

Synthesis and Characterization of Poly(amide–Imide)s and Their Precursors as Materials for Membranes

A. V. RAMI REDDY

Separation Technology Division, Central Salt and Marine Chemicals Research Institute, Bhavnagar 364 002, India

Received 5 March 1999; accepted 16 April 1999

ABSTRACT: Water soluble diamine amic acids (DAAs) were synthesized by reacting aliphatic diamines with pyromellitic dianhydride. Poly(amide–amic acid)s (PAAs) were prepared by interfacial polycondensation of DAAs in aqueous sodium hydroxide solution with isophthaloyl chloride in dichloromethane. Poly(amide–imide)s (PAIs) containing alternating (amide–amide)–(imide–imide) sequences were obtained by thermal cycloimidization of the PAA films at 175°C for 4 h in a forced air woven. The PAIs were readily soluble in polar aprotic solvents such as dimethylformamide, dimethylacetamide, dimethylsulfoxide, and *N*-methyl-2-pyrrolidone. The inherent viscosities of the polymers are in the range of 0.97–1.7 dL/g. The polymers were characterized by IR, ¹H nuclear magnetic resonance (NMR), and thermogravimetric analysis (TGA). Thin film composite membranes containing PAA ultrathin barrier layer were prepared by *in situ* interfacial polycondensation of DAA in water with trimesoyl chloride or isophthaloyl chloride in hexane on the surface of a porous polysulfone membrane. The membranes were characterized for water permeability and for the separation of NaCl and Na₂SO₄. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1721–1727, 2000

Key words: poly(amide–imide)s; composite membranes; interfacial polymerization

INTRODUCTION

In recent years, membrane separation techniques have been widely employed in processes of the chemical, medical, and food industries, environmental engineering, and so on. The performance of the membrane for any specified application depends strongly on the physical structure of the membrane as well as the chemical nature of the polymer. The physical structure of the membranes is strongly dependent on their preparation conditions such as polymer concentration, nature of the solvent, additives in the casting solution, casting temperature, and casting thickness. The relationships between preparation conditions and structure and performance of the membranes have been described by several researchers.^{1–5}

The successful application of membrane technology for various separation applications depends upon the availability of high-performance membranes tailored for each specific purpose. The salient features of polymers suitable as membranes are the inherent chemical, mechanical, and thermal properties, and their processability. Moreover, membranes suitable for materials separation should exhibit high permeability and high separation capability. Polysulfones, poly(vinylidene fluoride), polyamides, polyimides, poly(amide–imide)s (PAIs), and so on, are reported to be the most versatile class of polymers useful for a broad spectrum of membrane applications.^{6–10} As the range of applications expands, improved and cheap membranes with enhanced chemical stability and active life are sought.

In continuation of our work on PAIs^{11,12} for membrane applications, the preparation and characterization of novel soluble PAIs with alter-

nating (amide–amide)–(imide–imide) sequences by interfacial polymerization, and composite membranes containing poly(amide–amic acid) (PAA) ultrathin barrier layer by *in situ* interfacial polycondensation of diamine amic acids with a multifunctional acid chloride are reported in this paper.

EXPERIMENTAL

Materials

Pyromellitic dianhydride (PMDA), ethylenediamine (EDA), 1,2-diaminopropane (DAP), 1,3-propanediamine (PDA), 1,6-hexanediamine (HDA), *N*-(2-aminoethyl)piperazine (AEP), isophthaloyl chloride (IPC), and trimesoyl chloride (TMC) from Aldrich were used as received. All other reagents and solvents (AR grade) were obtained from various commercial sources and used without further purification.

Synthesis

Diamine Amic Acids (1–5)

In a typical procedure, the synthesis of *N,N'*-bis-(2-aminoethyl)terephthalamido-2,5-dicarboxylic acid (AETDC) from EDA and PMDA is described as follows. A mixture of PMDA (10.91 g) and 100 g of pure EDA was stirred at 5–10°C for 1 h, and at room temperature for 2 h. The solid AETDC was then filtered, washed with chloroform, and recrystallized from water–methanol mixture.

Similarly, *N,N'*-bis[(1-methyl-2-amino)ethyl]terephthalamido-2,5-dicarboxylic acid (MAETDC) or *N,N'*-bis[(2-amino-2-methyl)ethyl]terephthalamido-2,5-dicarboxylic acid (AMETDC), *N,N'*-bis(3-aminopropyl)terephthalamido-2,5-dicarboxylic acid (3APTDC), and *N,N'*-bis(2-piperazinyethyl)terephthalamido-2,5-dicarboxylic acid (PETDC) were obtained by the reaction of PMDA with DAP, PDA, and AEP, respectively. However, *N,N'*-bis(6-aminoethyl)terephthalamido-2,5-dicarboxylic acid (AHTDC) was obtained by the reaction of PMDA with a 4 M solution of HDA in dioxane (200 mL) under the similar conditions explained in the preparation of AETDC. The purity of the diamine amic acids (DAA) was verified by high-pressure liquid chromatography (HPLC) and was found to be above 96%. The melting points and the physico-chemical characteristics of the DAA are as follows:

1. AETDC: mp 200–202°C decompose. ANAL: Calcd for $C_{14}H_{18}N_4O_6$ (338.3): C, 49.70%; H, 5.36%; N, 16.56%. Found: C, 49.63%; H, 5.34%; N, 16.50%. IR (KBr, cm^{-1}): 3350 (N—H and O—H stretch), 1715 (acid C=O stretch), and 1665 (amide C=O stretch). 1H nuclear magnetic resonance (NMR) (D_2O): $\delta = 7.53$ (s, 2H, Ar—H) and 2.60–1.41 [m, 12H, $(CH_2CH_2NH_2)_2$].
2. MAETDC/AMETDC: mp 215–217°C decompose. ANAL: Calcd for $C_{16}H_{22}N_4O_6$ (366.4): C, 52.45%; H, 6.05%; N, 15.29%. Found: C, 52.38%; H, 5.97%; N, 15.22%. IR (KBr, cm^{-1}): 3325 (N—H and O—H stretch), 1710 (acid C=O stretch), and 1665 (amide C=O stretch). 1H NMR (D_2O): $\delta = 7.47$ (s, 2H, Ar—H), 2.58–2.38 [m, 10H, $(CH_2CHNH_2)_2$], and 0.98 [d, 6H, $(CH_3)_2$].
3. 3APTDC: mp 197–199°C decompose. ANAL: Calcd for $C_{16}H_{22}N_4O_6$ (366.4): C, 52.45%; H, 6.05%; N, 15.29%. Found: C, 52.35%; H, 5.99%; N, 15.23%. IR (KBr, cm^{-1}): 3360 (N—H and O—H stretch), 1715 (acid C=O stretch), and 1660 (amide C=O stretch). 1H NMR (D_2O): $\delta = 7.54$ (s, 2H, Ar—H) and 2.94–1.75 [m, 16H, $(CH_2CH_2CH_2NH_2)_2$].
4. AHTDC: mp 193–195°C. ANAL: Calcd for $C_{22}H_{34}N_4O_6$ (450.5): C, 58.65%; H, 7.61%; N, 12.43%. Found: C, 58.56%; H, 7.55%; N, 12.39%. IR (KBr, cm^{-1}): 3400 (N—H and O—H stretch), 1710 (acid C=O stretch), and 1670 (amide C=O stretch). 1H NMR (D_2O): $\delta = 7.52$ (s, 2H, Ar—H) and 2.84–1.43 [m, 28H, $\{(CH_2)_6NH_2\}_2$].
5. PETDC: mp 219–221°C decompose. ANAL: Calcd for $C_{22}H_{32}N_6O_6$ (476.5): C, 55.45%; H, 6.77%; N, 17.63%. Found: C, 55.39%; H, 6.74%; N, 17.58%. IR (KBr, cm^{-1}): 3400 (N—H and O—H stretch), 1715 (acid C=O stretch), 1660 (amide C=O stretch), 1350 (C—N—C stretch), and 1155 (C—NH—C stretch). 1H NMR (D_2O): $\delta = 7.59$ (s, 2H, Ar—H), 3.22–2.70 (m, 18H, CH_2 of piperazine moiety), and 1.42–1.35 [m, 8H, $(CH_2CH_2)_2$].

PAIs

To a solution of DAA (0.02 mol) and sodium hydroxide (5 g) in 100 mL of water was added IPC (4.06 g, 0.02 mol) in 75 mL of CH_2Cl_2 and stirred for 2 h at room temperature. Then, the PAA was

filtered, washed successfully with diluted HCl, water, and methanol, purified by reprecipitation into methanol from dimethylacetamide solution, and finally dried under vacuum.

A 10% dimethylacetamide solution of purified PAA was prepared, cast on a glass plate and the solvent was removed under vacuum. Then, the dried PAA film was stripped from the plate and cycloimidization to PAI was effected by heating it at 175°C for 4 h in a forced air oven.

Preparation of Thin Film Composite Membranes

Reinforced microporous polysulfone support membrane was prepared on a motor-driven mechanical membrane casting machine using 15% dimethylformamide solution of the polymer. The PAA thin film barrier layer was formed on a microporous polysulfone support by *in situ* interfacial polymerization of DAA in aqueous NaOH solution with TMC or IPC in hexane solution as described earlier.¹³ The polysulfone support (20 × 25 cm size) was soaked in aqueous NaOH (2%) solution of DAA (1.5%) for about 2 min, and the excess solution was decanted. Then, it was dried in air at room temperature for 5 min, and contacted with 0.15 wt % hexane solution of TMC or IPC for about 90 s. Thus, the nascent PAA composite membrane was cured at 75°C for 5 min.

Membrane Performance

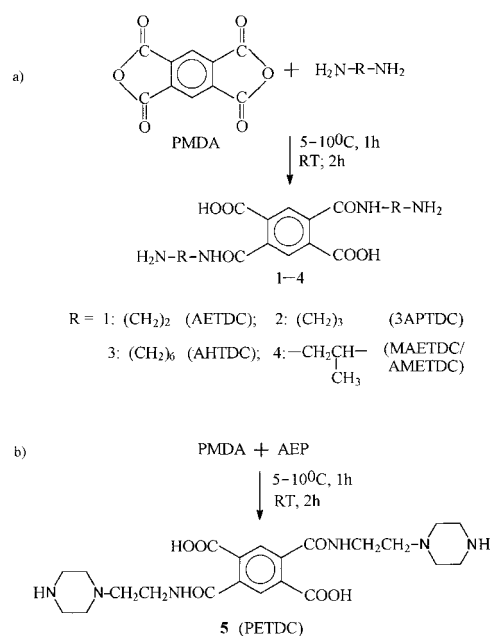
The performances of the composite membranes were tested for water permeability and for the separation of NaCl and Na₂SO₄ using a reverse osmosis test kit at the operating pressure of 100 psig. The feed concentrations of the salt solutions were 2000 ppm. The concentration of the salt in the permeate was determined using a calibration plot drawn between the salt concentration against the electrical conductivity of the solution. The salt separation of the membranes was computed using the expression:

$$\text{Salt separation (R\%)} = (1 - C_p/C_f) \times 100$$

where C_f and C_p are concentrations of the salt in the feed and permeate, respectively.

Techniques

Elemental analyses were performed with a Carlo Erba 1013 C—H—N analyzer (Milano, Italy). IR spectra of DAAs as KBr pellets and polymers as thin films were recorded using a Hitachi model



Scheme 1 Preparation of DAAs.

2750 IR (Tokyo, Japan) spectrophotometer. ¹H NMR spectra of DAAs in D₂O, and PAAs in dimethyl sulfoxide (DMSO)-_d₆ were obtained with a JEOL JNX-100 FT-NMR (Tokyo, Japan) spectrometer using tetramethylsilane (TMS) as an internal reference. Mettler TA 3000 thermal analyzer (Hiragau, Switzerland) at a heating rate of 15°C/min was used for thermogravimetric analysis (TGA) of the polymers.

RESULTS AND DISCUSSION

Synthesis of DAAs

DAAs (1-5), which contain free amine, carboxylic acid, and amide groups, were prepared quantitatively by the reaction of PMDA with aliphatic diamines (Scheme 1). The formation of higher oligomers could be avoided by reacting PMDA with either pure diamine or an excess amount of diamine solution in an organic solvent such as dioxane, dichloromethane, dimethylformamide (DMF), and so on. Symmetrical DAAs could be obtained when EDA, PDA, or HDA were reacted with PMDA. However, the reaction of DAP with PMDA may result in an asymmetrical DAA, in which the amic acid functional group may be attached to the amine on the primary carbon atom and/or a secondary carbon atom of the diamine, due to the asymmetry in the DAP itself.

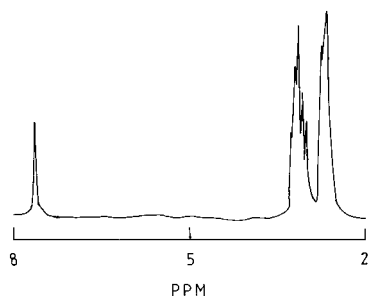


Figure 1 ^1H NMR spectrum of PETDC.

All the DAAs are freely soluble in water, which facilitates to utilize them for the preparation of PAAs by interfacial polymerization with a difunctional acid chloride such as IPC. Subsequently, the PAAs can be converted into the corresponding PAIs by thermal cycloimidization.

The elemental analyses data of the DAAs were in good agreement with the calculated values for the assigned structures. The IR spectra of DAAs exhibited strong characteristic absorptions at around 1710 and 1665 cm^{-1} due to the carbonyl stretchings of carboxylic acid and amide, respectively. In addition, PETDC shows strong characteristic bands around 1350 and 1155 cm^{-1} due to C—N—C and C—NH—C stretchings of piperazine moiety.

The ^1H NMR spectra of all the DAAs show distinct resonance absorptions for PMDA and diamine structural moieties. Figure 1 represents the ^1H NMR spectrum of PETDC. All the DAAs show a singlet around 7.55 ppm due to the two aromatic protons of PMDA moiety. The methylene as well as amine protons of alkylamine unit are observed as multiplets at 3.22–2.70 and 1.42–1.35 in PETDC, 2.60–1.41 ppm in AETDC, 2.85–2.38 ppm in MAETDC/AMETDC, 2.94–1.75 ppm in 3APTDC, and 2.84–1.43 ppm in AHTDC. In addition, MAETDC/AMETDC shows a doublet at 0.98 ppm due to methyl protons coupled to methine (CH) proton.

PAIs

The synthesis of PAIs, usually, consists of two steps: (1) preparation of PAA and (2) chemical or thermal cycloimidization of PAA to PAI. Generally, PAAs are prepared by low-temperature solution polymerization in polar aprotic solvents in a number of ways: (1) by polymerization of a diamine with a mixture of dicarboxylic acid chloride and dianhydride; (2) polymerization of a diamine

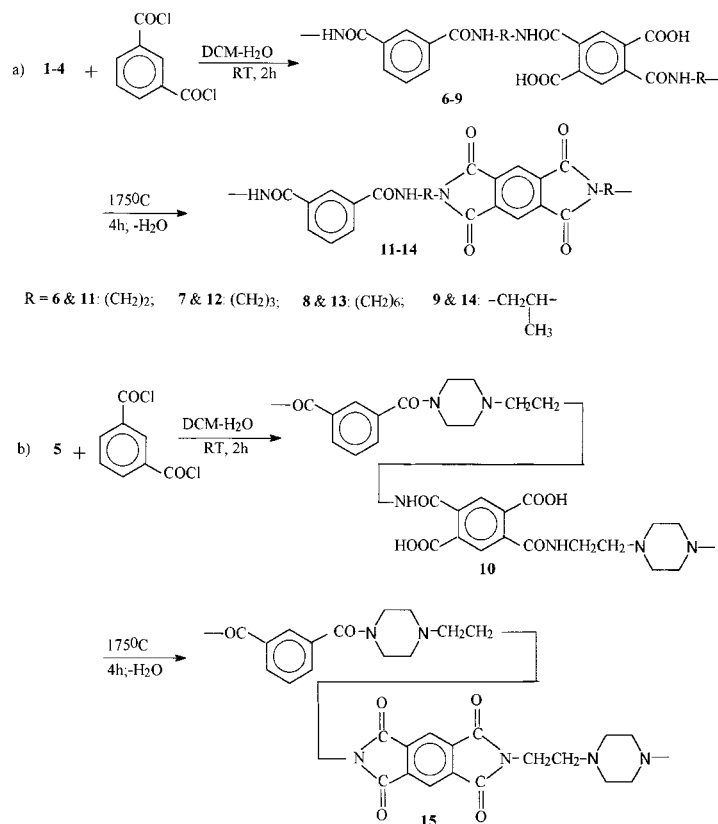
with a compound containing monoanhydride and monoacid chloride groups, for example, trimellitoyl chloride; and (3) polymerization of a diamine containing amide linkages with dianhydride.^{14–21}

In the present investigation, PAAs were prepared by interfacial polycondensation of DAAs (**1–5**) in aqueous NaOH solution with IPC in dichloromethane at room temperature (Scheme 2). Then, PAIs (**11–15**) with alternate (amide–amide)–(imide–imide) sequences in the polymer chain of tricomponent structures were obtained by thermal cycloimidization of the PAA films in a forced air oven. In the tricomponent polymer structure, such as diamine, diacid chloride, and dianhydride, one of the amino group of the diamine reacted with diacid chloride to form an amide linkage, and the other one attached as an imide linkage by reacting with dianhydride. This results in the regular distribution of amide and imide linkages along the polymer chain. The inherent viscosities of the polymers are in the range of 0.9–1.7 dL/g (Table I), and thus indicate that they have sufficiently high molecular weights for membrane preparation.

Polymer Characterization

Processability of the polymer in terms of solubility and tractability is one of the major requirements for the preparation of membranes by phase inversion method. Hence, the solubility of the PAIs was tested in various organic solvents. It was observed that all the PAIs were readily soluble in polar aprotic solvents such as DMF, dimethyl acetamide (DMAc), DMSO, and N-methyl-2-pyrrolidone (NMP) at room temperature, which are the common solvents for asymmetric membrane preparation by phase inversion process. They could be cast into tough and flexible films. The superior solubility of the PAIs can be apparently attributed to the presence of a flexible aliphatic chain between PMDA and IPC aromatic units. They were insoluble in protic solvents such as methanol, ethanol, and isopropanol, and chlorinated solvents such as CHCl_3 , CH_2Cl_2 , 1,2-dichloroethane, and so on.

The IR spectra of PAAs show broad absorptions around 3350 cm^{-1} due to amide N—H and carboxylic acid O—H stretchings, and strong bands at about 1710 and 1660 cm^{-1} due to carbonyl (C=O) stretchings of carboxylic acid and amide groups, respectively. PAIs show characteristic absorptions at around 1770 and 1710 cm^{-1} due to imide carbonyl stretchings, and at about 1665 cm^{-1} due to amide C=O stretchings.



Scheme 2 Preparation of PAIs.

In ¹H NMR spectra (Fig. 2), all the PAAs exhibit a multiplet at 8.74–7.45 ppm due to aromatic protons of PMDA and IPC units. The signals of the two aromatic protons of PMDA moiety, which appeared as a singlet at about 7.55 ppm in DAAs, were overlapped with those of the aromatic protons of isophthaloyl unit. They also show multiplet resonances at 3.52–1.58 ppm, which were assignable to the alkyl (CH₂ and CH) protons of the

diamine structural component. Polymer **9** shows an additional doublet at about 0.95 ppm due to methyl protons coupled to methine (CH) group.

Thermal Properties

The thermal stabilities of the PAIs were studied by TGA in air. Figure 3 shows the thermogravi-

Table I Inherent Viscosities and TGA Data of PAIs

Polymer No.	η_{inh} (dL/g)	IDT (°C)	T_{d10} (°C)
11	1.4	362	410
12	1.7	331	394
13	1.1	311	348
14	1.2	317	362
15	0.9	312	356

η_{inh} , Measured as 0.5 wt % dimethyl sulfoxide (DMSO) solution at 30°C; IDT, initial decomposition temperature; T_{d10} , temperature of 10% weight loss of polymer.

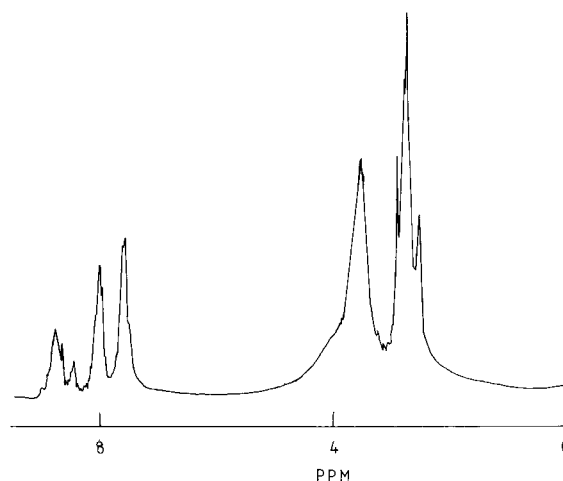


Figure 2 ¹H NMR spectrum of PAA **10**.

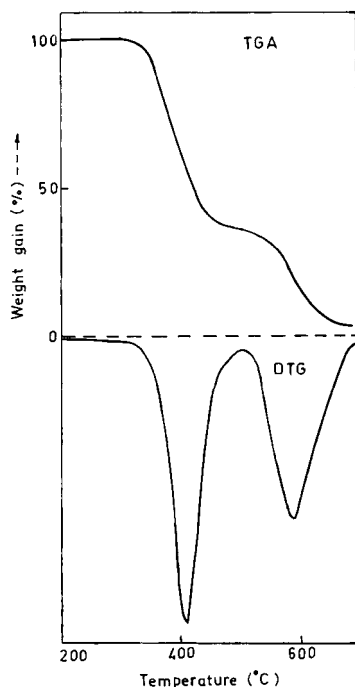


Figure 3 Thermogravimetric (TG) and derivative thermogravimetric (DTG) analysis curves of PAA **15**.

metric (TG) and derivative thermogravimetric (DTG) curves of polymer **15**. All the PAIs decompose in two stages, which is a characteristic of thermal oxidative degradation of most of the polymers. The major (>50%) weight loss of the polymers occurs in the first stage decomposition. The initial decomposition temperatures of the polymers are above 310°C, and the temperature at which 10% weight loss occurs is in the range of 348–410°C (Table I). Polymer **11**, which has shortest aliphatic (CH_2CH_2) chain possesses the highest initial decomposition temperature (IDT) value of about 362°C, whereas polymer **13** with isopropylidene unit has the lowest IDT value of about 311°C. The results clearly indicate that the polymers have good thermal stabilities with enhanced solubility in various organic solvents, which are normally used in the preparation of asymmetric membranes by phase inversion technique.

Thin Film Composite Membranes

DAAs were tested for the preparation of thin film composite membranes containing polysulfone (PSF)–PAA barrier layer by *in situ* interfacial polycondensation of the DAA in aqueous NaOH solution with TMC or IPC in hexane solution on

the surface of a microporous polysulfone support. Composite membranes with stable barrier layer of the reaction product of DAA and TMC or IPC were obtained.

The performances of the composite membranes have been tested using 2000 ppm aqueous feed solutions of NaCl and Na_2SO_4 at the operating pressure of 100 psig. The membranes have shown separations of 5–20% for both NaCl and Na_2SO_4 accompanied by very high water permeation rates (200–250 gfd). This may be due to the fact that the PSF–PAA composite membranes contain more open, less compact, and highly hydrophilic PAA barrier layer that allows higher permeation of both the solvent water as well as the solute. Because these composite membranes contain highly hydrophilic barrier layer of amide and carboxylic acid functional groups that greatly minimizes membrane fouling, they are expected to be the best candidates for the ultrafiltration separations of various biotechnological products such as BSA, globulins, and so on.

In general, the performance of the composite membranes is determined by the chemistry and preparation conditions of the ultrathin barrier layer. The former is an inherent property of the reactants taken to form the barrier layer. The preparation conditions that are decisive in determining the properties of the membrane are the concentration of the reactants, reaction time, curing time, and curing temperature. For any given pair of reactants taken to form the ultrathin film barrier layer the preparation conditions have to be optimized to obtain a membrane with optimum performance characteristics.¹³ Because these composite membranes contain PAA barrier that may be converted to PAI barrier layer, both the curing temperature and curing time would have a profound effect on the chemical nature and performance of the resultant membrane. The detailed investigations on the preparation of PSF–PAA and PSF–PAA–PAI composite membranes for the separation and concentration of various biotechnological products and for pervaporation applications are under progress, and these results will be reported elsewhere.

CONCLUSION

PAIs containing alternate (amide–amide)–(imide–imide) sequences were prepared by interfacial polymerization of DAAs with IPC, followed by the thermal cycloimidization of the resultant

PAA. The PAIs are soluble in polar aprotic solvents and could be cast into tough and flexible films. Composite membranes containing PAA ultrathin barrier layer were prepared by *in situ* interfacial polycondensation of DAA in water with TMC or IPC in hexane on the surface of a porous polysulfone membrane. The membranes have shown water permeation rates of 200–250 gfd at the operating pressure of 100 psig, thus indicating their application for ultrafiltration of various biotechnological products.

REFERENCES

1. Kesting, R. E. *Synthetic Polymeric Membranes*; John Wiley & Sons: New York, 1985.
2. Jiyan, C.; Scuchun, B.; Xindga, Z.; Lingying, Z. *Desalination* 1980, 34, 97.
3. Strathmann, H.; Kock, K. *Desalination* 1977, 21, 241.
4. Tsay, C. S.; McHugh, A. J. *J Polym Sci Part A Polym Phys* 1992, 30, 309.
5. Kesting, R. E. *J Appl Polym Sci* 1990, 41, 2739.
6. Matsuura, T.; Sourirajan, S. *Ind Eng Chem Process Des Dev* 1978, 17, 419.
7. Blais, P. In *Reverse Osmosis and Synthetic Membranes*; Sourirajan, S., Ed.; NRC: Canada, 1977; Chapter 9.
8. Strathmann, H.; Zschock, P. Ger Patent 2,940,447, 1981.
9. Parrini, P. *Desalination* 1983, 48, 67.
10. Iwama, A.; Kazuge, Y. *J Membr Sci* 1982, 11, 297.
11. Rami Reddy, A. V.; Sreenivasulu Reddy, P. *J Appl Polym Sci* 1995, 58, 1935.
12. Rami Reddy, A. V.; Sreenivasulu Reddy, P.; Anand, P. S. *Eur Polym J* 1998, 34, 1441.
13. Rami Reddy, A. V. Low pressure Polyamide thin film composite membranes by interfacial polymerization; IUPAC Interanational Symposium on Advances in Polymer Science and Technology; Chennai, India, Jan. 5–9, 1998.
14. Yang, C. P.; Chen, W. T. *J Polym Sci Part A Polym Chem* 1994, 32, 1101.
15. Kricheldorf, H. R.; Gurau, M. J. *J Polym Sci Part A Polym Chem* 1995, 33, 2241.
16. Perry, R. J.; Turner, S. R.; Blevins, R. W. *Macromolecules* 1994, 27, 4058.
17. Oishi, Y.; Kakimoto, M. A.; Imai, Y. *J Polym Sci Part A Polym Chem* 1991, 29, 1925.
18. Imai, Y.; Maldar, N. N.; Kakimoto, M. *J Polym Sci Part A Polym Chem Ed* 1985, 23, 2077.
19. Yang, C. P.; Chen, W. T. *J Polym Sci Part A Polym Chem* 1993, 31, 3081.
20. Ray, A.; Rao, Y. V.; Bhattacharya, V. K.; Maiti, S. *Polym J* 1983, 15, 169.
21. Kakimoto, M.; Akiyama, R.; Negi, Y. S.; Imai, Y. *J Polym Sci Part A Polym Chem* 1988, 26, 99.