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Effects of polydispersity on liquid–liquid equilibrium of polymeric fluids

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ABSTRACT

The effects of polymer polydispersity on the liquid–liquid equilibrium (LLE) of polymer solutions were investigated for the simple case of polydisperse polymer solutions: mixtures composed of a solvent and two monodisperse polymers of different molecular weights. Various quasi-binary cloud point curves including the upper critical solution temperature (UCST), lower critical solution temperature (LCST), both UCST and LCST, and closed loop miscibility were determined from thermal optical analysis (TOA). To describe the phase equilibrium of polydisperse polymer solutions, we extended the chain length contribution term in the modified double lattice chain length dependent model (extended MDL-CL). Phase equilibrium calculations were conducted for several ternary systems including hypothetical hourglass type LLE. The extended MDL-CL model appropriately described the effect of polymer polydispersity on the LLE of polymer solutions and the calculated results were in satisfactory agreement with the experimental data.

1. Introduction

Phase equilibria of polymer solutions have a broad range of applications in polymer processing, such as fractionation and creation of films for use in pharmaceuticals as well as membranes [1]. Appropriate descriptions of these processes require a satisfactory understanding of the equilibrium properties of a polymer solution. However, it is difficult to accurately describe the phase behavior of polymer solutions, not only because of the large difference in molecular size of the polymer and solvent, but also because most polymers are mixtures of molecules of different molecular weights.

It is well known that the polydispersity of a polymer has a significant effect on the LLE of polymer solutions, and also that phase diagrams for polydisperse polymer solutions are essentially different from those of monodisperse polymer solution [2]. To describe the phase behavior of polydisperse polymer solutions, two main approaches have been applied, namely, discrete and continuous method.

In the early stages, researchers developed a simple way of understanding the phase equilibrium of polydisperse polymer solution by considering ternary mixtures consisting of a solvent and two monodisperse polymers differing in molar mass only. This prototype of polydisperse polymer solution was investigated theoretically by Tompa [3], who identified the difference between precipitation threshold temperature and true critical point by applying Flory-Huggins theory to the ternary system. Similar theoretical approaches were investigated by Koningsveld and Staverman [4]. In addition, Flory and Schultz [5] reported the cloud point curve of ternary mixtures consisting of two polystyrenes (PS) and cyclohexane by varying the ratios of the polymer homologs. Reported phase diagrams of the ternary polymer solutions indicate that a small fraction of higher molecular weight components in polymer mixture have significant effects on the cloud point curve and threshold point. Similar results were obtained by Fujita and coworkers [6] for the same ternary system, and thermodynamic modeling was also conducted using a semi-empirical approach [7].

Continuous thermodynamic approaches have been investigated extensively by many researchers, and have replaced simple binary or ternary pseudo-components with a continuous distribution of molecular weight to represent the polydispersity of polymers. While a thorough review of relevant works is not the focus of the present study, works of Cotterman and co-workers [8,9], Hu and co-workers [10,11], Koningsveld [12] and Ratzsch and Kehlen [13] have all made significant contribution in this area.

In this work, we investigated the phase behaviors of ternary mixtures consisting of two monodisperse polymers and a solvent in

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order to better understand the effect of polydispersity on LLEs of polymer solutions. Cloud points were determined for closed loop miscibility, LCST and both UCST and LCST type LLE by varying the ratios of polymer homologs. To describe the polymer polydispersity effect on the various LLE types of polymer solution, the chain length dependent contribution in the MDL-CL model was extended by fitting Monte Carlo simulation data with chain length up to $r = 1000$, to incorporate the characteristics of long chain molecules. The extended MDL-CL model provides improved calculation results for phase behaviors of polymer solutions.

2. Experiments

2.1. Materials

Cloud point measurements were conducted for three sets of ternary mixtures consisting of two standard polymers and a solvent. PS, polyethylene glycol (PEG) and poly vinyl methyl ether (PVME) were purchased from Scientific Polymer Products and methyl acetate was purchased from Aldrich. All reagents were used as received. The molecular weights and polydispersity indices (Mw/Mn) for standard polymers are listed in Table 1. All of the PS and PEG had a sufficiently low polydispersity index and were regarded as monodisperse polymers.

2.2. Sample preparation

The weight fraction of the polymer with a large molecular weight in the polymer mixture ψ, and the total polymer weight fraction w were carefully determined gravimetrically. The weight fraction ψ is given by

$$\psi = \frac{w_{P1}}{w_{P1} + w_{P2}} \tag{1}$$

where the subscripts $P1$ and $P2$ represent the polymers with large and small molecular weight, respectively. The prepared polymer solution was then moved to a Pyrex tube (o.d. = 3 mm and i.d. = 1 mm) and sealed using conventional method [14]. For PS/PVME blend samples, two PSs and PVME were dissolved in toluene with 10 wt% total polymer weight fraction. The resulting solution was then cast onto a microscope slide and dried under vacuum at 70 °C for at least 2 days [15].

2.3. Determining cloud point

A thermal optical analysis (TOA) method was used to determine the cloud points for ternary systems as described in elsewhere [14]. All polymer solution systems studied are tabulated in Table 2. The sample was heated or cooled at a scan rate of 0.5 °C/min to determine the precise cloud point.

Table 1
Molecular weight and polydispersity indices of standard polymers.

Polymer	Molecular weight	M_w/M_n
PS1	498,000	1.05
PS2	45,300	1.01
PS3	151,000	1.09
PS4	61,800	1.07
PS5	48,100	1.01
PVME	90,700	1.95
PEG1	11,900	1.05
PEG2	4210	1.05

Table 2
Ternary systems consisting of two standard polymers and a solvent.

Type	Systems	Ref
UCST	PS1(1) + PS2(2) + Cylcohexane(3)	[6]
LCST	PS3(1) + PS4(2) + PVME(3)	This work
Both UCST and LCST	PS3(1) + PS5(2) + Methyl acetate(3)	This work
Closed Loop	PEG1(1) + PEG2(2) + water(3)	This work
Hourglass	Hypothetical description	–

3. Model development

Incorporating the chain length contributions appropriately is important when developing thermodynamic models. Previously, Ryu and Bae [16] developed the MDL-CL model by introducing a universal function based on Monte-Carlo simulation data. However, their longest chain length of simulation data, $r = 200$, is insufficient to represent the phase behaviors of polymer solutions. To obtain a better description of phase behaviors of the polymer solutions, we developed an extended MDL-CL model with simulation data utilizing a chain length up to $r = 1000$.

3.1. Helmholtz energy of mixing

The Helmholtz energy of mixing is given by the sum of entropy and energy contribution as follows [16]:

$$\begin{aligned} \frac{\Delta A_{mix}}{N_r kT} &= -\frac{\Delta S_{mix}}{N_r T} + \frac{\Delta U_{mix}}{N_r kT} \\ &= \sum_{i=1}^{K} \frac{\phi_i}{r_i} \ln \phi_i + \frac{1}{2} \sum_{i=1}^{K} \sum_{j=1}^{K} \xi_1 \phi_i \phi_j \left(\frac{1}{r_i} - \frac{1}{r_j} \right)^2 + \sum_{i=1}^{K} \sum_{j=1}^{K} a_{ij} \phi_i \phi_j \\ &\quad - \left(\sum_{i=1}^{K} \sum_{j=1}^{K} a_{ij}^{*} \phi_i \phi_j \right)^2 \end{aligned} \tag{2}$$

where T is the temperature, k is Boltzmann's constant and ϕ_i is the volume fraction of component i. The functions of chain length and reduced interchange energy, $a_{i,j}$ and $a_{i,j}^{*}$, have the form

$$a_{i,j} = \frac{\tilde{\varepsilon}_{ij}}{2} \left(\zeta_1 - \left(\frac{\phi_i}{r_i} + \frac{\phi_j}{r_j} \right) + \left(\frac{1}{r_i} + \frac{1}{r_j} \right) \right) \quad \text{and} \quad a_{i,j}^{*} = \tilde{\varepsilon}_{ij} \sqrt{\zeta_2 / 4} \tag{3}$$

where the interchange energy parameter $\tilde{\varepsilon}_{ij}$ represents the change of an unlike contact pair energy between the components i and j.

$$\tilde{\varepsilon}_{ij} = \frac{\varepsilon}{kT} = \frac{1}{T^{*}} = \frac{\varepsilon_{ii} + \varepsilon_{ij} - 2\varepsilon_{ij}}{kT} \tag{4}$$

The remaining parameters, ζ_1, ζ_2 and ξ_1, are given by a function of chain length or are a constant obtained by fitting simulation data.

Table 3
Universal constants in eq. (6).

Universal constant	Value
a_1	1.98489
a_2	−0.14949
a_3	0.00698
b_1	0.92309
b_2	0.54893
b_3	0.06670