate exclusively into two phases, the CPC is of traditional smooth shape (Figure 3j) and stable in its entire length. If, however, a solution of a given, say binary, polymer mixture undergoes a three-phase separation in a certain concentration and temperature interval, its experimental cloud-point curve APF will show an apparent break P (see Figure 3i).[9,22] In fact, the derivative $dT/d\phi$ at the point P is perfectly continuous, although double valued, and the CPC has to be viewed as proceeding from A to P and then becoming metastable as it plunges beneath the high-concentration branch and continues to the cusp point B. This is a singular point where the CPC abruptly reverses its course while keeping its slope $dT/d\phi$ constant (in the sense of a limit), becomes thermodynamically unstable, and moves along its innermost arc toward the other cusp point C. There its course is reversed, and the curve becomes metastable again (CP) and continues through P toward F. Since two stable branches intersect at the point P, a bulk phase of this composition and temperature will be equilibrated with two distinct incipient phases, thus forming the basis for development of a three-phase equilibrium. Hence the point P is referred to as the three-phase point of the CPC. Depending on the molecular weight distribution of the polymer mixture, the critical point may be located anywhere on the CPC, including its metastable and unstable parts.

If the critical point happens to coincide with either one of the cusp points, B or C, it is designated as a heterogeneous double critical point (D in magnified Figure 3a). The qualifier "heterogeneous" serves as a reminder that upon perturbation of the binary polymer mixture composition, the double critical point originally located say at B, becomes either single unstable (moving toward C) or single metastable, i.e., stable with respect to splitting into two infinitesimally close phases (moving toward P).

A substantial shift in the composition w_2 of the mixed polymer either way tends to reduce the extent of the triangular region PBC, until it shrinks to zero size, the points B, C, and P coalesce into one, the three-phase equilibrium ceases to exist, and the CPC becomes smooth again. At this stage, the critical point would be typically somewhere else on the CPC, above or below the location of the described event. Only if the chain-length ratio ρ_2 equals the prescribed value is the critical point located at the confluence of the points P, B, and C; i.e., it overlaps with two merged cusp points, and the CPC reverses its course twice in the immediate neighborhood of this point (see Figure 3b). Obviously, such a critical point can be viewed as a confluence of two heterogeneous double critical points and is referred to as a triple critical point T, and the CPC is of the apparently smooth type (Figure 3j).

Generalization to critical points of higher multiplicity that can exist in mixtures of more than three components is now evident. A quadruple critical point Q_a results as a confluence of three double critical points, i.e., as a superposition of three singular cusp points with a critical point in the CPC projection. This case is schematically represented in Figure 3c. The stable portion of the CPC itself is qualitatively indistinguishable from that of Figure 3a for a system with a double critical point, the only difference being an additional double reversal at the original point B; however, the phase development upon perturbation of the system is markedly different. The splitting of a quadruple critical point into stable (T_3) and unstable (T_2) triple critical points described in Figure 2 is projected onto the CPC as a shifting of a triple critical point away from the cusp along the metastable (Figure 1e) and unstable (Figure 1f) portions of the CPC, respectively. This indicates that a triple critical point T is not necessarily of the type displayed in (b) and (j) of Figure 3, with a "smooth" CPC; in quaternary and higher systems, T may be located on metastable or unstable portions of a CPC whose stable part shows a break (type of Figure 3i).

A quintuple critical point Q_i can be interpreted as a confluence of four double critical points, i.e., as an overlap of two pairs of cusp points with a critical point. Again, for a quaternary system, the CPC (Figure 3d) would be indistinguishable from that of Figure 3b with a simple stable triple critical point; the number of reversals, however, is doubled.

Generalizing the above, a critical point of multiplicity m is projected on the CPC as a confluence of the critical point with an $(m - 1)$-multiple cusp point. Critical points of even multiplicity are always located away from the stable portion of the CPC, whereas those of odd multiplicity may appear on the stable part. In general, it is impossible to recognize the multiplicity from the experimentally determined stable CPC alone without analyzing changes in CPC or phase behavior that occur upon perturbation of polymer composition and/or molecular weight distribution.

3.2. Effect of Concentration Dependence of g. The effect of the concentration dependence of the parameter g on the development of multiple critical points is best followed on a solvent–monodisperse polymer binary system, where eq 19–25 reduce to

$$n = -1: \quad (r\phi)^{-1} + (1 - \phi)^{-1} - 2g + 2(1 - 2\phi)g_1 + \phi(1 - \phi)g_2 = 0 \tag{27}$$

$$n = 0: \quad -(r\phi^2)^{-1} + (1 - \phi)^{-2} - 6g_1 + 3(1 - 2\phi)g_2 + \phi(1 - \phi)g_3 = 0 \tag{28}$$

$$n = 1: \quad 2(r\phi^3)^{-1} + 2(1 - \phi)^{-3} - 12g_2 + 4(1 - 2\phi)g_3 + \phi(1 - \phi)g_4 = 0 \tag{29}$$

$$n = 2: \quad -6(r\phi^4)^{-1} + 6(1 - \phi)^{-4} - 20g_3 + 5(1 - 2\phi)g_4 + \phi(1 - \phi)g_5 = 0 \tag{30}$$

and in general

$$(-1)^{n+1}(n + 1)!(r\phi^{n+2})^{-1} + (n + 1)!(1 - \phi)^{-(n+2)} - (n + 2)(n + 3)g_{n+1} + (n + 3)(1 - 2\phi)g_{n+2} + \phi(1 - \phi)g_{n+3} = 0 \tag{31}$$

For the ensuing discussion it is convenient to consider g as a power series in concentration

$$g = \sum_{i=0}^{k} a_i(T)\phi^i \tag{32}$$

Then, for a certain type of functionality (say, cubic, $k = 3$), all higher derivatives g_i, $i > 3$, disappear from the above equations, and the analysis is simplified.

The list of variables can be here extended by k values of a_i, $i = 1, 2, ..., k$. Although a particular system at a given temperature is characterized just by a single set of a_i's, inclusion of these quantities into variables enables one to take again a global view of the phase behavior. Variation of their values leads to similar effects as changes in chain lengths r_i and polymer composition w_i did for polydisperse polymers, namely, shifts in cloud-point curves, appearance and disappearance of multiple critical points, etc.

It is immediately apparent that a system with a linearly dependent g ($g_i = a_i = 0$ for $i > 1$) cannot ever satisfy eq 29; hence, such a system contains exclusively single critical points as specified by eq 27 and 28.

A system with a quadratic dependence of g on volume fraction can have at most a triple critical point. From eq 30, the critical concentration is then

$$\phi_T = (1 + r^{1/4})^{-1} \tag{33}$$

and from eq 29 and 28, the coefficients are

$$12a_{2,T} = (1 + r^{1/4})^4/r = (1 - \phi_T)^{-4} \tag{34}$$

$$12a_{1,T} = (1 + r^{1/4})^3(3r^{1/4} - 5)/r = 12a_{2,T}(3 - 8\phi_T) \tag{35}$$

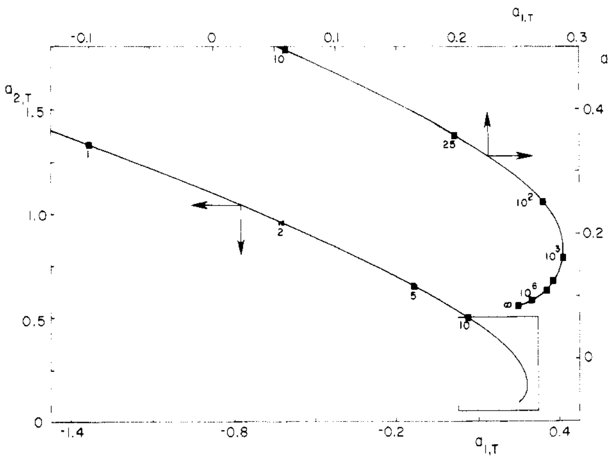

Figure 4. Relation between the interaction coefficients a_1 and a_2 required at a triple critical point of a binary system. The content of the inset is enlarged in the upper right portion of the figure. Chain length r appears as a parameter of the displayed functions.

All variables but one are thus fixed by the triple critical point condition; e.g., a chosen chain length r determines the critical concentration ϕ_T as well as the numerical values of coefficients a_1 and a_2 required. The relation between the latter two is depicted in Figure 4, with r as a parameter of the function. For a solution of a monomer, $r = 1$, the variables take values $\phi_T = {}^1/_2$, $a_{1,T} = -{}^4/_3$, $a_{2,T} = {}^4/_3$, and $a_{0,T} = {}^8/_3$, while in the limit for $r \to \infty$ we have $\phi_T \to 0$, $a_{1,T} \to {}^1/_4$, $a_{2,T} \to {}^1/_{12}$, and $a_{0,T} \to {}^3/_4$.

It might be worthwhile to note in passing that, within the framework of this analysis, the Θ point[8] can only very exceptionally represent a triple critical point, if ever. The majority of polymer–solvent systems known to date can be brought in a state of pseudoideality (Θ state) by appropriate adjustment of temperature and/or pressure. This has been found to be true irrespective of the number of components in the polymer, including strictly binary systems. The very special situation described here (fixed relation between $a_{1,T}$ and $a_{2,T}$) cannot be considered representative for such a general phenomenon. It should be emphasized that the present treatment deals with discrete phases in the Gibbs–van der Waals sense. While in equilibrium, such phases may, upon a change in variables, become identical and show critical behavior of various complexity. The term tricritical has also been used in a rather different context for the Θ point where a single polymer coil changes from a collapsed state below the Θ point to an expanded state above it. As noted by de Gennes,[27] such a transition is analogous to certain magnetic phase transitions and can be interpreted as a Griffiths tricritical point,[12–14] where "a first-order transition" (gas–liquid-like condensation of the coil below the Θ point) "turns into a λ transition" (excluded-volume chain expansion above the Θ-point). Although originally formulated just for an isolated chain, the concept of tricriticality was later extended to entire concentration regions around the Θ point, characterized by different scaling laws with regard to the temperature and concentration dependence of chain dimensions.[28–30] It is evident that such an approach cannot be reconciled with the present treatment based on true equilibrium phases in the classical sense.

Upon perturbation of a_1 and a_2 coefficients from the above values the triple critical point disappears from the system in one of three ways:

(1) It may split into a double and a single critical point. The condition for the existence of the former is given by eq 28 and 29, which can be recast as

$$a_{2,\mathrm{D}} = [(1 - \phi_\mathrm{D})^{-3} + r^{-1}\phi_\mathrm{D}^{-3}]/12 \quad (36)$$

$$a_{1,\mathrm{D}} = a_2(1 - 6\phi_\mathrm{D}) + \tfrac{1}{6}(1 - \phi_\mathrm{D})^{-3} \quad (37)$$

Note that in the concentration interval $0 < \phi_\mathrm{D} < 1$, the minimum of $a_{2,\mathrm{D}}$ of eq 36 coincides with the conditions (33) and (34) for a triple critical point. Hence at a given r, $a_{2,\mathrm{D}}$ for a system with a double critical point has to be greater than $a_{2,\mathrm{T}}$ of a triple critical point system, and the splitting requires a positive perturbation of a_2. It also follows from the above that there are two sets of double points, one with $\phi_\mathrm{D}' < \phi_\mathrm{T}$ and the other with $\phi_\mathrm{D}'' > \phi_\mathrm{T}$. The perturbation of a_1 has to conform with eq 38 obtained from derivatives of (36) and (37)

$$\delta a_1/\delta a_2 \simeq 1 - 4\phi_\mathrm{T} \quad (38)$$

i.e., it is positive for $r > 81$ ($\phi_\mathrm{T} < {}^1/_4$) and negative for $r < 81$ ($\phi_\mathrm{T} > {}^1/_4$). In general, this is true for both sets of double critical points; they differ from each other only by higher terms neglected in eq 38. A special situation arises at $r = 81$ ($\phi_\mathrm{T} = {}^1/_4$), where the upper set requires $a_1 \rightarrow -0$ while the lower set demands $a_1 \rightarrow +0$.

As expected, a system with a double (and a single) critical point(s) thus has two degrees of freedom: In addition to r, also, e.g., the coefficient $a_{2,\mathrm{D}} > a_{2,\mathrm{T}}$ can be chosen; these two parameters then determine a pair of values of ϕ_D and $a_{1,\mathrm{D}}$ (cf. eq 36 and 37). Noteworthy is the fact that single and double critical points may appear virtually at any concentration even if $r \rightarrow \infty$ (whereas the triple critical point in this limit is fixed at $\phi_\mathrm{T} = 0$).

(2) The triple critical point may decompose into three single critical points. The criterion for this instance can be deduced from Figure 5, illustrating the course of the critical state function F^c, rewritten from eq 28 as

$$F^\mathrm{c} \equiv (1 - \phi)^{-2} - (r\phi^2)^{-1} - 6a_1 + 6a_2(1 - 4\phi) \quad (39)$$

F^c is continuous in the interval (0, 1) and assumes values of opposite signs at the interval boundaries ($\lim_{\phi\rightarrow 0} F^\mathrm{c} = -\infty$, $\lim_{\phi\rightarrow 1} F^\mathrm{c} = +\infty$); hence it has to have an odd number of roots. It is apparent that three single roots will exist only if (a) F^c has a proper shape with a maximum and a minimum and (b) F^c is vertically positioned so that its maximum and minimum lie on the opposite sides of the axis of the abscissae (like curve 3 in Figure 5). The required shape is guaranteed by selecting $a_2 > a_{2,\mathrm{T}}$; as mentioned above, this choice leads to a pair of double critical points characterized by ϕ_D and $a_{1,\mathrm{D}}$ (cf. eq 36 and 37). The functions F^c for a pair of such systems are drawn in Figure 5 (curves 1 and 2); they are of identical shape, differing only by a vertical shift due to unequal values of $a_{1,\mathrm{D}}$. It becomes apparent from Figure 5 that these two curves also delineate boundaries of systems possessing three distinct critical roots, and the sought criterion reads $a_{1,\mathrm{D}}' > a_1 > a_{1,\mathrm{D}}''$. Furthermore, the two double critical root concentrations, ϕ_D' and ϕ_D'', separate the concentration range into three regions to which the three single critical roots are restricted. The condition for decomposition of a triple critical point into three single ones thus coincides with eq 38 for formation of a double critical point system, and the two events are in the first approximation indistinguishable.

(3) Finally, any perturbation of a_1 and a_2 coefficients other than specified by eq 38 leads to a system with one single critical point.

The above reflections are succinctly expressed in Figures 6 and 7, showing the distribution of various types of critical behavior in the a_1 vs. a_2 coordinates, computed for a typical low molecular weight ($r = 1$) and high molecular weight ($r = 10^4$) system. The triple critical point system is represented by the cusp point T. The two branches originating at T represent the two sets of double critical point systems, with the numbers attached specifying their concentration ϕ_D. The acute sector between the two branches maps systems with three single critical points, while the rest of the area (including the lower half-plane of negative a_2) corresponds to systems with one single critical point.

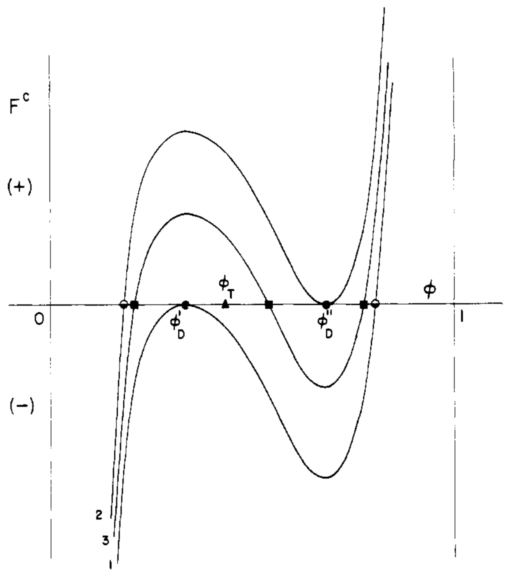

Figure 5. Critical state function F^c for three systems sharing a common value of $a_2 > a_{2,\mathrm{T}}$ but differing by values of a_1: (1) and (2), systems with a double (●) and a single (◒) critical point; (3), system with three single critical points (■).

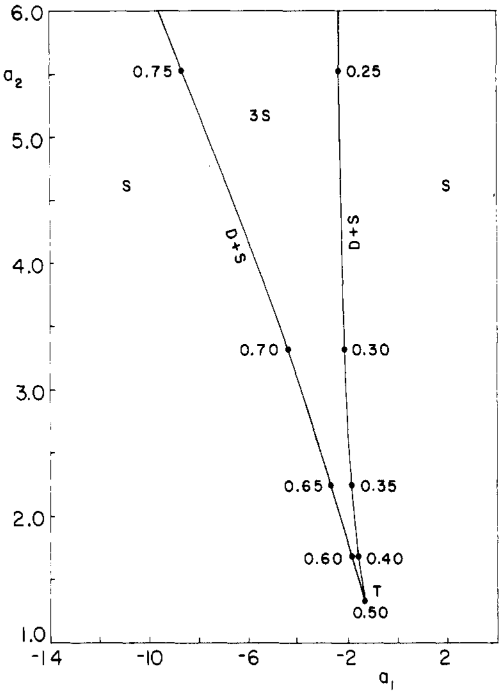

Figure 6. Critical point diagram of a binary system with $r = 1$ in a space of interaction coefficients. S, single critical point; the rest of the notation is identical with that of Figures 1 and 3. Numbers along the lines specify the polymer volume fraction at the multiple critical point.

Critical points of even higher multiplicities can appear in binary systems if the concentration dependence of g is stronger than quadratic. For instance, a quintuple critical point exists at the concentration $\phi = (1 + r^{1/6})^{-1}$ and "temperature" $a_0 = {}^{46}/_{15}$, if g is described by a fourth-order polynomial with coefficients $a_1 = -{}^{44}/_{15}$, $a_2 = {}^{76}/_{15}$, $a_3 = -{}^{64}/_{15}$, and $a_4 = {}^{32}/_{15}$. However, there does not seem to be much benefit in discussing these complicated cases in

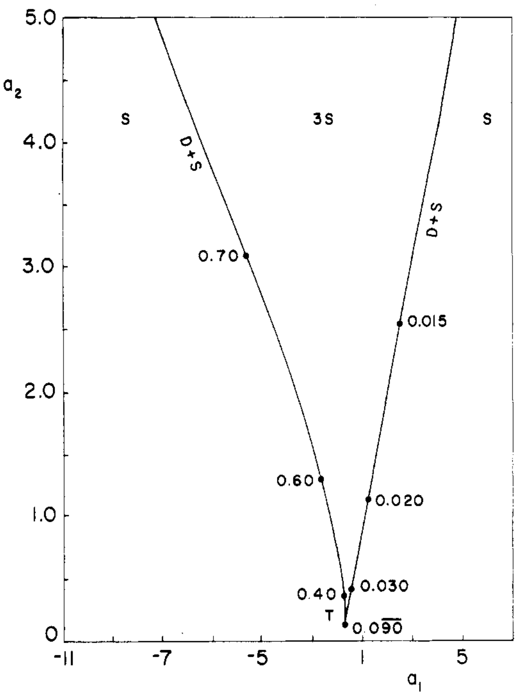

Figure 7. Critical point diagram of a binary system with $r = 10^4$ in a space of interaction coefficients. The notation is explained in the legend for Figure 6.

detail as long as there are no experimental indications of their actual existence in some specific system.

For binary systems, the cloud-point curves contain complete information on phase behavior since the equilibrium genuinely exists within the plane of the CPC. Hence, also the collection of single critical points composing a given multiple critical point lies within this plane, necessarily at an extremum of the CPC, contrary to what we have seen in polydisperse systems with concentration-independent g. This distinction has to result in markedly different genesis, appearance, and behavior of multiple critical points.

Indeed, a double critical point here arises as an isolated pair of CPC cups on the spinodal far away from the original CPC, rather than as a single cusp on the "old" CPC as before. It is not stable, and it is of heterogeneous nature in the sense of Korteweg[2] since upon perturbation of a_k it splits into unstable (N) and metastable (M) critical points. An example of such a slightly perturbed system with $r = 1$ is shown in Figure 8; the corresponding double critical point system might have parameters $a_{1,\mathrm{D}} = -2.000$, $a_{2,\mathrm{D}} = 2.628$, and $\phi_\mathrm{D} = 0.3284$. The new CPC appears very flat but its magnified display at the top reveals a shape of a sigmoidal loop. The metastable critical point is located at the maximum of its upper part while the unstable critical point is situated at the minimum of the lower portion. The other two extrema (the minimum of the upper and the maximum of the lower part) are located at the points of intersection of the spinodal with the new CPC and are at equilibrium with the corresponding cusp points (indicated by dotted lines). The entire new system is not stable and the only external sign of its existence is a profound shoulder observed on the original CPC.

Suitable variation of a_k (e.g., a decrease in a_2 at constant a_1) makes the new CPC grow, and eventually its metastable critical point M located at its maximum contacts the old CPC at its point of inflection with a horizontal slope. At this point the experimentally available (i.e., stable) portion of the CPC has two stable critical points but it still retains its smooth character.

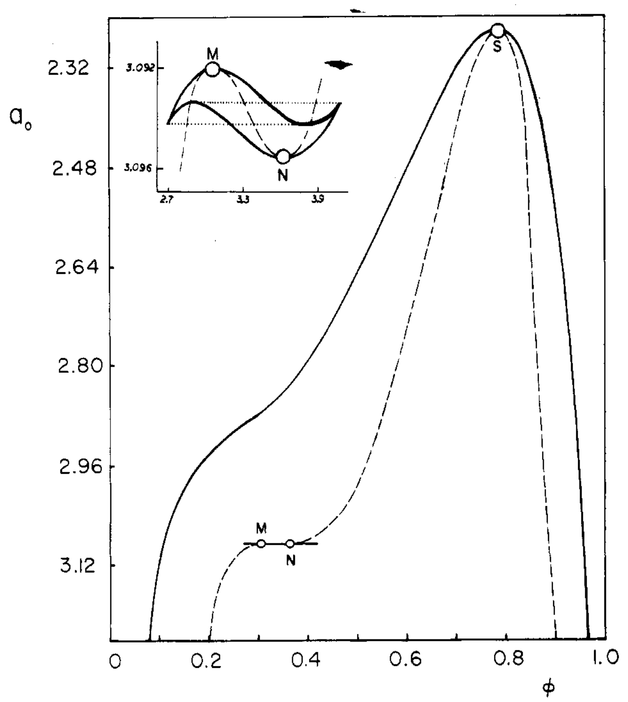

Figure 8. Cloud-point curve (—) of a slightly perturbed double critical point binary system ($r = 1$, $a_1 = -2.0$, $a_2 = 2.531$). (---) Spinodal; (O) critical points (M, metastable; N, unstable; S, stable).

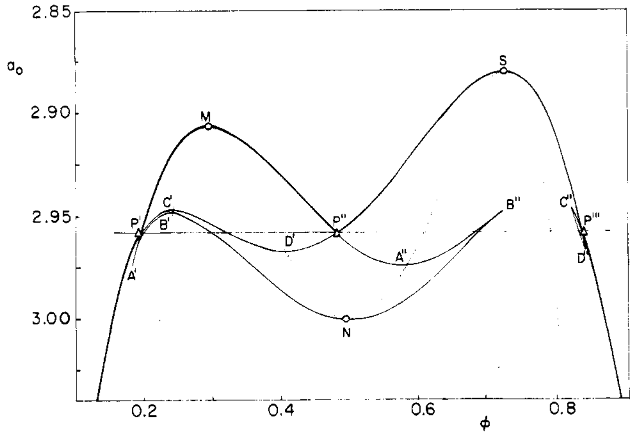

Figure 9. Composite cloud-point curve for a binary system with three single critical points ($r = 1$, $a_1 = -2.0$, $a_2 = 2.02$). (—) Stable and (—) not stable parts of CPC; (···) spinodal; (O) critical points (M, S, stable; N, unstable); P, three-phase equilibrium. Coexisting phases indicated by primed letters.

With further decrease of a_2, the old CPC develops a local maximum C′ and minimum D′ around its previous point of inflection. These features are not stable since they are "covered" by the stable arc of the new CPC, now protruding way above the old one (Figure 9). Their consequences, however, become apparent at the other end of the concentration scale, where a conjugated double-cusp system C″D″ develops on the CPC, with each cusp coexisting with one extremum of the old CPC. An experimental cloud-point curve now contains seemingly three singular break points P where its slope is apparently changed; in fact, however, the curve is well behaved at these points, and the apparent break points arise as points of intersection of two separate cloud-point systems (at $\phi < {}^1/_2$) or of two branches of the cusp system developed on the old curve (at $\phi > {}^1/_2$). It is evident that the triplet of break points P represents a special type of three-phase equilibrium that, unlike in previously discussed polydisperse systems, exists only at a single temperature. Because of

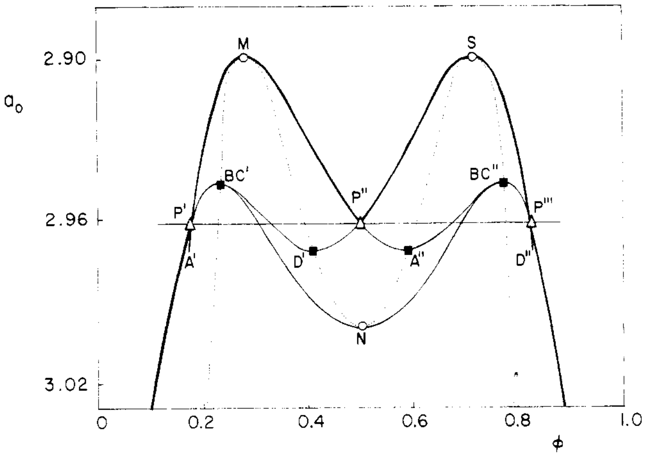

Figure 10. Composite symmetric cloud-point curve for a binary system with three single critical points ($r = 1$, $a_1 = -2.0$, $a_2 = 2.0$). The notation is identical with that of Figure 9.

its infinitesimal temperature range, it would be impossible to confirm its existence directly, but the coexisting phases should display a discontinuous change in composition upon cooling. This situation has been discussed before in relation to experimentally observed bimodal cloud-point curves, as well as curves with a shoulder.[31]

Finally, as $a_2 \rightarrow 2$, the right cusp of the new CPC, B'', approaches and eventually merges with the upper cusp C'' of the system developed at high concentrations, and the phase diagram becomes symmetrical about $\phi = {}^1/_2$ (cf. Figure 10). The system now contains three single critical points with coordinates $\phi_c = 0.2858$, ${}^1/_2$, and 0.7142. For the two stable critical points $a_0 \simeq 2.899$, whereas the unstable one has $a_0 = 3.0$. Here, the two CPC's become "fused" together, forming one complex continuous system. Similarly as in Figure 9, the spinodal separating metastable and unstable portions of the diagram intersects or contacts the CPC at the extremal points of the latter curve, as it has to. The noncritical points of intersection BC' and BC'' are conjugated with each other, while each of the points D' and A'' is at equilibrium with the opposite cusp point (D'' and A'). This system again exhibits a transient three-phase equilibrium between phases P', P'', and P'''.

It is apparent that with a further decrease of a_2 the process would be repeated in the reverse order and with switched sides: the two cusps would disengage on the left side at BC', creating a cusp system on the left-hand side and a separate closed-loop CPC on the right-hand side of Figure 10. The latter curve would gradually diminish and recede downward, its stable portion would become metastable, and eventually it would shrink to zero size at a heterogeneous double critical point characterized by parameters $a_1 = -2.000$, $a_2 \simeq 1.838$, $\phi_D \simeq 0.617$, $a_{0,D} \simeq 3.022$.

It is interesting to note that the genesis as well as the entire development and vanishing again of the closed-loop CPC described above strongly resembles the temperature behavior of binodal (isothermal) diagrams for simple liquid ternary three-phase systems.[7] Similar patterns have been also observed in pressure–composition diagrams for some vapor–liquid equilibria of binary systems.[3]

The CPC for a system with a triple critical point ($r = 1$, $a_{1,T} = -{}^4/_3$, $a_{2,T} = {}^4/_3$, $a_{0,T} = {}^8/_3$, $\phi_T = {}^1/_2$) is shown in Figure 11. As expected, it has a very flat top due to the triple critical root at $a_{0,T}$. For $r > 1$, the curve loses its symmetry and the maximum shifts to lower concentrations, but the flatness of the maximum is retained.

The principal new feature appearing in CPC's with at least quadratic dependence of g on polymer concentration, compared to systems with g constant or linearly dependent, is thus their possible composite character. They may consist of two or more separate curves, one of traditional convex shape and others of closed-loop sigmoidal type, with three or more critical points present. A corollary to this is the unpleasant fact that some points of the CPC may share a common value of σ; i.e., this parameter may no longer uniquely specify a particular equilibrium. Thus when solving eq 8 for ϕ at a given σ, one cannot stop the search after finding one root since there may exist more than one solution.

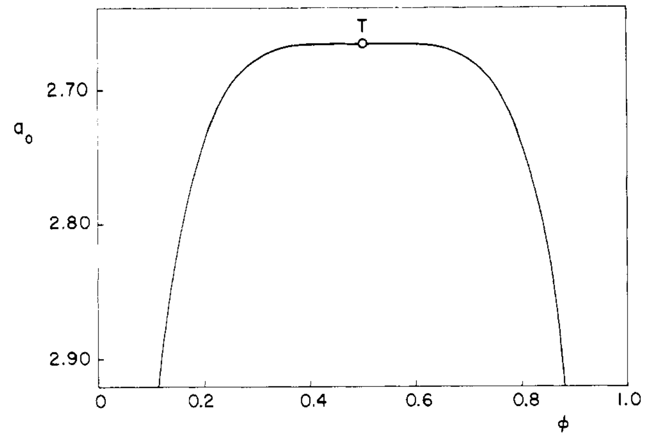

Figure 11. Cloud-point curve for a binary system with a triple critical point T ($r = 1$, $a_1 = -{}^4/_3$, $a_2 = {}^4/_3$).

4. Conclusions

The form of the cloud-point curve equation suggested for polydisperse polymer solutions in eq 8 and 9 allows for fast single-iteration solution if the interaction parameter g can be expressed as a sum of temperature and concentration functions, $g(T,\phi) = g^T(T) + g^\phi(\phi)$. Double iteration of two simultaneous equations is required only for the most general form of $g(T,\phi)$.

Some critical points may be of multiple character. This phenomenon may be caused by the asymmetry of the molecular weight distribution of the polymer or a strong concentration dependence of the interaction parameter $g(T,\phi)$. Criterion for a critical point of multiplicity m can be expressed in the form of $m + 1$ simultaneous equations in terms of polymer chain-length averages r_w, r_z, ..., r_{z+m-1}, the interaction parameter g, and its concentration derivatives up to the $(m + 2)$nd order, and the overall polymer concentration ϕ. General criteria thus obtained reduce to known expressions for some special cases.

The polydispersity effect alone may be responsible for the existence of critical points with multiplicities up to $2s - 3$ in an s-component system and its phase separation in up to s phases. Critical points of high multiplicities, $s \leq m \leq 2s - 3$, are rare in the sense that they exist only if the ratios of relative chain lengths of the polymer components, $\rho_j \equiv r_j/r_{j-1}$, satisfy certain relations. Hence, they exist only as subspaces of the ρ space of relative chain lengths and can be depicted as such in the form of critical point diagrams. They also delineate in ρ space regions of systems with different phase behavior. On the other hand, critical points of lower multiplicities, $s - 1 \geq m \geq 1$ exist in entire regions of ρ space and are thus permanent features (points, lines, surfaces, etc.) of phase diagrams drawn for certain sets of ρ_j's in the space of polymer mixture compositions, the so-called $\mathbf{w}$ space. A critical point of multiplicity m is projected onto the cloud-point curve (CPC) as a superposition of the critical point with an $(m - 1)$-multiple cusp point of the CPC. Only critical points of odd multiplicity may be located on the stable portion of the CPC. The cloud-point curve of systems with multiple critical

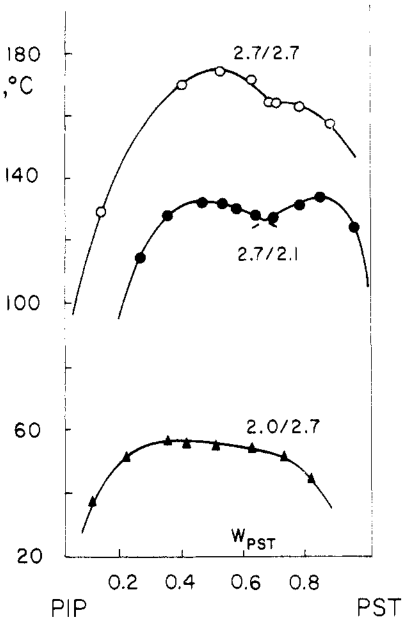

Figure 12. Cloud-point curves in the system polyisoprene (PIP)/polystyrene (PST). The constituents have narrow molar mass distributions (anionic polymers). Molar masses in kg/mol are indicated: (▲) McIntyre et al.;[34] (○, ●) our own work.[35] [Reprinted with permission from ref 35. Copyright 1977 John Wiley & Sons, Inc.]

points retains its character of a single continuous curve, although it contains singular cusp points where its course is abruptly reversed.

The effect of concentration dependence of the parameter $g(T,\phi)$ is best studied in a solution of a monodisperse polymer, assuming a power series form for g, $g = a_0 + a_1\phi + a_2\phi^2 + ...$ The dependence has to be at least of the second order if double and triple critical points are to be present. The existence of the latter point in a system demands that, for a given chain length r, the coefficients a_1 and a_2 assume certain fixed values $a_{1,\mathrm{T}}$ and $a_{2,\mathrm{T}}$. This requirement is relaxed for a double critical point having one more degree of freedom. The cloud-point curve of a system with three single critical points is composite, consisting of an "old" CPC of the common shape and a "new" CPC of sigmoidal closed-loop shape. The latter curve may be entirely not stable, creating just a shoulder in the old curve, or it may become partly stable, protruding above the old curve and giving rise to a special three-phase equilibrium and to two maxima and three apparent break points on the experimentally obtainable CPC. The genesis of the new CPC and its development and eventual disappearance resemble changes in binodals of three-phase ternary systems caused by varying temperature. The CPC of a system with a triple critical point displays a very flat maximum.

Some of the features here described on a theoretical basis have been verified by experiment (see ref 31–35). Figure 12, taken from ref 35, indicates an extreme sensitivity to chain length: the three shapes cloud-point curves may exhibit are all shown by the same system.

In conclusion we wish to note that the suggestions to classify critical points by their *order*, defined as the number of critically identical phases,[12,18] necessarily miss half of the points. In this notation, the common (single) critical point would be of the second order, the triple critical (tricritical) point would be of the third order, etc. At constant pressure and without a "lucky accident", the former case may appear in systems with at least two components, whereas the latter case requires at least four components. Quite generally, increasing thus defined order by one requires addition of two more components.[36] Does that mean that no new feature appears, say, in a three-component system, relative to a binary system? Surely not; ternary systems may contain Korteweg's double critical points[2] (extrema of the critical line[7]) which, however, do not fit into an order-based classification scheme since they do not represent stable critical states. Thus, totally missed are critical points of even multiplicities, inherently not stable, yet significant for understanding the genesis and development of multiple critical points with changing system parameters. Equally important for this purpose are critical points of high mulitplicities, $s - 1 < m \leq 2s - 3$, usually waived away as "lucky accidents". Their analyses in the space of material properties (such as chain length of polymer molecules or thermodynamic interaction parameters) enables drawing boundaries to various types of phase behavior.

It is apparent that all multiple critical points are not alike; this fact has been noted for tricritical points by Griffiths earlier[14] and is evident from comparison of sections 3.1 and 3.2 as well. A detailed study of scaling properties and other features of the critical point neighborhood, however, is beyond the scope of the present paper and will be carried out at some future date.

Acknowledgment. We thank Professors H. Fujita and Y. Einaga for their permission to use and quote their results prior to publication. Technical help by Mike Rozniak is gratefully acknowledged.

Appendix 1

In their analysis of the triple critical point condition, Fujita and Einaga[24] follow Tompa's method,[7] suitable specifically for ternary systems. Thus their approach is entirely different, and the equivalence of their and our results is not immediately apparent.

They assume a linear dependence of χ

$$\chi = \chi_0 + k\phi \tag{A1}$$

where χ is defined in terms of the chemical potential of the solvent. Corresponding to this choice, our parameter g is also a linear function[21]

$$g = \chi_0 + k(1 + \phi)/2 \tag{A2}$$

Equations 19 and 20 then read

$$(\phi r_\mathrm{w})^{-1} + (1 - \phi)^{-1} = 2\chi_0 + 3k\phi \tag{A3}$$

$$\phi^2/(1 - \phi)^2 - 3k\phi^2 = r_z/r_\mathrm{w}^2 \tag{A4}$$

while all the interaction terms disappear from eq 21 and 22 for the double and triple critical points, respectively.

Fujita and Einaga's criterion for a triple critical point is given in terms of parameters u, γ, and B, where, at the sought critical point

$$u = 2\chi_0(1 - \phi) - 1 \tag{A5}$$

$$\gamma = 3k(1 - \phi)^2 \tag{A6}$$

$$B^2 = r_z^{-1}(1 - \gamma)^{-3} \tag{A7}$$

It also follows from eq A4, A6, and A7 that

$$B = (1 - \phi)/[\phi r_\mathrm{w}(1 - \gamma)^2] \tag{A8}$$

Employing now a general relation between two consecutive averages of a binary polymer mixture

$$r_{s+1} = y - (x/r_s) \tag{A9}$$

where $x = r_1 r_2$ and $y = r_1 + r_2$, to eliminate r_{z+1} and r_{z+2}

from criteria (21) and (22) and substituting for r_z from eq A7, we get two linear equations for x and y in terms of B and γ than can be easily solved.

Finally, to obtain the condition for u, we first rewrite u of eq A5 by using (A3), (A6), and (A8) as

$$u = (1 - \phi)[(\phi r_{\mathrm{w}})^{-1} - 3k\phi] = B(1 - \gamma)^2 - \gamma\phi(1 - \phi)^{-1} \qquad \text{(A10)}$$

and compute the required $\phi/(1 - \phi)$ in terms of only B and γ from eq 21 and A7, with the aid of eq A9 for elimination of r_{z+1} and r_{w}.

All the results thus obtained are identical with those of Fujita and Einaga.

Appendix 2

The phase rule in its classical form

$$F = S + 2 - P \qquad \text{(A11)}$$

relates the numbers of components S and coexisting phases P to the number of free-to-choose variables F (such as pressure, temperature, and composition) for a given system.

On the other hand, the relations discussed in the section 3.1 differ from the above in several respects: (i) The pressure is assumed to be fixed at some constant value, i.e., it is not a variable. (ii) Since the chain-length distribution of the polymer is crucial for the existence of some multiple critical points, the list of variables includes the set of r_i's, $i = 1, 2, ..., s - 1$. Thus, our considerations are not limited to a particular system; rather they are based on a global view of all polymeric solutions with a given number of components. (iii) Whereas eq A11 refers to phase equilibria in general, we seek relations for m-multiple critical points which represent unique cases of phase equilibria, with compositions of all coexisting phases approaching each other.

With the number of independent variables equal to $2s - 1$ (temperature + concentration and chain length for $s - 1$ components) and the number of relations of the type (19)–(25) to be satisfied being equal to $m + 1$, the "critical point rule" takes the form

$$f = 2s - 2 - m, \qquad s > 1, \quad 1 \leq m \leq 2s - 3 \qquad \text{(A12)}$$

where f is the number of degrees of freedom for the respective critical point and s the number of components.

Equation A12 is in accord with the content of Table I. Although different, it is also consistent with the conclusions of other authors. For instance, Zernike's dimensionality (i.e., number of degrees of freedom) f of a critical point where ρ phases become identical is $f = s - 2\rho + 3$.[36] Realizing that the multiplicity of such a point is $m = 2\rho - 3$ (only critical points of odd multiplicities may correspond to stable physical states) and adding $(s - 1) - 1$ for r_i parameters and constant pressure, we recover from Zernike's result our formula (A12). Table I also confirms that, e.g., a liquid–liquid–liquid triple critical (tricritical) point is an invariant point in a quaternary system if manipulations with r_i's are not permitted, in conformity with conclusions of Kohnstamm,[11] Widom,[18] Griffiths,[12] and others.

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