

Estimation of Phase Diagrams for Copolymer-Diluent Systems in Thermally Induced Phase Separation

Rui Lv, Jing Zhou, Peng Xu, Qiangguo Du, Haitao Wang, Wei Zhong

Department of Macromolecular Science, Key Laboratory of Molecular Engineering of Polymers, Fudan University, 200433 Shanghai, China

Received 27 October 2005; accepted 3 January 2006

DOI 10.1002/app.26617

Published online 30 May 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The binary interaction model was introduced to estimate phase diagrams of copolymer-diluent systems in thermally induced phase separation. The crystallization curves and cloud points of poly(ethylene-co-vinyl alcohol) (EVOH) with 1,4-butanediol, EVOH/1,3-propanediol, and EVOH/glycerol were calculated and compared with experimental value or literature data. Fair agreement was obtained. To confirm the importance of incorporating intramolecular interactions, calculations with and without the consideration of intramolecular interac-

tions were performed and compared. It was found that better results can be obtained if intramolecular interaction was introduced. The reason for the small differences between the calculated value and the experimental data of the liquid-liquid phase separation is discussed. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 3513–3518, 2007

Key words: phase diagrams; binary interaction model; thermally induced phase separation; poly(ethylene-co-vinyl alcohol)

INTRODUCTION

Thermally induced phase separation (TIPS) has been widely used to prepare microporous membranes. In general, a homogeneous solution of polymer is prepared at an elevated temperature by blending the polymer with a diluent of high-boiling point, then the solution is cooled to induce solid-liquid (S-L) or liquid-liquid (L-L) phase separation, and finally a microporous structure is formed after the diluent is extracted by a volatile solvent. In the TIPS process, the phase diagram is always the focus of study because it provides crucial information about the phase behavior of polymer-diluent systems and the basis to control membrane morphology.^{1–3} Generally, the phase diagram is determined by experiments, which is usually time consuming especially for copolymer-diluent system because both the binodal line and crystallization line will change with copolymer composition significantly. There have been many attempts made to estimate the phase diagram. Kim et al. used the equation of state (EOS) theory to predict the L-S and L-L phase diagrams of isotactic polypropylene-diluents systems, and showed good agreement between their theory and experiments.⁴ However, EOS theory is rather complicated, and

many of its parameters are hard to obtain. McGuire et al. proposed a method for extrapolating the L-L phase boundary and predicting the melting point depression curve from cloud point data.⁵ The systems used in their research were all homopolymer diluent. As far as the phase behavior of copolymer mixtures is concerned, both intermolecular and intramolecular interactions of component units of copolymers should be considered. The existence of “miscibility windows” in homopolymer-copolymer blends has been rationalized in thermodynamic terms by means of a binary interaction model and other similar approaches.^{6,7} Miscibility in these systems does not require specific interaction but rather a “repulsion” between the different covalently bonded monomers of the copolymers. However, the binary interaction model has not been applied to estimate the phase diagrams for copolymer-diluent systems in TIPS.

Poly(ethylene-co-vinyl alcohol) (EVOH) is a semi-crystalline random copolymer with very low gas permeability, excellent chemical resistance, and mechanical properties.⁸ Like gas barrier films, it has been widely used as packing material for food, cosmetic, and chemical products.⁹ Recently, EVOH membranes have been the subject of significant research interest for water treatment applications, since hydrophilic EVOH copolymer has many superior properties over other hydrophobic polymers for the prevention of membrane fouling.¹⁰ Porous EVOH membranes can be conveniently prepared by TIPS process.^{10–13} Matsuyama and coworkers used a

Correspondence to: Q. Du (qgdu@fudan.edu.cn).

Contract grant sponsor: Ministry of Science and Technology; contract grant number: 2003CB615705.

serious of alcoholic diluents to prepared EVOH membrane via TIPS and found that the morphology of the membrane was affected by many factors such as diluents, ethylene content, polymer concentration, and cooling rate.^{11–15} Cheng et al. have studied EVOH membranes prepared using an immersion-precipitation method.¹⁶

In this paper the binary interaction model was utilized to estimate phase diagrams of copolymer-diluent systems in TIPS. EVOH was chosen as a research object, because its phase diagrams with many diluents have been extensively studied by Matsuyama, and so the estimated results and literature data could be readily compared.^{12,14} The phase diagrams of EVOH copolymer and 1,4-butanediol were experimentally measured in this article and used for comparison. The purpose of this article is to show the importance of considering the internal segment-segment interaction of copolymer in estimating the phase-separation behavior of copolymer-diluent systems.

THEORY

The simple thermodynamic model for describing polymer-solvent mixtures is developed by Flory and Huggins. The free energy of mixing is

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (1)$$

where ΔS_m and ΔH_m can be described by

$$\Delta S_m = -R(V_A + V_B) \left[\frac{\phi_A \ln \phi_A}{V'_A} + \frac{\phi_B \ln \phi_B}{V'_B} \right] \quad (2)$$

$$\Delta H_m = (V_A + V_B)B\phi_A\phi_B \quad (3)$$

where V'_i is the molar volume of the component i and V_A and V_B are the actual volumes of these components comprising the mixture; B is a binary interaction energy density.⁶ According to the concept of binary interactions, for a binary mixture of random copolymer EVOH, consisting of monomer 1 (ethylene) and monomer 2 (vinyl alcohol), and a diluent 3, the binary interaction energy density B can be expressed by

$$\begin{aligned} B &= \sum_{i>j}^{\text{Inter}} B_{ij}\phi_i\phi_j - \sum_{i>j}^{\text{Intra}} B_{ij}\phi_i\phi_j \\ &= B_{13}y + B_{23}(1-y) - B_{12}y(1-y) \end{aligned} \quad (4)$$

where y denotes the copolymer compositions, expressed in volume fractions, B_{12} , B_{13} , and B_{23} are interaction energy density between 1 and 2, 1 and 3, and 2 and 3, respectively.

B_{12} and B_{13} can be simply estimated with solubility parameters δ , because monomer 1 is a nonpolar unit.

$$B_{ij} = (\delta_i - \delta_j)^2 \quad (5)$$

For the estimation of B_{23} , in which some specific interaction between segments may exist, Hansen solubility parameters¹⁷ are applied to get more accurate values.

$$B_{ij} = (\delta_{di} - \delta_{dj})^2 + 0.25(\delta_{pi} - \delta_{pj})^2 + 0.25(\delta_{hi} - \delta_{hj})^2 \quad (6)$$

The solubility parameter components δ_d , δ_p , and δ_h can be directly obtained from the following equations.

$$\delta_d = \frac{\sum_i F_{d,i}}{V_m} \quad \delta_p = \frac{\left(\sum_i F_{p,i}^2\right)^{1/2}}{V_m} \quad \delta_h = \left(\frac{\sum_i E_{h,i}}{V_m}\right)^{1/2} \quad (7)$$

where i denotes the number of the structural groups, $F_{d,i}$ and $F_{p,i}$ the group molar attractions, and $E_{h,i}$ is the cohesive energy contributed from hydrogen bonding.¹⁸

B is also related to the more familiar interaction parameters χ by

$$B = RT \frac{\chi}{V_{\text{ref}}} \quad (8)$$

where V_{ref} is reference volume.¹⁹

Liquid-liquid phase-separation lines of the systems consisting of polymer and diluent were calculated using a method proposed by McGuire.⁵ By equating polymer chemical potentials in the two phases, two equations describing the binodal line or coexistence are obtained.

$$\left[(\phi_2^b)^2 - (\phi_2^a)^2 \right] \chi = \ln \left(\frac{1 - \phi_2^a}{1 - \phi_2^b} \right) + \left(1 - \frac{1}{r} \right) (\phi_2^a - \phi_2^b) \quad (9)$$

$$\begin{aligned} r \left[(1 - \phi_2^b)^2 - (1 - \phi_2^a)^2 \right] \chi &= \ln \left(\frac{\phi_2^a}{\phi_2^b} \right) \\ &+ (r-1) (\phi_2^a - \phi_2^b) \end{aligned} \quad (10)$$

where χ is the interaction parameter and ψ_2^a and ψ_2^b the volume fractions of the polymer in phase a and b , respectively. In addition, r is the ratio of the polymer molar volume to the diluents.

TABLE I
Properties of EVOH Used in This Work

Polymers	Ethylene content (mol %)	Density (gcm ⁻¹)	M_n
EVOH-38	38	1.17	30,900
EVOH-44	44	1.14	17,800

The theory of the melting point depression is adopted for estimating liquid–solid separation lines caused by crystallization.

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{RV_u}{\Delta H_u V_d} (\phi_d - \chi\phi_d^2) \quad (11)$$

where T_m and T_m^0 are the melting temperatures of the crystalline polymer in solution and melt, respectively, V_d and V_u are the molar volume of the diluent and the repeat unit, respectively, ΔH_u is the heat of fusion for the repeat unit, ψ_d is the volume fraction of the diluent, and χ is the Flory–Huggins interaction parameter between polymer and diluent.

EXPERIMENTAL

Materials

EVOH containing ~ 38 (EVOH-38) and 44 mol % ethylene (EVOH-44) were purchased from Aldrich Chemical Company (USA). 1,4-Butanediol was purchased from Shanghai Chemical Reagent and used without further purification.

The properties of EVOH were listed in Table I. The V_m of EVOH was calculated according to van Krevelen's expression.⁵ The average molecular weights were determined by GPC after acetylation by acetic anhydride and pyridine.²⁰ The heat of fusion for the repeat unit was determined by differential scanning calorimetry (DSC).

Determination of phase diagrams

L–S phase separation was determined according to the procedure described in reference.¹ PerkinElmer DSC-7 was used for data acquisition. The sealed aluminum DSC pan containing 3–5-mg sample was heated to 453 K and maintained at the same temperature for 5 min to ensure complete mixing and equilibration. It was then cooled down at 10 K/min. The onset of the exothermic peak during the cooling was taken as the dynamic crystallization temperature.

Cloud points were measured by small-angle light scattering. The sample was placed in the hole of the hot stage and quickly heated up to 120–180°C. The hot stage was maintained at this temperature for 5 min, and then cooled in air. A picture was taken every 5 s by a CCD camera, and the corresponding

TABLE II
Solubility Parameters for EVOH, Vinyl Alcohol, and the Diluents

Material	δ_d (MPa ^{0.5})	δ_p (MPa ^{0.5})	δ_h (MPa ^{0.5})
EVOH38	16.3	9.2	19.2
EVOH44	16.4	8.3	18.2
Vinyl alcohol	16	14.3	23.9
1,4-Butanediol	16.9	7.97	21.2
1,3-Propanediol	17.06	9.8	23.55
Glycerol	17.12	11.86	28.67

temperature was simultaneously recorded. The onset of diffractive halo was taken as the cloud point.

RESULTS AND DISCUSSION

The phase diagrams for TIPS for systems of EVOH with 1,4-butanediol, 1,3-propanediol, and glycerol were estimated, respectively. Table II lists the solubility parameters of polymers and the diluents. According to the formulae provided in the Theory section, the values of intersegmental binary interaction energy density, B_{ij} , were obtained and listed in Table III.

Figure 1 shows the measured crystallization temperature for the solutions of EVOH in 1,4-butanediol, and it can be seen that the crystallization temperature increased as the polymer concentration increased. The L–L phase separation for the systems was not observed above the crystallization temperature. The theoretically calculated curves of crystallization temperature and curves of binodal L–L phase separation were also listed in the figure. The results showed fair agreement between calculated crystallization temperature and the experimental data. The calculated binodal L–L phase-separation curves for both EVOH38/1,4-butanediol and EVOH/1,4-butanediol were all below the corresponding crystallization temperature curves, which indicated that L–L phase separation would not occur above the crystallization temperature. The estimated phase diagrams coincided with the experimental results.

TABLE III
The Values of Binary Interaction Energy Density for the Systems

Polymer	Diluent	B (MPa)	B_{12} (MPa)	B_{13} (MPa)	B_{23} (MPa)
EVOH44	1,4-Butanediol	21.39	75.69	77.37	12.65
EVOH38	1,4-Butanediol	18.73	75.69	77.37	12.65
EVOH44	1,3-Propanediol	34.54	75.69	117.54	6.22
EVOH38	1,3-Propanediol	29.31	75.69	117.54	6.22
EVOH44	Glycerol	64.63	75.69	186.15	8.43
EVOH38	Glycerol	55.75	75.69	186.15	8.43

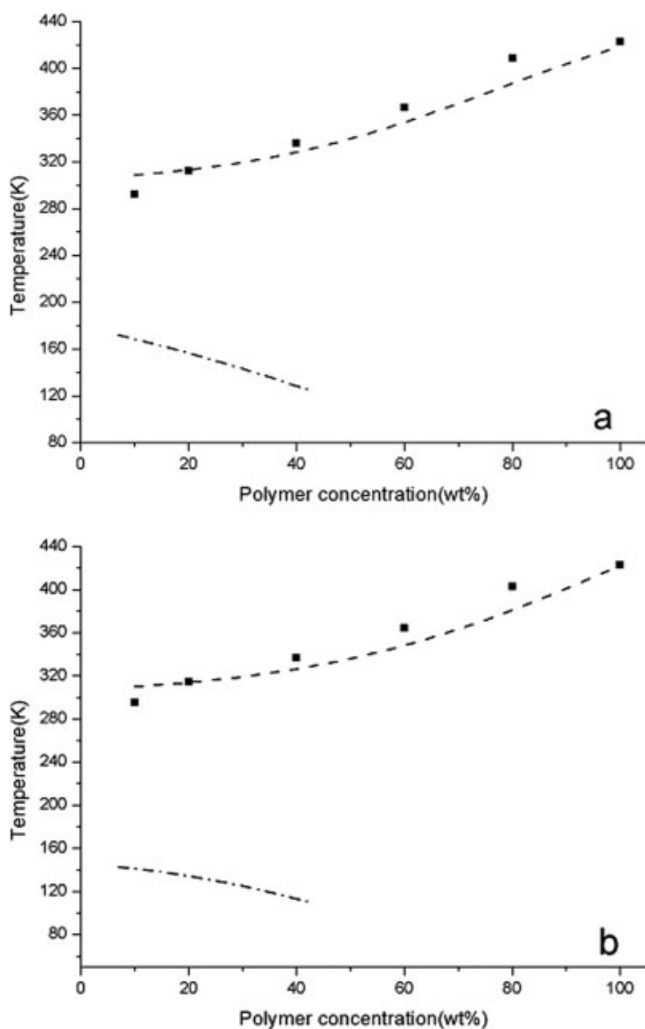


Figure 1 The phase diagrams of (a) EVOH44/1,4-butanediol and (b) EVOH38/1,4-butanediol (-----: calculated curve of crystallization temperature, ■:■: calculated curve of L-L phase separation, and ○: the measured crystallization temperature).

The same method was used to estimate the phase diagrams for the systems of EVOH44/1,3-propanediol and EVOH38/1,3-propanediol. The results are displayed in Figure 2, where the experimental data were taken from the literature.¹² Again, the experimental data and estimated curve of the L-S phase separation match reasonably well in the region of whole polymer concentration. From Figure 2, it can be seen that the calculated binodal boundaries of L-L phase separation for the systems were all under the crystallization temperature curves, which fitted the reference's results that this system was proceed by S-L phase separation rather than by L-L phase separation.

In the aforementioned two systems, there exists no L-L phase separation above the crystallization temperature; hence, it is difficult to compare the calculated L-L phase-separation temperature with the

real one. To validate the accuracy of this method, the system of EVOH/glycerol was investigated, in which the binodal boundary of L-L phase separation was observed experimentally by Matsuyama.¹² The raw data were taken from this reference, both crystallization lines and binodal lines were calculated, and the results were shown in Figure 3. Fair agreement is found between the experimental and estimated values for the system, as can be seen in Figure 3. The calculation of binary interaction energy density, B_{23} , from solubility parameter may be an important source of difference with experimental results, because there may be some special interaction between the two polar segments.

The calculations without considering the intramolecular interaction were also performed to assess the importance of consideration of bimodal interaction

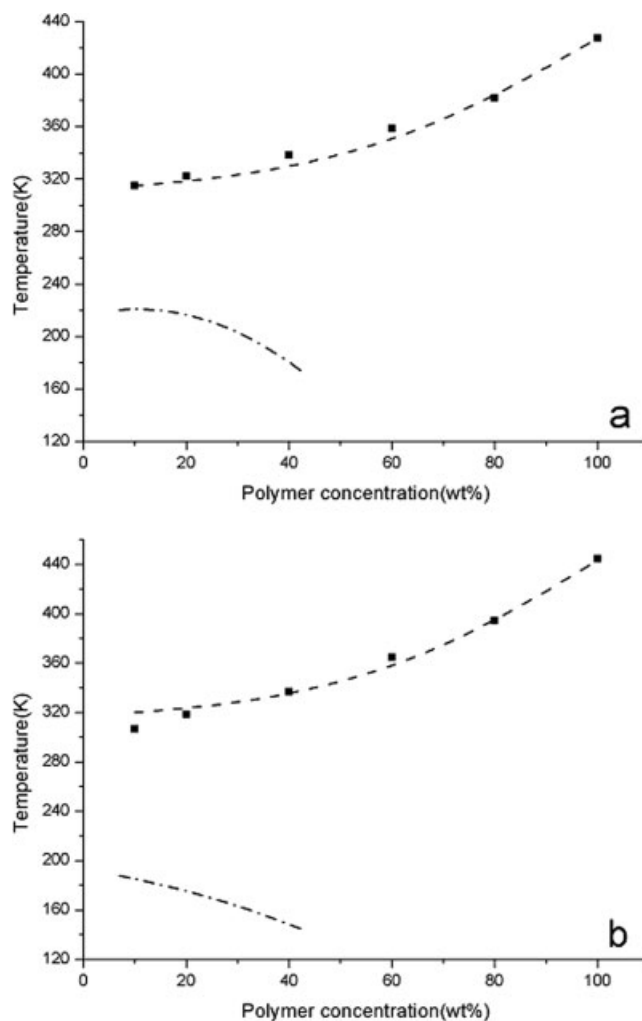


Figure 2 The correlation between the experimentally measured and the theoretically estimated phase diagram in EVOH/1,3-propanediol systems: (a) EVOH44 and (b) EVOH38. (-----: calculated curve of crystallization temperature, ■:■: calculated curve of L-L phase separation, and ○: the crystallization temperature of reference¹²).

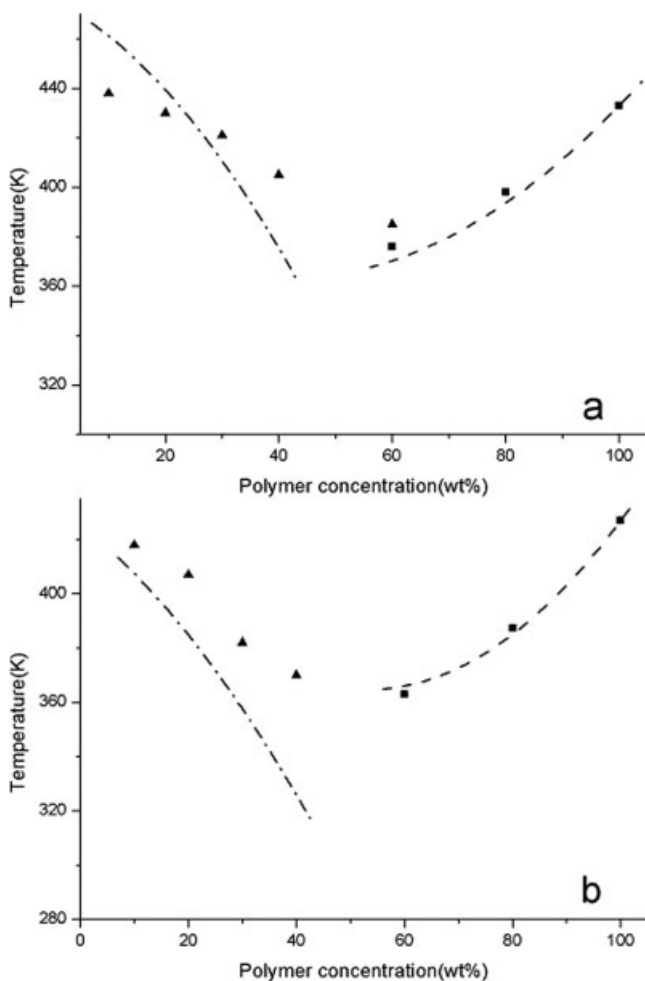


Figure 3 The correlation between the experimentally measured and the theoretically calculated phase diagram in EVOH-glycerol system; (a) EVOH44; (b) EVOH38. (----: calculated curve of crystallization temperature, ■: calculated curve of L-L phase separation, □: the crystallization temperature of reference¹², and ▲: the cloud point of reference¹²).

in the estimation of phase diagram for the systems of copolymer-diluent. In this case, the interaction parameter χ was obtained directly from solubility parameters as follows:

$$\chi_{ij} = \frac{V_{\text{ref}}}{RT} \left[(\delta_{di} - \delta_{dj})^2 + (\delta_{pi} - \delta_{pj})^2 + (\delta_{hi} - \delta_{hj})^2 \right] \quad (12)$$

where, $\delta_{d'}$, $\delta_{p'}$, and $\delta_{h'}$ are the solubility parameter components. Equation (12) was often used for the approximative estimation of χ in phase-inversion method.²¹

The comparison of calculated results with and without consideration of intramolecular interaction in the copolymer of EVOH was shown in Figures 4 and 5, where experimental data were also included. It can be seen that in estimating crystallization temperature, better agreement is obtained if binary interaction

model was used; and in estimating binodal line, binary interaction model was critical or tremendous discrepancy would be generated.

CONCLUSIONS

The binary interaction model was applied to estimate the phase diagrams of copolymer and diluent systems. The S-L and L-L phase-separation curves of EVOH/1,4-butanediol, EVOH/1,3-propanediol, and EVOH/glycerol have been calculated. The fair agreement between the experimental data and the calculated values indicated the feasibility to predict the phase-separation behavior of copolymer-diluent systems on the basis of binary interaction model. To

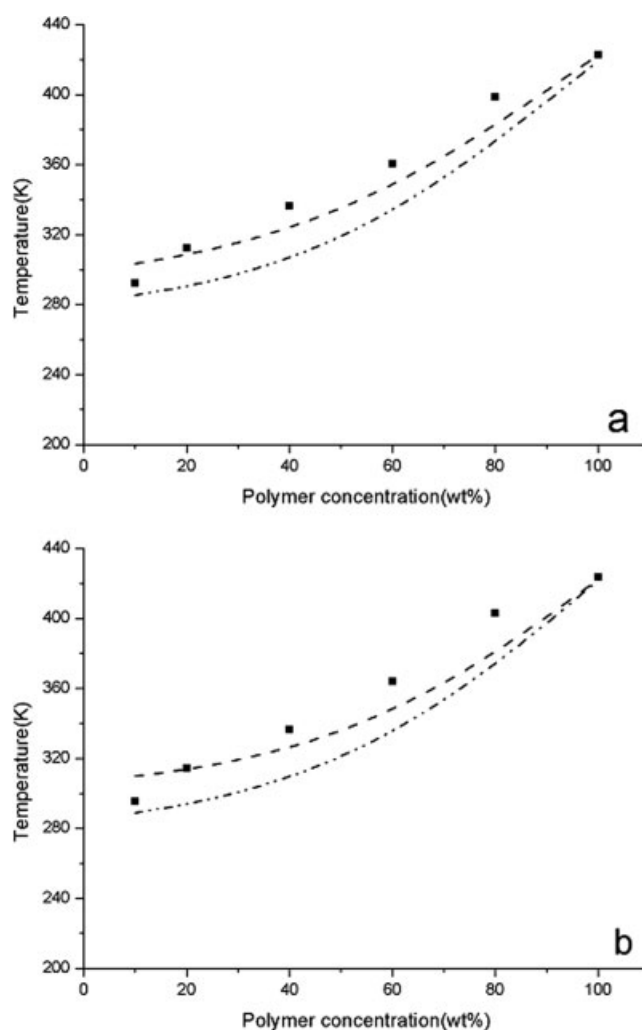


Figure 4 The comparison of crystallization temperature calculated with and without consideration of intramolecular interaction in the systems of EVOH/1,4-butanediol. (a) EVOH44; (b) EVOH38. (----: calculated curves by binary interaction model, ···: calculated curves without taking account of intramolecular interaction, □: the measured crystallization temperature).

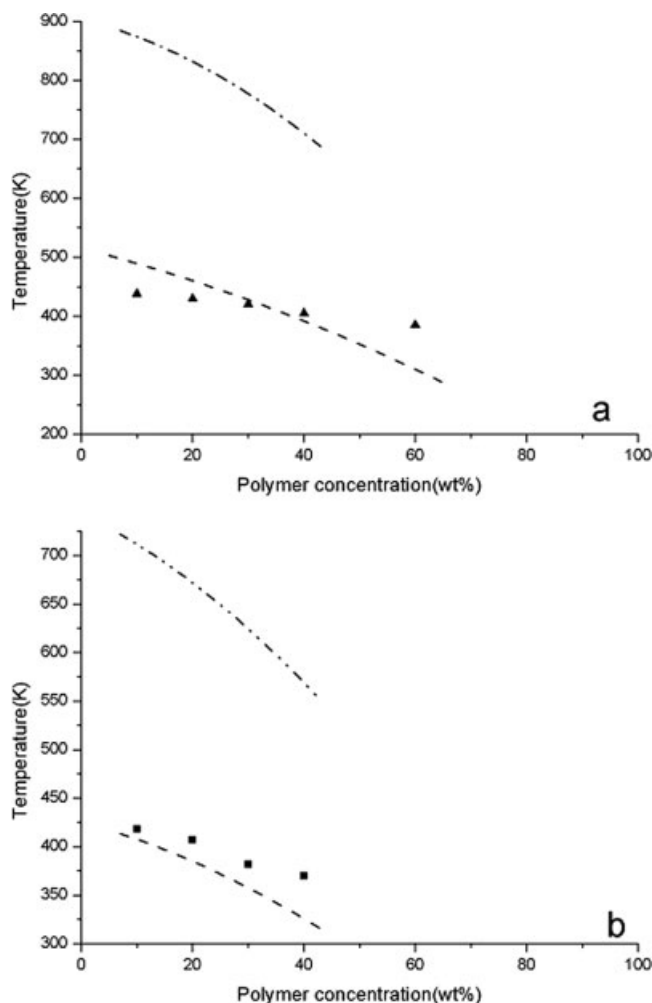


Figure 5 The comparison of binodal phase-separation temperature calculated with and without consideration of intramolecular interaction in the systems of EVOH/glycerol. (a) EVOH44 and (b) EVOH38. (----: calculated curves by binary interaction model, ■-■: calculated curves without taking account of intramolecular interaction, ▲: the cloud point of reference¹²).

confirm the importance of incorporating intramolecular interaction, calculations with and without the consideration of intramolecular interaction were performed and compared. Also, it was found that better

results were obtained if intramolecular interaction was introduced. But there are still small differences between the calculated value and the experimental data of the L-L phase separation. The calculation of B_{23} , the binary interaction energy density between polar vinyl-alcohol segments, and the polar diluent, from solubility parameter may be an important source of the difference, because there may be some special interaction. However, a simple way to estimate phase diagrams for the systems of copolymer and diluent was given in this work.

References

- Lloyd, D. R.; Kinzer, K. E.; Tseng, H. S. *J Membr Sci* 1990, 52, 239.
- Lloyd, D. R.; Sung, S. K.; Kinzer, K. E. *J Membr Sci* 1991, 64, 1.
- Liu, B.; Du, Q. G.; Yang, Y. L. *J Membr Sci* 2000, 180, 81.
- Kim, S. S.; Lloyd, D. R. *Polymer* 1992, 33, 1026.
- McGuire, K. S.; Laxminarayan, A.; Lloyd, D. R. *Polymer* 1994, 35, 4404.
- Paul, D. R.; Barlow, J. W. *Polymer* 1984, 25, 487.
- Cowie, J. M. G.; Reid, V. M. C.; Mcewen, I. J. *Polymer* 1990, 31, 486.
- Okaya, T.; Ikari, K. In: *Polyvinyl Alcohol Developments*; Finch, C.A., Ed.; Wiley: New York, 1992; Chapter 8.
- Zou, S. G. *New Chem Mater* 1999, 5, 10.
- Shang, M. X.; Matsuyama, H.; Teramoto, M.; Llyord, D. R.; Noboru, K. *Polymer* 200, 44, 7441.
- Matsuyama, H.; Iwatani, T.; Kiitamura, Y.; Tearamoto, M.; Sugoh, N. *J Appl Polym Sci* 2001, 79, 2449.
- Shang, M. X.; Matsuyama, H.; Maki, T.; Tearamoto, M.; Lloyd, D. R. *J Appl Polym Sci* 2003, 87, 853.
- Matsuyama, H.; Takida, Y.; Maki, T.; Tearamoto, M. *Polymer* 2002, 43, 5243.
- Matsuyama, H.; Kiyotaka, K.; Maki, T.; Tearamoto, M.; Tsuruta, H. *J Appl Polym Sci* 2001, 82, 2583.
- Shang, M. X.; Matsuyama, H.; Maki, T.; Tearamoto, M.; Llyord, D. R. *J Polym Sci Part B: Polym Phys* 2003, 41, 194.
- Cheng, L. P.; Young, T. H.; You, W. M. *J Membr Sci* 1998, 145, 77.
- Hansen, C. M. *Hansen Solubility Parameters*; Boca Raton, FL: CRC Press, 2000.
- van Krevelen, D. W. *Properties of Polymers*, 2nd ed.; Elsevier, Amsterdam, 1976.
- Cruz-Ramos, C. A.; Paul, D. R. *Macromolecules* 1989, 22, 1289.
- Matsumoto, T.; Nakamae, K.; Ochiuni, T.; Horie, S. *J Membr Sci* 1981, 10, 109.
- Xu, Z. L.; Qusay, F. A. *J Appl Polym Sci* 200, 233, 101.