Three-Phase and Four-Phase Cloud-Point Equilibria in Solutions of Polydisperse Homopolymers

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ABSTRACT: In the Flory–Huggins approximation, the cloud-point curves of polymers with very broad and asymmetric distribution of molecular weight may show *two triple points* at each of which the bulk phase of the solution is in equilibrium with two incipient phases of different compositions. By careful manipulation of the molecular weight distribution, the two stable triple points can be brought closer to each other and finally merged into a *quadruple point.* This point characterizes a four-phase equilibrium between the bulk phase and three incipient phases. The criterion for the appearance of a three-phase region on the cloud-point curve is formulated. It is argued that the existence of an extensive three-phase region in some systems presents a fundamental obstacle to the otherwise potentially feasible determination of the molecular weight distribution from the cloud-point curve.

In recent years it has been documented both experimentally and theoretically that solutions of polydisperse homopolymers in poor solvents may exhibit a three-phase region which, if extending up to the cloud-point curve (CPC), then results in the appearance of a triple point on the CPC, and sometimes also in a metastable critical point.[1–3] It seems desirable to examine closer the question under what conditions one could expect cloud-point equilibria involving more than two phases (for instance three or four) in a quasi-binary system where the phase separation occurs only because of vastly different molecular volumes of chemically identical x-mers.

Random search for a four-phase system would be futile since its occurence has to be rare. Fortunately there are some clues which aid in designing it. It is obvious that if one had a polydisperse polymer whose CPC contained *two* different stable triple points, then by careful manipulation of its molecular weight distribution one possibly could make the two triple points coalesce into the desired quadruple point. At this point, the bulk phase would be at equilibrium with three stable incipient phases of different compositions. The selection of a polymer with two triple points on its CPC, in turn, is assisted by analyzing our previous results. It has been shown[2,3] that a polymer with a logarithmic-normal (LN) distribution of molecular weight always exhibits a triple point and a metastable critical point. Hence, a triple point at relatively low polymer concentration should be ensured by choosing a high molecular weight polymer with a LN distribution as one prevailing constituent of a polymer mixture. On the other hand, triple points at high polymer concentrations have been observed, e.g., for polymers consisting of two monodisperse species of low but greatly differing molecular weights.[2] Employing such a polymer as the second constituent of the polymer mixture should tend to generate another triple point at higher concentrations. Finally, under favorable conditions, changing the ratio of the two constituents should result in moving the two triple points along the CPC and in generating a quadruple point.

For calculating the cloud-point curves, it is assumed that polymer solutions obey the Flory–Huggins thermodynamics with concentration-independent interaction parameter χ.[4] This approach is attractive for its simplicity and it is obvious that any unusual effects observed here will also exist, in principle, in systems with more complex behavior. CPC's are computed by previously reported methods.[2,3]

Results and Discussion

Synthetic mixtures of two polymer samples have been studied: *Sample A* is approximated by a logarithmic-normal distribution of molecular weight with average degrees of polymerization $x_n = 1 \times 10^4$ and $x_w = 2 \times 10^4$, and with the lower and upper limits of integration $x_{\min} = 10$, $x_{\max} = 1 \times 10^8$. With these parameters, the numerically computed averages x_n, x_w, x_z, and x_{z+1} differ from the ideal values by less than 10^{-4}%. *Sample B* consists of 99.5% of the species with $x = 50$ and 0.5% of the species with $x = 500$. Each sample alone shows a triple point on its CPC. The results for mixtures with A content varying from 40 to 3% are shown in Figures 1–4 and Table I. In order to avoid accumulating too many lines, CPC's and shadow curves are not always indicated in the regions where they are not thermodynamically stable.

Let us first discuss the features which are common to all mixtures examined in this work. The upper left part of each CPC, extending from the dilute region with $\chi \approx 0.5$ down to the first triple point encountered, is practically exclusively due to the component A with LN distribution. As such, it is virtually identical for all cases (only extending to higher concentrations for mixtures with lower contents of A sample), and it is indistinguishable from the analytical result $\chi^{-1} = 2(1 - \phi)$ derived for polymers with a *true* LN distribution. In all four mixtures, the metastable critical point is located in close proximity of the left singular point of the CPC, and the shadow curve follows very closely the CPC down to the first triple point, with the concentration difference between the two curves never exceeding 2×10^{-3} in the illustrated range. This behavior is in excellent agreement with our earlier analysis of systems containing polymers with LN distribution.[2,3] In particular, it illustrates the conclusion,[3] supported by experimental data of Klein et al.,[5] predicting that in such mixtures the portion of the CPC left off the (first) triple point is very little, if at all, dependent on the overall averages x_n, x_w, etc., commonly used to characterize polymers (cf. Table I).

At higher concentrations, the four mixtures differ in their behavior. In Figure 1 the A content of 40% appears to be high enough to overcome the tendency of the B sample to separate into three phases, and the CPC shows only one triple point, T_{12}, due to the LN distribution of the component A. The subscript attached to T here identifies the stable portions of the CPC which give rise to this particular triple point, with the portions being numbered somewhat arbitrarily from left to right as they appear in the sequence of Figures 1–4 (see Figure 2). Although the CPC shows a distinct depression at $\phi \approx 0.26$ in the place of the developing second triple point, the corresponding stable portion of the shadow curve remains continuous which clearly indicates that contrary to our previous belief[3] (and in accord with Koningsveld's and Kleintjens' suggestion[1]) not every depression on a CPC necessarily signifies the presence of a triple point.

The mixture containing 20% of A (Figure 2) already exhibits a second triple point T_{23}, due to the component B, at $\phi \approx 0.256$ as is apparent from the small triangular metastable region on CPC at this point as well as from the S-shaped form of the corresponding metastable part of the shadow curve. (The

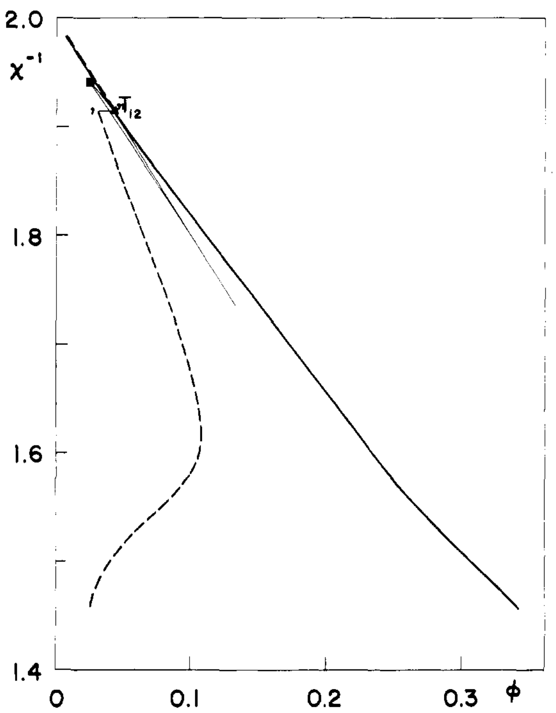

Figure 1. Cloud-point equilibrium for the mixture A–B = 40:60. (—) Cloud-point curve, (- - -) shadow curve. Bold lines indicate thermodynamically stable parts of both curves; thin lines indicate metastable or unstable parts. (■) Critical point, (▲) stable triple point T_{ij}. Single and double prime indicate the two incipient phases in equilibrium with the bulk phase at the triple point.

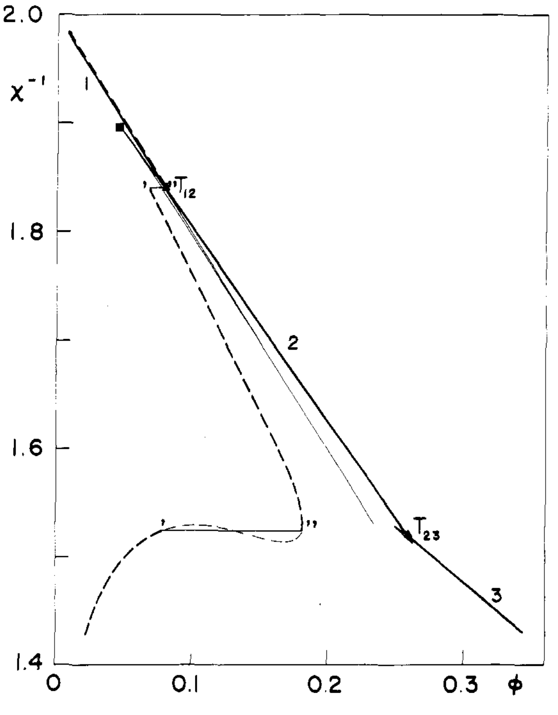

Figure 2. Cloud-point equilibrium for the mixture A–B = 20:80. Symbols are defined in Figure 1. Numbers 1, 2, and 3 identify the three parts of the cloud-point curve as employed for subscribing triple points T_{ij}.

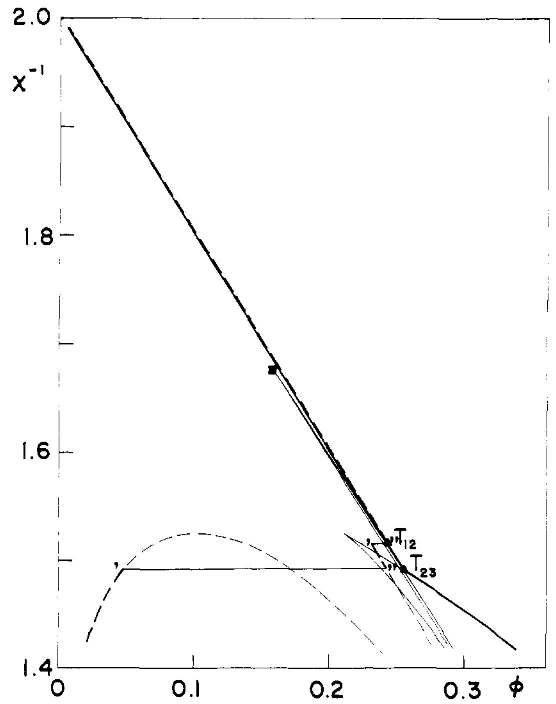

Figure 3. Cloud-point equilibrium for the mixture A–B = 5:95. Symbols are defined in Figure 1.

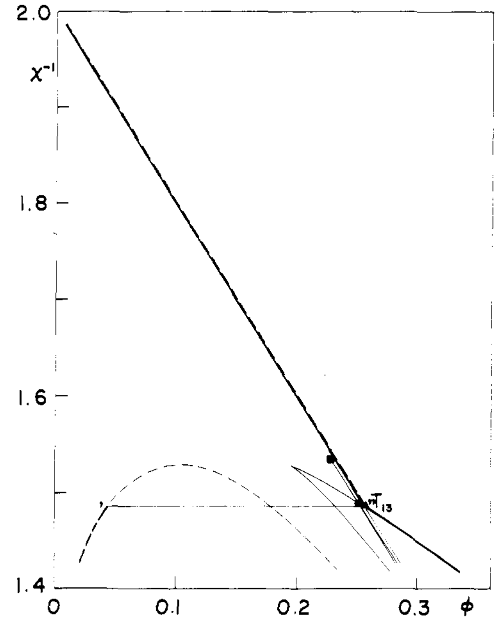

Figure 4. Cloud-point equilibrium for the mixture A–B = 3:97. Symbols are defined in Figure 1. (●) Metastable triple point T_{23}.

analogous S-shaped portion of the shadow curve associated with T_{12} has been omitted in all figures to maintain clarity of this region.) There are qualitative differences between the two triple points: whereas at T_{12} one incipient phase is always more concentrated and the other less concentrated than the bulk phase, at T_{23} both of the equilibrium incipient phases are less concentrated than the solution. As compared to Figure 1, both the triple point T_{12} and the critical point are shifted to higher concentrations because of decreased values of x_w and x_z. With a further decrease of A content, this trend then continues while T_{23} stays almost constant. For the mixture with 5% of A (Figure 3) the triple points T_{12} and T_{23}, both being still stable, approach each other within $\Delta\phi \approx 0.01$. The two triangular thermodynamically not stable portions of the CPC which in the previous case (Figure 2) were clearly separated here overlap giving rise to more triple points at the points of intersection. Most of these new triple points are inherenly not stable since they involve at least one triangular-base portion of the CPC which can never become thermodynamically stable; hence they are of no interest to us. The triple

Table I
Parameters Characterizing Three-Phase (T_{ij}) and Four-Phase (Q) Equilibria in the Examined Polymers

		Bulk phase				Incipient phases[a]					
	% A	x_n	x_w	χ	ϕ	ϕ'	ϕ''	x_n'	x_n''	x_w'	x_w''
T_{12}	40	83.4	8031	0.5223	0.0416	0.0307	0.0432	61.9	86.7	1979	3337000
	20	62.7	4042	0.5434	0.0788	0.0682	0.0804	54.5	64.0	850	1726000
	5	52.9	1050	0.6599	0.2414	0.2317	0.2427	51.0	53.1	194.5	474700
	3[b]	51.8	651	0.7493	0.3319	0.3224	0.3331	50.6	51.9	115.5	306700
T_{23}	20	62.7	4042	0.6564	0.2560	0.0792	0.1804	50.0	50.1	50.0	50.9
	5	52.9	1050	0.6697	0.2530	0.0483	0.2420	50.0	50.9	50.0	162.5
	3[b]	51.8	651	0.6712	0.2517	0.0461	0.2495	50.0	51.4	50.0	396.6
T_{13}	5[b]	52.9	1050	0.6694	0.2522	0.0487	0.2535	50.0	53.1	50.0	442200
	3	51.8	651	0.6725	0.2556	0.0443	0.2569	50.0	52.0	50.0	471000

		Bulk phase				Incipient phases[a]					
	% A	x_n	x_w	χ	ϕ	ϕ'	ϕ''	ϕ'''	x_n'	x_n''	x_n'''
Q	4.67	52.7	983	0.6700	0.2528	0.0479	0.2431	0.2541	50.0	50.9	52.9

[a] Incipient phases ordered according to increasing concentration. [b] Metastable or unstable triple point.

point T_{13}, however, is different. It is located at the intersection of the CPC portions 1 and 3, and although it is metastable for this particular system, it will become stable in the next examined polymer. It is too close to T_{23} to be separately plotted in Figure 3, but its coordinates are given in Table I. Finally, in the last examined system with only 3% of A, the triple point T_{12} has passed T_{23} (out of the scope of Figure 4) and become metastable. The triple point T_{23} is also metastable, and the CPC now contains only one stable triple point, T_{13}.

It is apparent that within the range of A content 5–3% there has to be a polymer mixture for which the three triple points T_{12}, T_{13}, and T_{23} merge into one quadruple point, and, correspondingly, six distinct incipient phases (some of them not stable) characterizing the above triple points reduce to three stable coexisting incipient phases (e.g., the phase ϕ' of T_{12} in Figure 3 becomes identical with the phase ϕ'' of T_{23}). Such a system has indeed been identified at $\approx$4.67% of A and is described in Table I. At the concentration $\phi \approx 0.2528$ and $\chi \approx 0.6699$, this mixture separates into four phases with one incipient phase being more concentrated and two incipient phases being less concentrated that the bulk phase of the solution.

The sequence of Figures 1–4 calls also for examination of another problem. It is apparent that in the composition range 20–40% A there exists a mixture for which the suspicously looking but still two-phase depression (similar to that of Figure 1) is just transformed into a true triple point T_{23} characterizing a three-phase equilibrium. It would be desirable to formulate some criterion for this state.

In any three-phase system, the left and right singular points of the CPC (acute angles of the CPC's triangular region) correspond to a maximum and a minimum on the shadow curve (see, e.g., the region of T_{23} in Figure 2). Using the previously established notation,[2,3] the condition of zero slope of the shadow curve can be written as

$$\mathrm{d}\chi/\mathrm{d}(\phi\nu_0) = 0 \tag{1}$$

where, in general,

$$\nu_k = \int_0^\infty w(x)x^k \exp(K\sigma x)\, dx \tag{2}$$

is the kth moment of the chain-length distribution in the incipient phase. This distribution is normalized so that $\phi\nu_0$ gives the polymer concentration in the incipient phase (i.e., at the shadow curve). The familiar nonnegative parameter σ describes the ratio in which the polymer species of chain length x is distributed between the concentrated ($''$) and dilute ($'$) phases,[4]

$$\phi_x''/\phi_x' = \exp(\sigma x) \tag{3}$$

K is a constant equal to $+1$ or -1, depending on whether the incipient phase is more or less concentrated that the bulk phase of the solution, and $w(x)$ is the chain-length distribution of the original polymer (i.e., of the polymer contained in the bulk phase).

Since $K\sigma$ changes monotonically along the entire length of the CPC, irrespective of possibly present three-phase regions, and since the CPC changes its direction at its singular points, such points will also be characterized by

$$|\mathrm{d}\sigma/\mathrm{d}\phi| \to \infty \tag{4a}$$

or, equivalently, by

$$\mathrm{d}\phi/\mathrm{d}\sigma = 0 \tag{4b}$$

By applying eq 1 and 4b to the relation for χ,

$$2\chi\phi(\nu_0 - 1) = K\sigma + \ln\,[(1 - \phi)/(1 - \phi\nu_0)] \tag{5}$$

and realizing that[2]

$$\mathrm{d}^n\nu_k/\mathrm{d}\sigma^n = K^n\nu_{k+n}$$

one can thus derive the equation which has to be satisfied at singular points of a three-phase region

$$2\chi = (\phi\nu_1)^{-1} + (1 - \phi\nu_0)^{-1} \tag{6a}$$

or more conveniently,

$$2\chi\phi^* = x_w^{*-1} + \phi^*/(1 - \phi^*) \tag{6b}$$

where $\phi^* \equiv \phi\nu_0$ and $x_w^* \equiv \nu_1/\nu_0$ denote the polymer concentration and the weight-average chain length of the polymer in the incipient phase.

Carried one step further, this method yields the answer to the problem posed above. In a system where, upon a small perturbation of the molecular weight distribution, the two-phase equilibrium will be transformed in a three-phase equilibrium, the two singular points of the CPC have to be superimposed. This then requires that in addition to eq 1 and 4 also eq 7 and 8 be satisfied

$$\mathrm{d}^2\chi/\mathrm{d}(\phi\nu_0)^2 = 0 \tag{7}$$

$$\mathrm{d}^2\phi/\mathrm{d}\sigma^2 = 0 \tag{8}$$

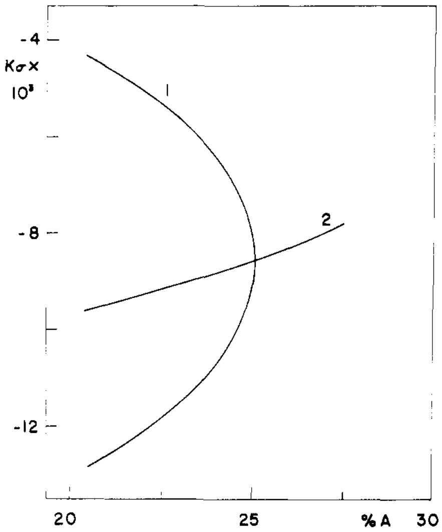

Figure 5. Plot of roots of eq 6b (curve 1) and eq 9 (curve 2) as functions of the A content in the mixture. For each mixture possessing a triple point T_{23} on its cloud-point curve, curve 1 specifies the two singular points. The first mixture exhibiting such a three-phase region is indicated by the point of intersection of curves 1 and 2.

Again in combination with eq 5, this translates into the criterion

$$\phi^*/(1 - \phi^*) = x_z^{*1/2}/x_w^* \qquad (9)$$

The applicability of eq 6b and 9 to our systems is illustrated in Figure 5. For a given polymer, $K\sigma$ is the only single parameter which unambiguously specifies a particular point of the CPC; all other parameters appearing in equilibrium equations (ϕ,ϕ^*,χ) may correspond to more than one point of the CPC, as apparent from Figures 1–4. Therefore, we plot $K\sigma$ satisfying the above equations as a function of the A content in the polymer mixture. In particular, curve 1 in Figure 5 represents the $K\sigma$ roots of eq 6b, i.e., it specifies the singular points of the CPC, and curve 2 shows $K\sigma$ roots of eq 9. The point of intersection of these two curves (which has to coincide with the flat extremum of curve 1) then defines the composition of the system and the value of $K\sigma$ at which the triple point T_{23} appears the first time; in our case it is ≈25.1% of A, $K\sigma \approx -8.575 \times 10^{-3}$.

The form of eq 6b and 9 looks familiar; if they referred to the bulk phase parameters rather than to the incipient phase parameters, they would define the critical point.[6] This also means that both equations will be satisfied at the critical point where the two phases become identical; however, this trivial solution is not interesting. Generally, the search for a nontrivial solution requires extensive calculation practically feasible only by employing a computer: for the examined system, many cloud-point equilibria have to be calculated, and for each point deviations from satisfying eq 6b have to be evaluated. If the deviations in dependence on polymer concentration show a minimum dropping almost to zero, this is an indication of the system being close to three-phase separation. A small change in molecular-weight distribution then usually results in the minimum crossing the zero line, i.e., in eq 6b having two real roots characterizing the singular points of a three-phase equilibrium. There is only one narrow group of cases where the three-phase equilibrium at the cloud point can be predicted immediately: if $x_{z+1} > 3x_z + 2x_z^{1/2}$, then the critical point itself is metastable, located between the two singular points of the CPC, and the CPC necessarily contains a triple point.[2]

The present numerical study confirms some points made in the past. Fractional precipitation (i.e., fractionation where the incipient phase is more concentrated than the bulk phase) of a polymer containing a component with a LN distribution may yield fractions with polydispersities sharply higher that the polydispersity x_w/x_n of the fractionated polymer. Moreover, unlike in polymers with converging distribution (e.g., Schulz–Zimm type), here this unpleasant effect grows worse by decreasing the size of the fraction.[7] For instance, at the four-phase equilibrium, the polydispersity of the polymer contained in the most concentrated phase is higher than 8000, compared to the original polydispersity of less than 20. At the same time, the phase separation may become difficult since the polymer concentrations (hence also the densities) of the bulk phase and the more concentrated incipient phase are very close to each other. The conditions are more favorable in the case of fractional solution (i.e., in our systems at concentrations higher than the first triple point concentration), where the polydispersity of a fraction is lower than that of the original polymer. This is particularly true if one goes beyond T_{23} or T_{13}; here the extracted fraction contains virtually pure lowest component present in the system, with $x_n \approx x_w \approx 50$ (cf. Table I).

The close similarity of the stable portions of CPC's for the four examined mixtures having very different molecular weight distributions suggests that, in general, it may be impossible to derive the molecular weight distribution from the experimentally observed CPC's alone. This task may be feasible for the cases where the CPC is in its entire length stable, i.e., where the experimentally observed CPC contains all the information about the distribution. However, if the CPC exhibits a triple point, the information stored in its metastable and/or unstable parts is lost and it becomes increasingly difficult to interpret the remaining stable part. This is true in particular if the critical point is not stable, since its neighborhood (the position, the slope of CPC at the critical point, etc.) contains the information about the most important low averages x_w, x_z, etc., not scrambled by higher averages.

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