Phase diagrams of quasi-binary polymer systems with *LCST/UCST* spinodals and hour-glass cloud-point curves

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A generalized Flory–Huggins theory is utilized to investigate liquid–liquid phase diagrams of quasi-binary polymer solutions and blends, in which one component may be polydisperse. A temperature and concentration dependent χ parameter is employed. It is illustrated that a polymer solution, in which the polymeric component has a Schulz–Zimm molecular weight distribution, may exhibit combined lower critical solution temperature/upper critical solution temperature spinodals and hour-glass cloud-point curves (CPCs). This is a direct consequence of the critical points being offset from the extrema of the CPCs and spinodals for quasi-binary systems, in contrast to true binary systems (such as solutions and blends of monodisperse polymers). Thus, for quasi-binary systems, it may be hazardous to infer the behaviour of spinodals from observations of CPCs or vice versa.

(Keywords: phase diagrams; quasi-binary systems; cloud-point curves)

Introduction

The determination of the liquid–liquid phase diagram of a polymer solution or blend is a critical first step in understanding the phase behaviour of these systems. Armed with this information the investigator is able to make informed judgements regarding the mechanism of phase separation under particular conditions, as well as assessing the useful temperature range in which a newly formulated blend may be successfully utilized. Experimentally it is known that there are five main types of phase diagrams[1,2]. These are lower critical solution temperature (*LCST*), upper critical solution temperature (*UCST*), combination of the two with the *LCST* lying above the *UCST*, closed loop and hour-glass. A modelling method has been described[3] that is capable of calculating all these types of phase diagrams for binary polymer solutions and blends. This method is based on a temperature and composition dependent χ interaction parameter of the form[3]:

$$\chi(T, \varphi_2) = (1 + b_1\varphi_2 + b_2\varphi_2^2)[d_0 + d_1/T + d_2 \ln(T)] \tag{1}$$

where the coefficients b_i and d_i are adjustable constants. This form of the temperature dependence follows from the assumption that the excess partial molar heat capacity of solution is independent of temperature. The quadratic composition dependence was chosen because it has been found to be sufficient to describe most of the experimentally determined χ parameters for solutions[4–6]. Finally, it is assumed that the temperature dependence of χ is uniform for all compositions. Recently, this method has been extended[7] to describe the liquid–liquid phase behaviour of polymer solutions and blends, in which one polymeric component may be comprised of a distribution of molecular weights.

When the coefficients of d_1 and d_2 in equation (1) are both positive, the resulting phase diagram is either of the combined *LCST/UCST* or hour-glass type. The classic example of a system that exhibits these types of phase diagrams is acetone/polystyrene, which undergoes a transition from combined *LCST/UCST* to hour-glass as the molecular weight of the polystyrene is increased[1]. Theoretical investigations of the coalescence of combined *LCST/UCST* spinodals, and binodals or cloud-point curves (CPCs), have been pursued previously[8–10]. A discussion of the scaling relation between composition and temperature near a critical point in the region of spinodal coalescence has been given by ten Brinke and Boots[8]. These authors showed that the exponent β, in the relation

$$|\varphi - \varphi_c| \approx |T - T_c|^\beta \tag{2}$$

is doubled for the coalescing case. Furthermore, Solc *et al.*[9] have discussed criteria for vertical coalescence and, more recently, for horizontal coalescence in systems with interaction parameters that depend strongly on concentration[10].

For a true binary system (solutions or blends of monodisperse polymers) the critical points, if any exist, are located at the extrema of the spinodals, which coincide with the extrema of the binodals. For these systems, the point where the two critical points of an *LCST/UCST* phase diagram coalesce is frequently called a double critical point. However, for quasi-binary systems the critical points are characteristically offset from the extrema of both the spinodals and the CPCs. Consequently, for quasi-binary systems undergoing vertical coalescence the extrema of the CPCs coalesce before those of the spinodals, and this can lead to some unusual phenomena. Here, we focus on a particular feature of quasi-binary phase diagrams that has not been generally appreciated; the fact that the CPCs and the spinodals for a particular system need not be of the same type.

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Phase equilibria in quasi-binary systems

The Gibbs free energy change on mixing a polydisperse polymer (component 2) with a monodisperse diluent or polymer (component 1) is given, for a mole of lattice sites, by:

$$\frac{\Delta G}{RT} = \frac{1-\varphi_2}{N_1}\ln(1-\varphi_2) + \sum_{i=1}^{n}\frac{\varphi_{2i}}{N_{2i}}\ln\varphi_{2i} + g(T,\varphi_2)\varphi_2(1-\varphi_2) \qquad (3)$$

The relative molar volume of component 1 is N_1; N_{2i} and φ_{2i} are the relative molar volume and volume fraction of the ith constituent in component 2; and φ_2 is the total volume fraction of component 2. The function $g(T, \varphi_2)$ is a residual free energy of mixing, which we take to be a function of temperature and composition. The relationship between g and χ is[3,11]:

$$\int_{\varphi_2}^{1}\chi(T,\varphi)\,\mathrm{d}\varphi = (1-\varphi_2)g(T,\varphi_2) \qquad (4)$$

The spinodal is calculated[7,11] from:

$$\frac{1}{N_1(1-\varphi_2)} - [2\chi(T,\varphi_2) + \varphi_2\chi'(T,\varphi_2)] + \frac{1}{\varphi_2 N_{2\mathrm{w}}} = 0 \qquad (5)$$

Critical point(s) are given[7,11] by solution(s) of:

$$\frac{N_{2\mathrm{z}}}{N_{2\mathrm{w}}^2\varphi_2^2} - \frac{1}{N_1(1-\varphi_2)^2} + [3\chi'(T,\varphi_2) + \varphi_2\chi''(T,\varphi_2)] = 0 \qquad (6)$$

Here, $N_{2\mathrm{w}}$ and $N_{2\mathrm{z}}$ are the weight-average and z-average relative molar volumes of component 2, respectively.

The CPC is obtained[7,12] by simultaneously solving the two equations:

$$\frac{1}{2}(1+\nu_0)\sigma + (\mu_{-1} - \nu_{-1}) + \frac{1}{N_1}(\nu_0 - 1) + \frac{1}{N_1}\left(\frac{1}{\varphi_2} - \frac{1+\nu_0}{2}\right)\ln\frac{1-\nu_0\varphi_2}{1-\varphi_2} + \frac{1}{2}\left\{(\nu_0-1)[\chi(T,\nu_0\varphi_2)(\nu_0\varphi_2) + \chi(T,\varphi_2)\varphi_2] - (\nu_0+1)\int_{\varphi_2}^{\varphi_2\nu_0}\chi(T,\varphi)\,\mathrm{d}\varphi\right\} = 0 \qquad (7)$$

and

$$\sigma - \frac{1}{N_1}\ln\frac{1-\nu_0\varphi_2}{1-\varphi_2} - \left[\nu_0\varphi_2\chi(T,\nu_0\varphi_2) - \varphi_2\chi(T,\varphi_2) + \int_{\varphi_2}^{\varphi_2\nu_0}\chi(T,\varphi)\,\mathrm{d}\varphi\right] = 0 \qquad (8)$$

The separation factor σ, as well as the statistical moments ν_k and μ_k $(k = -1, 0)$, are defined as[12]:

$$\frac{\varphi''_{2i}}{\varphi'_{2i}} = \exp(\sigma N_{2i}) \qquad (9)$$

$$\nu_k = \int N^k w(N)\exp(\sigma N)\,\mathrm{d}N \qquad (10)$$

and

$$\mu_k = \int N^k w(N)\,\mathrm{d}N \qquad (11)$$

where φ''_{2i} and φ'_{2i} are the volume fractions of component 2 in the incipient and original-solution phases, and where $w(N)$ is the relative molar volume distribution of component 2.

Phase diagrams

To illustrate phase diagrams that have CPCs and spinodals of different types for the same system, we use a hypothetical polymer solution consisting of a low molecular weight solvent ($M = 100$) and a polymer with a Schulz–Zimm molecular weight distribution. The polymer has $M_\mathrm{n} = 10\,000$, $M_\mathrm{w} = 13\,300$, $M_\mathrm{z} = 16\,700$, and a coupling constant $k = 3$. Both components have unit density. The five phase diagrams that are shown in *Figures 1–5* were generated for this polymer solution by using the interaction parameter:

$$\chi(T,\varphi_2) = \chi(T) = d_0 + 60.0/T + 0.18\ln T \qquad (12)$$

where $d_0 = -0.6370$ in *Figure 1*, $d_0 = -0.6366$ in *Figure 2*, $d_0 = -0.6361$ in *Figure 3*, $d_0 = -0.6350$ in *Figure 4* and $d_0 = -0.6300$ in *Figure 5*.

The remarkable feature of this sequence of phase diagrams is the transition in behaviour from the

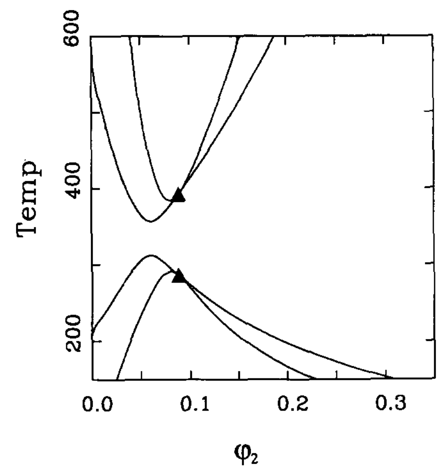

Figure 1 Phase diagram with *LCST/UCST* spinodal and CPCs; $d_0 = -0.6370$. The critical points are denoted by solid triangles

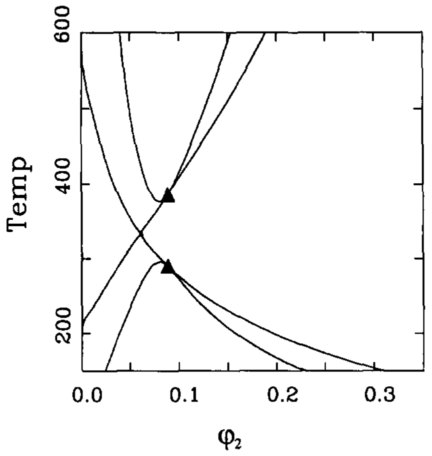

Figure 2 Phase diagram showing the initial coalescence of the CPCs; $d_0 = -0.6366$. The critical points are denoted by solid triangles

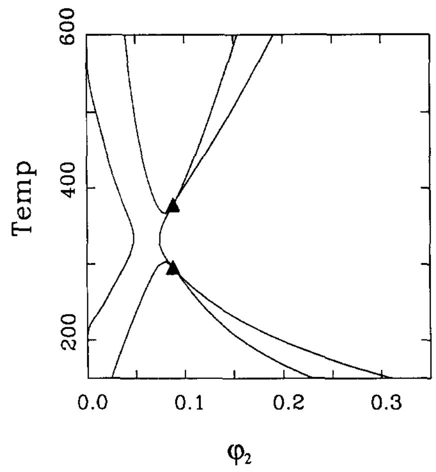

Figure 3 Phase diagram with *LCST*/*UCST* spinodals and hour-glass CPCs; $d_0 = -0.6361$. The critical points are denoted by solid triangles

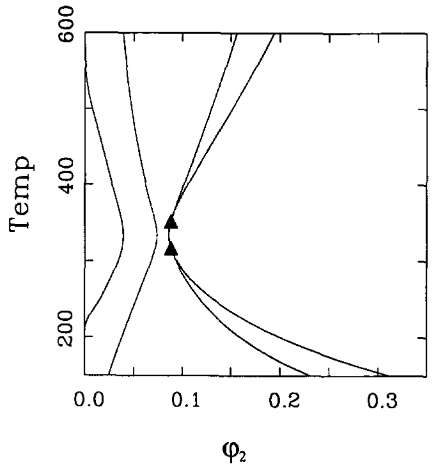

Figure 4 Phase diagram with hour-glass spinodals and CPCs; $d_0 = -0.6350$. The critical points are denoted by solid triangles

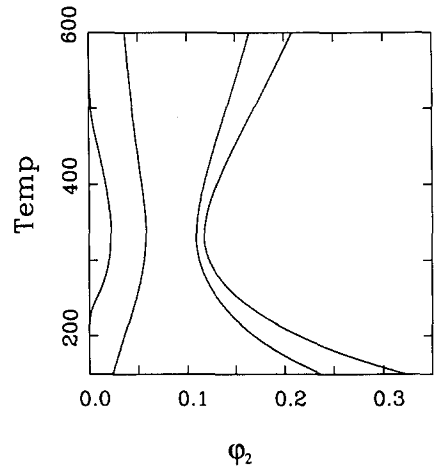

Figure 5 Phase diagram with hour-glass spinodals and CPCs; $d_0 = -0.6300$. No critical points exist for this system

LCST/*UCST* type to the hour-glass type for a relatively small change in the value of the χ interaction parameter, and the fact that the transition occurs in such a way (as seen in *Figure 3*) that the spinodals are of the former variety, while the CPCs are of the latter. Specifically, we see that in *Figure 1* ($d_0 = -0.6370$) the phase diagram is comprised of spinodals and CPCs that are both of the combined *LCST*/*UCST* type. Thus, there is a range of temperature over which the two components are miscible in all proportions. Note also that the critical points are characteristically offset from the extrema of both the spinodals and the CPCs towards higher volume fraction of polymer. As the value of d_0 is increased the temperature range of this miscibility gap decreases, and at $\sim d_0 = -0.6366$, as may be seen in *Figure 2*, the CPCs begin to coalesce. For slightly larger values of d_0 the CPCs become the hour-glass type while the spinodals retain their combined *LCST*/*UCST* form. This is illustrated in *Figure 3*, which was constructed with the coefficient d_0 set to -0.6361. Continuing to increase d_0 causes the spinodals curves to coalesce also. Note, in *Figure 4* ($d_0 = -0.6350$) for example, that even when the CPCs and spinodals are both of the hour-glass type, critical points may still exist for quasi-binary systems shortly after coalescence of the spinodals. This is in contrast to hour-glass phase diagrams for true binary systems, in which no critical points exist. For hour-glass phase diagrams, there is a range of composition over which the two components are immiscible at all temperatures, and further increasing the value of d_0 increases the width of this immiscible range. This may be observed in going from *Figure 4* ($d_0 = -0.635$) to *Figure 5* ($d_0 = -0.630$). In *Figure 5*, also note that there are no longer any critical points, and that the spinodal region at higher volume fraction of polymer is now continuous.

The authors have observed similar phenomena for quasi-binary solutions and blends in which the polydisperse component has other than the Schulz–Zimm molecular weight distribution described here. Other distributions investigated include: Gaussian, Flory and arbitrarily discrete.

We make no claim that such a transition in the form of the phase diagram could be seen in real systems. Rather it is our intent to point out that molecular weight distributions can have a profound effect on phase diagrams; and that, for such systems, it is at times hazardous to infer the behaviour of the spinodals from observations of the CPCs and vice versa. The type of phase diagram that a given system exhibits is exquisitely sensitive to the value of the χ interaction parameter, as these examples serve to illustrate.

Conclusions

A temperature and concentration dependent interaction parameter has been used to study liquid–liquid phase diagrams of quasi-binary polymer solutions and blends in which one component may have a molecular weight distribution. It has been demonstrated for such systems that the CPCs and spinodals need not be of the same type. Specifically, CPCs may be of the hour-glass type while spinodals are of the combined *LCST*/*UCST* type. This is contrary to the general consent, and underscores the possible danger of inferring the behaviour of spinodals from that of CPCs or vice versa.

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