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Synthesis of Soluble Anion-Exchange Copolyimides and Nanofiltration Membrane Performances

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ABSTRACT: Novel soluble anion-exchange copolyimides were synthesized by the two-step method. Copolyimides had inherent viscosities between 0.35 and 0.42 dL/g. Ion exchange capacity (IEC) of the polyimides was 0.18−0.33 mequiv/g. These IEC values were well explained with the degree of substitution. All polyimides were soluble in polar solvents such as *N*-methyl-2-pyrrolidone, *N*,*N*-dimethylformamide, and *N*,*N*-dimethylacetamide and showed amorphous patterns in X-ray diffraction studies. Soluble copolyimides synthesized in this study had glass transition temperatures between 220 and 265 °C. All unmodified polyimides were thermally stable below 560 °C. 10% weight loss temperatures were recorded in the range 560−600 °C in nitrogen. However, the 2-hydroxypropyl group of anion-exchange copolyimides was degraded at around 260 °C. The anion-exchange copolyimide nanofiltration membranes prepared from a cosolvent of diethylene glycol dimethyl ether and *N*-methyl-2-pyrrolidone showed better salt removal behavior than that of neutral copolyimides nanofiltration membranes.

Introduction

Aromatic polyimides are important engineering plastics due to their outstanding thermal stability, solvent resistance, and mechanical properties. However, they have the drawbacks of poor solubility in organic solvents and being unprocessable.[1−3] Many attempts have been made to modify the chemical structure of polyimide with the aim of minimizing the shortcomings of aromatic polyimides while preserving their outstanding properties. Several approaches such as introduction of bulky substituents along the polymer backbone[4−6] and incorporation of flexible bridging linkages[7,8] or ortho- or meta-oriented phenylene rings[9,10] led to considerable success in the preparation of soluble polyimides. Moreover, polyimide gas separation membranes have been intensively investigated because of their high permselectivity in order to separate gas mixtures.[11−14] Polyimide membranes can be also used in ultrafiltration separation applications because of their outstanding chemical stability, their excellent strength, and their good thermal stability.[15,16] Recently, we have reported the synthesis of soluble and highly thermally stable homopolyimides and copolyimides by the one-step and the two-step polycondensations. Previous articles described that bis[4-(3-aminophenoxy)phenyl]sulfone with pyromellitic dianhydride was effectively used to prepare a soluble aromatic polyimide.[17−21] Aromatic polymers containing heterocyclic rings such as triazine have good thermal stabilities.[22] However, these polymers are difficult to process due to their limited solublilities, thus improvement of their solublilities has become an important problem. Moreover, there will be cases in which salts should be removed from solutions at high temperatures above 100 °C. Commercially used membranes cannot endure severe conditions such as high temperature and organic solvents. In these cases ion-exchange polyimide membranes should be used.

In this work, we will describe the preparation and the characterization of soluble polyimides containing pyridine rings for anion-exchange polyimide applications. We also report on the modification of heterocyclic soluble copolyimides and their application as a nanofiltration membrane material.

Experimental Section

Materials. Reagent grade *N*-methyl-2-pyrrolidone (NMP) was obtained from Aldrich Chemicals and dried by refluxing over calcium hydride. All other solvents were used as received. Bis[4-(3-aminophenoxy)phenyl]sulfone (BAPS-m) and all dianhydrides (pyromellitic dianhydride (PMDA), 4,4′-oxyphthalic anhydride (ODPA), and 3,3′,4,4′-diphenyl sulfone tetracarboxylic dianhydride (DSDA)) were obtained from Tokyo Kasei Chemicals and purified by recrystallization in ethanol and acetic anhydride, respectively. 1,3-Diaminopyridine (DAP) and epichlorohydrin were purchased from Aldrich Chemicals and used as received.

Procedure. Soluble Anion-Exchange Copolyimide Synthesis. Random copolyimides were synthesized by the typical two-step method (Scheme 1). DAP could be dissolved in NMP by heating to 80 °C due to the poor solubility of DAP in NMP at room temperature. BAPS-m was added in DAP solution cooled to room temperature. Dianhydrides **I**, indicated in Table 1, were added in three portions within 30 min to form random copoly(amic acid)s intermediate **II**; copoly(amic acid) films prepared at 80 °C for 12 h were then thermally imidized to random copolyimides **III**: 2 h at 180 °C, 2 h at 230 °C, and finally 2 h at 270 °C. The resulting copolyimide **III** was dissolved in NMP at room temperature. Excess epichlorohydrin was added to the copolyimide **III** solution. That solution was stirred at 80 °C for 1 day. Modified polymer solution **IV** was cast onto a glass plate to a predetermined thickness of 250 μm with a doctor's knife and dried at 80 °C. Other soluble anion-exchange copolyimides were synthesized in the same way as above by changing the kinds of dianhydrides.

Nanofiltration Membrane Preparation and Performance Measurements. All polyimide nanofiltration membranes were prepared by the typical phase inversion method; a solution of 23 wt % polyimide in NMP and diethylene glycol dimethyl ether[23] (DGDE) as a cosolvent (NMP/DGDE = 8/2) was cast onto the polypropylene nonwoven fabric by means of a doctor's knife with a gap of adjustable height (200 μm). The proto membrane was prepared by evaporating solvent for 30 s in an atmosphere of air at temperature of 25 °C and relative humidity of 65% and then immersed into the gelation medium

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Scheme 1. Reaction Process for Soluble Copolyimides and Their Modification

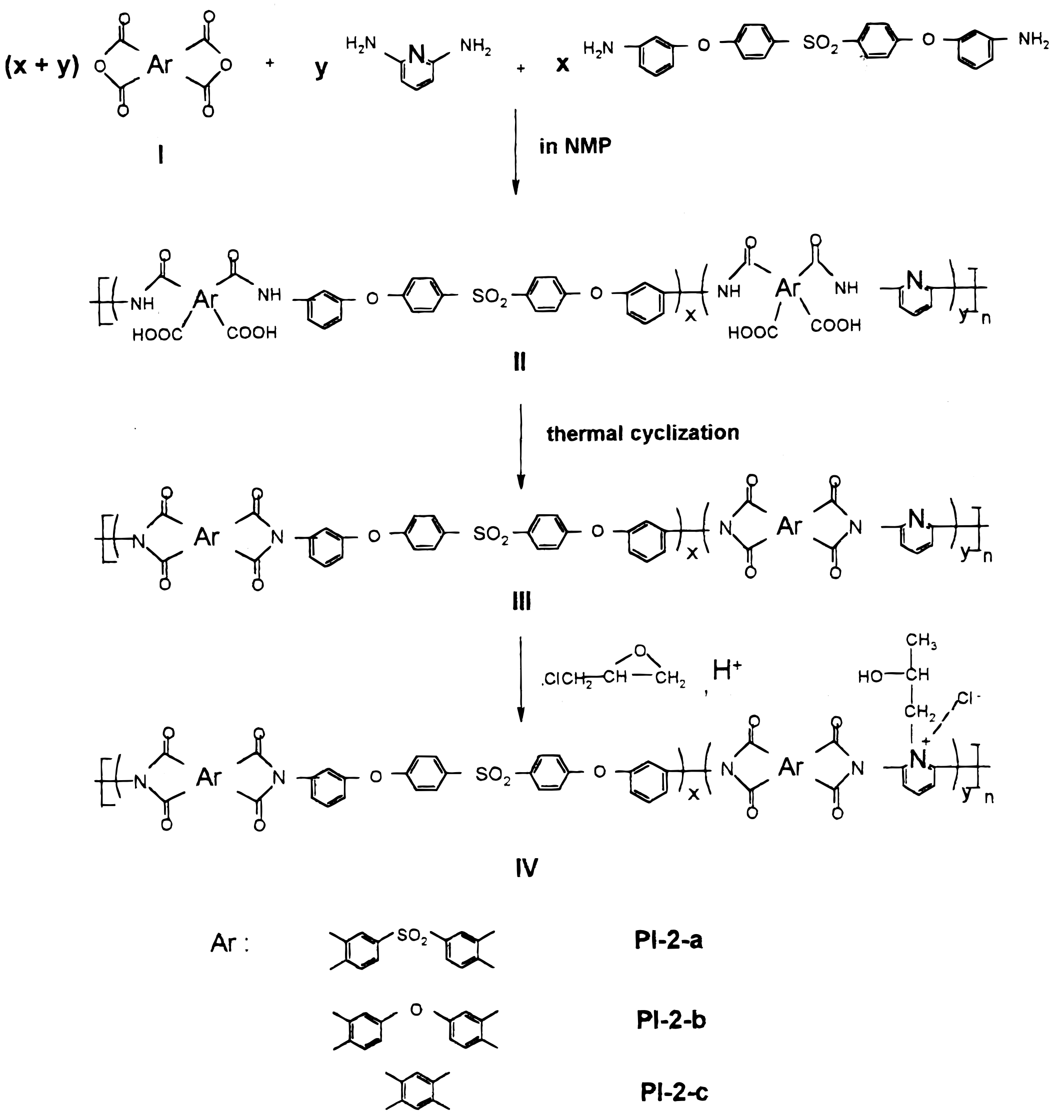
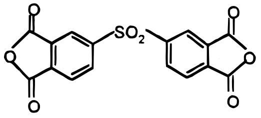
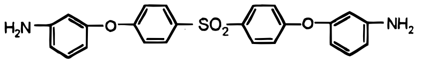
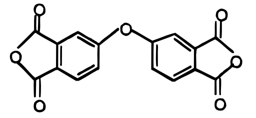
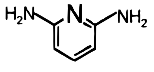
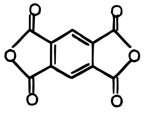


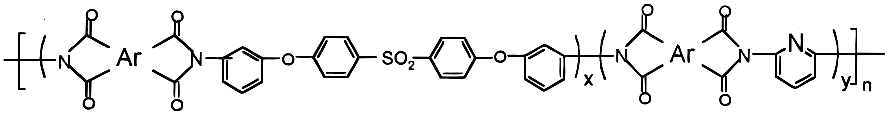
Table 1. Chemical Structures of Dianhydrides and Diamines Used in Polymerization

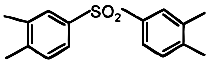
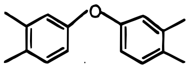
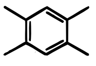
Code	Dianhydrides	Code	diamines
DSDA		BAPS-m	
ODPA		DAP	
PMDA			

of pure water at 4 °C. Membranes obtained in such a way were rinsed in water in order to remove the residual solvents. The permeation rate and solute rejection rate were measured in order to prepare membranes with similar membrane performance. The pure water flux was measured at 200 psi, 2.5 L/min, and 25 °C. The solute rejection rate was measured with PEG 600 under the same conditions as above. The permeate concentration was measured by HPLC equipped with a refractometer. To investigate the salt retention of the anion-exchange copolyimide membrane, 500 ppm of sodium chloride and magnesium sulfate aqueous solution were used as feed solution, respectively. The salt concentration was measured with conductometer. The membrane structures were examined by an Oxford scanning electron microscope (SEM). Membrane samples were fractured in liquid nitrogen and coated with gold to ~150 Å.

Cloud Point and Tie-Line. Polymer solutions with different compositions (1%, 3%, 6%, 10%, 15%) were placed in

Table 2. Molecular Structures and Molar Ratios of Soluble Random Copolyimides



Code	Ar	x	Y
PI-1-a[1)]		0.75	0.25
PI-1-b		0.83	0.17
PI-1-c		0.88	0.12

[1] PI-2 series are 2-hydroxypropyl-substituted polymers in pyridine ring.

Table 3. Relationship between Ion-Exchange Capacity (IEC) and Degree of Substitution of Soluble Ion-Exchange Copolyimides

code	IEC (mequiv/g)[a]	IEC (mequiv/g)[b]	DS[c]	DS[d]
PI-2-a	0.33	0.365	0.226	0.25
PI-2-b	0.24	0.255	0.160	0.17
PI-2-c	0.18	0.201	0.107	0.12

[a] Measured by the Fisher and Kunin method. [b] Predicted values when all of the pyridine rings are substituted: PI-2-a, IEC = 1000(DS/(754−278(DS))); PI-2-b, IEC = 1000(DS/(706−230(DS))); PI-2-c, IEC = 1000(DS/(614−138(DS))). [c] The following equations could be used for predicting DS (degree of substitution) with IEC values: (1) PI-2-a, $DS = (0.75 \times 754 + 0.25 \times 431)IEC/(1000-45(IEC))$; (2) PI-2-b, $DS = (0.83 \times 706 + 0.17 \times 431)IEC/(1000-45(IEC))$; (3) PI-2-c, $DS = (0.88 \times 614 + 0.12 \times 431)IEC/(1000-45(IEC))$. [d] DS values of the unmodified copolyimides.

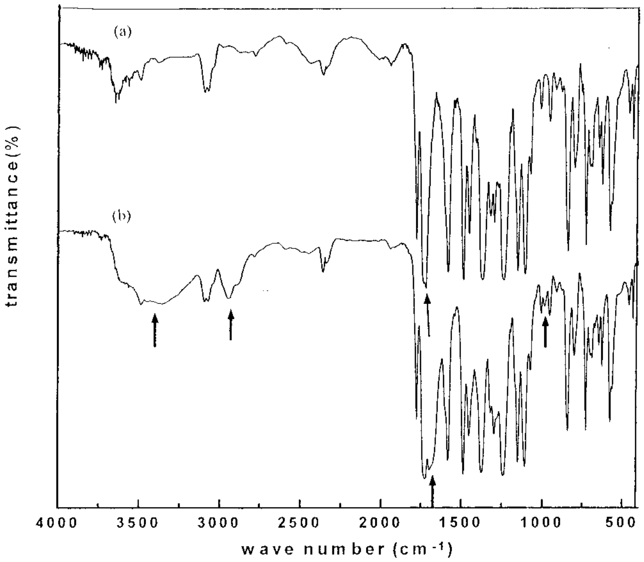


Figure 1. FT-IR spectra of the original copolyimide (a) PI-1-a (DSDA//BAPS/DAP(1.0//0.75/0.25)) and the anion-exchange copolyimide (b) PI-2-a in which PI-1-a is modified with epichlorohydrin.

tubes at 30 °C. Distilled water or a water/NMP mixture (4/1) was added to polymer solutions until turbidity occurred. On the basis of these data, the cloud point curve was determined in a ternary phase diagram. Alliquots of a polymer/NMP/water mixture were kept at 25 °C in a thermostated bath for over a month. The less viscous top layer was withdrawn. The water content in this mixture was determined by gas chromatography. The polymer content of the upper phase was determined from the weight after evaporation to dryness. Tie-line compositions were then calculated through material balance.[24]

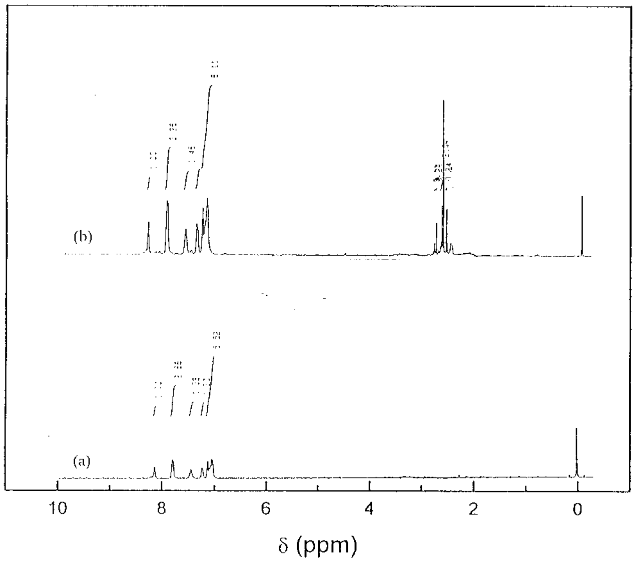


Figure 2. ^{1}H NMR spectra of the copolyimide (a) PI-1-a and the anion-exchange copolyimide (b) PI-2-a.

Characterization. Inherent viscosities of all soluble random copolyimides were measured in NMP at 30 °C using an Ubbelohde viscometer. The polymer concentration was 0.5 g/dL. Molecular weight distribution was obtained from the gel permeation chromatography (GPC, Waters 150 CV) with μ-Styragel 10 column (solvent, DMF; standard, polystyrene; flow rate, 1.5 mL/min). Polymer structure and thermal imidization were confirmed by using a Perkin-Elmer FT-IR. The ion-exchange capacity (IEC) of all copolyimides were evaluated by the back-titration method. A 1 g sample of anion-exchange copolyimide was soaked in 50 mL of 0.1 N HCl for 1 day. The converted polymer with chloride anion was filtered off. The remaining 20 mL of solution was titrated with 0.1 N NaOH using the auto titrator by the procedure described by Fisher and Kunin.[25] Glass transition temperatures (T_gs) shown in Table 3 were measured using a Perkin-Elmer differential scanning calorimeter (DSC) under nitrogen at a heating rate of 10 °C/min. DSCs were run twice and the second run taken for data. To investigate the thermal stability, thermogravimetric analysis (TGA), using a TA instrument, at a heating rate of 20 °C/min in nitrogen was used. Wide-angle X-ray diffraction (WAXD) was taken for each polymer using a ROTA FLEX RU-200 diffractometer (Rigaku, Tokyo) with wide-angle diffraction 2θ from 10 to 40°.

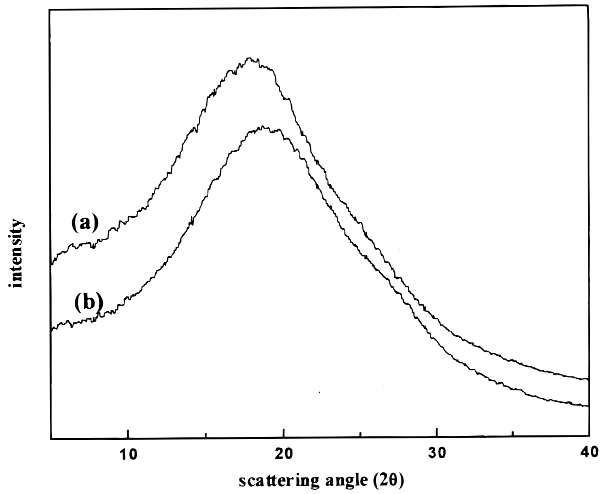


Figure 3. Wide-angle X-ray diffractograms of the copolyimide (a) PI-1-a and the anion-exchange copolyimide (b) PI-2-a.

Table 4. Thermal Properties of Soluble Copolyimides

		decomposition temperature (°C)[b]		
code	T_g (°C)[a]	T_i[c]	T_{10}[d]	T_{max}[e]
PI-1-a	230	570	600	630
PI-1-b	210	510	560	580
PI-1-c	240	560	580	615
PI-2-a	255	260[f]	600	630
PI-2-b	220	280	560	580
PI-2-c	265	260	580	615

[a] Glass transition temperature measured by DSC with a heating rate of 10 °C/min in N_2. [b] Decomposition temperature was measured by TGA with a heating rate of 20 °C/min in N_2. [c] Initial weight loss temperature. [d] 10% weight loss temperature. [e] Maximum weight loss temperature. [f] 2-Hydroxypropyl group was degraded to 1−3 wt % of the original films.

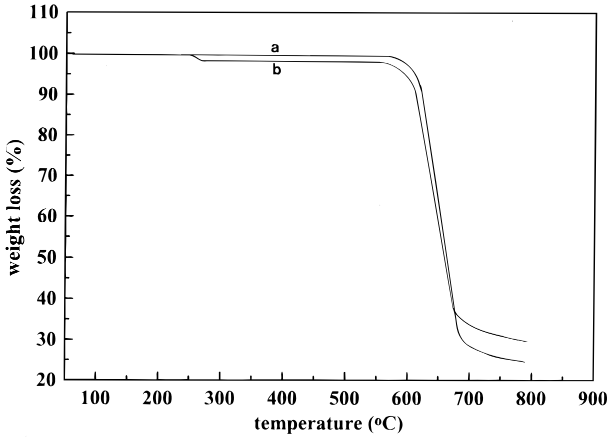


Figure 4. TGA thermograms of the copolyimide (a) PI-1-a and the anion-exchange copolyimide (b) PI-2-a.

Results and Discussion

Preparation of Soluble Anion-Exchange Copolyimides. The conditions to prepare soluble copolyimides were controlled by changing the ratio of BAPS-m and DAP. Table 2 shows conditions for soluble copolyimides. When DAP is used as a diamine, three homopolyimides are not soluble in polar solvents. However, if BAPS is used as a diamine instead of DAP, homopolyimides are soluble in polar solvents. Therefore, the ratio of BAPS-m and DAP at which the resulting copolyimides was soluble varied depending on the kind of dianhydride. This indicates that if more DAP is added in diamine solution, the resulting copolyimides cannot be soluble. DSDA having a dipolar sulfone bridging group increased solubility of the copolyimides compared to ODPA and PMDA. This fact indicates that when DSDA is used as a dianhydride, DAP can be incorporated more in copolyimides compared to that of ODPA- and PMDA-based copolyimides. This resulted in increasing IEC. Moreover, the sulfone group in DSDA activates the dianhydride. Therefore, the reactivity is increased.[2] The inherent viscosities of the copolyimides measured in NMP ranged from 0.35 to 0.42 dL/g. The reactivity of the DAP incorporating a pyridine ring is low. Therefore, as it incorporated the higher part of DAP, the viscosity was

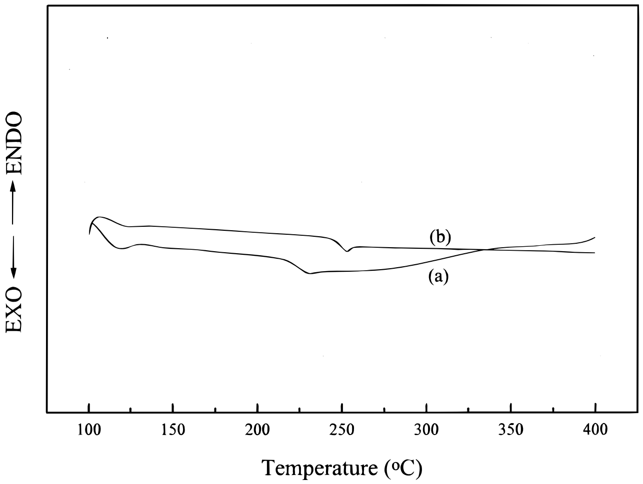


Figure 5. DSC traces of the original copolyimides (a) PI-1-a and the anion-exchange copolyimides (b) PI-2-a.

Table 5. Nanofiltration Membrane Performance

		solute rejection rate (%)		
code	PWF (L/m^2 h)	NaCl	$MgSO_4$	PEG 600
control[a]	132	53	99	99
PI-1-a	85	13	75	91
PI-2-a	91	54	89	96

[a] Hydranautics nanofiltration membrane which is prepared interfacially.

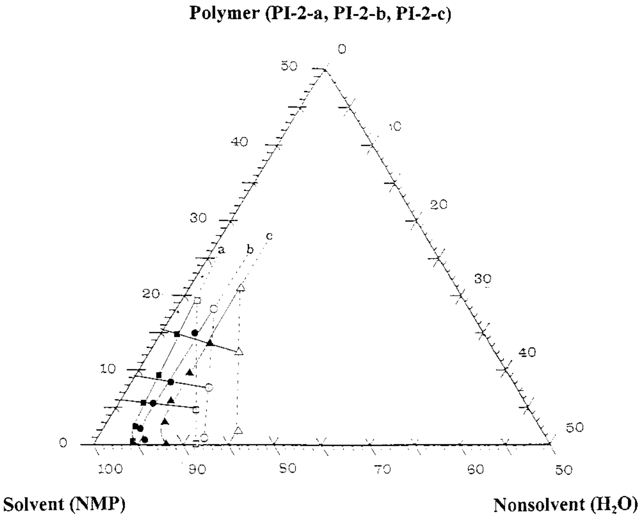
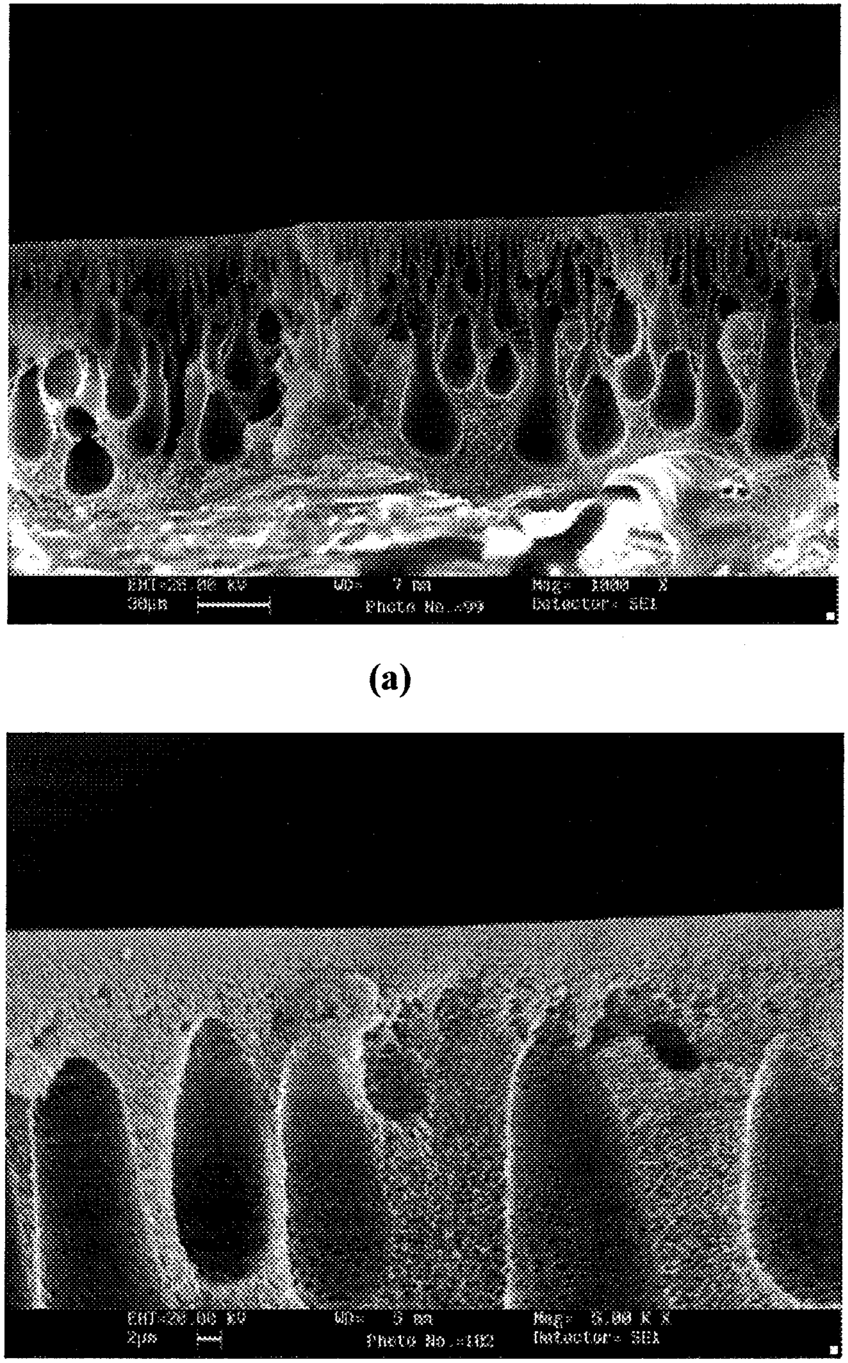


Figure 6. Polymer precipitation curves of (a) PI-2-c, (b) PI-2-b, and (c) PI-2-a. PI-1-a, PI-1-b (ODPA//BAPS/DAP(1.0//0.83/0.17)), and PI-1-c (PMDA//BAPS/DAP(1.0//0.88/0.12) were modified to PI-2-a, PI-2-b, and PI-2-c with epichlorohydrin, respectively.



(a)

(b)

Figure 7. SEM photographs of PI-2-a nanofiltration membranes of (a) cross section (×1000) and (b) skin layer (×5000).

lower than that of BAPS. However, the ether bridge in dianhydride, which is an electron-donating group, makes the reactivity lower. Because of these facts, ODPA was not useful for anion-exchange copolyimides. The thermal conversion of poly(amic acid) to polyimide and the degree of imidization were monitored by FT-IR spectroscopy. The amide I and II peaks (1650 and 1530 cm^{-1}, respectively) disappeared, and the absorption of the imide ring appeared (1782 and 1370 cm^{-1}), instead. According to the band ratio method,[26] namely, the ratio of the absorbance of the asymmetric carbonyl stretch at 1780 cm^{-1} and a reference aromatic stretch at 1500 cm^{-1}, the degree of imidization was analyzed. Figure 1 shows the FT-IR spectra of the unmodified PI-1-a and PI-2-a treated with epichlorohydrin. The hydroxyl and alkyl absorption peaks of PI-2-a were detected at 3400 and 2800 cm^{-1}, respectively. The C−O absorption peak of the hydroxyl could be observed in the range 1000−900 cm^{-1}. In addition, C=N absorption of the pyridine ring appeared in the range 1690−1640 cm^{-1} in both polymers. The 2-hydroxypropyl group could be also observed in ^1H NMR. In Figure 2, alkyl peak around 2−3 ppm could be monitored. Table 3 shows the IEC and degree of substitution (DS). From the definition of IEC and DS, the relationship between IEC and DS could be calculated. As can be seen in Table 3, the 2-hydroxypropyl group was successfully added to the pyridine ring.

Properties of Copolyimides. All three copolyimides synthesized by controlling ratio of diamines show good solubility in organic solvents such as DMAc, NMP, DMF, and DMSO. Moreover, three anion-exchange copolyimides which is modified with epichlorohydrin was also soluble in organic solvents which is meaning that the preparation of polymer solutions render these polyimides sufficiently tractible to permit their conversion from raw material into ultimate membrane configurations.

The crystallinity of the anion-exchange copolyimide films was evaluated by wide-angle X-ray diffraction analysis with 2θ ranging from 10 to 40°. As shown in Figure 3, all anion-exchange copolyimides showed amorphous patterns because of less efficient packing of the chains and less regular structures.

The thermal behavior of the copolyimides was evaluated by DSC and TGA. Table 4 shows the thermal properties of PI-1-a–2-c. TGA measurements were conducted with a heating rate of 20 °C/min in N_2. Anion-exchange copolyimides show a better decomposition behavior than the original soluble polyimides. The decomposition temperatures of PI-1 series incorporating pyridine ring are very high. Below 560 °C in N_2, no weight loss was observed. DSDA-based copolyimides show better thermoresistance. This fact is due to the higher solubility of DSDA-based copolyimides. However, the 2-hydroxypropyl group of anion-exchange copolyimides was degraded at around 260 °C. The weight loss percent of the 2-hydroxypropyl group was 1–3% of the original film. This is shown in Figure 4. The final decomposition of modified polymer begins at around 560 °C, which is almost same with the unmodified polymer. This degradation behavior of modified copolyimide with sulfonated polymers reported by Fu et al.[27] and Kruczek et al.[28] DSC data which is measured with a heating rate of 10 °C/min in N_2 show that anion-exchange copolyimides show higher T_g than the corresponding PMDA, ODPA and DSDA-based original copolyimides. The observed increase in T_g incurred by the introduction of ionic groups is due to the reduction of chain mobility by virtue of their bulkiness and by their ability to act as an interchain ionic cross-link. Anion-exchange copolyimides show T_gs of 220–265 °C. The T_gs of the anion-exchange copolyimides tend to increase in the order PI-2-c > PI-2-a > PI-2-b. Figure 5 shows the T_gs of PI-1-a and PI-2-a.

Nanofiltration Membrane Performances. Table 5 compares membranes prepared in our laboratory with Hydranautics nanofiltration membrane prepared interfacially. The pure water flux was in the range 85–96 (L/m^2 h) at 20 kg/cm^2. The molecular weight cutoff (MWCO) meaning that the solute retention rate of some solute is above 90% was poly(ethylene glycol) 600. Anion-exchange copolyimides showed better salt retention than neutral copolyimides due to the exchange of the anion with the cation incorporated in the anion-exchange copolyimides. By using DSDA and ODPA dianhydrides instead of PMDA, salt retention could be increased. This fact was due to the higher IEC values of DSDA- or ODPA-based copolyimides. Though performance of our membrane is lower than that of the commercial membrane, the polyimide membrane can be used under harsh conditions such as high pH and organic solution where commercial membrane is not available.

The miscibility regions shown in Figure 6 compare the degree of tolerance for water and the capacity of association with water for the original and modified polymers. The miscibility regions of the modified polymers which is more hydrophilic is wider compared to those of the original polymers. This fact indicates the modified polymer–polymer miscibility is lower. Therefore, solvents incorporated between polymers could be easily exchanged with nonsolvents.

Figure 7 shows the cross section structures of the membrane prepared from PI-2-a. Adding the DGDE in the casting solution makes the solvent/nonsolvent exchange difficult. This is the cause of forming thin skin-layer suitable for nanofiltration membranes.

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