# Phase Separation in Polyetherimide/Solvent/Nonsolvent Systems and Membrane Formation

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ABSTRACT: Phase separation phenomena of polyetherimide (PEI)/solvent/nonsolvent systems were investigated by measuring their precipitation values over the temperature range from 20 to 50°C. The solvents used are *N*-methyl-2-pyrrolidone (NMP), dimethylacetamide (DMAC), and dimethylformamide (DMF). Nine nonsolvents were employed including water, methanol, ethanol, 1-propanol, 2-propanol, acetic acid, propionic acid, ethylene glycol, and diethylene glycol. Based on the measured precipitation values, critical solubility parameters for PEI were calculated, and the partial solubility boundary for PEI was obtained in a two-dimensional solubility parameter coordinate graph. The relationship between solvent strength and membrane structure was examined using PEI hollow-fiber membranes prepared from binary polymer solutions containing NMP, DMAC, and DMF as solvents. Water was used both as internal and external coagulants. The cross-sectional structure and gas permeation properties of these hollow fibers were examined. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1789–1796, 1999

**Key words:** phase separation; polyetherimide/solvent/nonsolvent; asymmetric membrane

# **INTRODUCTION**

Commercially available polyetherimide (PEI) has several important advantages as a membrane material. This polymer has good chemical and thermal stability as well as membraneforming properties. Studies on gas permeation have revealed that PEI exhibits excellent separation properties, particularly for gases with small molecules (He and H<sub>2</sub>).<sup>1,2</sup> Recent studies made on pervaporation using PEI flat-sheet membranes show also that this polymer displays good selectivity for the 2-propanol/water system<sup>3</sup>; however, its permeability is low. The challenge is, therefore, to prepare a good asymmetric membrane with an ultrathin separating layer so as to achieve a high permeation flux. The formation of an asymmetric membrane deals with complicated thermodynamics, phaseseparation kinetics, and interfacial mass transfer during the membrane formation. An understanding of the phase-separation behavior of a polymer solution in the presence of a nonsolvent is therefore important in the development of "ideal" asymmetric membranes by the phaseinversion method. It can provide useful thermodynamic and kinetic information on controlling the membrane formation and morphology of the resulting membrane. Also, recent studies have demonstrated that the introduction of a suitable nonsolvent in the polymer solution plays a dominant role in preparing asymmetric membranes with good gas-separation performance and the desired membrane morphology.4-6 Studies on the phase separation of a polymer/

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solvent/nonsolvent system provide also information for the determination of the membrane dope composition.<sup>6</sup>

The incipience of phase separation in a polymer/solvent/nonsolvent system can be identified by determining the cloudy point of the dilute polymer solution based on a simple titration method. The term "precipitation value" has been defined as the grams of nonsolvent required to cause visual turbidity in a solution containing 100 g of solvent and 2 g of polymer.7 It has been demonstrated that the measured precipitation value could be used to indicate the initial occurrence of phase separation in a polymer/solvent/nonsolvent system.<sup>7</sup> Also, it has been shown that the precipitation value can provide a more precise indication of the strength of a solvent and a nonsolvent for a given polymer as well as information for the determination of the membrane dope composition.6,7

Phase-separation behaviors of PEI/solvent/ nonsolvent systems as a function of temperature were examined in detail by measuring their precipitation values. The partial solubility boundary for PEI on Hansen's two-dimensional coordinate graph was constructed based on the measured precipitation values. PEI asymmetric hollow-fiber membranes have been prepared from various solvents using water as a coagulant. The correlation between phase-separation behaviors based on precipitation values and the characteristics of PEI hollow-fiber membranes spun using different solvents is addressed.

# **EXPERIMENTAL**

# **Materials**

The polymer, polyetherimide (PEI, Ultam<sup>®</sup> 1000P), was purchased from General Electric Co., Waterford, NY. The solvents, *N*-methyl-2-pyrrolidone (NMP, 99+%), dimethylacetamide (DMAC, 99+%), and dimethylformamide (DMF, 99+%) were supplied by Merck, Darmstadt, Germany. The organic nonsolvents studied are methanol (MeOH, 100%, Baker Analyzed, Phillipsburg, NJ), ethanol (EtOH, 99.8%, Merck), 1-propanol (1-PrOH, 99+%, Ajax Chemicals, Auburn, Australia), 2-propanol (2-PrOH, 99.6%, Baker Analyzed), ethylene glycol (EgOH, 99.5%, Merck), diethylene glycol (DegOH, 99%, Merck), acetic acid (AA, 99.8%, Merck), and propionic acid (PA, 99+%, Merck). All these chemicals were used without further purification. Deionized water was also used as a nonsolvent. PEI was dried for at least 3 h at 150°C before being used in the experiments.

## Measurement of Precipitation Values (PVs)

The experimental apparatus and procedures for determining the PV by the titration method was described elsewhere.<sup>7</sup> The polymer solution with the ratio of 2 g polymer and 100 g solvent was placed in a glass-jacketed bottle, which can be easily operated at different temperatures. The temperature was controlled over the range of 20-50°C by a water thermostat. A pure nonsolvent was slowly added through a burette into the polymer solution under agitation until the original homogeneous solution became cloudy visually. The quantity in grams of the nonsolvent required to make the polymer solution turbid was obtained by measuring the change in the weight of the nonsolvent in the burette. The PV can, thus, be calculated from the amounts of nonsolvent used and the polymer solution in the bottle.

# Preparation and Characterization of Hollow-fiber Membranes

Polymer dopes were formulated using NMP, DMAC, and DMF individually as solvents. For each of the solvents used, two polymer dopes with the polymer concentrations of 20 and 25 wt %were prepared. The spinneret used has an orifice diameter of 0.6 mm and a tube inner diameter of 0.15 mm. Take-up velocity of the hollow fibers was kept at about 8 m/min. Hollow-fiber membranes were prepared by the wet-phase inversion method (air gap = 0). The internal water-injection rate was maintained at about 1.0-1.2 mL/ min. Spinning of the fiber was performed at the ambient condition (25  $\pm$  1°C, RH = 65%). The temperature of tap water was  $25 \pm 1^{\circ}$ C. The laboratory-scale spinning equipment used and the detailed spinning procedure were described elsewhere.<sup>6</sup>

The spun wet hollow fibers were dried under ambient conditions. Gas-permeation fluxes for He and  $N_2$  through these membranes were measured at a pressure difference of 1 bar and 25°C. Crosssectional morphologies of the membranes spun from the 25 wt % dopes were examined by scanning electronic microscopy. After silicone-coating, the gas-separation characteristics through these membranes were again examined at 5 bar and



**Figure 1** PVs of nonsolvents in the PEI/NMP system as a function of temperature.

25°C. The pressure-normalized fluxes and ideal slectivities for He and  $N_2$  were then obtained.

## **RESULTS AND DISCUSSION**

## PVs of PEI/NMP/Nonsolvent Systems

The PVs of H<sub>2</sub>O, MeOH, EtOH, 1-PrOH, 2-PrOH, AA, PA, EgOH, and DegOH in the PEI/NMP system were first measured over the temperature range from 20–50°C. The results are summarized in Figure 1. As depicted, the PVs for the nine nonsolvents increased in the order H<sub>2</sub>O < EgOH < MeOH < 2-PrOH < EtOH < DegOH < 1-PrOH < AA < PA. The PVs for water are substantially lower than those of the alcohols and the acids, indicating the low nonsolvent tolerance of the PEI–solvent solution for water. Water is a much stronger nonsolvent compared to the alcohols and acids. With increasing temperature, the PVs of all the nonsolvents in the PEI/NMP system were increased.

## PVs of PEI/DMAC/Nonsolvent Systems

Figure 2 presents the PVs of the nine nonsolvents

used in the PEI/DMAC system over the temperature range from 20 to 50°C. Similar to the case of the PEI/NMP system, water has the lowest PV compared to those of the organic nonsolvents used; moreover, the PVs for all the nonsolvents increased with increasing temperature. However, the PVs are generally much lower in the DMAC solvent systems than in the corresponding NMP systems.

### PVs of PEI/DMF/Nonsolvent Systems

The PVs of PEI/DMF/nonsolvent systems as a function of temperature are illustrated in Figure 3. It was observed that at temperatures below 20°C the polymer solutions had already turned cloudy prior to the addition of the nonsolvents. The PVs of the nine nonsolvents in the PEI/DMF solution are much lower than those in PEI/NMP and PEI/DMAC solutions, but the values increased sharply with increasing temperature.

### PVs and Nonsolvent Tolerance of a Polymer Solution

The PV of a nonsolvent in a polymer/solvent system offers a quantitative measure of the nonsol-



**Figure 2** PVs of nonsolvents in the PEI/DMAC system as a function of temperature.



**Figure 3** PVs of nonsolvents in the PEI/DMF system as a function of temperature.

vent tolerance of the polymer/solvent solution system. A greater compatibility of a nonsolvent with a solvent decreases the dissolving power of the solvent for the polymer; on the other hand, a lower compatibility of the nonsolvent and polymer promotes polymer aggregation and precipitation. Both these effects tend to lower the PV. For a given polymer/solvent/nonsolvent system, the compatibilities of the pairs, polymer/solvent, polymer/nonsolvent, and solvent/nonsolvent, depend on the polar and the nonpolar interactions of these components. The compatibility of a pair of components can be qualitatively indicated by their Hansen's solubility parameter difference and generally increases with a decreasing solubility parameter difference. Table 1 lists the Hansen's solubility parameters of the solvents and nonsolvents used in this study. The polar interaction of the components depends mainly on their hydrogen-bonding ability represented by the  $\delta_h$ component of the solubility parameter. The nonpolar interaction depends on the hydrophobic nature of the component. As shown in Figures 1–3, the nonsolvents (H<sub>2</sub>O, MeOH, and EgOH) with larger  $\delta_h$  values have lower PVs, which indicates weaker interaction between PEI and these nonsolvents. The results suggest that PEI is a very hydrophobic polymer. The nonsolvents with a lower value for  $\delta_h$  signify lower hydrogen-bonding ability and, hence, better nonsolvent/polymer compatibility and, consequently, higher PVs.

Among the three solvents examined, their  $\delta_h$  values follow the order DMF > DMAC > NMP as shown in Table I. Therefore, DMF is relatively more polar than are DMAC and NMP. The interactions between the DMF molecules and the PEI molecules are thus weaker than those of NMP–PEI and DMAC–PEI; on the other hand, the polar interactions of the nonsolvents and DMF are relatively more extensive compared to NMP and DMAC. These explain the significantly lower PVs

 Table I
 Hansen's Solubility Parameters for the Solvents and Nonsolvents Used in This Study<sup>8</sup>

Compounds	$\delta_p$	$\delta_h$	$\delta_d$	$\delta_t$
N-Methyl-2-pyrolidone (NMP)	12.27	7.16	18.0	22.93
N,N-Dimethylacetamide (DMAC)	11.45	10.23	16.77	22.74
Dimethylformamide (DMF)	13.70	11.30	17.40	24.86
Water $(H_2O)$	15.95	42.34	15.55	47.84
Methanol (MeOH)	12.27	22.30	15.14	29.61
Ethanol (EtOH)	8.80	19.43	15.75	26.51
1-Propanol (1-PrOH)	6.75	17.38	15.95	24.54
2-Propanol (2-PrOH)	6.10	16.40	15.80	23.50
Ethylene glycol (EgOH)	11.05	25.98	16.98	32.94
Diethylene glycol (DegOH)	14.73	20.46	16.16	29.94
Acetic acid (AA)	7.98	13.50	14.52	21.37
Propionic acid (PA)	6.14	12.07	14.73	20.01

Unit:  $(J/cm^{3})^{0.5}$ . The subscripts h, d, p, and t represent hydrogen-bonding, dispersive, polar, and total, respectively.

obtained for all the nonsolvents used in the PEI/ DMF systems and, also, the lower PVs in the PEI/DMAC systems compared to those in the PEI/NMP systems. The results further substantiate the hydrophobicity character of PEI. Based on the PVs measured for the three solvents, the solvent strength for PEI follows the sequence NMP > DMAC > DMF. Compared to the PVs reported for polysulfone (PSf) and polyethersulfone  $(PESf)^7$  for the same solvents and nonsolvents used, the observed PVs for PEI are much lower. This means that the interaction among the same polymer molecules is much stronger in PEI as compared to PS and PESf due to its very rigid and somewhat planar backbone. It appears to suggest that a strong solvent is needed for PEI in order to break the profusion of interchain bonds.

#### **Effect of Temperature**

The effect of temperature on the phase-separation behaviors of a polymer/solvent/nonsolvent system is complicated depending on the variations of polar and nonpolar interactions of the components with temperature. With increasing temperature, the Hansen's solubility parameter is generally decreased, particularly for the polar component caused by hydrogen bonding.<sup>9</sup> The nonpolar interactions of the nonsolvent/solvent and the nonsolvent/polymer may be expected to increase due to the significant decrease in the H-bonding ability. The dissolving power of a solvent for a polymer usually increases with temperature due to increasing molecular movement. It is believed that variations of the solubility parameters with temperature are different for different materials. Consequently, the effect of temperature on the PV depends on the magnitude of the polar and nonpolar interactions relative to the polymer-solvent interaction.

For a system with a strong H-bonding ability between a solvent or a solvent mixture and a polymer, the polymer solubility usually decreases with increasing temperature. Therefore, a lower critical solution temperature (LCST) exists. This phenomenon has been observed in investigating the phase separation of PESf/solvent/nonsolvent systems.<sup>7</sup> Since PEI is a more hydrophobic polymer compared to PESf, the H-bonding ability between PEI and the solvent or the nonsolvent is much weaker. The nonpolar interactions among the components are likely to be predominant; consequently, the polymer solubility increases with increasing temperature.

#### Partial Solubility Envelope of PEI

The Hansen's solubility parameter concept has been used for the selection of a suitable solvent or solvent mixture for a polymer and the formulation of a membrane-forming solution.<sup>10</sup> The solubility region of a polymer, referred to as the solubility envelop, is obtained by the solubility parameters of those solvents found to dissolve a particular polymer. Three-dimensional<sup>9</sup> and twodimensional<sup>10</sup> coordinate solubility parameters have been used to produce a polymer solubility diagram. However, it has been shown that there exists a certain dilemma and there is uncertainty at determining the boundaries of the solubility envelop because of the qualitative nature of the determination method.<sup>10</sup> With the introduction of a nonsolvent in the polymer solution, the dissolving power of the solvent is reduced and the solubility parameter of the solvent mixture moves toward the solubility parameter of the nonsolvent. At the cloudy point, the contact between polymer-polymer molecules is enhanced and the solubility of the polymer in the solvent mixture reaches its "critical condition." The solubility parameters of this solvent mixture can be calculated as the sum of solubility parameters of each component weighted by its mole fraction.<sup>10</sup> These "critical solubility parameters" can be used to construct the boundary of the solubility envelope for a given polymer. In this study, the critical solubility parameters for PEI were calculated from the measured PVs at 30°C for the NMP/nonsolvent, DMAC/nonsolvent, and DMF/nonsolvent systems. The partial boundary of the solubility envelope was then obtained and is shown in Figure 4. Although this method appears to be more accurate compared to the qualitative method, the determination of the exact composition at the boundary is still difficult as is illustrated in Figure 4. The critical solubility parameters determined from the different solvent/nonsolvent systems display some differences. For instance,  $\delta_p$  ranges from 10.5 to 12.5 (J/cm<sup>3</sup>)<sup>0.5</sup> and  $\delta_h$  varies from 8.5 to 11 (J/cm<sup>3</sup>)<sup>0.5</sup> for the NMP/nonsolvent and DMAC/nonsolvent systems. For the DMF/ nonsolvent systems, the determined parameters are very close to that of the DMF due to the very small PV values at 30°C for the various nonsolvents. As reported in our previous studies,<sup>7</sup> it is not reliable to precisely determine the composition of a membrane-forming polymer solution using the solubility envelope constructed based on the solubility parameter, particularly when the



Figure 4 Partial solubility boundary for PEI constructed from the PVs at 30°C.

solution composition required is close to the point of phase separation.

#### Membrane Formation and Characterization

The structure of a membrane and its separation characteristics are closely related to the "state" of a membrane-forming solution. The state depends critically on the interactions of the polymer-solvent-additive system. For a binary polymer solution containing only a polymer and a solvent, the stronger the polymer-solvent interaction and, conversely, the weaker the polymer-polymer interaction, the finer and more uniform will be the dispersion of the macromolecules or aggregates of the macromolecules in the solution. The membrane formed from this solution is expected to have a dense structure with small pores. As discussed above, the interaction strength of the polymer/solvent system can be indicated by the PV measured for a given nonsolvent. Based on the PVs measured in the PEI/NMP, PEI/DMAC, and PEI/DMF systems, the interaction strength of solvent-PEI follows the decreasing order NMP > DMAC > DMF. It is, therefore, expected that the porosity and pore size of the membranes formed will decrease according to the reverse order, that is, DMF > DMAC > NMP when the solvent and nonsolvent (coagulant) have good miscibility. On the other hand, a small PV means that the polymer solution is closer to the incipience of phase separation. Fast phase inversion tends to take place and the resulting membrane exhibits a thin and porous skin layer supported on a big macrovoid substructure. To elucidate the relationship between the PV and the membrane structure for the binary polymer solution system, PEI hollow-fiber membranes were prepared from the three solvents with water as a coagulant.

The gas-permeation properties of He and N<sub>2</sub> through the asymmetric membranes were measured at a pressure difference of 1 bar and at 25°C. The results are shown in Table II. As anticipated, the gas-permeation flux increased, while the selectivity for He/N<sub>2</sub> decreased following the solvent order NMP, DMAC, and DMF. For further investigating the skin-layer structure of the membranes, the membranes were coated using 3 wt % silicone (Sylgard-184) in *n*-pentane. The pressure-normalized fluxes of He and N<sub>2</sub> were measured at 25°C and a pressure difference of 5 bar. The results are also shown in the brackets in Table II. As illustrated, the membrane prepared from NMP yields higher selectivity but lower permeability compared to the other membranes spun from DMAC and DMF. The selectivities of the membranes prepared from DMF and DMAC at low polymer concentrations are quite small. These results further suggest the existence of big pores on the surface of these latter membranes which were not effectively sealed with silicone rubber. A comparison of the silicone-coated membranes prepared from NMP and DMAC at the polymer concentration of 25 wt % reveals that the membrane prepared from DMAC has a thinner skin layer than that of the membrane prepared from NMP.

An examination of the cross-sectional structures by scanning electronic microscopy (Figs. 5–7) of the three hollow-fiber membranes spun from the different solvents at a polymer concentration of 25 wt % reveals that the morphologies are different. Many small and long fingerlike macrovoids exist in the inner and outer edges of the hollow fiber spun from DMAC (Fig. 6). However, the fingerlike macrovoids in the outer edge are significantly reduced for the membrane spun from NMP as shown in Figure.5. The hollow fiber spun from DMF has big macrovoids in the inner

Membrane No.	Solvent Used	Polymer Concentration (wt %)	OD/ID (µm/µm)	$(P/L)_{He}$	$lpha_{ m He/N2}$
A1	NMP	20	510/254	$2.2 imes10^{-4}$	2.9
				$(5.2 imes10^{-5})$	(81)
A2	DMAC	20	509/230	$9.87 imes10^{-3}$	1.7
				$(4.0  imes 10^{-4})$	(2.9)
A3	DMF	20	509/236	$1.7 imes10^{-2}$	1.5
				$(9.7 imes10^{-4})$	(2.3)
B1	NMP	25	560/300	$2.49 imes10^{-5}$	29.2
				$(1.9  imes 10^{-5})$	(171)
B2	DMAC	25	509/227	$1.14 imes10^{-3}$	2.6
				$(6.5  imes 10^{-5})$	(123)
B3	DMF	25	500/227	$5.1 imes10^{-3}$	1.9
				$(9.5 imes10^{-5})$	(6.6)

Table II Pressure-normalized Fluxes of He and Ideal Selectivities of  $\rm He/N_2$  of the Membranes Prepared from NMP, DMAC, and DMF

OD: outer diameter of fiber; ID: inside diameter of fiber; (P/L): pressure-normalized flux,  $cm^3(STP)/cm^2 cmHg s$ ;  $\alpha$ : selectivity. Data in parentheses for silicone-coated membrane.

edge (Fig. 7). The formation of macrovoids in the substrate not only depends on the solvent used, but also on the membrane-formation condition. As shown in these graphs, the fingerlike voids are easily formed near the inner edge. This may be caused by the difference in coagulation rates between the inner and the outer skin due to the much smaller amount of coagulant (water) used in the fiber lumen. The weaker interaction between PEI and DMF results in the formation of big aggregates, which could contribute to the formation of big macrovoids.

# **CONCLUSIONS**

The PVs of several alcohols, acids, and water in three PEI/solvent systems, for example, PEI/



**Figure 5** Scanning electronic micrograph of crosssection structure of the PEI hollow fiber prepared from NMP.



**Figure 6** Scanning electronic micrograph of crosssection structure of the PEI hollow fiber prepared from DMAC.



**Figure 7** Scanning electronic micrograph of crosssection structure of the PEI hollow fiber prepared from DMF.

NMP, PEI/DMAC, and PEI/DMF, were measured at various temperatures. The observed PVs in the PEI/solvent systems are much smaller than those in the PESf/solvent and the PSf/solvent systems reported. The experimental results reveal that PEI is a more hydrophobic polymer than is PSf or PESf. The PVs generally increased with increasing temperature. The PVs for the nonsolvents and/or solvents with greater hydrogen-bonding ability such as H<sub>2</sub>O, MeOH, EgOH, and DMF are much smaller compared to those with a smaller hydrogen-bond ability. The solvent strength for PEI follows a decreased order as NMP > DMAC > DMF. The hollow-fiber membranes formed from a good solvent (higher PV) like NMP and DMAC exhibit a dense skin layer and good selectivity, whereas a porous skin layer tends to form from the poor solvent (much lower PV) such as DMF. The results are interpreted on the basis of polar and nonpolar interactions governing the structure of a polymer solution. The results also illustrate that the study of phase separation of a polymer/solvent/nonsolvent system based on the measured PVs may offer a rational physicochemical basis for the determination of the composition of a polymer membrane-forming solution and the choice of a suitable coagulant and operating conditions in making asymmetric membranes.

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