

Synthesis and Asymmetric Nanofiltration Membrane Performance of Heterogeneously Sulfonated Aromatic Polyimides

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ABSTRACT: Soluble sulfonated polyimides (PI) were heterogeneously synthesized by reacting soluble PIs with sulfur trioxide and dichloromethane solvent. The sulfonated PIs were soluble in polar solvents like *N*-methyl-2-pyrrolidone (NMP) and *N,N'*-dimethylformamide. The sulfonated PIs were characterized by Fourier transform infrared spectroscopy, proton nuclear magnetic resonance spectroscopy, differential scanning calorimetry, thermogravimetric analysis, triangular phase diagram, and back titration. Asymmetric nanofiltration membranes were prepared by the phase inversion method from the casting solution containing NMP

and diethyleneglycol dimethylether (DGDE). Introducing DGDE as an additive in the casting solution decreased pore size. The rejection rates of organic molecules and salts were investigated. The observed salt rejection of the membrane was of the order $R(\text{Na}_2\text{SO}_4) > R(\text{NaCl}) > R(\text{CaCl}_2)$. The membrane morphology was investigated by scanning electron microscopy. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2483–2489, 2003

Key words: polyimides; membranes; phase diagrams; additives

INTRODUCTION

Aromatic polyimides (PI) are of interest because of their various advantages, such as good mechanical properties, excellent solvent resistance, and thermal stability.^{1–5} However, PIs have application limits due to their processing difficulties and excessively high glass transition temperatures (T_g). The solubility of the PIs can be enhanced by introducing polar groups (amide, ester, ether, or other flexibilizing groups) or bulky substituents along the polymer backbone^{6–8} and by the incorporation of ortho- or meta-oriented phenylene rings.^{9,10}

We have synthesized ultrafiltration membranes with very high flux and 20 kDa molecular weight cut-off (MWCO) using soluble PIs.^{11,12} Moreover, anion-exchange PIs have been prepared by introducing a pyridine ring into the polymer backbone and by modifying with epichlorohydrin.¹³

Introducing additives to the casting solution can decrease the pore size of asymmetric membranes. We have prepared integrally skinned asymmetric polyetherimide nanofiltration (NF) membranes by the phase inversion method and by introducing additives

like diethyleneglycol dimethylether (DGDE), acetic acid, and 1,4-dioxane in the casting solution.^{14,15} However, because of the hydrophobicity of these additives, the flux through the membranes is lower than that through thin film composite NF membranes. Therefore, there is a need to improve the hydrophilicity of the membrane surface. Sulfonation is one method that has been widely used for the improvement of hydrophilicity and for the introduction of charge onto the membrane surface.^{16–19}

In this study, we synthesized and characterized the sulfonated PI NF membranes with small pore size.

EXPERIMENTAL

Materials

Reagent grade *N*-methyl-2-pyrrolidone (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) was purified by recrystallization in ethanol. Pyromellitic dianhydride (PMDA) was obtained from Tokyo Kasei Chemicals and purified by recrystallization in hot acetic anhydride. Sulfur trioxide (SO₃, Aldrich) and triethylphosphate (TEP, Aldrich) were used as received. Diethyleneglycol dimethylether (DGDE), dichloromethane (DCM), poly(ethylene glycol) of varying molecular weight (PEG 200, PEG 400,

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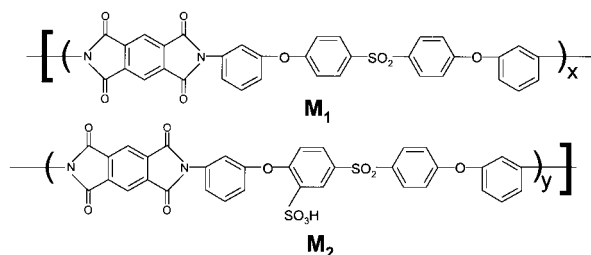


Figure 1 Molecular structure of PI and SPI-3.

PEG 600, and PEG 1000), and salts (NaCl, CaCl₂, and Na₂SO₄) were supplied from Junsei Chemicals (Japan) and used without further purification.

Polymer synthesis

Prior to sulfonation, soluble aromatic PIs were synthesized by a thermal two-step method. BAPS-m was dissolved in NMP at room temperature. A stoichiometric amount of PMDA was added in three portions within 30 min and vigorously mixed for 6 h to yield a homogenous and viscous poly(amic acid) intermediate solution and to reach constant viscosity. The solid content of the resulting solution was 20% by weight. Poly(amic acid) films prepared by evaporating NMP at 80°C for 12 h were then thermally imidized in a dry oven. Imidization conditions were as follows: 2 h at 180°C, 2 h at 230°C, and 2 h at 270°C. The PIs were sulfonated with SO₃. Before sulfonation, ₂SO₃·TEP complex was prepared by dissolving 0.5 mol of SO₃ in 0.25 mol of TEP for 48 h with vigorous stirring. The color of the solution turned a deep red. An amount of the sulfonating agent (₂SO₃·TEP) that was equimolar to the repeating unit of PI was added with a dropping funnel. Because PIs are not soluble in DCM, sulfonation was carried out heterogeneously at 25°C. The reaction time was varied as follows: 2 h for SPI-1, 4 h for SPI-2, and 6 h for SPI-3. The reacted PIs were filtered and then dried at 130°C for 12 h.

Polymer characterization

Ion-exchange capacity (IEC) was determined by converting the sulfonic acid group to sodium sulfonate with 0.1 N NaOH and by titrating with 0.1 N HCl according to the procedure described by Fisher and Kunin (back titration method).²⁰ The repeating units of sulfonated and nonsulfonated PIs are shown in Figure 1. Degree of sulfonation (DS) was calculated from the IEC as follows: the definition of DS is

$$DS = y/(x + y) \quad (1)$$

where x and y are the repeating unit of PI and sulfonated PI, respectively. The definition of IEC is

$$IEC = 1000y/(M_1x + M_2y) \quad (2)$$

where M_1 and M_2 are the molar mass of repeating unit of PI and sulfonated PI, respectively. Combining eqs. 1 and 2 results in eq. 3:

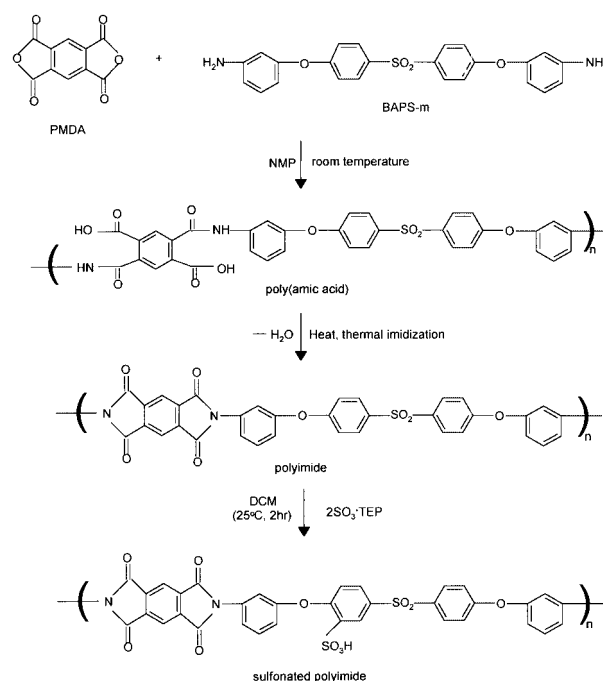
$$DS = M_1IEC/(1000 + IEC(M_1 - M_2)) \quad (3)$$

The Fourier transform infrared (FTIR) spectrum of PI was measured with a MIDAC model M2000 over the absorption range 4000–400 cm⁻¹. Characteristic major absorption bands at 1650, 1530, and 1720 cm⁻¹, corresponding to amide I, amide II, and the acid carbonyl group of poly(amic acid), respectively, completely disappeared. In their place, the absorption bands of the imide ring appeared at 1780, 1720 (carbonyl groups of imide ring), and 1370 cm⁻¹ (C–N group of imide ring).

Proton nuclear magnetic resonance (¹H-NMR) spectra were recorded for solutions in d₆-DMSO, employing ¹H measurements, with a Varian VXR 200 instrument operating at 50.42 MHz. DS was calculated from the ¹H-NMR spectra; that is, by evaluating the ratios between the peak area of aromatic proton located next to sulfonate group and the peak area of the other hydrogens, DS is obtainable.²¹

Differential scanning calorimetry (DSC; DSC 2910) was conducted under a nitrogen atmosphere at a heating rate of 20°C/min. All DSC scans were run twice, and the data from the second run were used.

Thermogravimetric analysis (TGA, Dupont model 951), at a heating rate of 20°C/min in nitrogen, was



Scheme 1 Reaction route of sulfonated polyimide.

TABLE I
Ion-Exchange Capacity (IEC) and Degree of Substitution (DS) of Soluble Cation-Exchange PIs

Code	Reaction time (h)	IEC (meq/g)	DS ^a	DS ^b
SPI-1	2	0.22	0.14	0.15
SPI-2	4	0.35	0.22	0.25
SPI-3	6	0.41	0.26	0.29

^a Calculated by the back titration method.

^b Calculated by the ¹H-NMR spectra method.

used to investigate thermal stability. The tests of solubility were performed in various solvents for 7 days at room temperature.

Cloud point and tie-line

Polymer solutions (1, 3, 6, 10, and 15 wt %) were placed in tubes at 30°C. In the cases of the polymer solutions with low polymer concentration (1 and 3 wt %), distilled water was slowly added until turbidity occurred. Water/NMP (4/1) was added to the other polymer solutions until turbidity occurred. The composition at the onset of turbidity, the so-called cloud point, represents the transition concentration between one-phase and two-phase regions. The cloud point curve can be interpreted as the binodal in a ternary phase diagram. Aliquots of a polymer/NMP/water mixture at its cloud point composition were kept at 25°C in a thermostatic bath for >1 month. Turbid polymer solutions developed into two clear liquid layers. The less viscous top layer was withdrawn, and the water content was determined by gas chromatography (GC). The polymer content of the upper phase was determined from the weight after evaporation to dryness, but the top and the bottom layers were separately removed and dried for 2 days until a constant weight of the polymer residue was observed. Tie-line compositions were then calculated by the method of material balance.^{22,23}

Membrane preparation

Asymmetric membranes were prepared by the phase inversion method. A casting solution was prepared by dissolving 20 wt % sulfonated PI in an NMP/DGDE mixture. Then, the solution was coated onto non-woven fabric (polyester). The nascent membrane was immersed into ice-cold water.

Membrane performance measurement

The flux was measured at 225 psi, a flow rate of 1.0 L/min, and a temperature of 25°C. The rejection rate of organic solute was measured with PEG 200, PEG 400, PEG 600, and PEG 1000 at the same conditions as just described. The feed concentration was 1000 ppm

in pure DI water. Salt rejection rate was measured with NaCl, CaCl₂, and Na₂SO₄ of different concentrations. The feed and permeate concentrations were measured by HPLC (Waters Company) with a chromatograph equipped with a refractometer.

Morphology of asymmetric membranes

The morphology (cross section and top layer) of asymmetric membranes was observed with a scanning electron microscope (SEM, JSM 1025, JEOL). The membranes were cryogenically fractured in liquid nitrogen and then coated with gold.

RESULTS AND DISCUSSION

Synthesis and characterization of sulfonated PIs

Synthesis

PI from PMDA and BAPS-m was heterogeneously sulfonated. We chose the 2SO₃·TEP complex instead of other sulfonation reactants, such as sulfuric acid and chlorosulfonic acid, because the latter degrade the polymer backbone, resulting in weak physical properties and shorter molecular chains. The reaction procedure for cation-exchange PIs containing sulfonic acid groups is shown in Scheme 1. Unfortunately, the synthesized PI was not soluble in chlorinated hydrocarbons, like DCM and dichloroethane, which were used as sulfonation solvents. Therefore, the reaction had to be carried out heterogeneously. IEC and DS values were dependent on the reaction time. The IEC values of the polymers are shown in Table I with reaction times. Even though IEC values were not high enough, a precipitation step could be omitted; therefore, the sulfonated polymers were filtered and dried without a precipitation step.

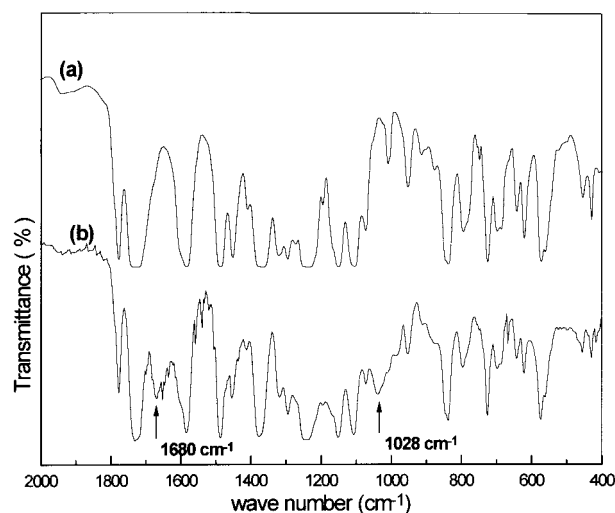


Figure 2 FTIR spectra of (a) PI and (b) SPI-3.

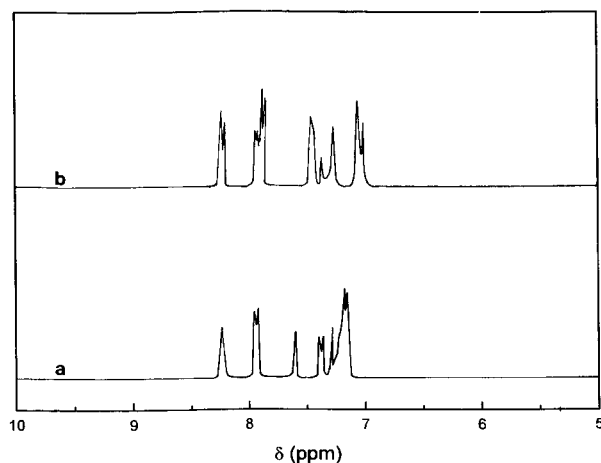


Figure 3 $^1\text{H-NMR}$ spectra of (a) PI and (b) SPI-3.

Characterization

The IEC and DS values of the sulfonated PIs obtained from back titration and by $^1\text{H-NMR}$ spectrum method with varying reaction times are also shown in Table I. Quantitative calculation of DS was possible by the back titration method.²⁰ In addition, these IEC and DS values show that the sulfonic acid groups were successfully substituted in the PI main chains. The measured value determined by the back titration method was lower than that determined by the $^1\text{H-NMR}$ spectrum method. Only surface ionic groups could be detected by the back titration method; that is, interior ionic groups could not be measured. However, when the $^1\text{H-NMR}$ spectrum method was used, all the sul-

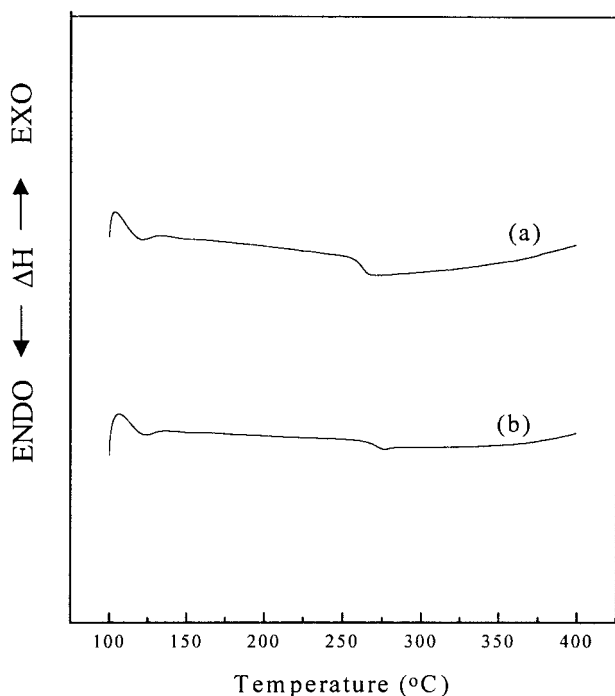


Figure 4 DSC traces of (a) PI and (b) SPI-3.

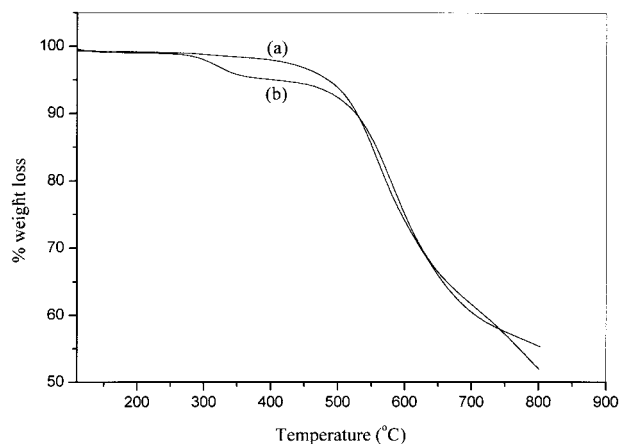


Figure 5 TGA thermograms of (a) PI and (b) SPI-3.

fonic acids were measurable because of the homogeneity of the polymer solution in DMSO.

FTIR and $^1\text{H-NMR}$ spectra in Figures 2 and 3, respectively, confirm the existence of sulfonic acid groups in the PI main chain. The FTIR spectrum in Figure 2 shows the typical absorption peaks of sulfonic acid groups at 1680 and 1028 cm^{-1} . In general, by introduction of sulfonic acid groups in the main chains, the band at 1028 cm^{-1} became evident by FTIR spectroscopy. The $^1\text{H-NMR}$ spectra of sulfonated and nonsulfonated PIs are compared in Figure 3. Sulfonic acid groups caused a downfield shift of aromatic hydrogen. The proton attached to the aromatic group of 7.50 ppm was shifted downfield to ~ 7.85 ppm. This downfield shift is attributed to the attachment of electron-withdrawing sulfonic acid group to the aromatic carbon. In our experiments of heterogeneous sulfonation of soluble PI, the results of FTIR and $^1\text{H-NMR}$ measurement indicate the introduction of a sulfonic acid group in the ortho-position at the aromatic ring.

In addition, the T_g (Figure 4) and thermal stability (Figure 5) of cation-exchange PIs containing sulfonic acid groups were examined by DSC and TGA, respectively. According to the results in Figure 4, the T_g of the sulfonated PI is higher than that of the nonsulfonated PI. This result confirms that the introduction of sulfonic acid groups to the aromatic carbon causes hydrogen bonds to form and, as a result, the T_g of the sulfonated polymer increases. The T_g increase can be

TABLE II
Thermal Properties of PI and SPIs

Code	IEC (meq/g)	T_g ($^{\circ}\text{C}$)	Decomposition temperature ($^{\circ}\text{C}$)		
			T_i	T_{10}	T_{max}
PI	0	244	481	505	660
SPI-1	0.22	256	295	520	650
SPI-2	0.35	261	305	510	660
SPI-3	0.41	270	310	510	640

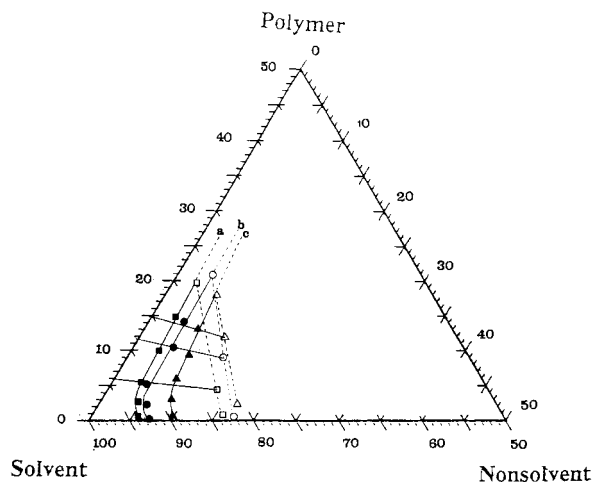


Figure 6 Phase diagrams of (a) PI, (b) SPI-2, and (c) SPI-3.

explained by the reduction of rotational freedom around the polymer main chains due to sulfonic acid groups. TGA curves in nitrogen, shown in Figure 5, exhibit two-stage degradation patterns. The sulfonated PI was first degraded at $\sim 200^\circ\text{C}$. This pattern may be attributed to the decomposition of the substituted sulfonic acid groups. The observed first weight loss increased with an increase in IEC values of sulfonated PIs. The second decomposition behavior was similar to that of the original polymer. Maximum weight loss temperature was relatively similar with IEC values. The results of DSC and TGA data and the IEC values are summarized in Table II.

All the sulfonated PIs showed good solubility in organic solvents, such as DMAc, NMP, DMF, and DMSO. However, the sulfonated PIs were insoluble in other solvents.

The miscibility regions, determined from polymer cloud points data, indicate the resistance to water with IEC or DS values and the capacity of the polymers to associate with water. The miscibility regions of the polymer solution become wider with increasing DS values, as clearly shown in Figure 6. The miscibility regions may be correlated with the flux of UF membranes. Association with more water means that precipitation in the coagulation bath can occur more quickly. Therefore, with increasing IEC values, faster instantaneous demixing can occur. The resulting membranes have an open porous structure. Moreover, the hydrophilic sulfonic acid groups increase the pure water flux by the increased driving force that results from the formation of hydrogen bonds with water and the enhancement of hydrophilicity. The UF membrane performance prepared from the polymers with different IEC values is shown in Table III. As shown, with increasing IEC values, the flux of membranes increased and the rejection rate decreased.

TABLE III
UF membrane Performance of PI and SPIs

Code ^a	IEC (meq/g)	PWF (L/m ² h) ^b	Rejection rate (%) ^c
PI	0	450	95
SPI-1	0.22	470	92
SPI-2	0.35	510	85
SPI-3	0.41	540	79

^a UF membrane was prepared by casting a solution of polymer/NMP (20/80 wt %).

^b Pure water flux measured at 2 kg/cm² and 25°C.

^c Measured with 1000 ppm aqueous solution of PEG 20 kDa.

Preparation and performance measurement of asymmetric NF membrane

The organic molecule and the salt rejection rate of NF membranes are shown in Figures 7 and 8, respectively. The NF membranes were prepared by the phase inversion method with the PIs and the sulfonated PIs. DGDE was used as an additive to decrease pore size. A small amount of water can be detrimental for making pores for nanofiltration. Therefore, water in DGDE should be almost completely removed. We prepared NF membranes with a different amount of DGDE in the casting solution. The formulation composition of casting solution for MWCO PEG 600-1000 was SPI-2/NMP/DGDE (20/32/48wt%). The pure water flux was in the range 85–96 L/m²h at 225 psi. As shown in Figure 7, the molecular weight of PEG for 90% rejection rate was 600, which means that the MWCO of the SPI-2 membrane was PEG 600. DGDE can form a sharp instantaneous film during precipitation in nonsolvent water. Therefore, the nonsolvent cannot easily penetrate into the casting solution during phase inversion. Instead, NMP and DGDE in the casting solution diffuse out of the coagulation bath. In general, if the penetration rate of nonsolvent of coagulation bath is

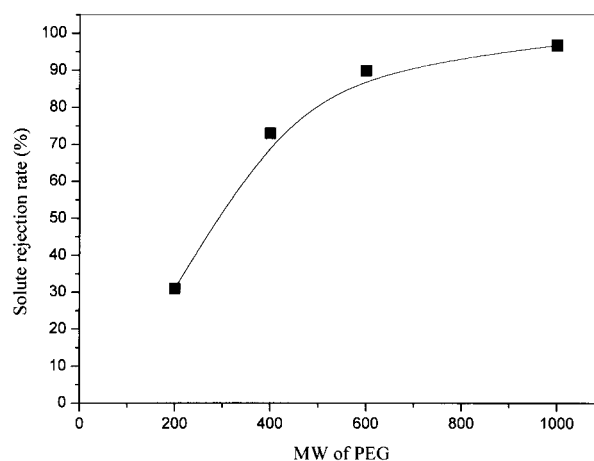


Figure 7 Rejection rate of different PEGs of SPI-2 membrane.

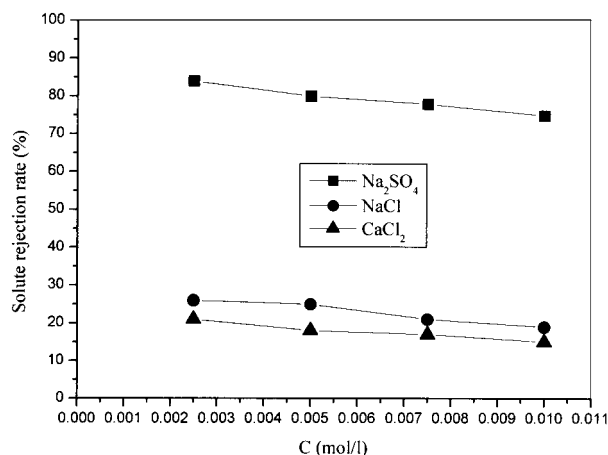


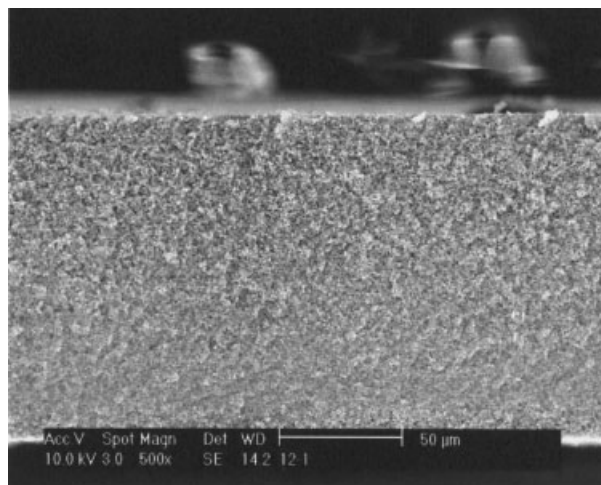
Figure 8 Rejection rate of different salts as a function of the feed concentration for an SPI-2 membrane.

faster than that of solvent, a membrane with denser skin layer can be formed. The salt rejection measurements of Figure 8 show that the behavior of the membranes can be classified into negatively charged NF membranes. In other words, the salt rejection sequence was of the following order: $R(\text{Na}_2\text{SO}_4) > R(\text{NaCl}) > R(\text{CaCl}_2)$. This behavior of salt rejection of the anionic membrane cannot be explained by the size exclusion effect. Instead, Donnan exclusion theory must be introduced. Although the size of hydrated calcium ions, shown in Table IV, is larger than that of sodium and chloride ions, the rejection rate of CaCl_2 was lower than that of NaCl . According to Donnan exclusion equilibrium, the Donnan equilibrium is dependent on the valence of the co-ion and the counterion. In other words, a divalent co-ion (sulfate ion) is much more rejected by the membrane than a monovalent co-ion (chloride ion). For two salts having the same co-ion, the membrane is richer in the divalent counterion (calcium ion) than the monovalent counterion (sodium ion). The observed salt rejection sequence reflects the Donnan equilibrium and the electroneutrality.

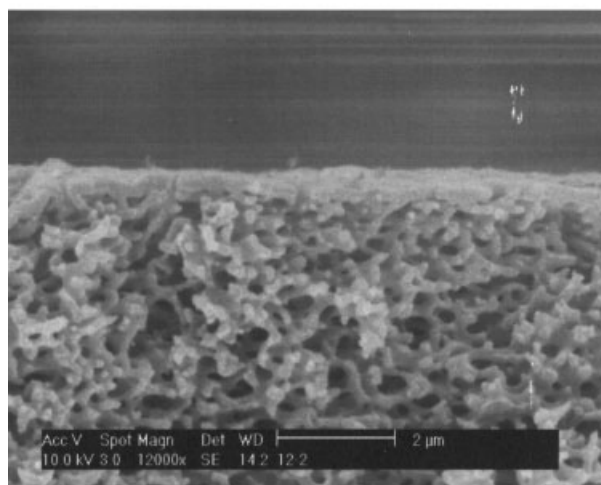
The morphology of the resulting NF membrane (SPI-2) is shown in Figure 9. We investigated the cross-sectional view of PI UF membrane prepared from the casting solution of PI/NMP.^{17,18} The membrane showed a straightforward finger-like structure. By introducing DGDE in the casting solution, the cross-

TABLE IV
Diffusion Coefficients and Hydrodynamic Radii for Several Ions in Water

Ion	D (10^{-9} m ² /s)	R (Å)
Na ⁺	1.33	1.64
Cl ⁻	2.03	1.07
Ca ²⁺	0.92	2.37
SO ₄ ²⁻	1.06	2.05



(a)



(b)

Figure 9 SEM photograph of an SPI-2 membrane: (a) cross-section ($\times 500$) and (b) top layer ($\times 12,000$).

section of the membrane changed significantly. The total cross-sectional view of the SPI-2 NF membrane shows a sponge-like structure instead of a finger shape one. A magnified view shows a very thin skin layer and an open porous sub-layer. This morphology explains why the flux of the asymmetric SPI-2 NF membrane is high. Obviously, DGDE as an additive in the SPI-2 casting solution decrease the pore size.

CONCLUSIONS

Soluble sulfonated polyimide was successfully synthesized by a heterogeneous sulfonation method with $2\text{SO}_3\cdot\text{TEP}$ complex under DCM solvent. The T_g increased with IEC values. Sulfonic acid groups were

degraded at $\sim 300^{\circ}\text{C}$., The IEC values were dependent on reaction time. The NF membrane was prepared by the phase inversion method. The introduction of DGDE as an additive in the casting solution significantly decreased the pore size. The MWCO of the membrane was PEG 600–1000. The salt rejection behavior was explained by the Donnan exclusion theory instead of the size exclusion theory. The membrane shows a very thin skin layer and an open porous sublayer.

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