Transactions of the Materials Research Society of Japan 25 [3] 757-758 (2000)

Phase Diagram of Polystyrene in Cyclohexane in ϕ-T-P Space

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The effect of pressure on the phase equilibrium of a ternary system, polystyrene I + polystyrene II + cyclohexane was studied by a numerical analysis of the generalized Flory-Huggins free energy. The calculation shows that an S-shaped three-phase coexistence curve appears in ϕ-T space at constant pressure, while various shapes of three phase coexistence curve appears in ϕ-P space at constant temperature. This complex phase equilibrium behavior was attributed to the coupling of three phase equilibrium and critical double point. The experimentally attainable condition for this phenomena is estimated.

Key word: three-phase equilibrium, coexistence curve in ϕ-P space, homotopy method

1. INTRODUCTION

The phase equilibria of multicomponent polymer solutions are involved and widely applied in the field of the chemical engineering, such as oil recovery, fractionation and clear/cloud glazing [1-3]. To understand the mechanism of the phase equilibrium behavior and to control the solubility should be quite fruitful. The previous studies showed that the three-phase equilibrium in bimodal polymer solutions is associated with a heterogeneous double plait point (HDPP), which appears in a limited range of interaction parameter χ or its integrated form g. At atmospheric pressure, the three-phase equilibrium is S-shaped and the two extrema are the critical end points [4]. It is worthwhile to study the three-phase equilibrium behavior in volume fraction (ϕ)-pressure (P) space, since χ and g depend on ϕ, temperature (T) as well as P. In polymer solutions, the critical temperature has a minimum against pressure, i.e., critical double point (CDP) appears and the location of CDP depends on molecular weight of the polymer. Thus, it is interesting to investigate the phase equilibrium behavior near the CDP. To determine all the composition variables at each temperature and pressure experimentally requires a laborious work in multicomponent systems, numerical analysis of free energy of the system is helpful. In this study we have carried out a calculation of the phase equilibrium behavior of the system polystyrene (PS) I + PS II + cyclohexane (CY) with using an empirically determined Gibbs free energy.

2. CALCULATION

The Gibbs free energy of mixing per unit volume for the system PS I + PS II + CY is given by [5]

$$\Delta G/(NRT) = (1-\phi_S)\ln(1-\phi_S) + (\phi_1/m_1)\ln\phi_1 + (\phi_2/m_2)\ln\phi_2 + g\phi_S(1-\phi_S) \qquad (1)$$

where N is the total number of moles of lattice sites, m_1 and m_2 the ratios of the molar volumes of two polymers and solvent, respectively, ϕ_1, ϕ_2 and ϕ_s the volume fraction of PSI , PSII and total PS, respectively and R the gas constant. The interaction parameter g was empirically determined from the molecular weight dependence of the critical temperature, the critical pressure and the critical composition of total polymer as a function of T, P and ϕ_s;

$$g = g_0(T,\phi_S) = \alpha + \beta(T)/(1-\gamma\phi_S) \qquad (2)$$

$$g(T,P,\phi_S) = g_0(T,\phi_S) + g_P(T,P) \qquad (3)$$

$$g_P = (A + B/T_c)P_c + (C + D/T_c)P_c^2 \qquad (4)$$

Here, the parameters are $\alpha = -0.1597$, $\beta = \beta_0 + \beta_1/T$ with $\beta_0 = 0.4987$ and $\beta_1 = 111.74$, and $\gamma = 0.2365$ determined by Koningsveld [6] and $A = -1.502\times10^{-3}$ MPa^{-1}, $B = 0.441$ KMPa^{-1}, $C = 1.680\times10^{-5}$ MPa^{-2}, and $D = -4.56\times10^{-3}$ KMPa^{-2}, respectively [7]. This phenomenological free energy provides a reasonable critical line for the binary system PS + CY for a wide range of molecular weight. The three-phase equilibrium in a ternary system is given by

$$\mu_0(T,P,\phi_1^\alpha,\phi_2^\alpha) = \mu_0(T,P,\phi_1^\beta,\phi_2^\beta) = \mu_0(T,P,\phi_1^\gamma,\phi_2^\gamma)$$

$$\mu_1(T,P,\phi_1^\alpha,\phi_2^\alpha) = \mu_1(T,P,\phi_1^\beta,\phi_2^\beta) = \mu_1(T,P,\phi_1^\gamma,\phi_2^\gamma)$$

$$\mu_2(T,P,\phi_1^\alpha,\phi_2^\alpha) = \mu_2(T,P,\phi_1^\beta,\phi_2^\beta) = \mu_2(T,P,\phi_1^\gamma,\phi_2^\gamma)$$

where ϕ_i is the volume fraction of polymer homolog i and α, β and γ denote the coexisting phases. μ_i is the chemical potential of mixing of i-th component. The solution was calculated by a homotopy method [8].

3. RESULTS AND DISCUSSION

Calculated *T-P* critical line of the binary system PS+CY has a minimum (CDP) when the molecular weight of the polymer M is larger than M_D=7.6x10^4. When M=M_D, the minimum appears at atmosphere. Three-phase coexistence curve of the ternary system PS I+PS II+CY was *S*-shaped far from the CDP in ϕ-*P* space just like ϕ-*T* space. On the other hand, near the CDP the two branches among the three branches of the three-phase coexistence curve coalesce at both upper and lower extrema to make a closed loop. Both above and below the critical end point pressure two-phase regions appear. A typical example is shown for the system PS I (m_1=880) + PS II(m_2=2.82x10^4) + CY at T= 21℃ and 21.5℃ in Figs. 1 and 2. Fig3 shows an illustration of the three-phase region in ϕ-*T-P* space. Both upper and lower critical lines have a minimum (upper critical double end point (UCDEP) and lower critical double end point (UCDEP)) against pressure as shown in Fig. 3. The change in the shape of the three-phase coexistence curve occurs due to this relative location of the critical line and three-phase region in ϕ-*T-P* space. This new type of reentrant phase equilibrium behavior can be observed by controlling the molecular weight of PS I, with keeping the molecular weight ratio of PS I and PS II, since the location of the center of the closed loop is reduced to an experimentally available positive pressure; the pressure of the center of the closed loop is decreased by 1.5MPa when the molecular weight of PS I is decreased by 100.

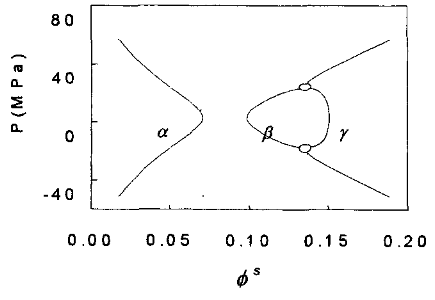

Fig.1 Coexistence curve in ϕ_s-*P* space at T=21.0^{0}C for the system polystyrene I (m_1=880) + polystyrene II (m_2=2.82x10^4) + cyclohexane with the overall volume fraction of PSI being 0.1377and that of PS II being 0.005. Open circles denote the lower critical end point(LCED). α,β,γ denotes upper, middle, lower phase respectively.

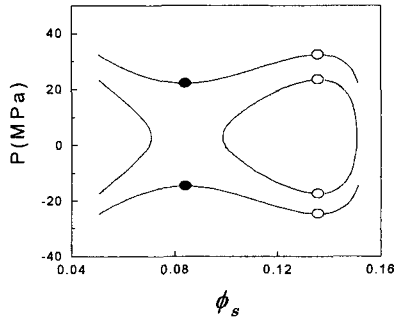

Fig.2 Three-phase coexistence curve for the same system as in Fig.1 at T=21.0^{0}C (chain line) and 21.5^{0}C (dashed line). Open and closed circles denote lower critical end point(LCED) and upper critical end point(UCED), respectively.

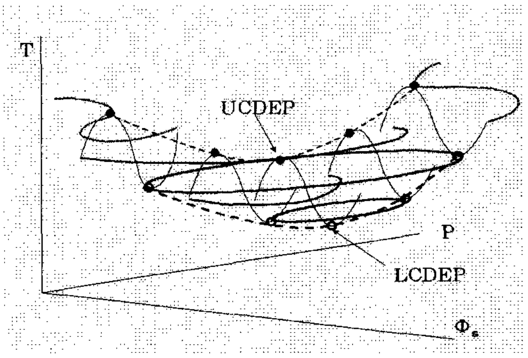

Fig.3 An illustration of three-phase region near the upper and lower critical double end points in ϕ-*T-P* space. Dashed line denote the upper and lower critical end line.

ACKNOWLEDGMENTS

TM is grateful to Mr. Takashi Sato for his helpful discussion. This work was partly supported by the Grant-in-aid by the Ministry of Education, Culture, Science and Sports under grant number 11640385.

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(Received December 17, 1999; Accepted March 31, 2000)