

# Preparation and Properties of Soluble Copolysulfoneimide and Performance of Solvent-Resistant Ultrafiltration Membrane

IN-CHUL KIM,<sup>1,2</sup> JONG-HO KIM,<sup>3</sup> KEW-HO LEE,<sup>2</sup> TAE-MOON TAK<sup>1</sup>

<sup>1</sup> Division of Biological Resources and Materials Engineering, College of Agriculture and Life Science, Seoul National University, Suwon 441-744, South Korea

<sup>2</sup> Membrane and Separation Research Center, Korea Research Institute of Chemical Technology, P.O. Box 9, Daedeog-Danji, Taejon 305-606, South Korea

<sup>3</sup> Department of Fiber Engineering, Sangju University, Sangju, South Korea

Received 22 June 2001; accepted 13 September 2001

**ABSTRACT:** Soluble copolysulfoneimides were synthesized by thermal two-step method in solution of *N*-methyl-2-pyrrolidone. The used aromatic diamines were bis[4-(3-aminophenoxy)phenyl]sulfone (BAPS-m) and 3,3'-diaminosulfone, and dianhydrides were pyromellitic dianhydride, 4,4'-oxyphthalic anhydride, and 3,3',4,4'-diphenylsulfone tetracarboxylic dianhydride. The molar ratio of diamines was changed to reduce the content of BAPS-m. The thermal and mechanical properties of polyimides were investigated. The polyimide ultrafiltration membrane with molecular weight cut-off of 10 kDa could be successfully prepared by phase-inversion method. Various solvent (water, alcohols, acetone, and hexane) fluxes were measured to investigate solvent-resistance and membrane behavior during solvent permeation. The activation energy relationship between hexane flux and viscosity with temperature was also studied. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1024–1030, 2002

**Key words:** copolysulfoneimide; ultrafiltration; phase inversion

## INTRODUCTION

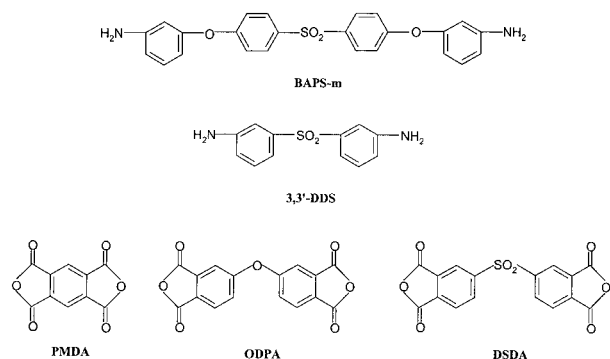
Aromatic polyimides were used as films or coatings where durability at high temperature is required.<sup>1–5</sup> They have various advantages such as good mechanical properties, excellent solvent resistance, and thermal stability. However, they have application limits because of their processing difficulties and high glass transition temperature ( $T_g$ ). Soluble polyimides such as polyetherimide and Matrimid<sup>®</sup> were not stable in solvents

such as chlorinated hydrocarbons and ketones. Therefore, soluble polyimide, which is stable in organic solvent and at high temperature, is required. The solubility of polyimide can be enhanced by introducing polar groups (amide, ester, ether, or other flexibilizing groups) or bulky substituents along the polymer backbone<sup>6–8</sup> and incorporation of *ortho*- or *meta*-oriented phenylene rings.<sup>9,10</sup>

If polyimide is soluble in polar solvents, membrane can be prepared by the phase-inversion method. The polyimide ultrafiltration (UF) membrane has been commercialized by Nitto Electric Co. since 1982.<sup>11</sup> Iwama and Kazuse investigated solvent stability and molecular weight cutoff

Correspondence to: T.-M. Tak (tmtak@snu.ac.kr).

*Journal of Applied Polymer Science*, Vol. 85, 1024–1030 (2002)  
© 2002 Wiley Periodicals, Inc.



**Scheme 1** Molecular structure of diamines and dianhydrides.

(MWCO) value in toluene solution with the membrane. This polyimide UF membrane was stable in various organic solvents except polar solvents such as *N*-methyl-2-pyrrolidone (NMP) and dimethylformamide (DMF).<sup>12</sup> Polyimide UF or nanofiltration (NF) membrane can be used in solute separation in organic solvent because of its outstanding chemical stability.<sup>13,14</sup> There are needs for membranes to endure at harsh conditions, including crude oil separation,<sup>15</sup> recycling of hot water, and soybean oil separation.<sup>16</sup> We have reported that bis[4-(3-aminophenoxy)phenyl]sulfone with aromatic dianhydride was effectively soluble in polar solvents such as NMP, DMF, and *N,N'*-dimethylacetamide (DMAc).<sup>17–20</sup>

In this work, we synthesized and characterized soluble copolysulfoneimides. With this polymer, UF membrane was prepared and the solvent permeation investigated.

## EXPERIMENTAL

### Materials

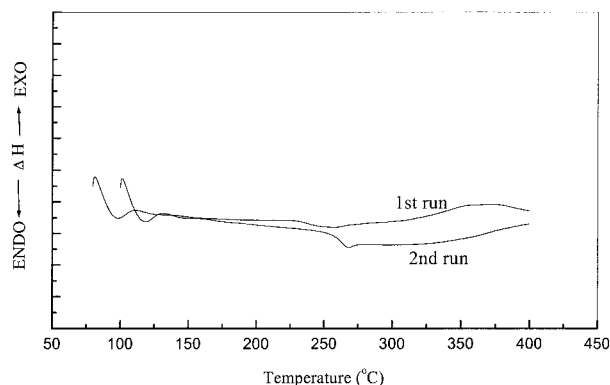
Reagent grade NMP (Aldrich, Milwaukee, WI) was dried by refluxing over calcium hydride. All other solvents were used as received. Bis[4-(3-aminophenoxy)phenyl]sulfone (BAPS-m; Tokyo Kasei, Tokyo, Japan) and 3,3'-diaminosulfone (3,3'-DDS, Aldrich) were purified by recrystallization in ethanol. Dianhydrides [pyromellitic dianhydride (PMDA), 4,4'-oxyphthalic anhydride (ODPA), and 3,3',4,4'-diphenylsulfone tetracarboxylic dianhydride (DSDA)] were obtained from Tokyo Kasei Chemicals and purified by recrystallization in hot acetic anhydride (Aldrich). Scheme 1 shows the molecular structures of monomers.

### Polymer Synthesis and Characterization

Random copolyimides were synthesized by two-step method. BAPS-m and 3,3'-DDS were dissolved in NMP at room temperature. A stoichiometric amount of dianhydride was added in three portions within 30 min and vigorously mixed for 6 h to yield a homogenous and viscous random copoly(amic acid) intermediate solution and to reach constant viscosity. The solid content of the resulting solution was 20% by weight. Copoly(amic acid) film prepared by evaporating NMP at 80°C for 12 h was then thermally imidized in a dry oven. The imidization conditions are as follows: 2 h at 180°C; 2 h at 230°C; and 2 h at 270°C. Other polyimides were prepared by changing the molar ratio of BAPS-m to 3,3'-DDS and dianhydrides. Percentage imidization was above 98%, measured with infrared spectrum.<sup>15</sup> Inherent viscosity of polymer solution (0.5 g/dL) was measured in NMP at 30°C by using an Ubbelohde viscometer. Fourier transform infrared (FTIR) spectra of polyimide and poly(amic acids) were made by using Midac model M2000, over 4000–400 cm<sup>-1</sup>. Characteristic major absorption bands at 1650, 1530, and 1720 assigned to amide I, amide II, and acid carbonyl of poly(amic acid) completely disappeared; instead, the absorption bands of the imide ring appeared at 1780 (asymmetric carbonyl group of imide ring), 1720 (asymmetric carbonyl group of imide ring), and 1370 (C–N band of imide ring). ( $T_g$  was measured by using differential scanning calorimetry (DSC; TA Instrument model DSC 2910) under nitrogen at a heating rate of 10°C/min. DSC was run twice and the second run taken for data to exclude the plasticizing effect by remaining solvents. To investigate the thermal stability, thermogravimetric analysis (TGA; DuPont model 951) at a heating rate of 20°C/min in nitrogen was used.

### UF Membrane Preparation and Performance

UF membrane was prepared by the phase-inversion method. A solution of 20 wt % polyimide in NMP was cast onto the polypropylene nonwoven fabric by means of a doctor knife with a gap of adjustable height (200 μm). The nascent membrane was prepared by evaporating solvent for 30 s in an atmosphere at a temperature of 25°C and relative humidity of 65% and then immersed into the gelation medium of pure water at 4°C. Membranes obtained in such a way were rinsed in flowing tap water to remove the residual solvents. The permeation rate and solute rejection rate



**Figure 1** The effect of reaction time of homopoly(amic acids) on the viscosity.

were measured to prepare membranes with similar membrane performance with an Amicon cell. The effective membrane area was 14.7 cm<sup>2</sup>. The pure water flux was measured at a pressure range of 1–4 atm with nitrogen gas and 25°C. The solute rejection rate was measured with poly(ethylene glycol) (PEG) of different molecular weights (6–35 kDa) at the same conditions as above. The concentration of PEG was 1000 ppm in water. The permeate concentration was measured by a HPLC equipped with a refractometer. The solute rejection rate  $R$  is defined as

$$R (\%) = (1 - C_p/C_f) \times 100$$

where  $C_p$  and  $C_f$  are the PEG concentration in the permeate and in the feed, respectively. Moreover, to investigate solvent resistance during membrane application, solvents such as alcohols, acetone, and hexane were permeated through the membrane.

## RESULTS AND DISCUSSION

### Polymer Synthesis

We have reported that aromatic homopolyimide with BAPS-m as a diamine and PMDA as a dianhydride is soluble in polar solvents such as NMP, DMAc, and DMF. However, in economical aspects, there is a need to reduce the content of BAPS-m.

Random copolysulfoneimides were prepared by the thermal two-step method in a solution of NMP. Diamines of BAPS-m and 3,3'-DDS were blended. Dianhydrides were PMDA, DSDA, and

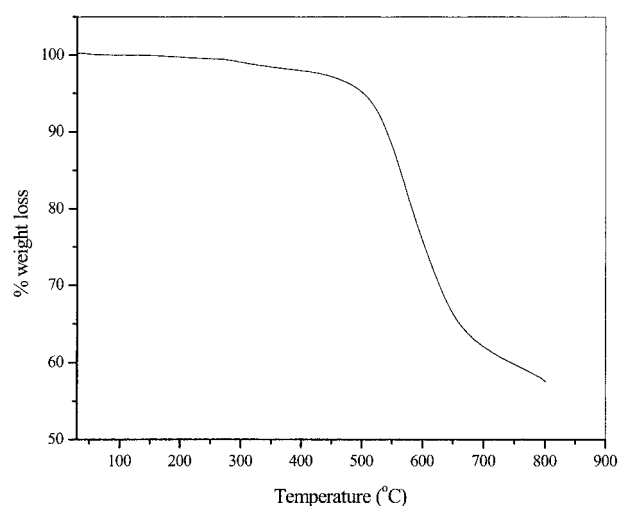
ODPA. Figure 1 shows the viscosity change of homopoly(amic acids) versus reaction time. This figure represents the extent of polymerization that increased sharply to 4 h; after that time, its viscosity change did not occur. The results may be the equilibrium between polymerization and depolymerization. When the rates of polymerization and depolymerization are equal, the viscosity does not change. The unequal mole ratio may stop polymerization at lower molecular weight (MW). This result shows that 4-h reaction time for poly(amic acid) synthesis is enough. The reaction between dianhydride and diamine occurs through a transfer of the carboxyl proton to the adjacent carboxamide group. Then, the anhydride's carbonyl carbon is nucleophilically substituted. It is not needed to remove the byproduct (carbonyl group) for the reaction completion because the byproduct is chemically bonded with the poly(amic acid). The equilibrium constant strongly depends upon the amine's nucleophilicity and electrophilicity of the dianhydride. In other words, BAPS-m's equilibrium content is larger than that of 3,3'-DDS because of the BAPS-m's larger basicity. The amine group of BAPS-m is linked to the ether linkage, which is the electron-donating group, whereas the amine group of 3,3'-DDS is linked to the sulfone linkage, which is the electron-withdrawing group. Therefore, the reactivity of BAPS-m is better than that of 3,3'-DDS. In the case of dianhydrides, the reverse fact is applied. The equilibrium constant of ODPA involving electron-donating ether group is smaller than that of DSDA having an electron-withdrawing sulfone group. In other words, the ether linkage, which is the electron-donating group, weakens the reactivity of the anhydride group, whereas the sulfone group which is the electron-withdrawing group strengthens one of the anhydride group. Figure 1 also shows that the reactivity order is PMDA > DSDA > ODPA. Table I exhibits the compositions, viscosities, and yields of homopolyimides and copolysulfoneimides when the kind of dianhydride was changed. The composition of diamines means the maximum ratio of BAPS-m to 3,3'-DDS for solubility. The viscosity and yield of copolysulfoneimides are lower than homopolyimides because of the lower reactivity of 3,3'-DDS. The sulfone linkage of 3,3'-DDS, which is the electron-withdrawing group, weakens the reactivity of the amine group. When DSDA is used as a dianhydride, more 3,3'-DDS can be involved in copolysulfoneimide than ODPA- and PMDA-based polyimides. This is due to the polar

**Table I Compositions, Viscosities, and Yields of Random Copolysulfoneimides Being Soluble**

Code	R1	R2	<i>x</i>	<i>y</i>	$\eta$ (dl/g)	Yield (%)
PI-1-a	PMDA	BAPS-m	1.0	0	0.47	>90
PI-1-b		3,3'-DDS	0.25	0.75	0.41	>80
PI-2-a	DSDA	BAPS-m	1.0	0	0.45	>90
PI-2-b		3,3'-DDS	0.09	0.91	0.40	>80
PI-3-a	ODPA	BAPS-m	1.0	0	0.41	>90
PI-3-b		3,3'-DDS	0.14	0.86	0.38	>80

sulfone bridge of DSDA. The sulfone bridge of DSDA can increase the solubility of polyimide and ODPA-based polyimide can incorporate more 3,3'-DDS than PMDA-based polyimide because of the flexible ether linkage of ODPA. Moreover, polar group introduction in polyimide main chain can be more soluble than flexible linkage. When DSDA was used as a dianhydride, the diamine ratio of BAPS-m to 3,3'-DDS was 1 to 10. In other words, by using DSDA, polyimide could be synthesized with the least BAPS-m because of polar sulfone bridge and *meta*-catenation of 3,3'-DDS. When ODPA and PMDA were used as dianhydrides, the diamine ratio of BAPS-m to 3,3'-DDS was 1 to 6 and 1 to 3, respectively.

Figure 2 shows the DSC curve of homopolyimide (PI-1-a) from PMDA and BAPS-m. When the film is first heated, the remaining solvent renders


**Figure 2** DSC curve of homopolyimide (PI-1-a).

the polyimide main chain plasticized. Therefore,  $T_g$  can be shown in slightly lower temperature than that of the second heated film. That is why the film should be heated a second time. Table II shows the thermal properties of homopolyimides and copolysulfoneimides. Introduction of 3,3'-DDS in the polyimide main chain increases the  $T_g$ . In BAPS-m, there is a flexible ether linkage, whereas in 3,3'-DDS a polar sulfone bridge is present. In general, a polar group in polymer chain increases the  $T_g$ . However, the polymer degradation pattern (thermal resistance) of copolysulfoneimide becomes worse than that of homopolyimide. In other words, as shown in Figure 3, in the cases of homopolyimides, initial degradation occurred above 500°C, whereas in the cases of copolysulfoneimides, initial degradation temperature is around 480°C. This is due to the asymmetric structure and lower reactivity of 3,3'-

**Table II Thermal Properties of Homopolyimides and Copolysulfoneimides**

Code	$T_g$ (°C) <sup>a</sup>	$T_i$ (°C) <sup>b</sup>	$T_{10}$ (°C) <sup>c</sup>	$T_{max}$ (°C) <sup>d</sup>
PI-1-a	250	550	580	650
PI-1-b	295	480	510	610
PI-2-a	247	545	570	650
PI-2-b	280	480	520	600
PI-3-a	213	530	570	630
PI-3-b	230	450	500	570

<sup>a</sup> Observed by DSC at a heating rate of 20°C/min.

<sup>b</sup> Initial decomposition temperature measured by TGA at a heating rate of 20°C/min.

<sup>c</sup> 10% weight loss temperature measured by TGA at a heating rate of 20°C/min.

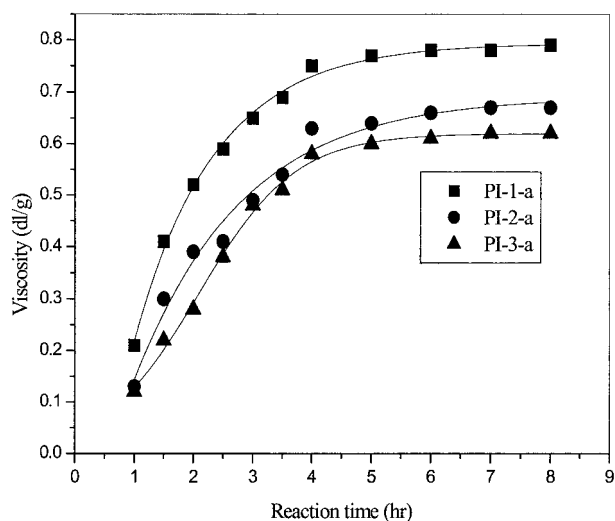
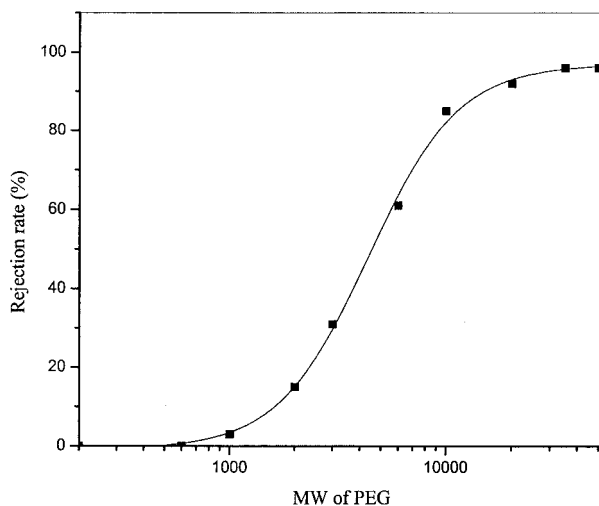
<sup>d</sup> Maximum weight loss temperature measured by TGA at a heating rate of 20°C/min.

**Table III Mechanical Properties of Homopolyimides and Copolysulfoneimides**

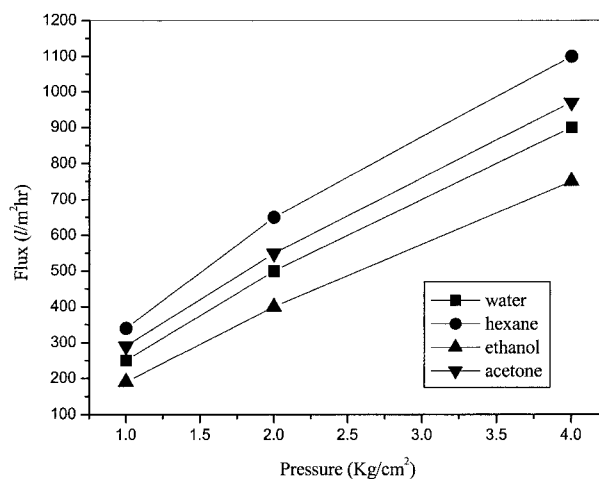
Code	Tensile Strength (psi)	Elongation (%)	Tensile Modulus (psi)
PI-1-a	11,800	6	235,000
PI-1-b	6100	5	145,000
PI-2-a	10,200	5	212,000
PI-2-b	8200	5	180,000
PI-3-a	7400	3	166,000
PI-3-b	7100	5	159,000

DDS. The asymmetric structure decreases the interaction between polymers. The lower reactivity renders the polymer chain length short. This result is also exhibited in mechanical properties of Table III. 3,3'-DDS in copolysulfoneimides decreased the tensile strength because of the above reasons.

That these polymers were dissolved in polar solvents implied that the phase inversion method can be used. A casting solution of 20 wt % in NMP could be prepared and UF membranes could be prepared by precipitation in ice-cold water. At first, pure water flux was measured. The permeation rates of these membranes are significantly high without adding additives to the casting solution. Moreover, the molecular weight cut-off values are approximately PEG 10 kDa. This membrane performance cannot be found in another polymeric UF membrane. Figure 4 shows the rejection rate of copolysulfoneimide (PI-2-b) UF membrane. The curve shows a very sharp

**Figure 3** TGA thermogram of homopolyimide (PI-1-a).**Figure 4** The rejection rate of PI-2-b ultrafiltration membrane in water.

pattern. Most commercial UF membranes show a broad rejection rate curve, which indicates that the separation characteristic of the membrane is not good. Figure 5 shows the various solvent fluxes for 10-kDa MW cut-off polyimide membranes at 25°C by changing the transmembrane pressures. To measure the hexane flux, the polyimide membrane should be wetted by passing alcohol. Hexane flux was highest because of the lowest viscosity. Figure 5 shows that the polyimide membranes are stable against the solvents. Moreover, when measured after being soaked for 2 months, the solvent flux was almost the same,

**Figure 5** Solvent flux for 10 kDa molecular weight cut-off membrane (PI-2-b) at 25°C with changing transmembrane pressure during dead-end filtration.



**Table IV Comparison of Solvent Fluxes and Physical Properties**

Solvent	$J$ (l/m <sup>2</sup> h)	$V$ (cm <sup>3</sup> /mol)	$\mu$ (cP)	$\epsilon$
Water	480	18	0.89	80.37
Methanol	410	40.4	0.55	33.62
Ethanol	360	58.4	1.08	24.30
Propanol	315	75.9	1.96	20.10
Butanol	260	91.5	2.53	17.80
Pentanol	220	108.2	3.27	13.90
Hexane	650	130.8	0.31	1.90
Acetone	520	73.3	0.32	20.85

implying that these membranes are stable in solvents for a long time.

Figure 6 exhibits the effect of temperature in the range of 20–40°C on hexane flux through the PI-2-b membrane. A temperature rise increased permeation flux because of a reduction in viscosity and diffusivity of solvent or a mobility increase of polymer chain.

The temperature effect on hexane flux can be correlated by the Arrhenius plot, given by:

$$J = A_J \exp(-E_J/RT)$$

where  $A_J$  is a frequency factor and  $E_J$  is a permeation activation energy. Figure 6 shows the results, yielding activation energy for PI-2-b membrane ( $E_J = 3.63$  kcal/mol). Because viscosity may be responsible for the flux increase with temperature, the datum for viscosity activation energy was taken from:

$$\mu = A_\mu \exp(-E_\mu/RT)$$

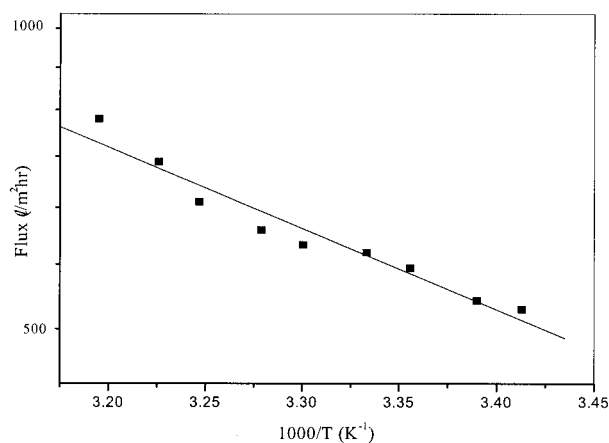
The hexane viscosity activation energy of  $E_\mu = 1.59$  kcal/mol was determined from viscosity data over a temperature range from 0 to 50°C. The flux/viscosity activation energy ratio was 2.28. It is thought that a viscosity decrease by temperature rise cannot be used to predict the permeation properties of hexane through the PI-2-b membrane.

Membrane-solvent interactions can be expected to vary with changes in solvent properties such as dielectric constant, molecular size, and dipole moment. Table IV lists flux measurements of several solvents having different physical properties. Fluxes were measured with the PI-2-b membrane, at room temperature and at a pressure of 2 kg/cm<sup>2</sup>.

Table IV shows that there are indeed significant variations in the flux stemming from the differences in physical properties. Higher fluxes are evident in the case of relatively hydrophobic solvents, such as acetone and hexane, whereas lower fluxes are indicated in the case of relatively hydrophilic solvents, such as butanol and water. Within the homologous series of linear alcohol, it was found that flux increases with decreasing molecular volume. The effect of the dielectric constant on solvent flux appears to be relatively small. This is due to the relatively high values of the dielectric constant of the solvents relative to that of the polymeric material. Except for the anomalous behavior of water, all other solvents show a consistent increase in flux with a decreasing viscosity. This result indicates that viscous forces represent one of the major parameters affecting solvent flow through PI-2-b membranes.

## CONCLUSION

Soluble copolysulfoneimides were synthesized by thermal two-step method. 3,3'-DDS was incorporated in the main chain (BAPS-m and dianhydride). By using DSDA as a dianhydride, 3,3'-DDS could be introduced more than PMDA- and ODPA-based polyimides. Lower reactivity of 3,3'-DDS made the viscosity and yield of the resulting polyimide decreased. The  $T_g$  of copolysulfoneimides were higher than those of homopolyimides because of the introduction of the sulfone bridge. However, the copolysulfoneimides were degraded at a lower temperature than the homopolyimide



**Figure 6** Arrhenius plot of the effect of temperature on hexane flux.

because of the low reactivity. The UF membrane with excellent performance could be prepared with the polymer. In other words, the membrane has very high flux and specific molecular weight cut-off value (10 kDa). Various solvent (water, alcohols, acetone, and hexane) fluxes could be measured, meaning that the polymer was stable in the solvents. Acetone and hexane, especially, which have lower viscosity and hydrophobic properties, could be permeated more than water and alcohols.

The authors are grateful to Dr. S. C. Kim, the president of the Korea Advanced Institute of Science and Technology Center Advanced Functional Polymers, for support of this work.

## REFERENCES

1. Polyimides: Materials, Chemistry, and Characterization; Feger, C.; Khojastech, M. M.; McGrath, J. E., Eds.; Elsevier: Amsterdam, 1989.
2. The Handbook of Polymer Synthesis; Kricheldorf, H. R., Eds.; Marcel Dekker: New York, 1991; Part B.
3. Polyimides; Wilson, D.; Stenzenberger, H. D.; Gengenrother, P. M., Eds.; Chapman and Hall: New York, 1990.
4. Imai, Y.; Malder, N. N.; Kakimoto, M. *J Polym Sci, Part A: Polym Chem* 1984, 22, 2189.
5. Polyimides: Synthesis, Characterization, and Application; Mittal, K. L., Ed.; Plenum: New York, 1984.
6. Jeong, H. J.; Kakimoto, M.; Imai, Y. *J Polym Sci, Polym Chem Ed* 1991, 29, 1691.
7. Oishi, Y.; Ishida, M.; Kakimoto, M.; Imai, Y.; Kurosaki, T. *J Polym Sci, Polym Chem Ed* 1992, 30, 1027.
8. In Structure—Solubility Relationships in Polymers; Harris, F. W.; Lanier, L. H.; Seymour, R. B., Eds.; Academic Press: New York, 1977.
9. St. Clair, T. L.; St. Clair, A. K.; Smith, E. N. *Polym Prepr* 1976, 17, 359.
10. Bell, V. L.; Stump, B. L.; Gager, H. *J Polym Sci, Polym Chem Ed* 1976, 14, 2275.
11. Polyimide Membranes; Ohya, H.; Kudryavtsev, V.; Semenova, S. I., Eds.; Kodansha: Tokyo, 1996.
12. Iwama, A.; Kazuse, Y. *J Membr Sci* 1982, 11, 303.
13. Hayashi, Y.; Yuzaki, S.; Kawanishi, T.; Shimizu, N.; Furukawa, T. *J Membr Sci* 2000, 177, 233.
14. White, L. S.; Nitsch, A. R. *J Membr Sci* 2000, 179, 267.
15. Okazaki, I.; Ohya, H.; Semenova, S. I.; Aihara, M.; Nehishi, Y. *J. Membr Sci* 1998, 141, 277.
16. Iwama, A. *Membrane* 1986, 11 (2), 99.
17. Kim, I. C.; Tak, T. M. *J Appl Polym Sci* 1999, 74, 272.
18. Kim, I. C.; Park, K. W.; Tak, T. M. *J Appl Polym Sci* 1999, 73, 907.
19. Kim, I. C.; Kim, J. H.; Lee, K.-H.; Tak, T. M. *J Appl Polym Sci* 2000, 75, 1.
20. Kim, I. C.; Tak, T. M. *Macromolecules* 2000, 33, 2391.