

# Preparation of Soluble Polyimides and Ultrafiltration Membrane Performances

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**ABSTRACT:** Various soluble polyimides with bis[4-(3-aminophenoxy)phenyl]sulfone and three kinds of dianhydrides were prepared in a polar *N*-methyl-2-pyrrolidone solvent by the traditional chemical two-step method. All the polymers synthesized had good solubilities in polar solvents and excellent thermal properties. Wide-angle X-ray diffraction studies showed that all polyimides were amorphous. Polyimide ultrafiltration asymmetric membranes were successfully prepared by the traditional phase-inversion method. The cross sections of the polyimide ultrafiltration membranes showed a very thin surface layer and a porous sublayer. The pure water flux was very high and the solute rejection rate at poly(ethylene glycol) of MW 20,000 was above 90%. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1–9, 2000

**Key words:** soluble polyimides; ultrafiltration asymmetric membrane

## INTRODUCTION

In recent years, membrane processes have been used in a wide range of applications and the number of such applications are still growing.<sup>1–3</sup> Ultrafiltration (UF) membrane materials, including cellulose acetate, cannot be used for organic solutions because of their poor chemical instabilities.<sup>4,5</sup> Furthermore, commercially available UF membranes made of organic polymers are limited to operating temperatures at above 100°C. Even at below this temperature, their lifetimes are often short. There are needs for membranes to en-

sure at harsh conditions, including crude oil separation,<sup>6</sup> recycling of hot water, and soybean oil separation.<sup>7</sup> As a suitable material to overcome these drawbacks, polyimide, with excellent thermal stability combined with good chemical stability and mechanical stability, is one. However, the major limitations of aromatic polyimides for membrane applications are their high melting points and poor solubility in organic solvents.<sup>8,9</sup> Although preparing polyimide membranes with poly(amic acid) is possible, their complexity and uncontrollable fabrication do not make them applicable. Therefore, there is a need to prepare an asymmetric UF membrane by the convenient and economical phase-inversion process. To prepare polyimide membranes by the phase-inversion method, polyimide should be soluble in polar solvents. In recent years, we reported that soluble polyimide can be synthesized by a two-step

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method with bis[4-(3-aminophenoxy)phenyl]sulfone as a diamine and pyromellitic dianhydride as a dianhydride.<sup>10–15</sup>

In this article, we describe the synthesis and characterization of soluble aromatic polyimides. Furthermore, with these soluble polymers, asymmetric UF membranes by the phase-inversion method were prepared and characterized.

## EXPERIMENTAL

### Materials

Bis[4-(3-aminophenoxy)phenyl]sulfone (BAPS-m, Wakayama Seika Kogyo, Osaka, Japan) and dianhydrides such as 4,4'-oxydiphthalic anhydride (ODPA, Tokyo Kasei, Tokyo, Japan), pyromellitic dianhydride (PMDA, Aldrich Chemicals, Milwaukee, USA), and 3,3',4,4'-diphenylsulfonetetracarboxylic dianhydride (DSDA, Tokyo Kasei) were purified by recrystallization three times from ethanol and acetic anhydride, respectively. *N*-Methyl-2-pyrrolidone (NMP, Aldrich) was refluxed over calcium hydride and then stored in a sealed, dark flask over molecular sieves. Diamine and dianhydrides that were purified were vacuum-dried at 140°C for 6 h before use. Polyethersulfone (PES, BASF, Ludwigshafen, Germany) and polysulfone (PSf, Amoco, Chicago, USA) were dried at 130°C and used for the preparation of UF membranes. The performances of these two membranes were compared to those of membranes prepared in this work. Dichloromethane (DCM) was purchased from Aldrich and used with no further purification for the preparation of PES and PSf membranes.

### Polymer Synthesis

Polyimide was prepared by the traditional chemical method: A poly(amic acid) solution was synthesized in a glass flask with a mechanical stirrer, a condenser, and a nitrogen inlet tube. BAPS-m was completely dissolved in NMP and then ODPA was precisely added at a 1 : 1 molar ratio in three portions within 30 min. The reaction was carried out overnight at room temperature under a nitrogen atmosphere. A mixture of acetic anhydride and pyridine (volume ratio 2 : 1) was added slowly to the obtained poly(amic acid) and the resulting solution was held at 110°C for 6 h. The polymer was not precipitated during the reaction, which implied that polyimide was soluble in NMP. The

polymer solution was poured into methanol. The precipitates were filtered, washed with methanol and water, and dried at 110°C in a vacuum. The inherent viscosity of polyimide was measured in an NMP solution with a 0.5 g/dL concentration at 30°C. Other polyimides were synthesized by the same procedure as above.

### Measurements

Infrared (IR) spectra of polyimide were examined using a MIDAC Model M 2000. The molecular weight distribution was obtained from gel permeation chromatography (GPC, Water 150 C) with a  $\mu$ -Styragel 10 column (solvent: DMF, standard: polystyrene, flow rate: 1.5 mL/min). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on a TA Instrument under nitrogen at heating rates of 20 and 10°C/min, respectively. All DSCs were run twice and the second run taken for the data. Wide-angle X-ray diffraction (WAXD) was taken for each polymer using a ROTA FLEX RU-200 diffractometer (Rigaku, Tokyo) with wide-angle diffraction  $2\theta$  from 10° to 40°.

### Membrane Preparation

Various concentrations of the polyimide polymer were dissolved in NMP as a solvent for 24 h at 60°C. The homogeneous polymer solution was cast onto a polypropylene nonwoven fabric with a doctor knife gap of 200  $\mu$ m. The membrane was precipitated by immersing in deionized ice-cold water just after casting in an environment of  $65 \pm 5\%$  relative humidity,  $25 \pm 1^\circ\text{C}$ , and evaporation for 0.5 min. After 1 h, the remaining solvent was completely removed from the precipitated membrane by immersing it in deionized water. The PES and PSf membranes used commercially in the separation area were prepared to compare them with the polyimide membranes. DCM was used as an additive to control the solute rejection rate of the PES and PSf membranes.

Cross sections of the precipitated membranes were observed using scanning electron microscopy (SEM, JSM-5410LV). Air-dried membrane samples were fractured under cryogenic conditions using liquid nitrogen. The fractured membranes were coated with gold before SEM photographs were taken.

### Membrane Performances

All membranes were initially subjected to deionized water of 3 kg/cm<sup>2</sup> for 2 h before testing.

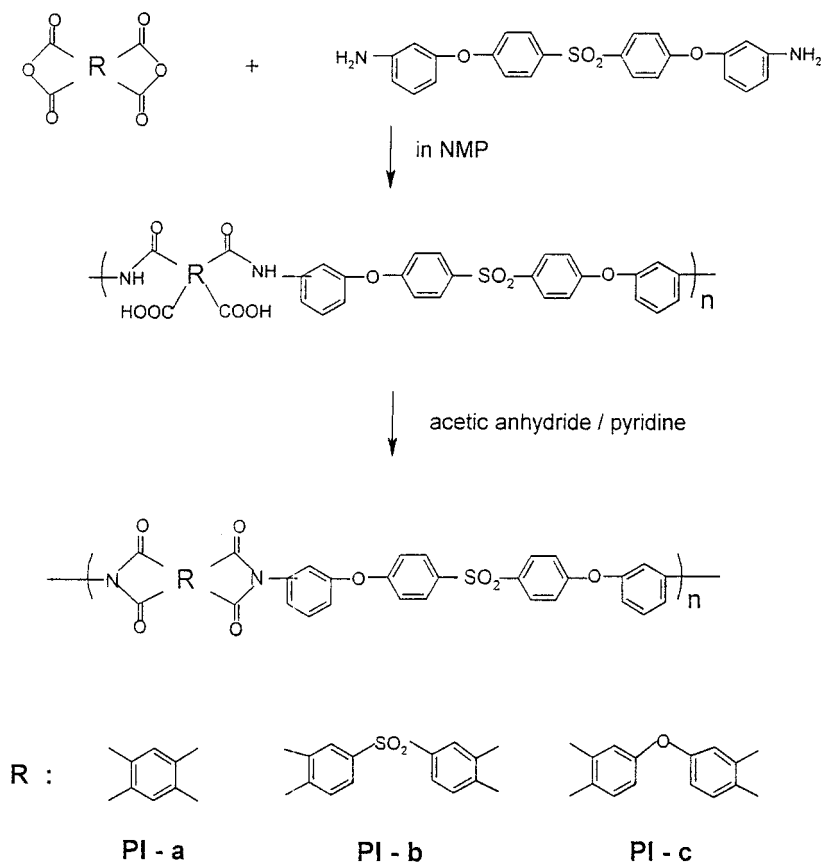


Figure 1 Polyimide synthesis scheme.

Operating conditions were  $25 \pm 1^\circ\text{C}$  and  $1 \text{ kg/cm}^2$ . Poly(ethylene glycol)s (PEG MW 6000, 10,000, and 20,000) were used as solutes ( $1000 \text{ mg/L}$ ) in the feed solution. The solute concentrations in the feed and the permeate were determined by high-performance liquid chromatography (Waters 410) measurements. 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 concentrations in the permeate and in the feed, respectively.

## RESULTS AND DISCUSSION

### Polymer Synthesis

Soluble polyimide was synthesized by the traditional chemical two-step method. The synthetic route is shown in Figure 1. No precipitation took

place during chemical imidization, which implied that the polymer was soluble in NMP. Table I shows the results of the inherent viscosities, molecular weights, and solubilities. Film-forming properties of all the polyimides were good, implying that membranes can be prepared successively by the phase-inversion method. The inherent viscosity and number-average molecular weight of the polyimide synthesized from dianhydride (DSDA) having an electron-withdrawing group (sulfone group) was higher than that of dianhydride (ODPA) having an electron-donating group (ether group). That is the same result as that of Yang et al's report.<sup>16</sup> The structure of the polyimide was confirmed by FTIR. As can be seen in Figure 2, the major peaks at  $1650$  and  $1530 \text{ cm}^{-1}$  assigned to amide I and amide II, respectively,<sup>17</sup> disappeared entirely after imidization. In place of these bands, imide ring absorptions appeared at  $1782$  and  $1370 \text{ cm}^{-1}$ , attributed to the asymmetric and symmetric stretches of the carbonyl group of imide and the C—N band.

**Table I** Inherent Viscosities, Number-average Molecular Weights and Solubilities of Three Polymers

$\eta_{inh}$ (dL/g) <sup>a</sup>	Code	$M_n$ <sup>b</sup>	Solubility <sup>c</sup>					
			NMP	DMAc	DMF	DMSO	THF	Toluene
0.27	PI-a	22000	++	++	++	+	-	-
0.25	PI-b	19000	++	++	++	++	-	-
0.21	PI-c	14000	++	++	++	+	-	-

<sup>a</sup> Measured in NMP at 30°C on 0.5 g/dL.

<sup>b</sup> Number-average molecular weight taken by GPC.

<sup>c</sup> ++, soluble: +, partially soluble: -, insoluble.

### Polymer Properties

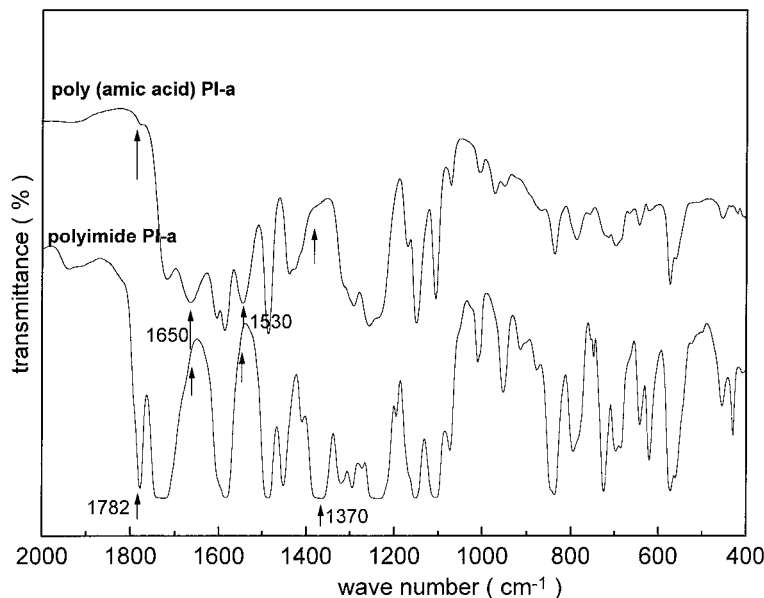
The thermal properties of all the polymers were evaluated by DSC and TGA. Figure 3 shows DSC data of the polyimides. All the polyimides had excellent thermooxidative stability and also showed a high glass transition temperature. The  $T_g$ 's tended to decrease in the order PI-a > PI-b > PI-c. Introduction of the sulfone group in the polyimide main chain results in more intermolecular association (polar interaction) and, accordingly, in a higher  $T_g$ . Furthermore, rotational freedom reduction of the sulfone group around the main chain was higher than that of the ether group. A melting endotherm was not observed, which means the absence of a melting point, which is attributed to the essentially amorphous character. Figure 4 shows the thermal stability by TGA. All the polymers possessed good thermal

stabilities with no significant weight loss up to approximately 420°C in nitrogen. The  $T_g$ 's of the new polymers were found in the range of 420–450°C, indicating good thermal stabilities at highly elevated temperatures. The thermal properties of all the polymers are summarized in Table II.

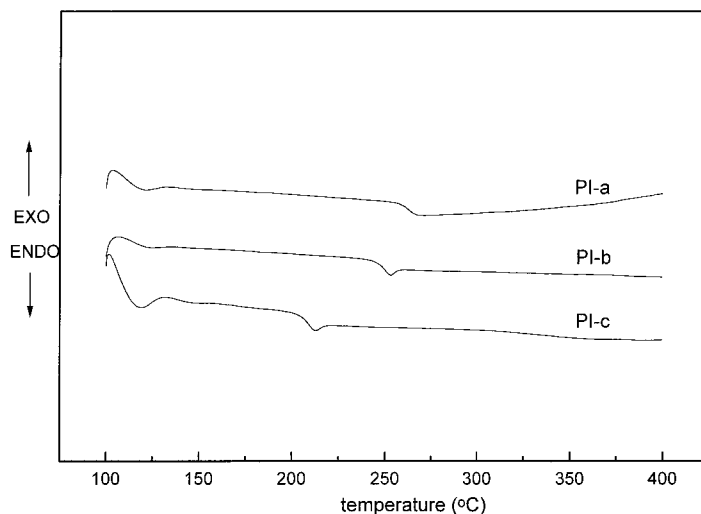
Wide-angle X-ray patterns of the polymers with  $2\theta$  from 10° to 40° are shown in Figure 5. All the polyimides exhibited only one slightly stronger reflection, indicating that they were amorphous. This is due to less stereoregularity of BAPS.<sup>17,18</sup>

### Membrane Preparation and Performances

To prepare an UF membrane with polyimide which is not soluble in organic solvent, poly(amic acid) should be used. This membrane preparation



**Figure 2** FTIR spectra of poly(amic acid) PI-a and polyimide PI-a.

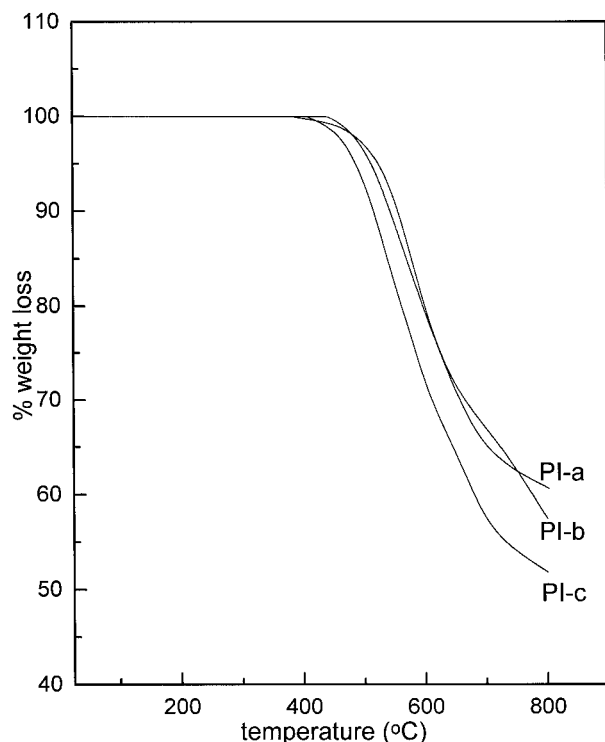


**Figure 3** DSC thermograms (at a heating rate of  $10^{\circ}\text{C min}^{-1}$ ) of three polyimides.

method is very complex and uncontrollable. It is almost impossible to prepare a UF membrane with poly(amic acid) for mass production. UF membranes were prepared by the traditional phase-inversion method, which is very economical and reproducible. A polyimide casting solution dissolved in NMP was cast onto a polypropylene

nonwoven fabric and then immersed into an ice-cold water nonsolvent bath. The polyimides prepared in this study showed good solubilities in polar solvents such as NMP, DMAc, DMF, and DMSO, implying that it is possible to prepare membranes by the dry-wet phase-inversion method.

Figure 6 shows the cross sections of the polyimide membranes. The membranes had straight-forward fingerlike voids in the sublayer and a hyperthin top skin layer in contrast to other polymeric membranes. These SEM pictures indicate the type of liquid-liquid phase separation that occurs, when the polyimide/NMP casting solution is immersed into a water gelation bath, is instantaneous demixing.<sup>19,20</sup> Where a high mutual affinity between solvent and nonsolvent, such as NMP/H<sub>2</sub>O, exists, a porous membrane with high flux is obtained, whereas in the case of low mutual affinity, a nonporous membrane with low flux is obtained.<sup>1</sup> To prepare membranes for UF, mu-



**Figure 4** TGA traces of three polymers. Heating rate is  $20^{\circ}\text{C min}^{-1}$ .

**Table II** Thermal Properties of Polyimides

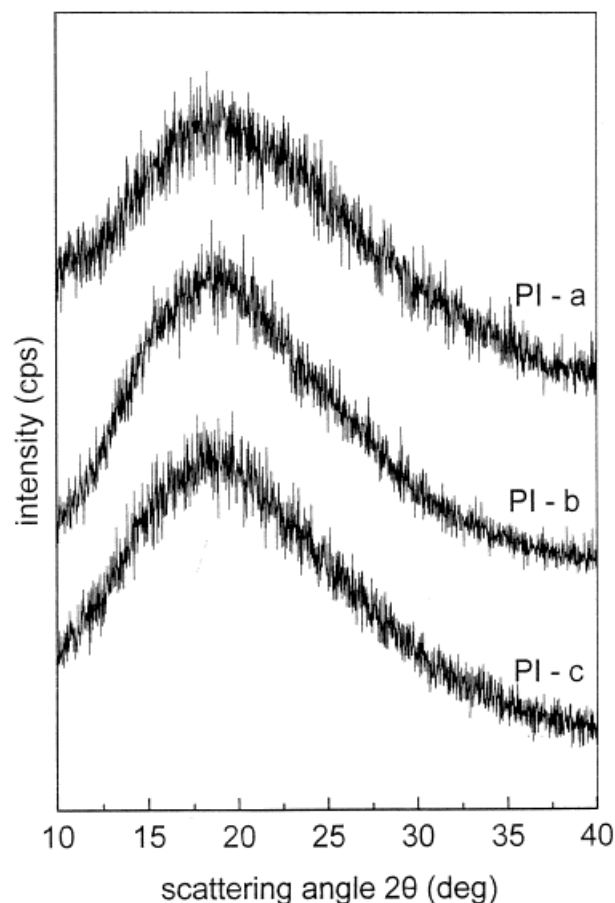
Code	$T_g$ ( $^{\circ}\text{C}$ ) <sup>a</sup>	$T_i$ ( $^{\circ}\text{C}$ ) <sup>b</sup>	$T_{10}$ ( $^{\circ}\text{C}$ ) <sup>c</sup>	$T_{\max}$ ( $^{\circ}\text{C}$ ) <sup>d</sup>
PI-a	267	430	520	610
PI-b	255	450	560	670
PI-c	213	420	510	595

<sup>a</sup> Glass transition temperature from DSC at a heating rate  $10^{\circ}\text{C/min}$ .

<sup>b</sup> Onset decomposition temperature.

<sup>c</sup> Temperature which 10% weight loss was recorded by TGA at a heating rate of  $20^{\circ}\text{C/min}$ .

<sup>d</sup> Maximum polymer decomposition temperature.



**Figure 5** WAXD diagrams of the polyimides.

tual affinity and demixing should be high and instantaneous, respectively. Figures 7–10 show the membrane performances as a function of the polymer concentration. The porous membrane selectivity is determined mainly by the dimensions of the pores but the choice of the material affects phenomena such as adsorption and chemical stability under the condition of actual application and membrane cleaning. This implies that the requirements for the polymeric material are not primarily determined by the flux and rejection but also by the chemical and thermal properties of the membrane material.

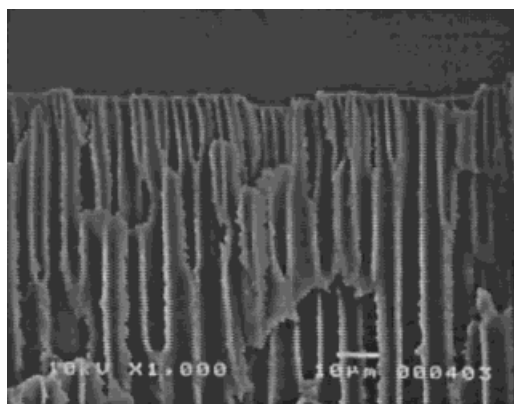
In the case of applications in nonaqueous mixtures or at high temperatures, the chemical and thermal resistances of the polymeric material are the most important factors. The molecular weight of PI-a is higher than that of PI-b and PI-c. This leads to a much higher polymer fraction at the interface compared to that of low molecular weight of polyimide. In general, increasing the initial polymer concentration leads to a much

higher polymer concentration at the interface. This implies that the volume fraction of polymer increases and, consequently, a lower porosity is obtained. Therefore, the pore size of the top layer can be controlled by changing the molecular weight of the polymer and polymer concentration. As a result, the polyimide structure is not related to UF application. However, in the case of gas separation, the polyimide structure can determine the membrane performance (permeability and selectivity). Also, a high  $T_g$  of the polyimide can affect the permeation rate because of the high free volume.

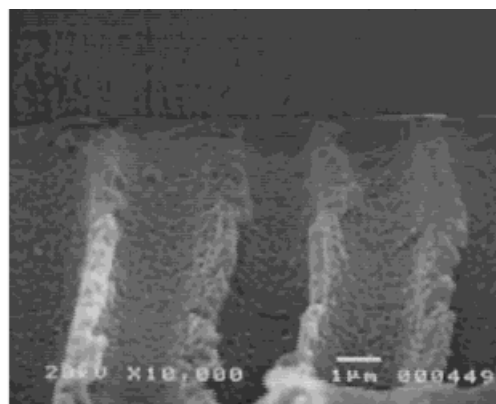
The polyimide membranes prepared in this study show very good membrane performance in contrast to other organic polymers. Pure water flux was very high compared to that of other polymeric UF membranes. Furthermore, polyimide membranes can retain PEG 20,000 to 90% at above 20% polymer concentration. This fact is very specific in the field of UF membranes. As can be seen in Table III, other polymeric membrane materials such as polysulfone and poly(ether sulfone) can retain PEG 20,000 to 90%. However, pure water flux is low ( $60\text{--}120\text{ L m}^{-2}\text{ h}^{-1}$ ) compared to that of the polyimide membranes prepared in our article. This has not been clearly shown up to now. We will expand on this specific UF membrane performance in a future publication.

## CONCLUSIONS

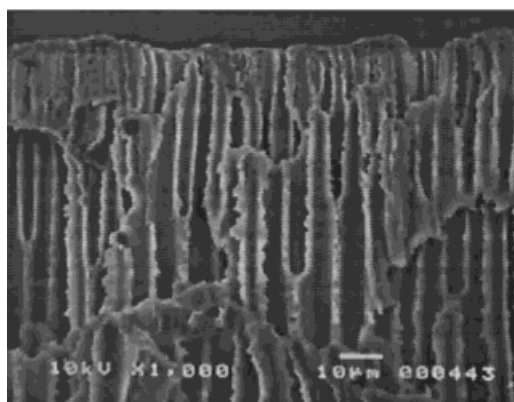
Soluble aromatic polyimides were synthesized by the typical chemical two-step method from BAPS-m as a diamine, and PMDA, ODP, and DSDA, as dianhydrides. They were soluble in polar solvents such as NMP, DMAc, DMF, and DMSO. The inherent viscosities were 0.21–0.27 dL/g. Their  $T_g$ 's were 213–267°C. TGA data showed that all the polymers synthesized had good thermal stabilities; initial weight loss temperature was in the range of 420–450°C. WAXD data indicated that they are all amorphous. UF polyimide membranes were successfully prepared by the traditional phase-inversion method from a polyimide/NMP casting solution. All the membranes had excellent UF membrane performance; a high permeation rate and high solute rejection rate at PEG MW 20,000 was compared to those of other polymeric membranes such as PES and PSf. The cross-section view showed a very thin top layer and a porous sublayer, indicating a very high flux.



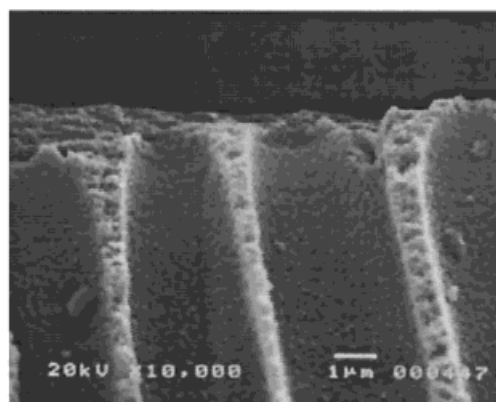
(a)



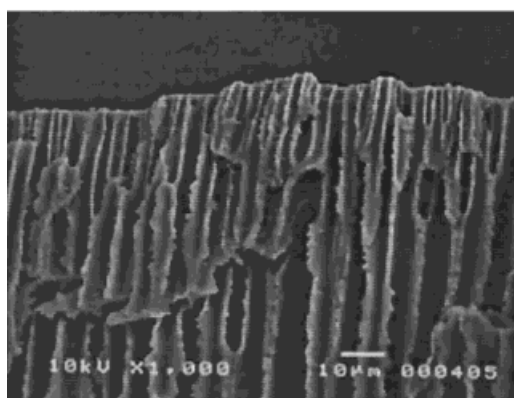
(a')



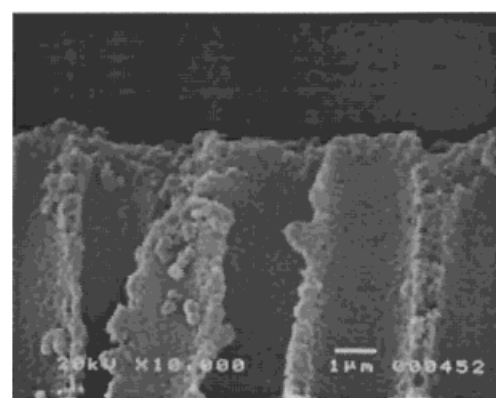
(b)



(b')

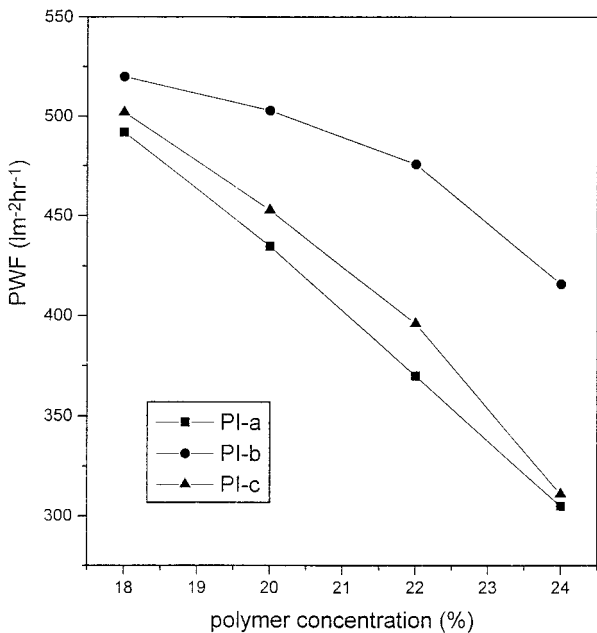


(c)

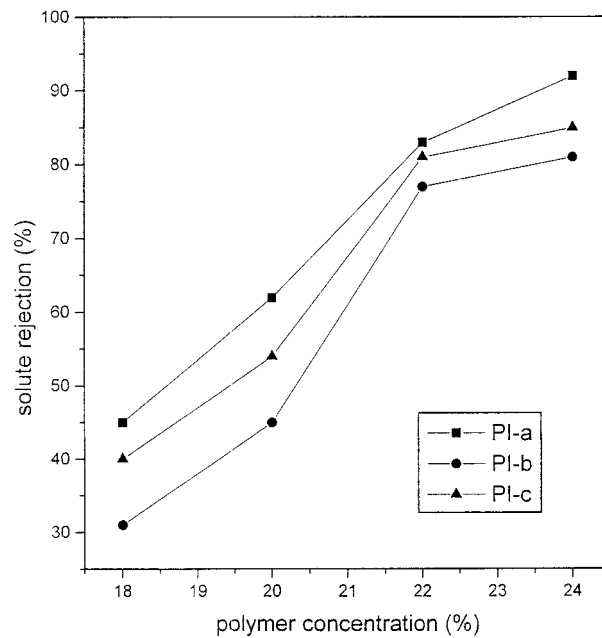


(c')

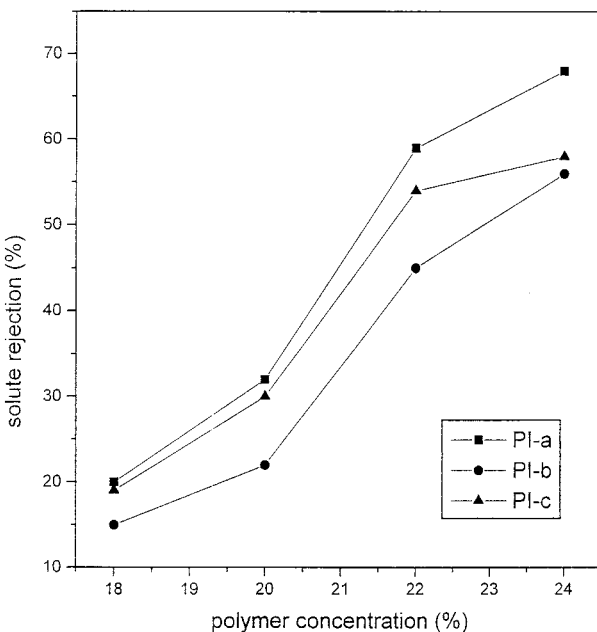
**Figure 6** Cross sections of three polyimides: (a) PI-a; (b) PI-b; (c) PI-c.



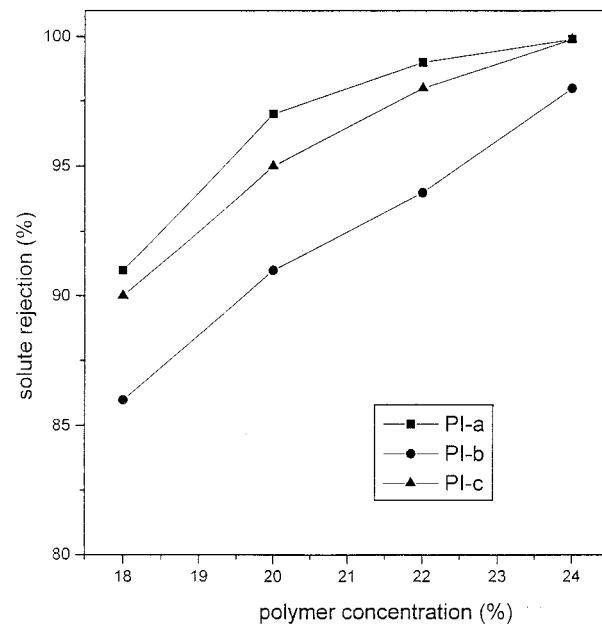
**Figure 7** Pure water permeability as a function of polyimide concentration.



**Figure 9** Solute rejection rate of PEG MW 10,000 for membranes prepared with different concentrations of polyimide.



**Figure 8** Solute rejection rate of PEG MW 6000 for membranes prepared with different concentrations of polyimide.



**Figure 10** Solute rejection rate of PEG MW 20,000 for membranes prepared with different concentrations of polyimide.



**Table III Comparison of the Membrane Performances Between Three Polyimides and Other Polymers**

	PI-a <sup>a</sup>	PI-b <sup>a</sup>	PI-c <sup>a</sup>	PES <sup>b</sup>	PSf <sup>c</sup>
PWF (L m <sup>-2</sup> h <sup>-1</sup> ) <sup>d</sup>	375	470	450	63	95
Solute rejection (%) <sup>e</sup>	98	93	97	94	91

<sup>a</sup> All polyimides membranes were prepared with the casting solution consisted of 22/78 polyimide/NMP.

<sup>b</sup> PES. The casting solution consisted of 22/73/5 PES/NMP/dichloromethane.

<sup>c</sup> PSf. The casting solution consisted of 20/75/5 PSf/NMP/dichloromethane.

<sup>d</sup> PWF was tested in the conditions of pressure 1 kg/cm<sup>2</sup>, flow rate 2.5 L/min, and feed temperature 25°C.

<sup>e</sup> Solute rejection was measured with PEG MW 20,000.

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