The phase diagrams of mixtures of EVAL and PEG in relation to membrane formation

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Abstract

The phase diagrams of various ethylene–vinyl alcohol (EVAL) copolymer with different hydroxyl (OH) group contents and poly(ethylene glycol) (PEG) with different molecular weights (ranging from 200 to 600) are determined. It is found experimentally that both the liquid–liquid (L–L) phase boundaries and the crystallization curves are shifted to higher temperature when the OH group contents in EVAL increase. On the other hand, only the L–L phase boundaries shift to higher temperature when the molecular weights of PEG increase. These phenomena are interpreted by using solubility parameters ($\delta_d$, $\delta_p$) to estimate the Flory–Huggins interaction parameters, $\chi^*$, of the mixtures. By extrapolating the L–L bi-phasic curves from cloud points of temperature ($T_{\text{cloud}}$), the experimental interaction parameters $\chi$ are obtained, which are linearly correlated to the theoretically estimated interaction parameters, $\chi^*$. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Phase diagram; EVAL; PEG; TIPS; Interaction parameter

1. Introduction

The thermally induced phase separation (TIPS) process has recently been introduced to forming microporous membrane and is gaining much interest for the advantages over the conventional membrane preparation technique [1–4]. The TIPS process is applicable to a wide range of polymers, including semi-crystalline polymers, such as polypropylene (PP), polyethylene (PE), poly(vinylidene fluoride) (PVF), and polysulphone (PSF) [5–8]. However, most of these membranes are hydrophobic and thus the separation flux tends to decline during the operations due to solute adsorption and pore blocking [9–11]. This disadvantages become significant in the case of protein separation because the hydrophobic interactions between proteins and the membrane surface bring about non-selective irreversible adsorption of proteins onto the membrane surface. Moreover, since hydrophobic membranes are non-wettable by water, a pressure gradient is needed to pass water through the membrane pores. Thus, hydrophilic microporous membranes are highly desirable [12]. The surfaces of hydrophobic membranes have been made hydrophilic by physical and chemical post-treatment. For example, methods of surface modifications include adsorption of surfactant on the membrane surface [13], plasma treatment [14–16] and the surface grating of hydrophilic species [17,18]. However, the instabilities in the treated sections can cause problems in the practical use of the membranes [12].

An alternative way to make stable hydrophilic microporous membranes is to use co-polymers with both hydrophobic and hydrophilic components [12].
Chung and Lee prepared hydroxylated polypropylene (PP-OH) and a membrane of hydrophilic PP/PP-OH blends [19]. Llody prepared microporous membrane from ethylene–acrylic acid copolymer salts and studied the effects of the initial polymer concentration and cooling rate on resultant membrane structure [12].

Ethylene–vinyl alcohol (EVAL) has been widely used as food packaging material due to its excellent gas barrier properties and harmlessness to health (FDA approved). EVAL can crystallize over the whole composition range of ethylene and has good thermal stability and high chemical resistance [20]. Yamashita utilized (20 years ago) EVAL to produce membranes processing improved permeability for the dialysis of blood [21]. Recently, EVAL membranes have attracted plenty of research interest in several fields of biomedical science [22,23]. All of these EVAL membranes were prepared by the immersion–precipitation process.

In this current research, with poly(ethylene glycol) (PEG) as diluent EVAL has been used to produce hydrophilic microporous membranes via TIPS process. The phase diagrams provide crucial information about phase behavior of polymer–diluent systems. When thermal energy is removed from a homogeneous polymer–diluent mixture, the TIPS can occur via solid–liquid (S–L) or L–L phase separation depending on the polymer–diluent interaction, the composition and the thermal driving force. Moreover, the L–L phase separation has two mechanisms: nucleation growth and spinodal decomposition, which result in different characteristic morphologies, and thus a phase diagram is essentially important. Although many studies on the effects of various diluent on the TIPS process have been reported [24–27], the effects of polymer properties on the membrane morphology have not yet been studied and few studies have been reported on the formation of microporous membrane from hydrophilic copolymers. Therefore, the study on phase diagrams of EVAL/PEG, especially the effect of OH group content of EVAL, is very important as it has a strong influence on the membrane properties, such as the pore shape and size, the surface hydrophilicity, etc.

2. Experiment

2.1. Materials

EVAL containing 47 (G110, G156) and 44 mol% ethylene (E105) were kindly supplied by Kuraray Co. Ltd., Japan. EVAL containing ca. 27 (EVAL-27), 32 (EVAL-32), 38 (EVAL-38) and 44 mol% ethylene
Table 1

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Ethylene content (mol%)</th>
<th>Density (g cm(^{-1}))</th>
<th>(T_m) (°C)</th>
<th>(T_g) (°C)</th>
<th>(M_n)</th>
<th>(M_w)</th>
<th>(M_w/M_n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EVAL-27</td>
<td>27</td>
<td>1.20</td>
<td>191</td>
<td>72</td>
<td>40,000</td>
<td>71,900</td>
<td>1.80</td>
</tr>
<tr>
<td>EVAL-32</td>
<td>32</td>
<td>1.19</td>
<td>183</td>
<td>69</td>
<td>21,500</td>
<td>61,100</td>
<td>2.83</td>
</tr>
<tr>
<td>EVAL-38</td>
<td>38</td>
<td>1.17</td>
<td>175</td>
<td>62</td>
<td>30,900</td>
<td>64,800</td>
<td>2.10</td>
</tr>
<tr>
<td>EVAL-44</td>
<td>44</td>
<td>1.14</td>
<td>165</td>
<td>55</td>
<td>17,800</td>
<td>58,800</td>
<td>3.30</td>
</tr>
<tr>
<td>E105</td>
<td>44</td>
<td>1.14</td>
<td>165</td>
<td>55</td>
<td>14,600</td>
<td>45,800</td>
<td>3.14</td>
</tr>
<tr>
<td>G156</td>
<td>47</td>
<td>1.12</td>
<td>160</td>
<td>48</td>
<td>15,400</td>
<td>48,200</td>
<td>3.14</td>
</tr>
<tr>
<td>G110</td>
<td>47</td>
<td>1.12</td>
<td>160</td>
<td>48</td>
<td>15,100</td>
<td>39,100</td>
<td>2.59</td>
</tr>
<tr>
<td>EVA28/150</td>
<td>88.8</td>
<td>0.95</td>
<td>73</td>
<td>–</td>
<td>31,100</td>
<td>78,700</td>
<td>2.53</td>
</tr>
</tbody>
</table>

(EVAL-44) were purchased from Aldrich Co. EVA28/150 was purchased from Shanghai Chemical Industry Institute (shown in Table 1). Their average molecular weights were determined by GPC after acetylation by acetic anhydride and pyridine [28]. Fig. 1 is a typical IR spectroscopy of reacetylated EVAL (for example, G156), which shows that most of OH in EVAL have been reacetylated. The homologous series of PEG and dimethyl tetraethylene glycol (DMTEG) were commercially available. All the chemicals in this study were not purified further.

EVAL-88.8 copolymer containing 88.8 mol% ethylene was prepared from EVA28/150 using the following procedure [29]. EVA28/150 (10 g) was dissolved in iso-butyl alcohol (200 ml) solution of Na iso-butoxide (6 g). The mixture was refluxed for 3 h and then neutralized with 50% acetic acid, and centrifuged after 20 h. Then, white EVAL powder was obtained. The EVAL was purified by reprecipitation in benzene/methanol solutions by adding very dilute acid, followed by washing with pure water and drying in a vacuum oven for 2 days at 90°C. IR spectroscopy (Fig. 1) revealed that the hydrolysis was complete.

2.2. Procedure

EVAL and PEG were blended by solvent casting method using a mixture of \(i\)-propanol (vol. 80%) and water (vol. 20%) as a solvent. Blends prepared by solvent casting were dried at 75°C for 48 h in a vacuum oven to remove the solvent. An alternative method to prepare the blend is to mix EVAL and PEG melts at 210°C in a mill. It was confirmed by thermal–optical analyses that the phase behaviors are essentially the same for the samples obtained by different preparation methods.

The phase boundaries were measured at the cooling rate of 1°C per min by optical microscopy. In each experiment, the sample was placed on a glass slide coated with conductive indium tin oxide (ITO). To explore the upper critical solution temperature (UCST) behavior, the immiscible sample was heated to the temperature ~20°C above the expected phase boundary or melting point of EVAL. After maintaining the sample at this temperature for 5 min to ensure complete mixing and equilibration, another glass slide coated with ITO was placed on the sample to form a polymer film and to avoid solvent loss by evaporation during TIPS process.

Videomicroscopy was used to determine the optical phase separation temperature. Fig. 2 shows a schematic diagram of the equipment for examining the phase boundary [30]. The transmitted light intensity was recorded during the sample cooling. The temperature at which the intensity first drops was

Fig. 1. The IR spectroscopy of reacetalized G156 and EVAL88.8, which confirms that most of the OH groups in G156 have been reacetylated and EVA28/150 has been completely hydrolyzed to EVAL88.8.
taken as the phase separation temperature. Another more convenient method is to watch the appearance of the diluent drops with parallel polarizers or crystal formation with cross polarizers under polarizing microscope. The onset of the domain formation on cooling was taken as the phase separation temperature. For the sake of reliability, six observations for each sample were performed and averaged. The deviation of the phase boundaries measured by two methods for the same sample is less than 1°C, which is in the error range of this experiment. For the concentration of EV AL is higher than 40 wt.%, the error range of these measurements is less than ±1°C in the S–L phase region, while it is less than ±3°C in the L–L phase region. When the concentration of EVAL is lower than 40 wt.%, the error range in the L–L phase region could be as large as ±5°C.

3. Results and discussion

3.1. Phase diagram

All the phase diagrams showed the UCST type L–L phase behavior. Since EVAL is a semi-crystalline polymer, the L–L phase boundary is expected to be intersected with a crystallization curve, the intersection of which is called a monotectic point. At room temperature the samples are turbid, it reveals that the samples are phase separated and/or crystallized. The crystallization curve inside the L–L phase envelope was not determined, because the L–L phase separation retarded the observation of crystallization in optical microscopy. However, the crystallization curve inside the L–L phase region is almost horizontal, many of the earlier studies revealed the typical behavior of L–L phase separation [31].

3.2. The effect of the conductive glass slide

The glass slide coated with conductive ITO is necessary when the concentration of EVAL is lower than 40 wt.%, because the mixture is so mobile on the surface of glass slide uncoated that it prevents the precise determination of diluent drop or crystal formation. It is known that there are many OH on the surface of glass slide, which makes the surface be highly hydrophilic. As PEG is highly hydrophilic, it is so easy to be spread through the glass surface to the board while leaving EVAL in the center of the surface. The hydrophobicity of the glass surface is improved after coated with ITO, therefore, the wetability of PEG on the surface reduced significantly. It makes the observation of phase separation much easier when the concentration of EVAL is lower than 40 wt.%. The effect of glass slide coated with ITO on the kinetics of L–L phase separation have been studied [32]. It shows that the rate of spinodal decomposition is reduced and the final phase structure is also altered. However, it has little effect on the phase boundaries, which is determined mainly by the bulk properties.

3.3. Effects of molecular weight and its distribution of EVAL

The phase diagrams for EVAL-44/PEG400 and E105/PEG400 are shown in Fig. 3a. Comparing with the system of E105/PEG400, the L–L phase boundary of EVAL-44/PEG400 shifts to the higher temperature. This character can be explained by the Flory–Huggins theory [33,34]. In this simple theory, the interaction parameter is essential to the qualitative understanding of the phase diagram. The phase boundary of the mixture can be calculated from the following Gibbs free energy of mixing:

\[
\frac{\Delta G_{\text{mix}}}{RT} = \left( \frac{\phi_d}{N_d} \right) \ln \phi_d + \left( \frac{\phi_p}{N_p} \right) \ln \phi_p + \chi \phi_d \phi_p
\]
Fig. 3. $T_{\text{cloud}}$ and temperature of crystallization point ($T_c$). (a) EVAL-44/PEG400 and E105/PEG400, (b) G156/PEG600 and G110/PEG600, (c) G156/PEG400 and G110/PEG400, which show that the higher molecular weight leads the L–L phase boundary to the slightly higher temperature and the molecular weight distribution has little effect on the L–L phase boundary.

where $\phi_d$ and $\phi_p$ are the volume fractions of polymer and diluent, respectively, $N_d$ and $N_p$ the chain lengths of polymer and diluent molecules and $\chi$ the Flory–Huggins interaction parameter. The first two terms usually correspond to the very small (but favorable) contribution from combinatorial entropy. Here we should note that the number averaged molecular weight of EVAL-44 and E105 are 17,800 and 14,600, respectively. The molecular weight distributions are almost the same. Therefore, in both systems of EVAL-44/PEG400 and E105/PEG400, $\chi$ and $N_d$ should be the same, and therefore the shift of the phase boundaries of EVAL-44/PEG400 and E105/PEG400 can only attribute the effect of $N_p$.

Contrast to EVAL-44/E105, G110/G156 has nearly the same number averaged molecular weights. However, the polydispersities of G110 and G156 are 2.59 and 3.14, respectively. When these samples are mixed with PEG400 or PEG600, respectively, the phase diagrams of G110/PEG400 and G156/PEG400 (Fig. 3b), or G110/PEG600 and G156/PEG400 (Fig. 3c) are obtained. We can conclude that the molecular weight distribution has little effect on the L–L phase boundary.

3.4. Effects of OH content of EVAL

The phase diagrams for PEG400 with various EVAL systems are shown in Fig. 4a. It shows that the L–L immiscible region is enlarged when the OH content of EVAL increases. The monotectic point of EVAL-27/PEG400 is at approximately 82 wt.% EVAL concentration, while that of G156/PEG400 decreases to approximately 40 wt.% EVAL concentration. They are approximately 81, 80 and 61 wt.% for the systems of EVAL-32/PEG400, EVAL-38/PEG400 and EVAL-44/PEG400, respectively. The upper critical temperature of the mixture of G156/PEG400 is about 165°C. However, the upper critical temperatures of the mixtures of EVAL-27/PEG400, EVAL-32/PEG400 and EVAL-38/PEG400 are higher than 200°C. Therefore, for these systems, the critical temperatures are difficult to measure as the ether bonds in PEG could be easily decomposed.

The same results are shown in the phase diagrams for the systems of PEG300 with various EVAL (Fig. 4b). The monotectic points of EVAL-27/PEG300, EVAL-32/PEG300, EVAL-38/PEG300 and EVAL-44/PEG300 are approximately 70, 50, 34 and
Fig. 4. $T_{\text{cloud}}$ and $T_c$ of various OH content EV AL with (a) PEG400, (b) PEG300, which show that when the OH content in EV AL increases, both the L–L phase boundary and the crystallization shift to the higher temperature.

28 wt.%, respectively. The L–L phase boundary for the system of EV AL156/PEG300 cannot be observed because the OH content in this system is very low.

As one can see from Fig. 3, the effects of the molecular weight and molecular weight distribution of EV AL on the mixture compatibility are not strong, the miscibility of the system studied here primarily depends on the unfavorable contributions from enthalpy, embodied in $\chi$ parameter (Eq. (1)). When $\chi$ becomes more positive (i.e. the polymer–diluent system becomes less compatible), the binodal line shifts to higher temperature at a fixed polymer concentration. The interaction parameter $\chi$ can be estimated from the difference of the solubility parameters between polymer and the diluent by using the following expression.

$$\chi = \frac{V_m}{RT} \left[ (\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + (\delta_{h1} - \delta_{h2})^2 \right].$$  \hspace{1cm} (2)

where $V_m$ is a reference volume which equals to the molar volume of the specific repeating unit size of the polymer. In order to distinguish the theoretically estimated interaction parameter from the experimentally measured one, we have denoted the estimated interaction parameter in Eq. (2) as $\chi^*$. Obviously, the closer the values of the solubility parameters of the two compounds, the smaller the magnitude of $\chi^*$, which, in turn, effectively reduces the unfavorable contribution to the Gibbs free energy. The solubility parameters of PEG and EV AL (Table 2) are calculated by using the group molar attraction constants given by van Krevelen [35,36]. The $V_m$ of EV AL is calculated according to idea expressed by Coleman [37,38]. The $V_m$ of diluent is the molecular weight divided by its density. Hansen’s parameters, such as $\delta_d$, $\delta_p$ and $\delta_h$ can be directly calculated from the following equations.

$$\delta_d = \frac{\sum_i F_{d,i}}{V_m},$$  \hspace{1cm} (3)

$$\delta_p = \frac{\left( \sum_i F_{p,i}^2 \right)^{1/2}}{V_m},$$  \hspace{1cm} (4)

$$\delta_h = \left( \frac{\sum_i - U_{h,i}}{V_m} \right)^{1/2},$$  \hspace{1cm} (5)

where $i$ numbers the structural groups, $F_{d,i}$ and $F_{p,i}$ the group molar attractions and $U_{h,i}$ is the cohesive energy contributed from hydrogen-bonding. As expected, the dispersive component of the solubility parameter ($\delta_d$) for all the EV AL and PEG are quite similar and therefore van de Waals-type interaction cannot explain the observed differences between PEG and EV AL with different OH contents. The hydrogen-bonding contribution to the solubility parameter ($\delta_h$) can be plotted against the polar contribution ($\delta_p$) in an attempt to account for both types of interactions between PEG and EV AL. The ratings for both EV AL and PEG are consistent with the trends illustrated in Fig. 5. EV AL with different OH contents and PEG with different molecular weights show significant differences in terms of their participation into polar and hydrogen-bonding interactions. To a given PEG, as the OH contents in EVAL increase from G156 to EVAL-44, EVAL-38, EVAL-32 and EVAL-27, both the hydrogen-bonding contribution to the solubility parameter ($\delta_h$) and the polar contribution ($\delta_p$) increase accordingly. Therefore, the difference between the values of PEG and
Table 2
Solubility parameters for PEG and EVAL

<table>
<thead>
<tr>
<th>Material</th>
<th>( V_m ) (cm(^3) mol(^{-1}))</th>
<th>( \delta_d ) (Mpa(^{0.5}))</th>
<th>( \delta_p ) (Mpa(^{0.5}))</th>
<th>( \delta_h ) (Mpa(^{0.5}))</th>
<th>( \delta_l ) (Mpa(^{0.5}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEG200</td>
<td>177.65</td>
<td>16.7</td>
<td>5.6</td>
<td>16.7</td>
<td>24.3</td>
</tr>
<tr>
<td>PEG300</td>
<td>265.98</td>
<td>16.6</td>
<td>4.4</td>
<td>14.5</td>
<td>22.5</td>
</tr>
<tr>
<td>PEG400</td>
<td>354.45</td>
<td>16.6</td>
<td>3.7</td>
<td>13.3</td>
<td>21.6</td>
</tr>
<tr>
<td>PEG600</td>
<td>530.97</td>
<td>16.6</td>
<td>3.2</td>
<td>12.1</td>
<td>20.8</td>
</tr>
<tr>
<td>EVAL-27</td>
<td>46.87(^a)</td>
<td>16.2</td>
<td>10.7</td>
<td>20.7</td>
<td>28.4</td>
</tr>
<tr>
<td>EVAL-32</td>
<td>50.05(^a)</td>
<td>16.3</td>
<td>10.0</td>
<td>20.0</td>
<td>27.6</td>
</tr>
<tr>
<td>EVAL-38</td>
<td>54.50(^a)</td>
<td>16.3</td>
<td>9.2</td>
<td>29.2</td>
<td>26.8</td>
</tr>
<tr>
<td>EVAL-44</td>
<td>60.09(^a)</td>
<td>16.4</td>
<td>8.3</td>
<td>18.2</td>
<td>25.9</td>
</tr>
<tr>
<td>G156</td>
<td>63.31(^a)</td>
<td>16.4</td>
<td>7.9</td>
<td>17.8</td>
<td>25.5</td>
</tr>
<tr>
<td>EVAL-88.8</td>
<td>287.27(^a)</td>
<td>16.9</td>
<td>1.7</td>
<td>8.3</td>
<td>18.9</td>
</tr>
<tr>
<td>DMTEG</td>
<td>222</td>
<td>15.8</td>
<td>4.0</td>
<td>8.2</td>
<td>18.2</td>
</tr>
</tbody>
</table>

\(^a\) Average repeating unit size that contains one OH group.

EVAL becomes bigger and the polymer–diluent system becomes less compatible as OH content in EVAL increases. For example, EVAL-27, with significantly highest hydrogen-bonding characteristics, leads to the largest L–L bi-phasic region when mixed with PEG. On the contrary, G156 has best compatibility with PEG. This agrees with the experimental observations, though the quantitative calculation is more difficult.

3.5. Effects of molecular weight of PEG

The phase diagrams for the mixtures of EVAL and different PEG are shown in Fig. 6. As the molecular weight of PEG increases, the L–L phase boundaries shifts to the higher temperatures. When the molecular weight of PEG is higher than 600, the mixtures cannot form homogenized phase at a temperature below the thermal degradation temperature of the sample. On the other hand, the L–L phase boundary cannot be observed when the molecular weight of PEG is smaller than 200.

Another important influential factor could be the OH end groups in PEG. We should mention that the content of the OH end groups is inversely proportional to the molecular weight of PEG. Kim [39] has discussed the effect of PEG molecular weight on the structure of Nylon12 membrane via TIPS process. They found that the interaction energy can be strongly influenced by the OH end groups of PEG. In the system of this study, the interaction energy between ethylene oxide and EVAL segments is weaker than that between OH end groups and EVAL segments. Since the relative content of OH end group in PEG decreases with the molecular weight increases and the L–L phase boundary will shift to higher temperature accordingly.

To a given EVAL, as the molecular weight of PEG increase, both of the hydrogen-bonding contribution to the solubility parameter (\( \delta_h \)) and polar contribution (\( \delta_p \)) decrease (see Fig. 5). Therefore, the difference between the solubility values of PEG and EVAL becomes bigger accordingly. This is also consistent with the experimental observations about the effects of PEG molecular weight on phase diagram.

In order to tackle the effect of OH end groups in PEG, we have chosen non-OH terminated PEG, i.e. DMTEG as diluent. The phase diagram of G156/
Fig. 6. $T_{\text{cloud}}$ and $T_c$ of various PEG with (a) EVAL-27, (b) EVAL-32, (c) EVAL-38, (d) EVAL-44, (e) G156, which show that when the molecular weight of PEG increases, the L–L phase boundary shifts to the higher temperature.
Fig. 7. $T_{\text{cloud}}$ and $T_c$ (a) G156/DMTEG, which show that the OH end group in PEG plays a significant role in phase diagram, (b) various PEG with EV AL-88.8, which shows that the L–L immiscible region is slightly enlarged when the molecular weight of PEG increases.

DMTEG is shown in Fig. 7a. Although the molecular weight of DMTEG is low (ca. 220), the L–L phase boundary can still be observed as it is higher than crystallization curve when the polymer concentration is lower than 0.7. Compared with DMTEG, PEG200 is more compatible with EVAL and thus the L–L phase boundaries of PEG200 and any of the EVAL used in this study are below the crystallization curve of EVAL. It is obvious that the differences between the molecular weights and the basic structure of these two diluents are very small. Therefore, we can conclude that the OH end group in PEG plays a significant role in phase diagram. Hansen’s parameters, such as $\delta_d$, $\delta_p$ and $\delta_h$ of DMTEG were listed in Table 2 and shown in Fig. 5. It can be seen from Fig. 5 that the distance between DMTEG and various EVAL is much larger than that of PEG200. It agrees with the discussions given above.

In fact, when the molecular weight of PEG increases, two factors make the L–L phase boundary shift to higher temperature. Of cause, one is the increase of $N_d$. The other is the decrease of the relative content of OH end group per unit volume of PEG if the molecular weight is high. In order to distinguish these two factors, EVAL-88.8 with less OH content was prepared. The position of Hansen’s parameters in Fig. 5 lies on the other side of PEG compared with other EVAL. The distance between EVAL-88.8 and PEG600 is closest in Fig. 5, while in the sequence of PEG400, PEG300 and PEG200, the distance of position between EVAL and PEG become larger. The phase diagram shown in Fig. 7b reveals that the L–L immiscible region is slightly enlarged when the molecular weight of PEG increase, while the L–L immiscible region for other EVAL with various PEG shown in Fig. 6 is significantly different.

3.6. Theoretical fit of L–L phase boundary

The thermodynamics of polymer–diluent system has been thoroughly studied. For example, Kim used the equation of state theory to predict the phase behavior, and show good agreement with experiments [40], but the generation of the required thermodynamic data is extremely time-consuming. Therefore, McGuire proposed a simple method for extrapolating the L–L phase boundary from cloud data for polymer–diluent systems [41]. By equating polymer chemical potentials in the two phases, two equations describing the binodal line or coexistence are obtained.

\[
\frac{\left(\phi_a^2 - \phi_b^2\right)}{2} - \frac{\left(\phi_a^2 - \phi_b^2\right)}{2} \ln \frac{1 - \phi_b^2}{1 - \phi_a^2} + \frac{1}{r} \left(\frac{\phi_a^2 - \phi_b^2}{\phi_a^2 - \phi_b^2}\right) \chi \\
= \ln \left(\frac{1 - \phi_a^2}{1 - \phi_b^2}\right) + \left(1 - \frac{1}{r}\right) \left(\phi_a^2 - \phi_b^2\right),
\]

(6)

\[
\frac{\left(\phi_a^2 - \phi_b^2\right)}{2} - \frac{\left(\phi_a^2 - \phi_b^2\right)}{2} \ln \frac{1 - \phi_b^2}{1 - \phi_a^2} = \frac{\phi_a^2}{\phi_b^2} + \left(\phi_a^2 - \phi_b^2\right) \chi \\
= \ln \left(\frac{\phi_a^2}{\phi_b^2}\right) + \left(\phi_a^2 - \phi_b^2\right),
\]

(7)

where $\chi$ is the interaction parameter based on the diluent molar volume fraction and $\phi_a^2$ and $\phi_b^2$ 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 diluent molar volume. If the interaction para-
Fig. 8. Temperature dependence of the interaction parameter for G156/PEG600.  

The interaction parameter is assumed to have a temperature dependence of \( \chi = \alpha + \beta/T \), as is often the case with polymer solutions. By simultaneously solving Eqs. (6) and (7) with \( \phi^0_b \) (cloud point of temperature (\( T_{\text{cloud}} \))) known, \( \gamma \) can be determined as a function of temperature. In system of G156/PEG600, for example, Fig. 8 shows that a plot of \( \chi \) against \( 1/T \) gives a straight line. Using this temperature dependence of the interaction parameter, a typical calculated binodal line was plotted in Fig. 9 along with the \( T_{\text{cloud}} \). The generation of binodal line in this manner is essentially an elegant line fit based on Flory’s theory. Moreover, the spinodal line can also be obtained simultaneously, which differs the unstable region from the metastable region. The portion of the binodal line beneath the crystallization curve, where experimental generation of \( T_{\text{cloud}} \) data is not possible, represents only a kinetically attainable state, and thus, it is not actually a part of the equilibrium phase diagram. One benefit of generating a phase diagram from \( T_{\text{cloud}} \) is that it allows to estimate the spinodal lines (and hence the resulting morphology) for quenches well below the equilibrium crystallization curve of polymer solution, i.e. if the phase separation has the mechanisms of nucleation-growth or spinodal decomposition. The interaction parameters \( \chi \) of various EVAL/PEG, determined from \( T_{\text{cloud}} \) using Lloyd’s method, are listed in Table 3.

The theoretically estimated interaction parameters \( \chi^* \) in 298 K are calculated from solubility parameters in Eq. (2) using the datum in Table 2. The relation between \( \chi \) and \( \chi^* \) in 298 K are shown in Fig. 10.

**Table 3**  
The interaction parameter \( \chi = \alpha + \beta/T \) from \( T_{\text{cloud}} \)

<table>
<thead>
<tr>
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<th>( \alpha )</th>
<th>( \beta )</th>
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Fig. 9. The correlation between the experimentally measured and the theoretically calculated phase diagram for G156/PEG600. The parameters used in this calculation are listed in Table 3.

Fig. 10. Plot of \( \chi^* \) against \( \chi \) for EVAL and PEG. It shows the linear correlation with slop of \(-3.5\).
which shows that the linear correlation between $\chi$ and $\chi^*$.

4. Conclusion

Hydrophilic microporous membranes were prepared from various EVAL with different OH contents via TIPS process. PEG with different molecular weights ranging from 200 to 600 is used as diluent. The phase diagrams of these polymer–diluent systems were determined by videomicroscopy on glass slide coated with conductive ITO, which can effectively reduce diluent spreading. It is found that all the phase diagrams in which L–L phase boundary occurs show the UCST type phase behavior. When the molecular weight of EVAL increases, the mixture becomes less compatible, which shifts the L–L phase boundary to higher temperature, but the effect of molecular weight distribution of EVAL on phase diagram is less significant. As the OH content in EVAL co-polymer increases, both the L–L phase boundary and the crystallization shift to the higher temperature. The possible reason is that the solubility parameters ($\delta_h$, $\delta_p$) increase with the increase of OH contents in copolymers, which limit the interaction between polymer and diluent and reduce the compatibility. As the molecular weight of PEG increases, the phase boundary shifts to the higher temperature. The OH end groups of PEG play an important role on the interaction energy in these systems. When the relative content of OH end group in PEG decreases with the increase of molecular weight, the solubility parameters ($\delta_h$, $\delta_p$) decrease, and the compatibilities of these systems are reduced accordingly. We should mention that the binodal curves can be theoretically fitted by Flory–Huggins theory and the results are quite compatible. By using Lloyd’s method of extrapolating the L–L phase boundary from cloud data for polymer–diluent systems, the experimental interaction parameters $\chi$ can be obtained. It is important to note that the correlation between experimental $\chi$ and the theoretically estimated $\chi^*$ in 298 K is linear with the slope of 3.5.

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