

"ZERO" AND "OFF-ZERO" CRITICAL CONCENTRATIONS IN SOLUTIONS OF POLYDISPERSE POLYMERS WITH VERY HIGH MOLAR MASSES

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Polymer solutions with a concentration-dependent interaction parameter $g(\phi)$ are known to have sometimes critical polymer concentrations ϕ_c converging to a non-zero value (a so-called "off-zero" limiting critical point (CP)), as the chain length, m , grows to infinity, rather than to zero as usual (a "zero" limiting CP). In this report the criteria for the existence of both types, known for binary solutions with a linear $g = g_0 + g_1\phi$, are extended to cover polydisperse polymers with a quadratic interaction function $g(\phi)$. Its coefficients g_2 and $\Delta g_2 \equiv g_2 - g_1$ determine the number and type of limiting CPs. Accordingly, the plane $g_2, \Delta g_2$ is divided into the regions I (a zero CP), II (an off-zero CP), and III (a zero + two off-zero CPs). The region II is restricted to the half-plane with $\Delta g_2 < -1/6$, whereas the other half-plane with $\Delta g_2 > -1/6$ is shared by I and III. By varying the interactions, two limiting CPs may be brought together and merged in a heterogeneous double limiting CP. Such instances define the boundaries between the regions: at the I/III line, two off-zero CPs merge, whereas at the II/III line an off-zero CP coincides with a zero CP. A first-order perturbation theory of the latter double CPs, and a second-order perturbation theory of single "zero" CPs are developed, enabling meaningful extrapolations of data on polymers with high but finite molar masses. The latter theory yields extrapolation formulas for determination of Θ -temperature, taking into account the polymer polydispersity and the concentration dependence of g . Solutions of polyisobutene in diphenyl ether and, possibly, in benzene appear to present experimental examples of off-zero limiting critical concentrations.

In the original Flory–Huggins–Staverman (FHS) systems^{1–6} with a concentration-independent interaction parameter g , the behavior of the critical point (CP) for solutions of

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polymers with very high molar mass M (and chain length m) is trivial: in the limit for $m \rightarrow \infty$, the critical polymer concentration, ϕ_c , goes to zero, and the critical value of the interaction parameter, g_c , approaches $1/2$. The situation is more complex when the interaction parameter g depends on polymer concentration ϕ as often happens, particularly in systems with strong interactions⁷. If the *zero* limiting root (i.e., root with $\phi_c \rightarrow 0$ as $m \rightarrow \infty$) is found at all, it is usually displaced from its classical position at $g_c \rightarrow 1/2$. Furthermore, another non-zero critical concentration (or two) sometimes appears, representing an *off-zero* limiting CP (ref.⁸). Although, strictly speaking, the two italicized qualifiers apply only to the limits for $m \rightarrow \infty$, it is convenient to use them for finite m as well to characterize the CPs leading to one or the other limit. When employed in the latter broader sense, these terms will be distinguished by quotation marks.

Flory and Daoust⁹ first drew attention to the problem in an experimental study of the system benzene–poly(2-methylpropene) in which the effect was noticed from values of the interaction parameters determined by osmotic pressure measurements. The authors noted that the experimental errors involved make a decision about the actual occurrence of the phenomenon difficult. A quite convincing example was presented a few years later by Dusek¹⁰ who studied the system aliphatic alcohol–poly(2-hydroxyethyl methacrylate). Its cross-linked analogue was also one of the systems in which Sedlacek et al.¹¹ investigated by light-scattering techniques inhomogeneities in gels induced by micro-phase separation or by the cross-linking process. The problem of off-zero limiting CPs was also investigated in studies of poly(2-methylpropene) dissolved in benzene¹² and in diphenyl ether¹³. Recent work on the system water–poly(*N*-isopropylacrylamide) indicates that even in this case an off-zero critical concentration for infinitely long chains may occur, which phenomenon may also be behind the observed demixing of swollen cross-linked polymer phases¹⁴. The system water–poly(vinyl methyl ether) appears to present another case in point, while preliminary data on the system 2-nonanone–poly(methyl methacrylate) indicate that the latter might present an example of type III behavior with a “zero” plus two “off-zero” CPs (ref.¹⁵).

Although for the special case of a monodisperse polymer solution with linearly-dependent interaction parameter, $\chi = \chi_1 + \chi_2\phi$, this phenomenon was analyzed by Dusek more than 25 years ago¹⁰, it seems to be remaining a well kept secret for the polymer community at large, as occasional conversations with its members clearly suggest. In this paper the above issue is reexamined under broader conditions, particularly for polymers polydisperse in their molar mass, and for interaction functions with stronger than linear concentration dependence. The criteria for the existence of both types of limiting CPs are derived, and their validity is confirmed by some numerically computed examples. Also, perturbation theories of “zero” CPs and of “zero” heterogeneous double CPs are developed for systems with high, but not infinite, polymer molar masses.

In order to avoid excessive cluttering of equations with indices, the subscript c specifying the critical state values will be omitted at g -related derivatives and coefficients.

THEORETICAL

We start our analysis from the familiar relations for the spinodal and the critical concentration^{16,17}

$$[\varphi_c/(1 - \varphi_c)] + \varphi_c[-2g_c + 2(1 - 2\varphi_c)g^{(1)} + \varphi_c(1 - \varphi_c)g^{(2)}] + m_w^{-1} = 0, \quad (1)$$

$$[\varphi_c/(1 - \varphi_c)]^2 + \varphi_c^2[-6g^{(1)} + 3(1 - 2\varphi_c)g^{(2)} + \varphi_c(1 - \varphi_c)g^{(3)}] - m_z/m_w^2 = 0, \quad (2)$$

where φ_c is the critical volume fraction of the polydisperse polymer, and m_w and m_z are its weight- and z-average chain lengths. The concentration-dependent interaction function, $g \equiv g(\varphi, T)$, introduced in the FHS lattice theory, is defined in terms of the free energy of mixing, and $g^{(i)}$ denotes its i -th concentration derivative, $g^{(i)} \equiv (\partial g^i / \partial \varphi^i)_T$. Dusek's results¹⁰, on the other hand, are expressed in terms of the interaction parameter χ defined by the chemical potential of the solvent. For a linearly-dependent parameter g , the two are related by equations¹⁸:

$$\begin{aligned} g &= g_0 + g_1\varphi & \chi &= \chi_1 + \chi_2\varphi \\ g_0 &= \chi_1 + \chi_2/2 & \chi_1 &= g_0 - g_1 \\ g_1 &= \chi_2/2 & \chi_2 &= 2g_1 \end{aligned} \quad (3a)$$

"Zero" Critical Points

Since the focus here is on the very dilute region, $\varphi \rightarrow 0$, it is particularly advantageous to express g as a power series

$$g = \sum_{i=0}^k g_i \varphi^i \quad (3b)$$

with the derivatives

$$g^{(1)} = \sum_{i=1}^k i g_i \varphi^{i-1}, \quad g^{(2)} = \sum_{i=2}^k i(i-1) g_i \varphi^{i-2}, \text{ etc.} \quad (3c)$$

Each g_i may be a function of temperature.

By expanding the denominators of the first terms and by substituting for $g^{(j)}$ from Eq. (3c), the critical conditions (1) and (2) take the form

$$\varphi_c [1 + 2 \Delta g_1 + \varphi_c(1 + 6 \Delta g_2) + \varphi_c^2(1 + 12 \Delta g_3) + O(\varphi_c^3)] + m_w^{-1} = 0, \quad (4a)$$

$$\varphi_c^2 [1 + 6 \Delta g_2 + 2\varphi_c(1 + 12 \Delta g_3) + O(\varphi_c^2)] - \zeta/m_w = 0, \quad (5a)$$

where Δg_i stands for the difference of two consecutive coefficients, i.e., $\Delta g_1 \equiv g_1 - g_0$, $\Delta g_2 \equiv g_2 - g_1$, etc., and ζ denotes the ratio m_z/m_w . It is interesting to note that only the coefficient's differences, Δg_i , but not their separate values, appear in both equations. This circumstance has unwelcome consequences for the evaluation of interaction coefficients from critical data (see below).

Mere consideration of signs in each of the Eqs (4a) and (5a) alone puts already limits on the existential boundaries of "zero" CPs. Since both the φ_c and chain-length averages m_q are positive, the above two equations can be satisfied for φ_c approaching 0 only if, at the critical temperature,

$$1 + 2 \Delta g_1 \leq 0, \quad \text{or,} \quad g_0 \geq (1/2) + g_1, \quad (6a)$$

and

$$1 + 6 \Delta g_2 \geq 0, \quad \text{or,} \quad g_2 \geq g_1 - (1/6). \quad (7)$$

In fact, simultaneous consideration of Eqs (4a) and (5a) shows (Appendix I) that in the limit of $m_w \rightarrow \infty$, the condition for Δg_1 is even narrower than that: the relation (6a) is limited strictly to equality, i.e.,

$$1 + 2 \Delta g_1 = 0, \quad \text{or,} \quad g_0 = (1/2) + g_1. \quad (6b)$$

Zero limiting CPs are thus restricted to the region $\Delta g_2 \geq -1/6$, essentially regardless of higher coefficients g_i , $i > 2$. More significantly, they also have to satisfy Eq. (6b), indicating that the traditional value of 1/2 has to be assumed by the difference $g_0 - g_1$, not simply by g_0 or g_c (except for the trivial case where $g_1 = 0$). Equations (6b) and (7) reproduce Dusek's Eq. (8b) (ref.¹⁰) derived for a linearly dependent $g(\varphi)$. The present derivation, however, is general, valid for any interaction function $g(\varphi)$.

Note that when discussing criteria of this nature, we tacitly assume that the temperature T can always be adjusted to make $g_0(T)$ fit the required relation for it (in this instance Eq. (6b)). This may not always be possible in practice where, for a given system under consideration, the required g_0 may lie outside the experimentally accessible range.

It is well known that for monodisperse polymers with a constant interaction parameter $g \equiv g_0 \equiv \chi$ of the form

$$g_0 = \alpha + \frac{\beta}{T} = \frac{1}{2} + \Psi \left(\frac{\Theta}{T} - 1 \right) \quad (8a)$$

the "zero" critical temperatures are predicted^{19,20} to obey the relation

$$T_c^{-1} = \Theta^{-1} + (\Theta\Psi)^{-1}[m^{-1/2} + (2m)^{-1}] . \quad (9a)$$

Thus a simple linearized plot of T_c^{-1} vs the expression in brackets of Eq. (9a) yields the thermodynamic parameters Θ and Ψ characterizing the system. Equation (8a) also guarantees that at the temperature $T = \Theta$ the parameter χ assumes the value of 1/2, i.e., the second virial coefficient A_2 equals 0.

It is obvious that for polydisperse systems with an interaction function $g(\varphi)$, the resolution of critical variables will not be that simple. As shown by Dusek for monodisperse polymers¹⁰, linear interactions alone of the type $g_i = \alpha_i + \beta_i/T$, $i = 0, 1$, lead already to an uncomfortable quartic equation for the critical concentration φ_c . For interaction functions stronger yet, a perturbation approach seems to be the only one feasible (other than numerical iteration in more than one variable).

The perturbation theory of "zero" critical roots for solutions of high-molar mass polydisperse polymers with any $g(\varphi)$ function can be developed from Eqs (4a) and (5a) (see Appendix I). Since it is more convenient to work with finite nonvanishing quantities, we introduce the scaled variables

$$\Phi \equiv \varphi_c m_w^{1/2} \quad \text{and} \quad \Gamma \equiv -(1 + 2 \Delta g_1) m_w^{1/2} , \quad (10)$$

where $\Gamma \geq 0$. Then the second-order result for the critical concentration can be written (cf. Eq. (A1.2)) as

$$\Phi \approx \left(\frac{\zeta}{1 + 6 \Delta g_2} \right)^{1/2} \left[1 + (\zeta/m_w)^{1/2} \frac{1 + 12 \Delta g_3}{(1 + 6 \Delta g_2)^{3/2}} \right]^{-1} \quad (11a)$$

Similarly, the second-order perturbation form of the condition (4a) for a “zero” CP is obtained from Eq. (A1.5) as

$$\Gamma \approx (\zeta^{1/2} + \zeta^{-1/2}) (1 + 6 \Delta g_2)^{1/2} + \frac{1 + 12 \Delta g_3}{(1 + 6 \Delta g_2) m_w^{1/2}} \quad (12)$$

It is satisfying to see that our approximate formulas (11a) and (12) developed by this method for polydisperse polymers with a concentration-dependent interaction function $g(\phi)$, reproduce the exact results for systems with a constant parameter $g \equiv g_0$ obtained years ago. Specifically, Eq. (11a) reduces to the Stockmayer's critical concentration formula¹⁶

$$\Phi_c = \frac{m_z^{1/2}/m_w}{1 + m_z^{1/2}/m_w} \quad (11b)$$

whereas Eq. (12) yields for monodisperse fractions with $g \equiv g_0$ the Shultz–Flory extrapolation formula (9a). Hence, the approximations contained in Eqs (11a) and (12) should concern only the effects of polydispersity (Eq. (12)) and of the concentration dependence of $g(\phi)$ (Eqs (11a) and (12)).

In the following we shall discuss the Shultz–Flory-type extrapolations for two more realistic cases. First, with interactions still kept constant, the effect of polydispersity alone on Eq. (9a) is simple: Equation (12) shows that the extrapolation procedure remains the same except for modification of the bracketed term plotted on the x -axis. Equation (9a) now becomes a function of both the weight- and z -average chain lengths

$$T_c^{-1} = \Theta^{-1} + (\Theta\Psi)^{-1} \left(\frac{\zeta^{1/2} + \zeta^{-1/2}}{2m_w^{1/2}} + \frac{1}{2m_w} \right) \quad (9b)$$

Compared to a “monodisperse” plot employing the weight-average m_w for m in Eq. (9a), polydispersity thus shifts the plotted points to higher x -values, since the function $Z(\zeta) \equiv (\zeta^{1/2} + \zeta^{-1/2})/2$ is always greater than 1 for $\zeta \equiv m_z/m_w > 1$. Inspection of $Z(\zeta)$ shows, however, that the simple plot (9a) with $m = m_w$ is remarkably tolerant of polydispersity, and for reasonably good fractions the ζ -correction should not be very substantial. It is applied only to the more significant first term $m_w^{-1/2}$, and it increases slowly

with growing relative "ζ-polydispersity" $\Delta\zeta \equiv \zeta - 1 = (m_z - m_w)/m_w$, as follows from the series expansion

$$Z(\zeta) = 1 + [(\Delta\zeta)^2/8] [1 - \Delta\zeta + (15/16) (\Delta\zeta)^2 - \dots].$$

Even for a relatively large $\zeta = 2$, i.e., $m_z = 2m_w$, $Z(\zeta)$ would increase merely by $\approx 6\%$ to 1.061. This insensitivity has to be at least partly responsible for traditionally good fits obtained with Eq. (9a), even when using data on polymer fractions of undetermined (and probably varying) polydispersity.

It should be noted that the effect of polymer polydispersity on the Shultz-Flory extrapolation formula, Eq. (9a), has been studied before, although under quite different circumstances: Based on an empirical fit of numerically generated data, Shultz²⁰ analyzed the polydispersity effect for polymers with Schultz-Flory distribution of molar mass, assuming that the easier measurable precipitation threshold data were employed instead of the hard-to-obtain true critical data.

For the most general case, we first redefine Eq. (8a) as

$$g_0 - g_1 \equiv \frac{1}{2} + \Psi \left(\frac{\Theta}{T} - 1 \right). \quad (8b)$$

Since the relation $\chi_1 \equiv g_0 - g_1$ of Eq. (3a) holds in fact for any interaction polynomial function $g(\varphi)$ (ref.¹⁸) it is apparent that with the above definition (8b), the A_2 is guaranteed to be zero at $T = \Theta$ where $\Delta g_1 + 1/2 = 0$. Also, Eq. (12) together with the definition of Γ (Eq. (10)) and Eq. (8b) indicate that such a point will mark the critical temperature of a polymer with $m \rightarrow \infty$. Thus, one can conclude that in case of "zero" CPs, the temperature obtained by correct extrapolation of T_c s for $m \rightarrow \infty$ is identical to the Θ -temperature where $A_2 = 0$, independently of nature of the interaction function. For linearly dependent χ , the same conclusion was reached earlier by Dusek¹⁰.

With the definition (8b), the approximate Eq. (12) yields the equivalent of Eq. (9a) in the form

$$T_c^{-1} \approx \Theta^{-1} + (\Theta\Psi)^{-1} \left[\frac{\zeta^{1/2} + \zeta^{-1/2}}{2m_w^{1/2}} (1 + 6\Delta g_2)^{1/2} + \frac{1 + 12\Delta g_3}{2m_w(1 + 6\Delta g_2)} \right]. \quad (9c)$$

Equations (8b) and (9c) remind us again (just as noted below Eq. (5a)) that analysis of critical data alone, however accurate the data is, cannot provide values of separate interaction coefficients; at best, one can hope for obtaining their differences Δg_1 , Δg_2 and Δg_3 . In reality, even that feat may be too much to ask. Evidently, with two unknown interaction terms present in the bracket of Eq. (9c), this relation alone contains too many unknowns to permit their full determination. However, a resolution is

possible if also critical concentration data of sufficient accuracy are utilized, and if the higher differences of interaction coefficients, Δg_i , $i > 1$, are independent of temperature (an often employed assumption). Equation (11a) can be rearranged to read

$$\frac{\zeta^{1/2}}{\Phi} \approx (1 + 6 \Delta g_2)^{1/2} + \frac{1 + 12 \Delta g_3}{1 + 6 \Delta g_2} \frac{\zeta^{1/2}}{m_w^{1/2}} \quad (11c)$$

Hence, the ϕ_c data should be linearized by plotting $m_z^{1/2}/(\phi_c m_w)$ vs $(\zeta/m_w)^{1/2} \equiv m_z^{1/2}/m_w$, yielding an intercept of $(1 + 6 \Delta g_2)^{1/2}$ and a slope of $(1 + 12 \Delta g_3)/(1 + 6 \Delta g_2)$. Furthermore, the Δg_2 and Δg_3 terms thus resolved can now be used to evaluate the bracket of Eq. (9c). Finally, plotting the T_c^{-1} vs the said bracket should result again in a linear plot, with the familiar intercept of Θ^{-1} and the slope of $(\Theta\Psi)^{-1}$.

The situation is no better when the original expanded series of Eqs (4a) and (5a) are used for data treatment. Neglecting the higher-order terms, Eq. (5a) can be rearranged as

$$\zeta/m_w \phi_c^2 \approx 1 + 6 \Delta g_2 + 2\phi_c(1 + 12 \Delta g_3) \quad (5b)^*$$

and used to linearize critical concentration data by plotting $m_z/(m_w \phi_c)^2$ vs ϕ_c , with an intercept of $(1 + 6 \Delta g_2)$ and a slope of $2(1 + 12 \Delta g_3)$. The resolved interaction terms Δg_2 and Δg_3 could then be used to evaluate the bracketed ϕ_c coefficient in the recast form of Eq. (4a):

$$T_c^{-1} \approx \Theta^{-1} + (\Theta\Psi)^{-1} \{ (2\phi_c m_w)^{-1} + \phi_c [1 + 6 \Delta g_2 + \phi_c(1 + 12 \Delta g_3)]/2 \} \quad (4b)$$

Plotting of T_c^{-1} vs the expression in the braces of Eq. (4b) should then yield a linear graph with the same intercept and slope as those of Eq. (9c). Again, the resolution of unknown g_i coefficient is not complete.

Although the relations (4b) and (5b), based directly on the series (4a) and (5a) contain fewer approximations than their twins (9c) and (11c), it remains an open question which ones are more effective for data treatment; only their comparison with actual experimental data can yield the answer. Furthermore, it is not clear whether experimental errors would allow significant figures to arise from such analyses, unless the typical

* It is apparent that Eq. (5b) could also be obtained by squaring Eq. (11c) and substituting for $(\zeta/m_w)^{1/2}$ from Eq. (11a); this fact attests to the internal consistency of the present treatment.

experimental data accuracy is enhanced. Also, note that for polydisperse polymers the present study assumes true critical data being available, i.e., it does not provide at all for an error committed by employing the easier-to-obtain precipitation threshold data instead of the critical ones¹⁷⁻²⁰.

"Off-zero" Critical Points

The origin of this type of critical point is apparent from the rearranged form of Eqs (1) and (2). For instance, Eq. (2) may be written as

$$\varphi_c^2 [(1 - \varphi_c)^{-2} - 6g^{(1)} + 3(1 - 2\varphi_c)g^{(2)} + \varphi_c(1 - \varphi_c)g^{(3)}] - m_z/m_w^2 = 0 \quad (13)$$

Evidently for $m_w \rightarrow \infty$ with ζ finite, Eq. (13) can be satisfied not only by $\varphi_c \rightarrow 0$ (the classical zero root) but also if its bracket approaches zero, i.e.,

$$(1 - \varphi_c)^{-2} - 6g^{(1)} + 3(1 - 2\varphi_c)g^{(2)} + \varphi_c(1 - \varphi_c)g^{(3)} = 0 \quad (14)$$

Similarly, Eq. (1) yields another condition

$$(1 - \varphi_c)^{-1} - 2g_c + 2(1 - 2\varphi_c)g^{(1)} + \varphi_c(1 - \varphi_c)g^{(2)} = 0 \quad (15)$$

Note that for the original Flory's constant parameter $g \equiv g_0$ this alternative leads to a physically impossible situation: Eq. (14) would require that φ_c diverge. In other words, an off-zero limiting CP can never appear in original FHS systems. Only the concentration-dependent interactions can bring it into the physical concentration range (0,1). Also, the general Eq. (15) contains no requirement that $g_0 - g_1$ be equal to 1/2, i.e., the off-zero limiting critical temperature is not identical to the Θ -temperature where the second virial coefficient vanishes. The same conclusion was reached earlier for systems with linear interactions^{9,10}.

In the general case, Eqs (14) and (15) are too complex to draw any simple criteria from them, and they have to be numerically examined for each particular case to see whether there are any physically relevant roots. However, some analysis is feasible for the special case where the interaction function $g(\varphi)$ is expressed as a power series, Eq. (3b), no stronger than quadratic. As shown in the Appendix II, several regimes can be distinguished in such a case, differing by the number of off-zero limiting CPs present in the system. Existential boundaries of these regimes in the space of interaction parameters g_2 and Δg_2 are shown in Fig. 1 and discussed below:

1. For $\Delta g_2 < -1/6$, Eq. (14) has one physically significant (i.e., within the range $0 < \varphi_c < 1$) root for any value of g_2 (region II).

2. For $\Delta g_2 > -1/6$, the number of relevant roots of Eq. (14) depends on g_2 :

2.1. For $g_2 < 1/12$, there are no such roots (region I).

2.2. For $g_2 > 1/12$, the number of such roots depends on the value of Δg_2 relative to the criterion $G(g_2)$ defined as

$$G(g_2) \equiv 4g_2 - (12g_2)^{2/3} / 2. \quad (16)$$

2.2.1. There are no such roots if $\Delta g_2 > G$ (region I).

2.2.2. For $\Delta g_2 = G$, Eq. (14) has a double root at

$$\varphi_c = 1 - (12g_2)^{-1/3} \quad (17)$$

(the boundary between I and III).

2.2.3. For $-1/6 < \Delta g_2 < G$, Eq. (14) has two single roots, typically one smaller and one greater than φ_c of Eq. (17) (region III).

The usefulness of relations derived for a quadratic $g(\varphi)$ may be greater than realized at first sight. Since in the neighborhood of CPs the compositions of the coexisting phases are usually close to each other, the second-order expansion of any interaction

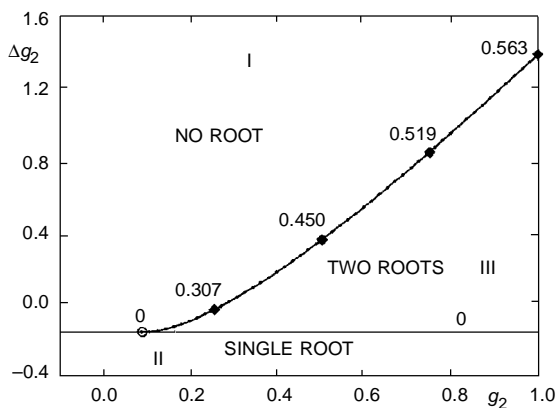


FIG. 1

Existential boundaries of various off-zero limiting CPs in the plane of interaction parameter coefficients g_2 , Δg_2 for systems with a quadratic interaction function $g(\varphi)$. Numbers specify the concentrations φ_c of HEDLCPs; Roman numerals mark various regions; the zero CPs present for $\Delta g_2 > -1/6$ in I and III are not included

function $g(\varphi)$ in the critical region should be a good enough approximation to yield reasonable results.

RESULTS AND DISCUSSION

Linearly Dependent Interaction Parameter

In this case one has

$$g = g_0 + g_1\varphi, \quad g_i = 0 \quad \text{for } i \geq 2. \quad (18)$$

From earlier work^{10,21} it is anticipated that only one critical point should exist under these conditions. This expectation is confirmed by the criteria derived above. From Eq. (7) it is apparent that the zero critical root will appear for a polymer with $M \rightarrow \infty$ only if

$$g_1 \leq 1/6. \quad (19)$$

On the other hand, according to Eq. (14) the off-zero limiting critical point requires that

$$6g_1 = (1 - \varphi_c)^{-2} \quad (20)$$

which in effect means that g_1 cannot be lower than $1/6$. Thus the case with $g_1 = 1/6$ takes on the crucial role of a transition between zero and off-zero limiting CPs. For instance, in a sequence of systems with $M \rightarrow \infty$ and g_1 gradually increasing from negative to positive values, the CP keeps adjusting its T_c to maintain $g_0 = g_1 + 1/2$ (cf. Eq. (6b)), but stays anchored at zero polymer concentration as long as $g_1 \leq 1/6$. Only then it detaches from $\varphi_c = 0$ and starts moving to off-zero concentrations, with the actual value of φ_c always consistent with Eq. (20). In the diagram of Fig. 1, representative points of such a sequence of systems would spread from top to bottom along the vertical passing through $g_2 = 0$, crossing from I (no off-zero CP, one zero CP) directly to II (one off-zero CP, no zero CP).

The relation between the critical interaction coefficients and the critical concentration for both zero and off-zero limiting CPs is illustrated in Fig. 2. The left portion of the figure shows the linear dependence between $g_c \equiv g_0$ and g_1 (cf. Eq. (6b)) in the range $g_1 < 1/6$ where the CP stays anchored at zero concentration, $\varphi_c = 0$. The right-hand side, on the other hand, displays the triplet of interaction terms, g_c , g_0 and g_1 , required for an

off-zero limiting CP of concentration φ_c , where $0 < \varphi_c < 1$. Equations (15), (18) and (20) were used to compute the curves. Note that both types of systems have just one degree of freedom: e.g., by choosing g_1 (for zero CPs) or φ_c (for off-zero CPs), all remaining quantities are fixed. It is interesting that for both types of CPs even negative values of g_c can lead to partial miscibility, albeit under different circumstances: in the case of zero CPs such phase separation occurs for highly negative slopes g_1 , whereas for off-zero limiting CPs highly positive slopes g_1 at high φ_c are required, g_0 then being more negative than g_c .

Quadratically Dependent Interaction Parameter

Here it is assumed that

$$g = g_0 + g_1\varphi + g_2\varphi^2, \quad g_i = 0 \text{ for } i \geq 3. \quad (21)$$

Summarizing the results of the Theoretical, the plane of interaction coefficients $g_2, \Delta g_2$ is here divided into three regions I, II and III, as shown in Fig. 1, distinguished by how many and what kind of limiting CPs a corresponding system with $m \rightarrow \infty$ possesses: It has a zero CP if located in I; an off-zero CP if contained in II; and two off-zero CPs and one zero CP if positioned in III. Of particular interest will be the events occurring at the boundaries where some CPs may appear or disappear.

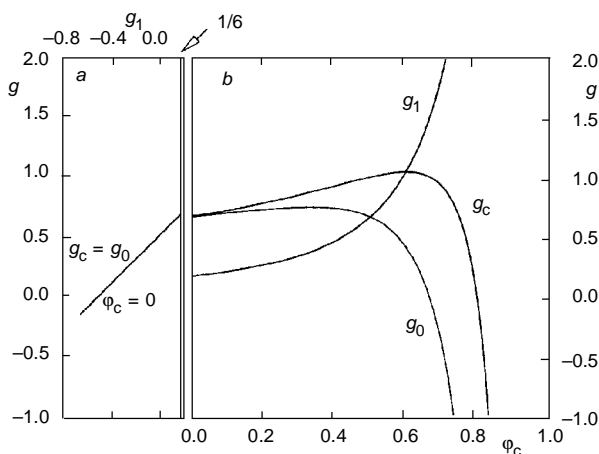


FIG. 2

A composite plot of values of interaction coefficients required at the limiting CPs for systems with a linear interaction function. **a**: A plot of $g_c \equiv g_0$ vs g_1 for zero CPs with $\varphi_c = 0$. **b**: A plot of g_c , g_0 and g_1 vs φ_c for off-zero CPs. The vertical scale is common for all listed interaction terms

The simplest process – a switch in category – occurs at the I/II boundary (i.e., at $\Delta g_2 = -1/6$ for $g_2 < 1/12$) where single CPs present on both sides of the line merely differ in their type. By comparing the zero CP criterion (7) with the condition 1. of the section “*Off-zero*” *Critical Points* (see Theoretical), it is recognized that the boundary limiting the existence of zero CPs to $\Delta g_2 > -1/6$, is identical to the boundary restricting the single roots of the off-zero CPs to $\Delta g_2 < -1/6$. Therefore a zero limiting CP, existing above it, disengages from the zero polymer concentration and starts moving to off-zero ϕ_c as the line is crossed, thus becoming an off-zero limiting CP.

The events at the other two boundaries are more complex since they involve a change in the total number of limiting CPs by two, typically associated with double CPs. Indeed, the double-root character of the solutions of the critical condition (14) along the I/III boundary has been established already in section “*Off-zero*” *Critical Points*, suggesting the presence of double CPs. It is consistent with the diagram of Fig. 1 indicating that, when crossing this boundary upwards, the system should lose both of its off-zero limiting CPs (which merge into a double limiting CP and then disappear from real space), and keep only its zero CP.

As apparent from Fig. 1, two limiting CPs also disappear when crossing the boundary III/II (at $\Delta g_2 = -1/6$ for $g_2 > 1/12$) downwards. However, here the merger involves CPs of different types: one zero CP and one off-zero CP. The double-root character of this boundary could not have been discovered in the Theoretical where each category of CPs was examined separately, but it will be documented below.

Examples by Model Calculation

In order to independently test the results derived above, cloud-point curves (CPCs) have been generated by standard methods for solutions of a series of polymers with various chain lengths, corresponding to different thermodynamic conditions (i.e., different combinations of interaction coefficients g_i). Critical points, computed from formulas (1) and (2), fit well the plotted CPCs in all cases, and are consistent with criteria derived in this paper. The usual critical subscript c may be replaced by Z, L or H, letters employed for zero, off-zero, and heterogeneous double limiting CPs, respectively; and if need be, the finite analogues of these three types would be distinguished by an apostrophe. In order to facilitate comparison, in all examples (except for Figs 9 and 10) the “constant” coefficient g_0 is kept identical, $g_0 = 0.5 + 50/T$.

To confirm the prediction^{9,10} that even a linear $g(\phi)$ suffices to produce the unfamiliar off-zero limiting CP behavior, we examine the case of $g_1 = 2/3$ (or, in quadratic notation, $g_2 = 0$, $\Delta g_2 = -2/3$). Both the Eqs (19) and (20), and the criterion 1. of the “*Off-zero*” *Critical Points* (see Theoretical) section, predict one off-zero CP but no zero CP. The CPCs generated for chain lengths 10, 20, 100, and 1 000 and plotted with their CPs in Fig. 3, indeed converge to a limiting CPC with its off-zero critical point L (\square) at $\phi_L = 1/2$,

$g_L = 1$ and $g_0 = 2/3$, i.e., at $T_L = 300$ K, as required by Eqs (15), (18) and (20), and in accord with Fig. 2. There are two noteworthy features:

A) the critical concentrations ϕ_c change remarkably little in the sequence of m 's ranging from 10 to infinity;

B) also the convergence of T_c 's towards their infinite limit is quite fast above $m \approx 1\,000$.

For the quadratic $g(\phi)$ function, several examples are shown corresponding to the systems located in various regions of the CP diagram of Fig. 1. Unless otherwise indi-

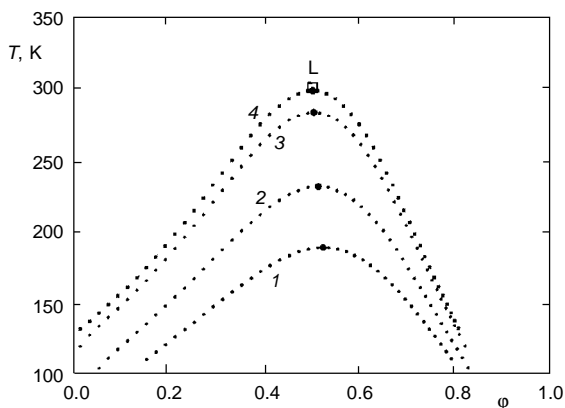


FIG. 3

Phase diagrams for systems with $g_0 = 0.5 + 50/T$, $g_1 = 2/3$, $g_2 = 0.0$. CPCs and CPs (●) computed for chain lengths (m): 1 10, 2 20, 3 100, 4 1 000; □ a limiting CP for $m \rightarrow \infty$

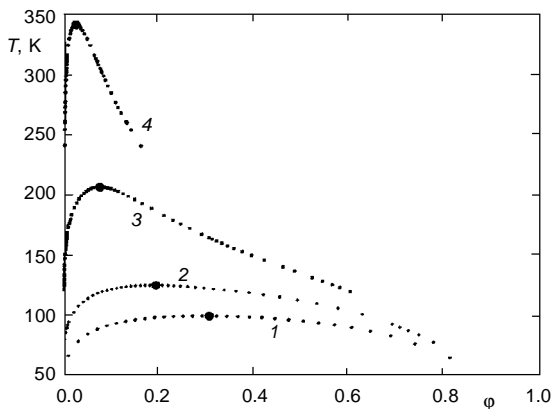


FIG. 4

Phase diagrams for systems with $g_0 = 0.5 + 50/T$, $g_1 = 0.1$, $g_2 = 0.3$. Notation is the same as in Fig. 3

cated, the quadratic coefficient is kept constant at $g_2 = 0.3$, making the I/III criterion $G \approx 0.0255$; only the value of the difference Δg_2 is varied from 0.2 downwards, moving the representative point along a vertical from the region I to III and to the boundary III/II.

The CPCs for systems of type I ($g_1 = 0.1$, $g_2 = 0.3$, i.e., $\Delta g_2 > G$) with the same sequence of chain lengths as in the previous case, are shown in Fig. 4. As predicted for this region, it is a classical system with its only CP clearly approaching zero concentration as $m \rightarrow \infty$. However, in contrast to the items A) and B) described above for the

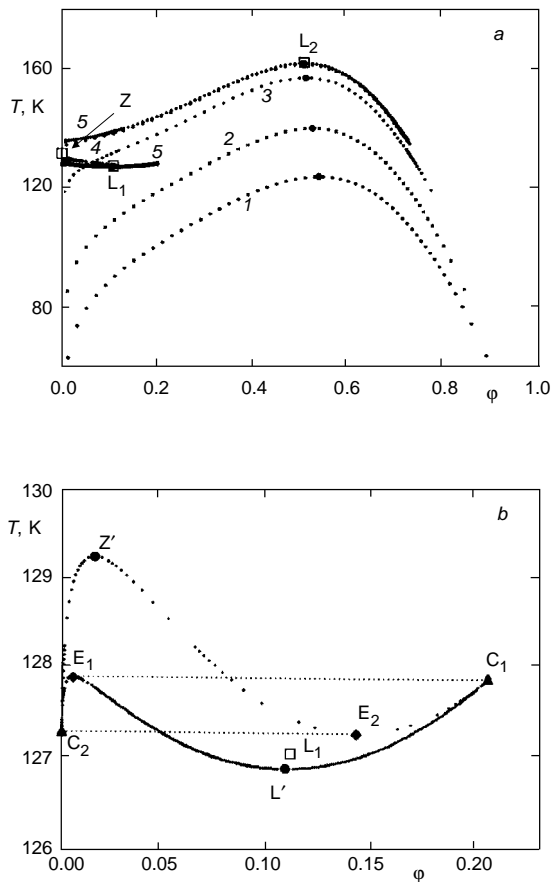


FIG. 5

Phase diagrams for systems with $g_0 = 0.5 + 50/T$, $g_1 = 0.38$, $g_2 = 0.3$. Notation is the same as in Fig. 3. **a**: Curve 5, additional CPC for $m = 10\,000$. **b**: Enlarged portion of **a**, depicting the new sigmoidal binodal for $m = 10\,000$. \blacklozenge E_1 , E_2 , noncritical extrema; \blacktriangle C_1 , C_2 , cusp points of the binodal; \dots tie-line

“off-zero” CPs, the rate of convergence towards infinite-chain behavior is here much slower, and the critical concentrations φ_c vary considerably for individual curves. In fact, the critical temperature T_c for $m \rightarrow \infty$ (i.e., Θ -temperature) is at 500 K, way out of the scale of Fig. 4.

A system of type III is the most intriguing since it should combine two off-zero CPs with a zero CP. The interaction coefficients chosen here are $g_1 = 0.38$ and $g_2 = 0.3$ (i.e., $\Delta g_2 = -0.08$). Thus, the condition 2.2.3. (cf. “Off-zero” Critical Points in Theoretical) for the region III, $-1/6 < \Delta g_2 < G$, is clearly satisfied; the same is apparent by plotting the coordinates $g_2, \Delta g_2$ into the diagram of Fig. 1. The CPCs computed for this system are shown in Fig. 5a. To our initial dismay, the first four curves (1–4) obtained for the above employed sequence of $m = 10, 20, 100$ and 1 000 showed each only a single “off-zero” CP, eventually converging for $m \rightarrow \infty$ to its limit L_2 with $\varphi_{L_2} \approx 0.5087$ and $T_{L_2} \approx 161.39$ K. However, for the next higher examined chain length of $m = 10\,000$ (curve 5), two additional CPs appeared on a newly formed sigmoidal binodal in the low-concentration area, hiding under the stable portion of curve 5 (that hardly differed from the previous curve 4 for $m = 1\,000$). The new CPC is enlarged in Fig. 5b. It has two noncritical extrema E_i , each of them at equilibrium with the opposite cusp C_i . More importantly, it also has two critical extrema (●): a left metastable maximum Z' on the upper curve, representing a new “zero” CP, and a right unstable minimum L' on the lower curve, corresponding to a new “off-zero” CP. With m growing from 10 000 to ∞ , the latter CP hardly shifts, to the off-zero limiting critical point L_1 (□) at $\varphi_{L_1} \approx 0.10782$ and $T_{L_1} \approx 127.03$ K, whereas its left “zero” twin moves out of the scope of Fig. 5b to $\varphi_Z = 0$ and $T_Z = 50/0.38 \approx 131.58$ K. As before, this system shows a much faster convergence of the “off-zero” CPs, compared to the “zero” CPs. All three limiting CPs (□) are depicted in Fig. 5a.

The new sigmoidal binodal resembles the one observed earlier²¹ under similar circumstances, i.e., in binary systems with a quadratic interaction function, where its origin was traced to a heterogeneous double critical point (HEDCP). In order to confirm that the same genesis applies to our pair of a “zero” and an “off-zero” CP in Fig. 5b, twin CPs have been computed from Eqs (1) and (2) in the range $0 < \varphi_c < 0.11$ for a series of chain lengths with $m > 1\,000$, and the stability criterion, H , evaluated for each one of them, using the relation²¹

$$H \equiv (m\varphi_c^3)^{-1} + (1 - \varphi_c)^{-3} - 12g_2 \quad (22)$$

Critical points for a sequence of m 's raising from 1 200 to ∞ are plotted in Fig. 6. The resulting critical line (CL) forms a curve with a minimum H' and two branches: the left one (+) picturing the (meta)stable ($H > 0$) “zero” CPs, ending in the zero limiting critical point Z , and the right one (×) tracing the unstable ($H < 0$) “off-zero” CPs,

ending in the off-zero limiting CP L_1 . (Both Z and L_1 also appear in Fig. 5a.) For the chain length $m_{H'} \approx 1185.4$, both branches meet at the curve's minimum H' at $\phi_{H'} \approx 0.07107$ and $T_{H'} \approx 125.61$ K, where $H = 0$. Evidently, these parameters specify an HEDCP that exists in the system with $m = m_{H'}$. When the chain length drops below $m_{H'}$, there are no CPs present in the low-concentration range, only a single "off-zero" CP at $\phi_c > 1/2$ (cf. Fig. 5a, curves 1–4). This example graphically reinforces the point that the critical diagram of Fig. 1 is valid only for true limiting off-zero CPs; at finite m , every point of the region III may not necessarily represent a system with two "off-zero" and one "zero" CPs.

If the above scheme is truly consistent, the two branches of the CL of Fig. 6 should retain their opposite stability character all along, unless there exists another HEDCP where the CP stability would switch again. Both branches have been examined in this respect, with the results confirming the expectations:

1) It can be proven that "zero" CPs of Fig. 6 stay metastable (or stable) even in their limit Z for $m \rightarrow \infty$ where $\phi_c \rightarrow 0$. Note that here the product $m\phi_c^3$ approaches a positive zero since from Eq. (10) we have $m\phi_c^3 = \phi_c\Phi^2 \rightarrow 0^{(+)}$. Thus the stability criterion H (Eq. (22)) grows to ∞ but stays positive as $\phi_c \rightarrow 0$, confirming the (meta)stability of the zero limiting critical point Z .

2) The right branch in Fig. 6 formed by "off-zero" CPs, on the other hand, ends for $m \rightarrow \infty$ in an off-zero limiting critical point L_1 at $\phi_{L_1} \approx 0.10782$ and $T_{L_1} \approx 127.03$ K, in accord with Eqs (14) and (15). A numerical check shows that even in this limit, the stability criterion H of Eq. (22) stays negative, i.e., the right branch of the CL of Fig. 6

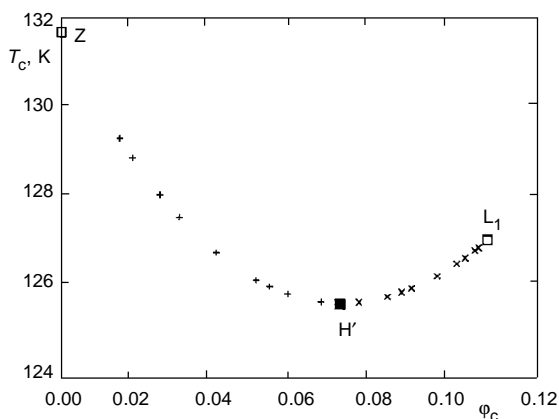


FIG. 6

Critical line (CL) with $\phi_c < 0.11$ for systems with interactions specified in Fig. 5: \square limiting CPs for $m \rightarrow \infty$; \blacksquare an HEDCP for $m_{H'} \approx 1185$. Pairs of points raising from H' to the limits Z and L_1 are for $m = 1200, 1300, 1400, 1500, 2000, 3000, 4000, 7000, 10000$

is unstable in its entire length. The question now is whether by modifying the interactions (which until now have been kept fixed), one could close the gap in the CL between the two off-zero limiting CPs, namely the unstable one (L_1 of Figs 5, 6), and the stable one at $\phi_{L_2} \approx 0.51$, $T_{L_2} \approx 161.4$ K (L_2 in Fig. 5a). Such a merger of two off-zero limiting CPs of opposite stabilities should constitute another HEDCP, this time qualified as a heterogeneous double limiting critical point (HEDLCP) since it exists for the limit of $m \rightarrow \infty$. It has to satisfy Eqs (14), (15), and the condition

$$g_2 = [12(1 - \phi_c)^3]^{-1} \quad (23)$$

derived for $m \rightarrow \infty$ from the HEDCP criterion $H = 0$ (cf. Eq. (22)).

This supposition is indeed confirmed by the following example: With critical polymer concentration of the prospective HEDLCP arbitrarily chosen to be $\phi_{HL} = 0.25$, g_2 is fixed by Eq. (23) at $g_2 = 16/81 \approx 0.1975309$; Eq. (14) yields $g_1 = 8/27 \approx 0.296296$; and from Eq. (15) one has for this point $g_0 \approx 0.814815$, i.e., $T_{HL} \approx 158.82$ K if $g_0 = 0.5 + 50/T$. The CL computed with these interaction coefficients for a sequence of chain lengths is displayed in Fig. 7. As anticipated, now the CL is continuous throughout its entire length, and it has two extrema (H' and H), each corresponding to one HEDCP. The maximum is also a limiting off-zero critical point L , matching the above coordinates for an HEDLCP, and separating the right (meta)stable branch from the middle unstable one

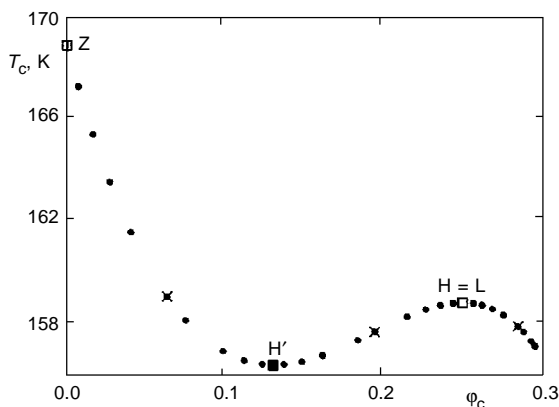


FIG. 7

CL for systems with interactions $g_0 = 0.5 + 50/T$, $g_1 = 8/27$, $g_2 = 16/81$. Notation is identical to that of Fig. 6; $m_{H'} \approx 526.91$. Triplets of points raising from H' and from the right end of the curve ($\phi_c = 0.29503$, $T_c = 157.21$) towards Z and $H \equiv L$ are for $m = 530, 550, 600, 800, 1\ 000$ (\times), $2\ 000, 4\ 000, 10\ 000, 50\ 000$

(H'-H), both consisting of "off-zero" CPs. The minimum H' of the CL, reached for $m_{H'} \approx 526.91$ at $\phi_{H'} \approx 0.1308$ and $T_{H'} \approx 156.37$ K, is of the same type as H' of Fig. 6. It separates the left branch of (meta)stable "zero" CPs from the middle branch of unstable "off-zero" CPs. Finally, the left branch ends again in a zero limiting critical point Z at $\phi_Z = 0$ and $g_0 \approx 0.796296$, i.e., at $T_Z \equiv \Theta \approx 168.75$ K.

Mathematically speaking, the HEDLCP ($H \equiv L$ of Fig. 7) is a double root of the off-zero critical Eq. (14), and in the limiting critical diagram of Fig. 1 it should lie on the double-root boundary line separating I from III. Comparison of its parameters given above with the diagram shows that indeed this is the case. More significantly, Eq. (23) characterizing all off-zero HEDLCPs is equivalent to Eq. (17) derived for double off-zero limiting critical roots, which proves the above statement in general.

After having clarified the physical meaning of the boundary line between the regions I and III, we turn our attention to the horizontal $\Delta g_2 = -1/6$ separating for $g_2 > 1/12$ the regions II and III (cf. Fig. 1). From analyses in the Theoretical it is apparent that a system with $m \rightarrow \infty$, crossing the horizontal from III to II, should lose its zero as well as one of its two off-zero limiting CPs, being left with a single remaining off-zero limiting CP. Evidently, this could happen if the off-zero limiting critical point L_1 of Fig. 6 merged with the zero limiting critical point Z. At the same time the opposite stabilities of the CL parts H'-Z and H'- L_1 , squeezed between the approaching L_1 and Z, should guarantee that the collapsed CP at $\phi_c \rightarrow 0$ has a double-heterogeneous character.

A quick look at the HEDLCP criterion (23) seems to contradict such a possibility since for $\phi_c \rightarrow 0$ Eq. (23) is satisfied only for $g_2 = 1/12$ (i.e., at the cusp in the diagram of Fig. 1 where all three regions meet together), but not for any $g_2 > 1/12$. However, this argument is wrong. Equation (23) was derived for off-zero HEDLCPs where both merging limiting CPs are of off-zero nature. On the other hand, in the above-assumed collapse at the III/II boundary one of the participants is a zero limiting CP. Clearly, one has to inspect the general forms of critical Eqs (1) and (2), and of the HEDCP condition which, for quadratic interactions and a polydisperse polymer solute, reads²¹

$$H \equiv m_z(m_{z+1} - 3m_z) - 2m_w^3\phi_c^3 [(1 - \phi)^{-3} - 6g^{(2)}] = 0 \quad (24)$$

A first-order perturbation theory, valid for very high chain lengths and small ϕ_c , can be applied to Eqs (2) and (24). Closed expressions in terms of interaction coefficients g_i result for $m_{H'}$ and $\phi_{H'}$ associated with such a "zero"/"off-zero" HEDCP, and $T_{H'}$ is then obtained from Eq. (1) as usual. General conditions for polydisperse polymer solutions are given in Appendix III as Eqs (A3.3) and (A3.4). In case of monodisperse polymers they reduce to simple relations

$$m_{H'} \approx \frac{(12g_2 - 1)^2}{(1 + 6 \Delta g_2)^3} \quad (25)$$

$$\varphi_{H'} \approx \frac{(1 + 6 \Delta g_2)}{(12g_2 - 1)} \quad (26)$$

It is immediately obvious that for the III/II boundary with $\Delta g_2 = -1/6$ and $g_2 > 1/12$, Eqs (25) and (26) indeed guarantee $\varphi_{H'} \rightarrow 0^{(+)}$ with $m_{H'}$ simultaneously growing to ∞ . Interesting is, however, the rate of convergence: here the HEDCP's concentration $\varphi_{H'}$ approaches zero as $m_{H'}^{-1/3}$ [as can be seen by eliminating $(1 + 6 \Delta g_2)$ from the two equations], whereas for a regular single "zero" CP its φ_c varies as $m^{-1/2}$. The reason for different behavior along the two paths involves the interaction term $(1 + 6 \Delta g_2)$ which changes drastically in the former case but is kept constant in the latter.

The collapse of the critical line $Z-H'-L_1$ of Fig. 6 to zero size at zero concentration is illustrated in Fig. 8 displaying three other CLs, all of the same structure as that of Fig. 6 (albeit without special marking for points Z , H' and L_1 to avoid overcrowding). For each of the three CLs shown, the interaction coefficients are kept fixed at $g_2 = 0.3$, and $g_1 = 0.42$ (curve 1), 0.44 (2) and 0.45 (3), respectively; $g_0 = 0.5 + 50/T$ as usual. Obviously, the CL of Fig. 6 with $g_1 = 0.38$ can be considered as part of the sequence, although it is too remote for the scale of Fig. 8. Along each of the four CLs the chain lengths grow from their minimal values of $m_{H'} \approx 1\,190$, $7\,950$, $44\,000$ and $180\,000$, respectively, characterizing the curves' minima, up to infinity, reached at the zero limiting critical point Z at $\varphi_c = 0$ on the left side, and at the limiting off-zero critical point L_1 on the right side (end of the line). It is apparent that with Δg_2 dropping from -0.08

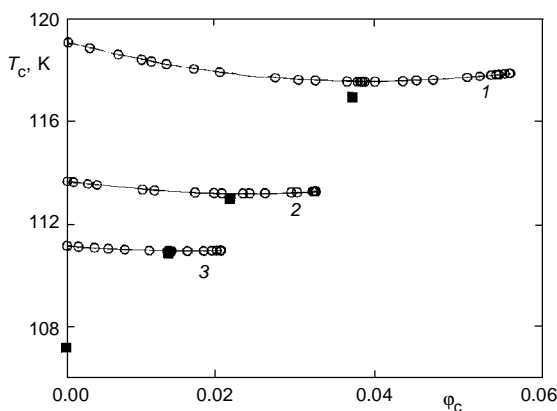


FIG. 8

CLs for three high-molar mass systems with $g_0 = 0.5 + 50/T$, $g_2 = 0.3$, and $\Delta g_2 = -0.12$ (1), -0.14 (2), and -0.15 (3), converging to a single point at $\varphi_c = 0$ for $\Delta g_2 = -1/6$; ■ HEDCPs approximated by Eqs (1), (25) and (26)

(Fig. 6) to -0.12 (curve 1), -0.14 (2) and -0.15 (3), both the ϕ_c - and m -ranges of displayed curves shrink, ready to collapse into a point at $\phi_c \rightarrow 0$ and $T_c \rightarrow 107.14$ K for $m \rightarrow \infty$ and $\Delta g_2 \rightarrow -1/6$. Full squares in Fig. 8 mark the HEDCPs approximated by Eqs (25) and (26), together with Eq. (1). It is evident that the critical data contained in Fig. 8 is consistent with the above theoretical predictions.

In the system of Figs 5a and 5b the effect of two additional CPs on the experimentally determined CPC may be hard to detect: For $m < 1$ 185 they do not exist at all; for $m > 1$ 185 they are present, born from an HEDCP, but the new sigmoidal binodal never becomes stable. Note that even the zero limiting CP for $m \rightarrow \infty$ (Z in Fig. 5a) stays metastable, hiding under the stable portion of the CPC. However, not always behave the new binodals so inconspicuously. An example of a very prominent effect of the additional CPs of type III on the experimentally accessible CPC is shown in Figs 9a and 9b. They are based on a quadratic $g(\phi)$ function applied to a polymer with $m \rightarrow \infty$, and the coefficients g_1 and g_2 were calculated with Eq. (2) after choosing suitable values for the two off-zero limiting CP concentrations. The relevant values of g_0 follow from Eq. (1) and yield the two off-zero limiting critical temperatures.

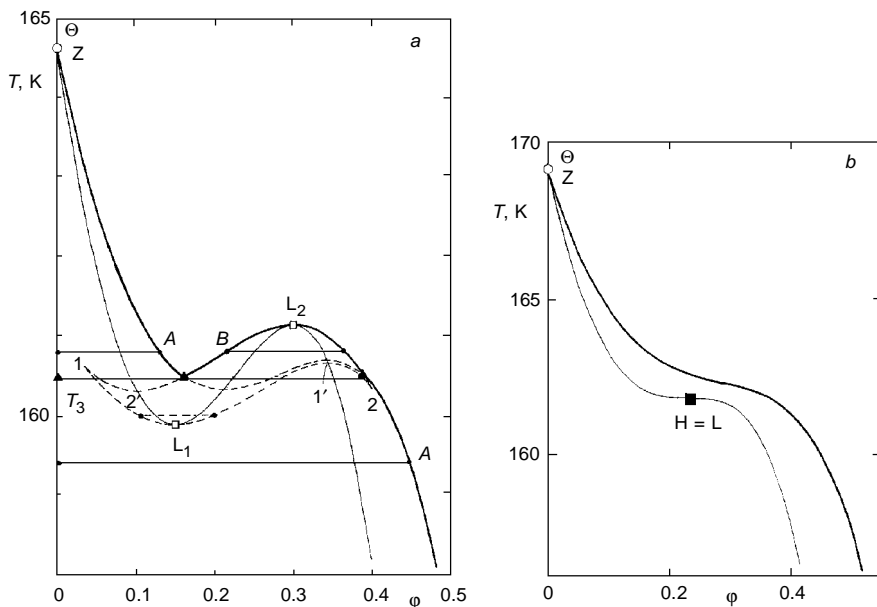


FIG. 9

Limiting phase diagrams for $m \rightarrow \infty$. Spinodal: light-drawn curve; binodal: heavy-drawn curve; dashed line marks portions that are not stable; \circ a zero limiting CP. **a** A III-type system with $g_1 \approx 0.30365$, $g_2 \approx 0.18243$, $G \approx -0.11327$, $\Delta g_2 \approx -0.12122$, $\Theta \approx 164.66$ K; \square L_1 , L_2 , off-zero limiting CPs; tie-lines: \bullet — \bullet , \bullet — \bullet — \bullet . **b** A I/III type system with $g_1 \approx 0.29570$, $g_2 \approx 0.18243$, $\Delta g_2 = G \approx -0.11327$, $\Theta \approx 169.09$ K; \blacksquare an off-zero HEDLCP

In Fig. 9a with off-zero limiting CPs L_1 and L_2 at $\phi_c = 0.15$ and 0.3 , respectively, some tie lines have been drawn in to further elucidate the course of the two binodals. Some refer to equilibria between pure solvent and polymer solution (**A**), others to equilibria between two polymer solutions of different concentrations (**B**). In this case the “new” sigmoidal binodal protrudes through the “regular” one, becoming partly stable. The two binodals intersect at T_3 (nonvariant three-phase equilibrium). According to classic rules^{14,22,23} the non-critical nonstable extrema ($1'$, $2'$) of the new binodal are intersected by the spinodal, and coexist with cusps (1, 2) in other parts of the binodal. [The seemingly missing cusps, that should accompany similar extrema on the regular CPC, coincide with the temperature axis at $\phi = 0$ (cf. Fig. 4j of ref.²³ for finite m).]

In Fig. 9b the two off-zero limiting CPs have coincided in an HEDLCP ($H = L$) defined by the I/III boundary line condition (17). Keeping the g_2 value of Fig. 9a unchanged, we find the concentration $\phi_{HL} \approx 0.22985$ from Eq. (17), the corresponding g_1 and g_0 with Eqs (1) and (2), and can then calculate the phase diagram. As usual, the HEDCP is not amenable to direct experimental observation, and its proximity can only be guessed from the shoulder on the stable part of the CPC.

Poly(2-methylpropene) Solutions

GPC data on ζ and m_w , as well as critical concentrations measured with the phase-volume-ratio method¹⁷, are available for solutions of high-molar mass poly(2-methylpropene) in benzene and in diphenyl ether^{12,13}. Assuming a quadratic $g(\phi)$, we may use Eq. (2) to evaluate the interaction parameters g_1 and g_2 supposed independent of temperature. Curves of ζ/m_w against w_c , the critical mass fraction of polymer, so obtained are shown in Fig. 10. The off-zero limiting critical concentration ϕ_L can be computed with the equation obtained by setting the bracketed expression in Eq. (13) equal to zero.

For diphenyl ether we find $g_1 \approx -0.13861$ and $g_2 \approx -0.34089$. Thus, $\Delta g_2 \approx -0.20228$, lower than $-1/6$. The calculated value for w_L is as large as 0.02085 , at a g_0 value of 0.36027 . Note that the limiting critical state is not quite a Θ -state, in which the second virial coefficient vanishes. In the latter case we should have $g_0 - g_1 = 1/2$, instead of 0.49888 .

Such an analysis for the benzene data leads to the light-drawn curve in Fig. 10, and the extrapolation to zero ζ/m_w covers a twice as large concentration range as with diphenyl ether. We obtain $g_1 \approx 0.13083$, $g_2 \approx -0.04140$, and $\Delta g_2 \approx -0.17223$, close to $-1/6$. The calculated off-zero limiting critical concentration is 0.01102 , and the quantity $g_0 - g_1$ now equals 0.4999 . The experimental errors involved render a firm conclusion impossible in this case, which is in line with the relevant remarks made by Flory and Daoust⁹.

CONCLUDING REMARKS

The conclusions drawn in the preceding sections do not depend on the particular $g(\varphi)$ function chosen here. The practically always found dependence of g on φ may have various reasons, primary among which is the difference in size and shape of the molecular species in the system. A simple expression for $g(\varphi)$ is due to Staverman²⁴ who assumed the number of nearest-neighbor contacts to be proportional to the van der Waals surface area of molecules and repeating units. The $g(\varphi)$ function then takes a simple closed form²⁵ that can be expanded in a power series as in Eq. (3b)

$$g = a + \frac{b_s + b_h/T}{1 - c\varphi} = a + (b_s + b_h/T) (1 + c\varphi + c^2\varphi^2 + c^3\varphi^3 + \dots) , \quad (27)$$

where a and b_s are empirical entropy corrections, b_h is an enthalpic term similar to β of Eq. (8a), and $c = 1 - s_2/s_1$ is related to the two molecular surface areas s_1 and s_2 .

Following the same procedure as used for Fig. 9a one finds $a \approx 0.21505$, $b_s \approx 0.57986$, $b_h \approx 12.584$ K, $c \approx 0.56569$, and obtains a phase diagram, essentially identical to Fig. 9a, except for small shifts in some variables; for instance, Θ is now 165.06 K, versus 164.66 K before. The temperature T_3 is the same: 160.5 K. On the other hand, setting Θ and the concentrations and temperatures of the double CP equal to those of Fig. 9b we obtain $a \approx 0.21641$, $b_s \approx 0.57158$, $b_h \approx 13.568$ K, $c \approx 0.56492$, and a phase diagram that can hardly be distinguished from Fig. 9b.

These examples demonstrate that the phenomena discussed in this paper do not depend on the chosen model for $g(\varphi)$ and may be expected not to represent rare exceptions, in view of the quite reasonable parameter values employed.

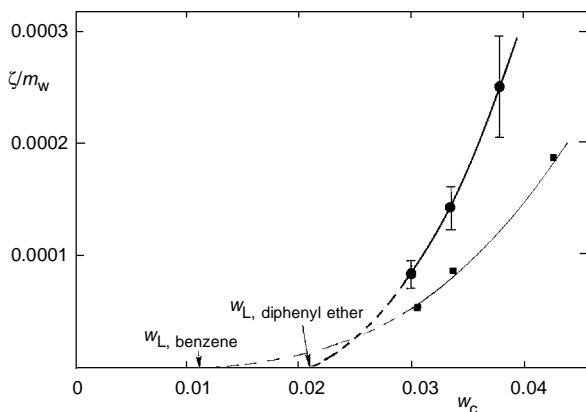


FIG. 10

Experimental data for the quantity ζ/m_w against w_c , the critical mass fraction of poly(2-methylpropene). Solvent: benzene (light-drawn curve), diphenyl ether (heavy-drawn curve)

APPENDIX I

After neglecting quadratic and higher terms in the bracket of Eq. (5a), the critical concentration can be written

$$\varphi_c \approx (\zeta/m_w)^{1/2} [1 + 6 \Delta g_2 + 2\varphi_c(1 + 12 \Delta g_3)]^{-1/2} \quad (A1.1)$$

which, after expanding the square-root bracket into a φ_c -series and substituting from Eq. (A1.1) can be approximated as

$$\varphi_c \approx \left(\frac{\zeta/m_w}{1 + 6 \Delta g_2} \right)^{1/2} \left[1 + (\zeta/m_w)^{1/2} \frac{1 + 12 \Delta g_3}{(1 + 6 \Delta g_2)^{3/2}} \right]^{-1} . \quad (A1.2)$$

The spinodal condition requires more care: It is apparent from Eq. (A1.1) that, in general, the product $\varphi_c m_w^{1/2} \equiv \Phi$ retains a finite non-zero positive value even as $m_w \rightarrow \infty$ and $\varphi_c \rightarrow 0$. Thus in order to satisfy Eq. (4a), here recast as

$$\Phi [1 + 2 \Delta g_1 + \varphi_c(1 + 6 \Delta g_2) + \varphi_c^2(1 + 12 \Delta g_3) + O(\varphi_c^3)] + m_w^{-1/2} = 0 ; \quad (A1.3)$$

the leading term in the bracket, $1 + 2 \Delta g_1$, has to approach a negative zero, i.e.,

$$g_0 \rightarrow (1/2) + g_1 + 0^{(+)} . \quad (A1.4)$$

As expected, simultaneous matching of both Eqs (4a) and (5a) puts a stricter condition on Δg_1 than just the inequality (6a).

Handling of (A1.3) is facilitated by introducing another finite non-zero product based on Eq. (A1.4), namely $\Gamma \equiv -(1 + 2 \Delta g_1)m_w^{1/2}$, where $\Gamma \geq 0$; Eq. (A1.3) then becomes

$$\Phi [-\Gamma + (1 + 6 \Delta g_2)\Phi + (1 + 12 \Delta g_3)\Phi\varphi_c + O(\varphi_c^2)] + 1 = 0 . \quad (A1.5)$$

From Eq. (A1.5) it is apparent that an error would be committed had we treated Eq. (4a) the same as Eq. (5a), namely, had we neglected the quadratic term in the bracket of (4a).

APPENDIX II

If the interaction function $g(\varphi)$, Eq. (3b) is no stronger than quadratic (i.e., $k < 3$), Eq. (14) is reduced to an equation cubic in φ_c ,

$$[6(1 - \varphi_c)^2]^{-1} = 4g_2\varphi_c - \Delta g_2. \quad (A2.1)$$

Criteria for the existence of the roots φ_c in the interval $(0, 1)$ can be derived by comparing separately the left- and right-hand sides of Eq. (A2.1) displayed as functions of φ_c in Fig. 11. The former expression, denoted as Y , is a monotonous function growing from $Y = Y_0 = 1/6$ at $\varphi_c = 0$ to $Y \rightarrow \infty$ for $\varphi_c \rightarrow 1$, whereas the latter one, y , is a straight line with an intercept $y_0 = -\Delta g_2$ and the slope $s = 4g_2$. For two displayed cases, the corresponding straight lines are marked by 1 and t .

It is apparent that when the intercept y_0 is greater than Y_0 (dashed line 1 in Fig. 11), i.e., $\Delta g_2 < -1/6$, the line intersects the function Y in the physical interval $0 \leq \varphi_c \leq 1$ once and only once for any slope, positive, zero or negative. Hence, in this case there exists a single meaningful solution φ_c of Eq. (A2.1). However, when the intercept y_0 is smaller than Y_0 , i.e., $\Delta g_2 > -1/6$, physically significant limiting root(s) can exist only with certain parameter boundaries. These are revealed by examining the tangent to the function Y (line t in Fig. 11) with the slope S , given by

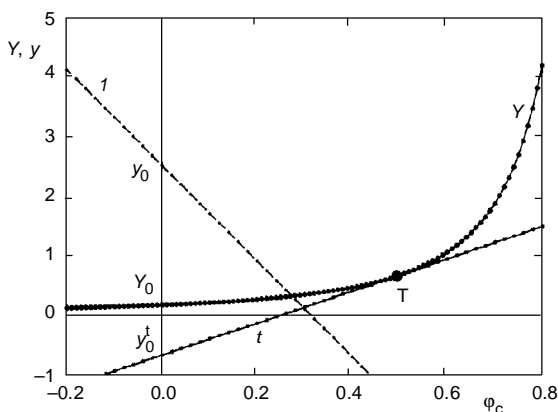


FIG. 11

Graph displaying the left- and right-hand sides of Eq. (A2.1), denoted as Y and y , respectively. For the two cases shown here, straight line y is denoted by 1 and t . The intercepts cut off on the vertical axis ($\varphi_c = 0$) are marked by 0 subscripts. A tangent t to the curve Y makes a contact with it at the point T .

$$S \equiv dY/d\varphi_c = [3(1 - \varphi_c^T)^3]^{-1} , \quad (A2.2)$$

where the superscript T specifies the coordinate of the contact point T. Conversely, the slope S can be used to define the contact point by expressing its coordinates as

$$\varphi_c^T = 1 - (3S)^{-1/3} \quad Y^T = (S^2/3)^{1/3}/2 , \quad (A2.3)$$

which, in turn, determine the tangent's intercept y_0^t at $\varphi_c = 0$ as

$$y_0^t = \frac{(3S)^{2/3}}{2} - S . \quad (A2.4)$$

The crucial factor $G(g_2)$ can now be identified by comparing the parameters of the line y (the right-hand side of Eq. (A2.1)) with those of the tangent t as

$$G(g_2) \equiv 4g_2 - (12g_2)^{2/3}/2 . \quad (A2.5)$$

Three cases can be distinguished:

a) It is obvious that if the line y is identical with the tangent t ($\Delta g_2 = -y_0^t$ and $4g_2 = S$, i.e., $\Delta g_2 = G$), Eq. (A2.1) has a double root at

$$\varphi_c^T = 1 - (12g_2)^{-1/3} . \quad (A2.6)$$

Since the root has to be within the range $0 \leq \varphi_c^T \leq 1$, the slope g_2 cannot be lower than $1/12$.

b) If the line y is shifted downwards, i.e., $\Delta g_2 > G$, there is no interaction with the function Y , i.e., there are no physically relevant roots of Eq. (A2.1).

c) If, on the other hand, the line y is shifted upwards with Δg_2 dropping below G , i.e., $\Delta g_2 < G$, and $g_2 \geq 1/12$, Eq. (A2.1) has initially two physically significant roots, one lower and one greater than φ_c^T of Eq. (A2.6). As Δg_2 keeps further decreasing and crosses the value of $-1/6$, the lower root passes through $\varphi_c = 0$ (cf. Eq. (A2.1)), thus becoming physically irrelevant. Then the system is left with only one physical root (the higher one of the original couple).

APPENDIX III

In a polymer solution with quadratic interactions, approximate relations for a heterogeneous double critical point (HEDCP) in the range of low concentrations, $\varphi_c \rightarrow 0$, are derived from the HEDCP criterion, Eq. (24), and from the CP condition (2). From the former relation we obtain

$$(m_w \varphi_c)^3 \approx \frac{m_z(3m_z - m_{z+1})}{2(12g_2 - 1)}, \quad (A3.1)$$

whereas the latter one yields

$$(m_w \varphi_c)^2 \approx \frac{m_z}{1 + 6 \Delta g_2}. \quad (A3.2)$$

By eliminating one or the other variable from Eqs (A3.1) and (A3.2), one can isolate the effect the quadratic interactions have on the location of the HEDCP H' (cf. Figs 6–8). Specifically, we get

$$m_z^{1/2} (3 - \zeta_1) \approx 2 \frac{12g_2 - 1}{(1 + 6 \Delta g_2)^{3/2}}, \quad (A3.3)$$

$$\varphi_c \approx \frac{\zeta(3 - \zeta_1)}{2(12g_2 - 1)} (1 + 6 \Delta g_2), \quad (A3.4)$$

where $\zeta \equiv m_z/m_w$ and $\zeta_1 \equiv m_{z+1}/m_z$. These results confirm the significance of the horizontal line $\Delta g_2 \rightarrow -1/6$ (cf. Fig. 1) where, independently of the type of polymer molecular-weight distribution, the HEDCP concentration φ_c approaches zero (cf. Eq. (A3.4)) for a polymer with its chain length m_z growing to infinity. The rate of approach, however, does depend on the polymer's m -distribution, as well as on the interaction coefficient g_2 .

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