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# Phase Equilibria for Polymer Mixtures[1]

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The perturbed hard-sphere-chain (PHSC) equation of state is applied to calculate phase diagrams of ternary mixtures containing polymers. Special attention is given to the effects of polymer molecular weight, pressure, temperature, and various molecular parameters.

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**KEY WORDS:** equation of state; phase diagrams; polymer solution; ternary systems.

## 1. INTRODUCTION

It has been recognized for some time that thermodynamic properties of polymer mixtures depend on the properties of solvents and polymers and equations of state provide useful tools for correlating and estimating thermodynamic properties of polymer mixtures [1, 2]. For example, the equation-of-state theory has successfully explained both lower critical solution temperature (LCST) and upper critical solution temperature (UCST) phenomena for polymer solutions. The classical Flory–Huggins equation [3] ignores the thermodynamic properties of pure components and completely fails to describe LCST behavior.

In general, an equation-of-state approach to polymer mixtures starts with describing properties of the pure components; extensions to mixtures follow soon after success for pure systems. This approach usually involves using arbitrary mixing and combining rules to obtain parameters from the pure components for mixtures [4]. Recently, there have been an increased interest in developing statistical/mechanical based equations of state for polymer mixtures. Although a rigorous statistical/mechanical treatment for polymers is difficult, because of their asymmetric structure, their large number of internal degrees of freedom, and the strong coupling between

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intra- and intermolecular interactions, a number of equations of state have been developed based on a relatively simple model, hard-sphere chains, in which a molecule is modeled by a series of freely jointed tangent hard spheres [5–12]. Among them is the perturbed hard-sphere-chain (PHSC) equation of state, which takes the hard-sphere chains as its reference system plus a van der Waals term as the perturbation [10–12].

For pure fluids and polymers, the PHSC equation of state is characterized by three molecular parameters: segment number per molecule $r$, segment size $\sigma$, and nonbonded segment–segment interaction energy $\varepsilon$; they can be obtained from readily available data for thermodynamic properties such as vapor pressures, densities, and compressibilities [10, 12]. For mixtures containing polymers, no mixing rules are required for the hard-sphere-chain contribution. Only the perturbation needs the van der Waals one-fluid mixing theory. The PHSC equation of state can reproduce all types of fluid phase equilibria that have been found experimentally in binary mixtures containing polymers, including the lower critical solution temperature (LCST), the upper critical solution temperature, and the hour glass-shaped phase behavior [11]. For several binary mixtures containing polymers, calculated liquid–liquid coexistence curves are in good agreement with experiment [12].

In this paper, we apply the PHSC equation of state to ternary mixtures containing polymers. We are particularly concerned here with liquid–liquid equilibria of ternary systems because of the variety of observed phase behavior reported in the literature. We present some calculated phase diagrams for ternary mixtures and investigate the effects of polymer molecular weight, pressure, and temperature. Conclusions are summarized in the last section.

## 2. PERTURBED HARD-SPHERE-CHAIN EQUATION OF STATE

The derivation of the PHSC equation of state for mixtures follows a rigorous first-order statistical–mechanical perturbation theory based on a mixture of hard-sphere chains as the reference system plus a van der Waals term as the perturbation; details are given in previous publications [10, 12]. Here we reproduce only the main steps necessary for describing the model.

In general, the PHSC equation of state is applicable to fluid mixtures containing any number of components over the entire range of fluid conditions. Its form for pure fluids is [10]

$$\frac{p}{\rho k_B T} = 1 + r^2 b \rho g(d^+) - (r-1)[g(d^+) - 1] - \frac{r^2 a \rho}{k_B T} \qquad (1)$$

where $p$ is the pressure, $\rho = N/V$ is the number density ($N$ is the number of molecules and $V$ the volume), $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, $g(d^+)$ is the radial distribution function of hard spheres at contact, and $d$ is the effective hard-sphere diameter; $g(d^+)$ is calculated from the Carnahan–Starling equation [13]:

$$g(d^+) = \frac{1-\eta/2}{(1-\eta)^3}, \qquad \eta = \frac{rb\rho}{4} \tag{2}$$

In Eq. (1), the first three terms represent the reference equation of state for hard-sphere chains, and the last term is a van der Waals-type perturbation to take into account attractive forces. The three segment-based parameters in Eq. (1), $r$, $b$, and $a$, all have a direct physical interpretation. Parameter $r$ represents the number of effective hard spheres per molecule. Parameter $b$ represents the second virial coefficient of hard spheres; it is an effective van der Waals covolume. Parameter $a$ reflects the strength of attractive forces between two nonbonded segments. In the PHSC theory, both $a$ and $b$ are temperature dependent according to the Song–Mason method [14]:

$$a(T) = \tfrac{2}{3}\pi\sigma^3\varepsilon F_a(k_B T/\varepsilon), \qquad b(T) = \tfrac{2}{3}\pi d^3(T) = \tfrac{2}{3}\pi\sigma^3 F_b(f_B T/\varepsilon) \tag{3}$$

where $\varepsilon$ and $\sigma$ are pair-potential parameters; $\varepsilon$ is the depth of the minimum in the pair potential and $\sigma$ is the separation distance between segment centers at this minimum. In Eq. (3), $F_a$ and $F_b$ are two universal functions of the reduced temperature, $k_B T/\varepsilon$. They are determined from thermodynamic properties of fluid argon and methane over wide ranges of temperature and density and they are accurately represented by the following empirical formulae [12]:

$$\begin{aligned} F_a(k_B T/\varepsilon) = {} & 1.8681 \exp[-0.0619(k_B T/\varepsilon)] \\ & + 0.6715 \exp[-1.7317(k_B T/\varepsilon)^{3/2}] \end{aligned} \tag{4}$$

$$\begin{aligned} F_b(k_B T/\varepsilon) = {} & 0.7303 \exp[-0.1649(k_B T/\varepsilon)^{1/2}] \\ & + 0.2697 \exp[-2.3973(k_B T/\varepsilon)^{3/2}] \end{aligned} \tag{5}$$

Extension of Eq. (1) to mixtures is straightforward [11, 12]:

$$\begin{aligned} \frac{p}{\rho k_B T} = {} & 1 + \rho \sum_{ij}^{m} x_i x_j r_i r_j b_{ij} g_{ij}(d_{ij}^+) - \sum_{i}^{m} x_i (r_i - 1)[g_{ii}(d_{ii}^+) - 1] \\ & - \frac{\rho}{k_B T} \sum_{ij}^{m} x_i x_j r_i r_j a_{ij} \end{aligned} \tag{6}$$

where $x_i = N_i/N$ is the number fraction of molecules, $r_i$ is the number of segments comprised of component $i = 1, 2, \ldots, m$, and $g_{ij}(d_{ij}^+)$ is the $ij$ pair radial distribution function of hard-sphere mixtures at contact. For each unlike pair of components $(i \neq j)$, additional parameters, $b_{ij}$, and $a_{ij}$ are needed for the mixture; $b_{ij}$ is the second cross virial coefficient of hard-sphere mixtures, and $a_{ij}$ is the parameter reflecting attractive forces between two unlike nonbonded segments. A combining rule is not necessary for calculating $b_{ij}$ because hard-sphere diameters are additive:

$$b_{ij}(T) = \tfrac{2}{3}\pi d_{ij}^3(T) = (b_i^{1/3} + b_j^{1/3})^3/8, \qquad d_{ij}(T) = [d_i(T) + d_j(T)]/2 \quad (7)$$

The parameter $a_{ij}$ can be obtained by extending Eq. (3) to mixtures,

$$a_{ij}(T) = \tfrac{2}{3}\pi\sigma_{ij}^3\varepsilon_{ij}F_a(k_B T/\varepsilon_{ij}) \quad (8)$$

where, like in pure fluids, $\sigma_{ij}$ and $\varepsilon_{ij}$ are associated with a pair potential between unlike segments; they can be determined from the pure-component parameters by using appropriate combining rules:

$$\sigma_{ij} = \tfrac{1}{2}(\sigma_i + \sigma_j), \qquad \varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{1/2}(1 - \kappa_{ij}) \quad (9)$$

where $\kappa_{ij}$ is the adjustable binary parameter. Finally, to obtain a complete equation of state from Eq. (6), a suitable mathematical form for $g_{ij}(d_{ij}^+)$ is needed and given by the Boublik–Mansoori–Carnahan–Starling equation for hard-sphere mixtures [15]:

$$g_{ij}(d_{ij}^+) = \frac{1}{1-\eta} + \frac{3}{2}\frac{\xi_{ij}}{(1-\eta)^2} + \frac{1}{2}\frac{\xi_{ij}^2}{(1-\eta)^3} \quad (10)$$

with

$$\eta = \frac{\rho}{4}\sum_i^m x_i r_i b_i, \qquad \xi_{ij} = \frac{\rho}{4}\left(\frac{b_i b_j}{b_{ij}}\right)^{1/3}\sum_k^m x_k r_k b_k^{2/3} \quad (11)$$

## 3. PHASE DIAGRAMS OF TERNARY SYSTEMS

The PHSC equation of state has been applied successfully to correlate thermodynamic properties for pure fluids and polymers and binary systems containing polymers [10–12]. Here we focus our application on model calculations of liquid–liquid phase diagrams of ternary mixtures containing polymers. One of the most common ternary system containing polymers is that of one solvent with a pair of polymer species. Figure 1 shows a model calculation of such a system in which the only difference between two

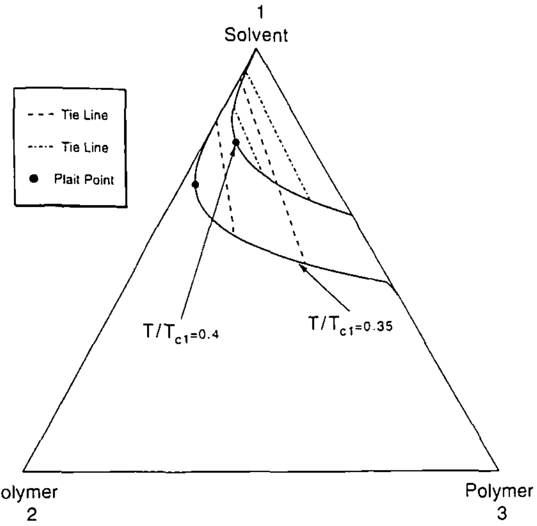

**Fig. 1.** Liquid–liquid phase diagram for a ternary mixture containing one solvent and two polymers. The parameters used are as follows: $r_1 = 5$, $r_2 = 50$, $r_3 = 500$, $\sigma_{11} = \sigma_{22} = \sigma_{33}$, $\varepsilon_{11} = \varepsilon_{22} = \varepsilon_{33}$, $\kappa_{12} = \kappa_{13} = 0.01$, $\kappa_{23} = 0$, $p\ p_{c1} = 0.01$. $p_{c1}$ and $T_{c1}$ are the critical pressure and temperature of the solvent, respectively. Each apex represents a pure component and each sideline represents the composition range of a binary.

polymers is their molecular weights. The lighter polymer (component 2) is miscible with the solvent in all proportions but the heavier polymer (component 3) has limited solubility with the solvent. Each coexistence curve corresponds to a fixed temperature. Since this system shows the upper critical solution temperature, arising the temperature decreases the size of the two-phase region because the energetic effect becomes smaller and the entropy of mixing becomes more important.

Another common ternary system is that of one polymer with one solvent and one nonsolvent as shown in Fig. 2. In such a system, it is interesting to see how much the polymer molecular weights can affect the solubility gap. In general, raising the molecular weights of the polymers increases the size of the two-phase region because the process reduces the opportunities of polymer–solvent contacts.

Figure 3 shows the phase diagram of a ternary system at the lower critical solution temperatures, which can be calculated only by using an equation of state. In this system, the only difference among components is their molecular weights or chain lengths, as given by different values of $r$'s,

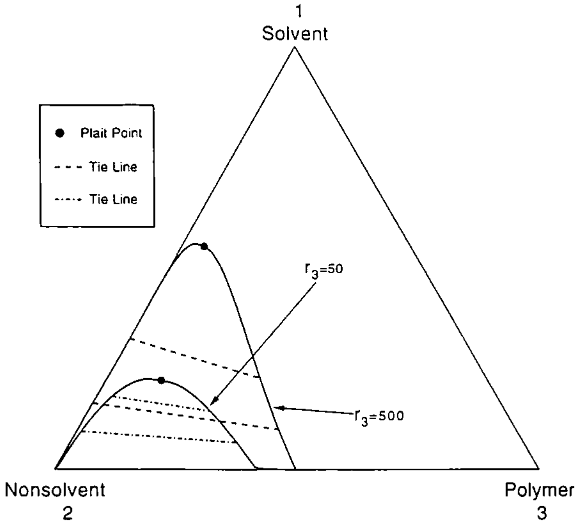

**Fig. 2.** Phase diagram for a ternary mixture containing one polymer with one solvent and one non solvent, exhibiting the molecular weight effect. $r_1 = 2$, $r_2 = 1$, $\sigma_{11} = \sigma_{22} = \sigma_{33}$, $\varepsilon_{11} = \varepsilon_{22} = \varepsilon_{33}$, $\kappa_{12} = \kappa_{13} = \kappa_{23} = 0$, $T/T_{c1} = 0.45$, $p/p_{c1} = 0.1$.

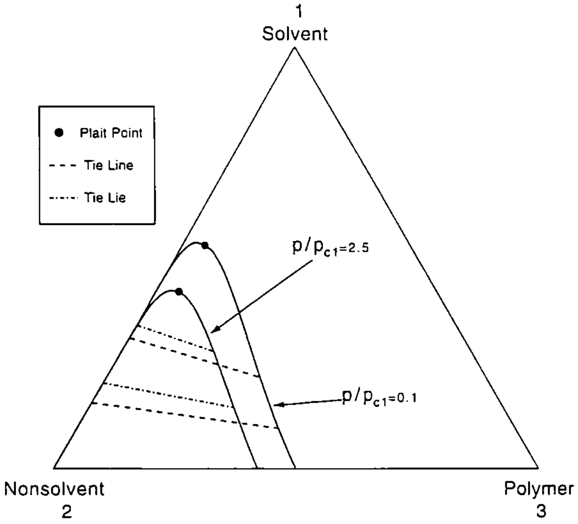

**Fig. 3.** Phase diagram for a ternary mixture exhibiting the free-volume effects and the pressure effects, both leading to lower critical solution temperatures. $r_1 = 2$, $r_2 = 1$, $r_3 = 500$, $\sigma_{11} = \sigma_{22} = \sigma_{33}$, $\varepsilon_{11} = \varepsilon_{22} = \varepsilon_{33}$, $\kappa_{12} = \kappa_{13} = \kappa_{23} = 0$, $T/T_{c1} = 0.45$.

which cause the free-volume effects leading to a lower critical solution temperature between the polymer and the non solvent. It also shows that, at the lower critical solution temperature, the mixture is readily compressible, therefore, a small change in the pressure can make a significant volume change in the mixture.

Figure 4 shows two binodal curves of a ternary system caused by free-volume effects at two difference temperatures. Contrary to the behavior of the UCST shown in Fig. 1, raising the temperature increases the size of the two-phase region. The physical reason is that the volume changing increases when the temperature goes up.

Figure 5 shows an example, of unexpected phase behavior in a ternary system in which there are two compatible polymers and a good solvent to both polymers. One would expect that they should still be miscible in all proportions in the ternary. But what actually happens is that two compatible polymers become incompatible on the addition of solvent, giving rise to a closed two-phase region in the ternary phase diagram. The physical explanation is that the addition of solvent, on the one hand, reduces the opportunities of polymer–polymer contacts and, on the other hand, may introduce an effective repulsion between two polymers.

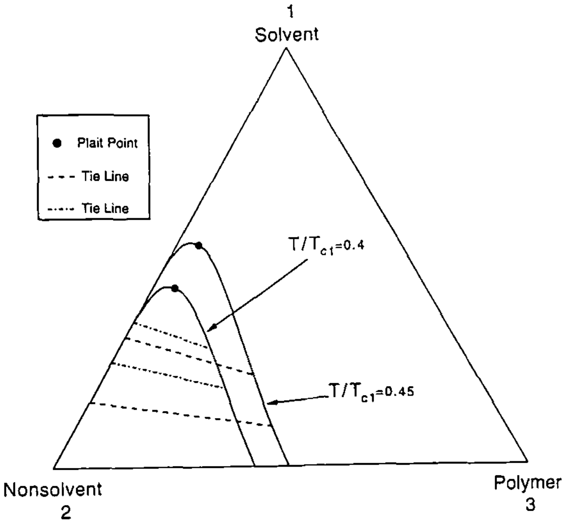

Fig. 4. Phase diagram for a ternary mixture exhibiting the temperature effect at the lower critical solution temperature. $r_1=2$, $r_2=1$, $r_3=500$, $\sigma_{11}=\sigma_{22}=\sigma_{33}$, $\varepsilon_{11}=\varepsilon_{22}=\varepsilon_{33}$, $\kappa_{12}=\kappa_{13}=\kappa_{23}=0$, $p/p_{c1}=0.1$.

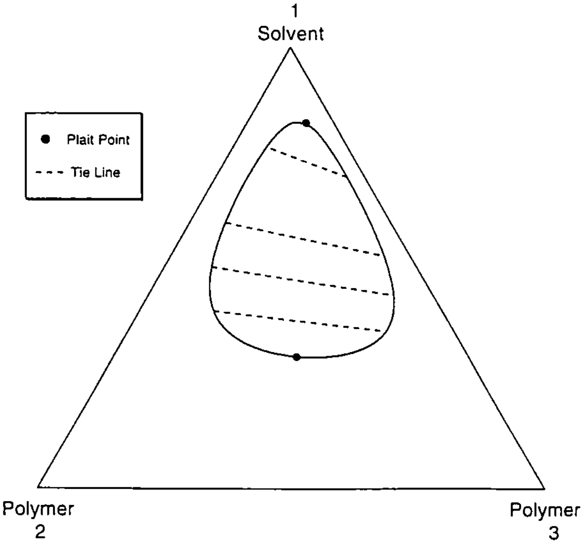

**Fig. 5.** Phase diagram for a ternary mixture containing a solvent with two compatible polymers, exhibiting an unexpected phase behavior. $r_1 = 5$, $r_2 = r_3 = 1000$, $\sigma_{11} = \sigma_{22} = \sigma_{33}$, $\varepsilon_{22}/\varepsilon_1 = 1$, $\varepsilon_{33}/\varepsilon_{11} = 1.02$, $\kappa_{12} = \kappa_{23} = 0$, $\kappa_{13} = 0.01$, $T/T_{c1} = 0.7$, $p/p_{c1} = 0.1$.

## 4. CONCLUSIONS

Phase diagrams are presented for a variety of ternary systems containing polymers using the PHSC equation of state. Although this equation is applicable to any number of components, we are particularly concerned with liquid–liquid equilibria in ternary mixtures because liquid–liquid equilibria provide a much more critical test of the theory. Using physically reasonable parameters, the PHSC equation of state successfully reproduces phase diagrams of ternary systems with effects from polymer molecular weights, temperatures, pressures, and various molecular parameters.

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