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Polymer 46 (2005) 5524–5532

polymer

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Synthesis, characterization and thermal properties of soluble aromatic poly(amide imide)s

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Received 3 January 2005; received in revised form 23 April 2005; accepted 23 April 2005

Abstract

Novel diamines such as *N*,*N*′-bis(aminoaryl)terephthalamido-2-carboxylic acids (BATCA), which contain primary amine, amide and carboxylic acid groups and are soluble in dilute aqueous NaOH solution, were synthesized by reacting aromatic diamines with trimellitic anhydride chloride in dimethylformamide. Poly(amide imide)s containing 3:1 ratio of amide:imide groups in the polymer chain were prepared by low temperature solution polymerization of BATCAs with isophthaloyl chloride or terephthaloyl chloride in dimethylformamide at 5–10 °C to form poly(amide amic acid)s, and followed by treating with a mixture of triethylamine and acetic anhydride. The PAIs were soluble in polar aprotic solvents like dimethylformamide, dimethylacetamide, dimethylsulphoxide and *N*-methylpyrrolidone, and have inherent viscosities in the range of 0.30–0.66 dL/g. The PAIs were characterized by IR, ^{1}H NMR and ^{13}C NMR techniques. Thermogravimetric analysis (TGA) has shown that the initial decomposition temperatures of the polymers are in the range of 250–440 °C, depending upon the structures of diamine and diacid chloride. The glass transition temperatures of the PAIs are in the range of 128–320 °C. The IDT and T_g values of the polymers containing terephthaloyl unit are higher by about 20–40 °C than those of the polymers with isophthaloyl unit. BATCA could be utilized for the preparation of thin film composite membranes having PAA/PAI barrier layer on PES by in situ interfacial polymerization with IPC/TPC/TMC.

Keywords: *N*,*N*′-bis(aminoaryl)terephthalamido-2-carboxylic acids; Poly(amide imide)s; Characterization, thermal properties

1. Introduction

Polyimides are well known for their excellent mechanical and thermal and chemical resistance properties. They are being used for a variety of applications such as aerospace programs, automobile and electrical industries, insulations, coatings, solvent resistant membranes applications, etc. [1–5]. However, the main limitation in employing polyimides for different applications is their poor processability due to low solubility in common organic solvents and high melting or softening temperatures. Hence, polyimides are generally employed in their precursor polyamic acid form, and then it will be converted into imide form by heating at different temperatures for different time periods, usually at 80–100, 150–175 and 225–250 °C for 1–2 h at each temperature. To overcome this problem, considerable efforts have been made to modify their chemical structure to improve their processability and solubility, and to change their properties with regard to a specific application or to a particular property. The various approaches followed are: (1) attachment of bulky substituents or pendant groups to the rigid polyimide backbone, (2) introduction of flexible bridge groups like ether, sulfone, etc. in the polymer chain, and (3) synthesis of poly(amide imide)s and poly(ester imide)s by incorporating amide or ester functionality at regular intervals in the polyimide chain [6–12]. Poly(amide imide)s containing different extent of amide to imide ratios have been reported by following different synthetic pathways [13–20]. The present paper reports the synthesis, characterization and thermal properties of poly(amide imide)s containing amide to imide ratio of 3:1 and are distributed randomly in the polymer chain.

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doi:10.1016/j.polymer.2005.04.056

2. Experimental

2.1. Materials

Trimellitic anhydride chloride (TMAC), *m*-phenylenediamine (MPD), 3,3′-diaminophenyl sulphone (3DPS), 4,4′-diaminophenyl sulphone (4DPS), 4,4′-oxydianiline (ODA), 4,4′-diaminophenylmethane (DPM), 3,5-diaminobenzoic acid (DAB) were purified by recrystallization from ethanol. Isophthaloyl dichloride (IPC), terephthaloyl chloride (TPC) and trimesoyl chloride (TMC), from Aldrich Co., USA, were recrystallized from dichloromethane–hexane mixture. All the other reagents and solvents were of analytical grade samples and were purified as per standard methods.

2.2. Synthesis of N,N′-bis(aminoaryl)terephthalamido-2-carboxylic acids (BATCA)s (**1**–**6**)

In a typical procedure, the synthesis of *N*,*N*′-bis(3-aminophenyl)terephthalamido-2-carboxylic acid (BPTC, **1**) is described as follows. To a cooled (5–10 °C) and well stirred solution of *m*-phenylenediamine (2.16 g, 0.02 mol) in 15 mL dimethylformamide was added at once a solution of trimellitic anhydride chloride (2.10 g, 0.01 mol) in 15 mL DMF, and the reaction mixture was stirred at 5–10 °C for 1 h, and at room temperature for 2 h. The product, BAPTCA, was then isolated by adding the reaction solution to ice cold water, filtered, washed with methanol and dried at 65–70 °C under vacuum.

Similarly, *N*,*N*′-bis(3-amino-5-carboxyphenyl)terephthalamido-2-carboxylic acid (BCPTC, **2**), *N*,*N*′-bis[4-(4′-aminophenylmethylene)phenyl]terephthalamido-2-carboxylic acid (BPMPTC **3**), *N*,*N*′-bis[4-(4′-aminophenoxy)phenyl]-terephthalamido-2-carboxylic acid (BPOPTC, **4**), *N*,*N*′-bis[3-(3′-aminophenylsulfonyl)phenyl]terephthalamido-2-carboxylic acid (B3PSPTC, **5**) and *N*,*N*′-bis[4-(4′-aminophenylsulfonyl)phenyl]terephthalamido-2-carboxylic acid (B4PSPTC, **6**) were prepared by reacting DAB, DPM, ODA, 3DPS and 4DPS, respectively, with TMAC. The BATCAs did not show any obvious melting points and decompose at temperatures of above 210 °C. The structures of BATCAs were confirmed by elemental analysis, IR and ^{1}H NMR techniques.

2.3. Synthesis of poly(amide imide)s

Poly(amide amic acid)s were synthesized by low temperature solution polycondensation of BATCAs with IPC/TPC in dimethylformamide and then converted them into poly(amide imide)s by treating with acetic anhydride and triethylamine mixture. To a well stirred solution of BATCA (0.01 mol) and triethylamine (0.02 mol) in 25 ml dimethylformamide at 5–10 °C was added slowly a solution of IPC/TPC (2.02 g, 0.01 mol) in 10 mL DMF, stirred at 5–10 °C for 1 h and at room temperature for 12 h. After diluting with 20 mL DMF, a mixture of 1.3 mL acetic anhydride and 1.8 mL TEA was added to the reaction solution and stirred at 60–70 °C for 6 h, and at room temperature for 12 h. Poly(amide imide)s were finally isolated by adding the reaction mixture to excess of methanol, filtered washed with methanol and dried at 100–120 °C.

2.4. Preparation of thin film composite membranes

Reinforced porous polyethersulfone support membrane was prepared on a motor-driven mechanical membrane casting device using 15 wt% dimethylformamide solution of the polymer. Poly(amide amic acid) skin layer on the top of porous polyethersulfone support was formed by in situ interfacial polymerization of BATCA (1.0 wt%) in aqueous NaOH solution (0.01 wt%) with trimesoyl chloride (0.1 wt%) in hexane. Polyethersulfone support ($15\times 20\ \mathrm{cm}^2$ size) was fixed in a glass trough at the edges and soaked in BATCA solution for about 2 min, and the excess solution was decanted. Then, it was allowed in air at ambient temperature for 4 min, and contacted with TMC solution for 90 s. This results in the formation of poly(amide amic acid) thin film on the top of polyethersulfone support by the interfacial polycondensation of BATCA at the pore surface of the support with TMC in hexane. Thus, the nascent PAA composite membrane was cured at 70 °C for 4 min in air circulating oven.

2.5. Membrane performance

The performances of the membranes were tested in a reverse osmosis test kit at the operating pressure of 20 kg/cm^2 using 2000 ppm aqueous feed solutions of NaCl, Na_2SO_4 and $CaCl_2$. Initially, pure water was passed for about 1 h at 22 kg/cm^2 and then salt solution was passed at 20 kg/cm^2 and measured the permeate flux after 20/40 min. Salt concentration in feed and permeate solutions was determined by measuring the electrical conductivity of the salt solution. The solute separation was then computed using the following expression:

$$\text{Solute rejection } (R\%) = \left(1 - \frac{C_\mathrm{p}}{C_\mathrm{f}}\right) \times 100$$

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

2.6. Measurements

IR spectra were recorded as KBr pellet using a Perkin–Elmer Spectrum GX FT-ATIR spectrophotometer. ^{1}H NMR spectra were obtained with a Bruker Avance DPX 200 MHz FT-NMR spectrometer. Spectra were recorded in DMSO-*d*6 using tetramethylsilane as the internal standard. Mettler Toledo 822$^\mathrm{e}$ and 851$^\mathrm{e}$ thermal analyzers were used for DSC and TGA, respectively. Polymer sample of about 5 mg for

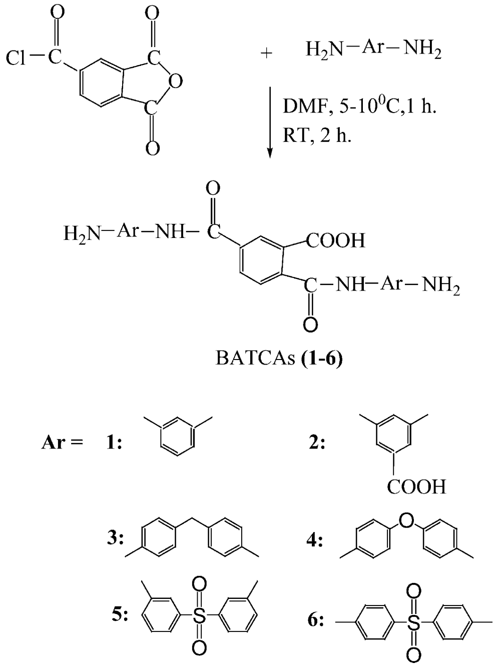
DSC was heated at a rate of 10 °C/min to 300 °C under nitrogen atmosphere, quenched to 50 °C and again heated to 350 °C. All the T_g values reported in this paper were obtained from DSC second heating curves of the polymers. TGA thermograms were recorded in air at a heating rate of 10 °C/min.

3. Results and discussion

3.1. Synthesis of N,N′-bis(aminoaryl)terephthalamido-2-carboxylic acids (BATCAs)

Six *N*,*N*′-bis(aminoaryl)terephthalamido-2-carboxylic acids such as BPTC, BCPTC, BPMPTC, BPOPTC, B3PSPTC and B4PSPTC, which contain two primary amine (NH_2), amide (C=O NH) and carboxylic acid (COOH) groups were synthesized by reacting MPD, DAB, DPM, ODA, 3DPS and 4DPS, respectively, with trimellitic anhydride chloride in dimethylformamide (Scheme 1). Under the experimental conditions, the reaction leads to the formation of BATCAs with two units of diamine and one unit of TMAC. However, there is also a possibility for the formation of minor amount of amic acid diamines containing two units of TMAC and three units of diamine with end primary amine functionality. These structures leads to the formation of poly(amide imide)s with random distribution of amide and imide units along the polymer chain.

All the BATCAs show characteristic strong IR bands at about 1725 and 1665 cm^{-1} corresponding to the carbonyl stretchings of carboxylic acid and amide groups, respectively. They exhibit a broad absorption at 3300–3400 cm^{-1} due to carboxylic acid O–H and amide N–H stretchings. The band at 1500 cm^{-1} may be assigned to aromatic ⟩C=C⟨ stretchings.



Scheme 1. Synthesis of *N*,*N*′-bis(aminoaryl)terephthalamido-2-carboxylic acids (BATCAs).

^1H NMR spectra (Fig. 1) of BATCAs exhibit resonance signals at 10.4–11.0 ppm due to the protons of carboxylic acid O–H and amide N–H groups which were formed at *ortho*-position to each other due to the opening of anhydride group of TMAC. They show two characteristic multiplets corresponding to the aromatic protons. The multiplet at 8.5–7.9 ppm corresponds to Ar–H of TMAC unit, and the second multiplet at 6.5–7.6 ppm may be assigned to the aromatic protons of amine unit. The signals due to amide N–H protons are overlapped with those of TMAC unit around 8.0 ppm. Resonance signals corresponding to primary amine group appear around 3.8 ppm.

3.2. Synthesis of poly(amide imide)s

Poly(amide imide)s which contain 3/1 ratio of amide/imide groups and are distributed randomly along the polymer chain were synthesized in two steps as outlined in Scheme 2. In the first step, poly(amide amic acid)s were prepared by low temperature solution polymerization of BATCAs with isophthaloyl chloride or terephthaloyl

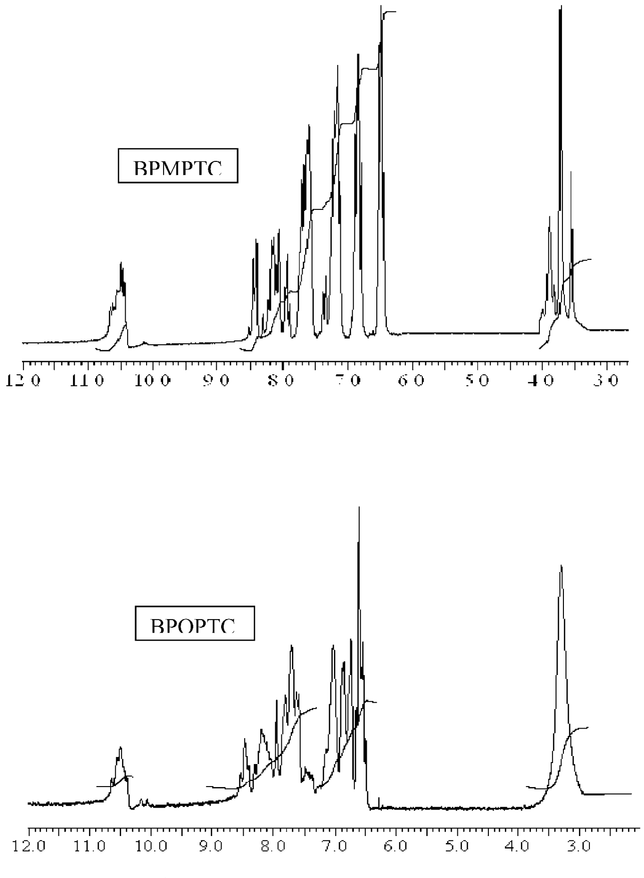
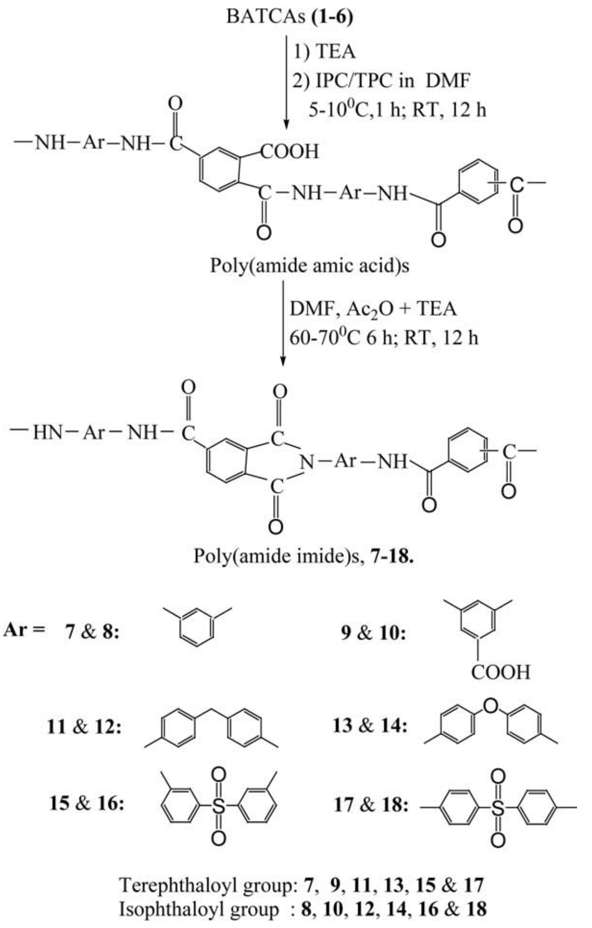


Fig. 1. ^1H NMR spectra of BPMPTC and BPOPTC.



Scheme 2. Synthesis of poly(amide imide)s.

chloride in dimethylformamide at 5–10 °C. Poly(amide imide)s were then obtained by cycloimidization of poly (amide amic acid)s with a mixture of triethylamine and acetic anhydride for several hours.

3.3. Polymer characterization

Solubility of the polymer is a major factor that shows its processability for different applications, and hence the solubilities of the PAIs have been tested in various solvents. It was observed that all the polymers were easily soluble in polar aprotic solvents like DMF, DMAc, DMSO, NMP, etc. and insoluble in chlorinated and hydroxy group containing solvents. The enhanced solubility of these polymers may be attributed to the random distribution of amide and imide functionalities, which hinders the packing of polymer chain. The inherent viscosities (Table 1) of the polymers are in the range of 0.30–0.66 dL/g in dimethylformamide solution.

The IR spectra of poly(amide amic acid)s show a broad band around 3400 cm^{-1} due to carboxylic acid O–H as well as amide N–H stretchings, strong bands at about 1715 and 1660 cm^{-1} corresponding to carbonyl (C=O) stretchings of carboxylic acid (COOH) and amide (C=O–NH) groups, respectively. IR spectra (Fig. 2) of poly(amide imide)s show characteristic bands corresponding to imide moiety at 1775–1780 and 1715–1725 cm^{-1} due to symmetric and asymmetric stretchings, respectively, of C=O of imide group, and at 1650–1660 cm^{-1} corresponding to amide C=O stretchings. Bands are also observed at 1370–1385 cm^{-1} due to C–N stretch of imide ring, and at 720–730 cm^{-1} due to C=O bending of imide group. PAIs also show a broad band centered at 3300–3350 cm^{-1} which is assignable to amide N–H stretchings. However, the intensity of this band is considerably lower than the band observed around 3400 cm^{-1} for poly(amide amic acid)s. This may be attributed to the loss of amic acid moiety (COOH and N–H) upon cycloimidization.

^{1}H NMR spectra (Fig. 3(a) and (b), Table 2) of the PAAs of poly(amide imide)s **7**–**18** exhibit a multiplet between 6.55 and 8.75 ppm corresponding to the aromatic protons of all the three reactants such as TMAC, TPC/IPC and diamine. They also show two peaks between 10.10 and 11.10 ppm which are assignable to hydrogen bonded protons of amide N–H and carboxylic acid group.

^{13}C NMR spectra (Fig. 4(a) and (b)) of the PAAs exhibit a group of resonance signals at 111.3–142.1 ppm due to aromatic carbons. The signals at 149.9 ppm may be assigned to the aromatic carbon at an *ortho*-position to carbonyl group. In addition, the polymers show resonance signals at 162.3–167.4 ppm corresponding to carbonyl carbons of amide (C=O NH) and carboxylic acid group.

3.4. Thermal properties

Thermal oxidative stabilities of the polymers were measured by thermogravimetric analyses in air. Fig. 5 shows the TGA thermogram of polyimide prepared from TMAC, IPC and DPM. The data on initial decomposition temperatures (IDT), the temperature at which 10 wt% loss occurred, and decomposition temperature ranges for all the polymers are presented in Table 3. The initial decomposition temperatures of all the polymers, except polymer **10**, are above 250 °C and this indicates their good thermal stabilities. The PAIs undergo decomposition in two stages, which is a characteristic of thermooxidative degradation of most of the polymers. A weight loss of about 10–30% was observed for most of the polymers in the first stage decomposition up to the temperature of about 450 °C. Then, a fast decomposition was occurred in the second stage

Table 1
Inherent viscosities of the polymers

Polymer no.	7	8	9	10	11	12	13	14	15	16	17	18
η_{inh} (dL/g)	0.36	0.53	0.57	0.36	0.30	0.30	0.66	0.52	0.55	0.55	0.51	0.61

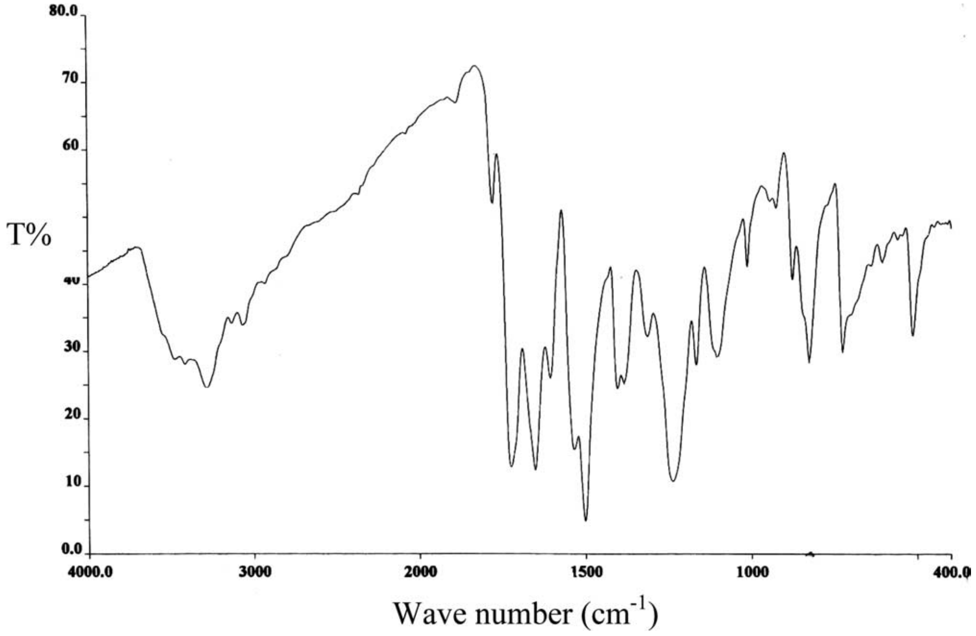


Fig. 2. IR spectrum of polymer **14**.

in the temperature range of 460–800 °C. The data in Table 3 clearly indicate that the nature of diamine has a considerable effect on the thermooxidative degradation of poly(amide imide)s reported in this paper. Polymers having MPD unit possess higher thermal stability with a weight loss of about 52–55% upto the temperature of 800 °C. About 63–65% weight loss was observed up to 800 °C for polymers with DPM unit. In the case of other polymers, the weight loss was about 85–98% at 800 °C. The TGA data clearly indicate that polymers having SO_2 group in the diamine unit undergo almost complete decomposition (92–98%). The data also strongly suggest that polymers with a single benzene ring in the diamine unit were more stable than those having a diamine unit with two benzene rings which are joined together by –CH_2–, –O– or –SO_2– group. However, polymers having –CH_2– group have shown somewhat higher thermal stability than those polymers having –O– or –SO_2– interconnecting group. Another important observation was that the difference in the weight loss (2–5%) of the polymers having either TPC or IPC unit is very minimum when compared with the variation of diamine unit. The above observations strongly suggest that the nature of diamine unit has a profound effect on the thermal oxidative stability of the poly(amide imide)s having TMAC-IPC/TPC-diamine units in the chain. The thermal stabilities of the polymers based on diamine unit are as follows: MPD (55–57%) > DBA ≅ DPM (63–65%) > ODA (82–85%) > 4APS ≅ 3APS (92–98%).

Table 2
^{1}H NMR data of poly(amide amic acid)s

Polymer no.	Chemical shift (ppm)	
	Aromatic	COOH, CO–NH
7	6.82–8.53	10.31–10.69
9	7.21–8.36	10.24–10.41
11	7.22–8.62	10.34 and 10.56
12	6.90–8.72	10.10–10.64
14	6.55–8.75	10.45–10.78
15	6.75–8.52	10.81–11.05
16	6.62–8.60	10.58–11.10
17	6.52–8.39	10.59–10.69
18	6.40–8.35	10.64 and 10.70

Table 3 shows the glass transition temperatures of the polymers determined by differential scanning calorimetry. The glass transition temperatures of the polymers are in the range of 199–270 °C thus indicating the higher stiffness nature of the polymer chain. Polymers **11** and **12** with DPM unit have shown lower T_g values, whereas, higher T_g values were observed for polymers with MPD and 4DPS unit. Interestingly, polymers containing isophthaloyl unit exhibited somewhat higher glass transition temperatures than those with *para*-(terephthaloyl) unit. Generally, polymers having terephthaloyl linkages exhibit somewhat higher T_g values than those of isophthaloyl unit. The difference in the T_g values of both *meta*- and *para*-substituted polymers in the present case may be attributed to the presence of rigid aromatic structures with compact imide ring bridged units, which exerts a profound effect on glass transition temperature.

3.5. Composite membranes

Composite membranes containing poly(amide amic acid) skin layer on the top of a microporous polyethersulfone support were prepared by in situ interfacial polymerization of diamine amic acid in aqueous NaOH solution with TMC in hexane solution. The chemical structures of the skin layer

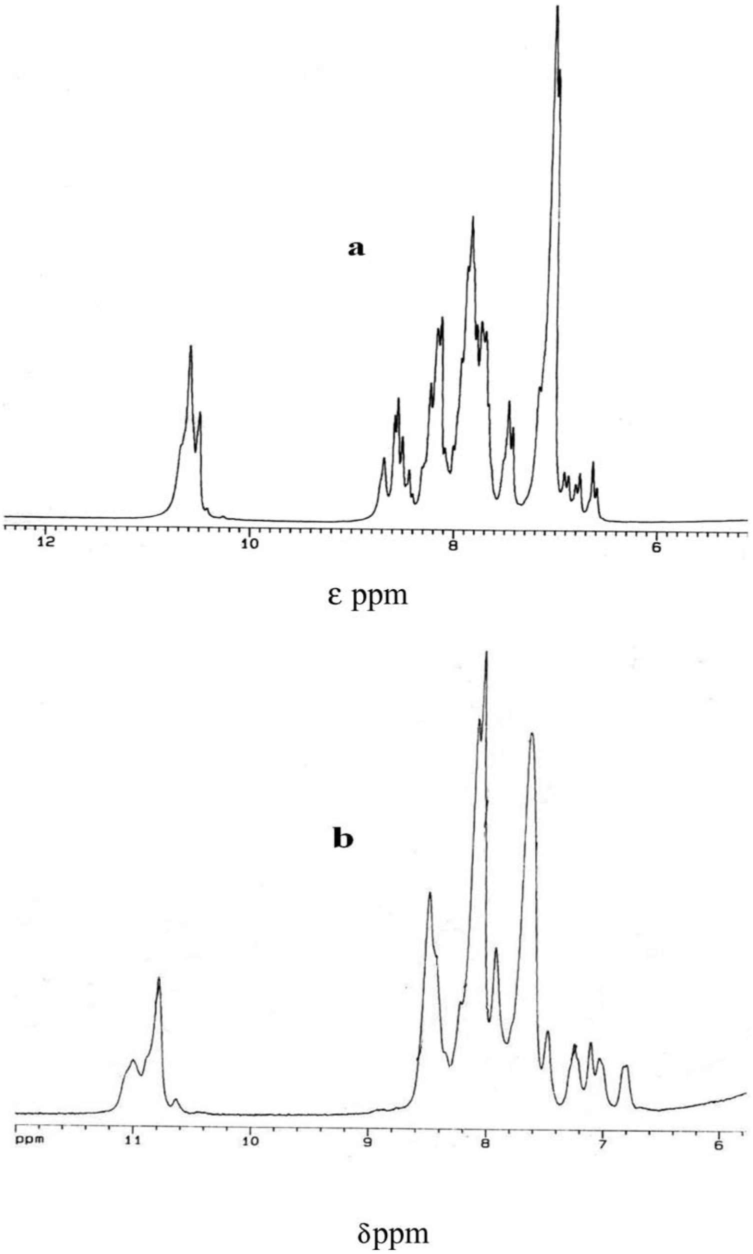


Fig. 3. ^{1}H NMR spectra of: (a) polymer **14** and (b) polymer **15**.

formed on PES support are shown in Fig. 6. It was observed that the poly(amide amic acid) skin layers formed by interfacial polymerization of BATCAs **1–4** with TMC were stable for performance evaluation. However, the films formed with other BATCAs (**5** and **6**) were brittle and were collapsed during performance evaluation.

The performances of the composite membranes were tested using 2000 ppm aqueous feed solutions of NaCl, $CaCl_2$ and Na_2SO_4, and the data are presented in Table 4. The membranes have exhibited separations of 24–77% for NaCl and 46–81% for Na_2SO_4, and 6–68% for $CaCl_2$ with water fluxes of 4–172 L/m^2 h at the operating pressure of 20 kg/cm^2. Membrane **2**, which has a DBA unit, exhibited lower salt separations and very high water fluxes, whereas, membrane **4** with ODA unit has shown very low water fluxes with considerably good salt rejections (40–73%). However, membrane **1**, which has a skin layer of TMAC–MPD–TMC unit, exhibited higher salt rejection with good water fluxes. The lower salt rejection and higher water flux of membrane **2** may be attributed to the formation of more open and less compact poly(amide amic acid) skin layer with more hydrophilic functional groups like carboxylic acid associated with DBA, which allows higher permeation of both the solvent water as well as solute. These membranes are expected to be the best candidates for ultrafiltration applications involving various biotechnological products such as enzymes, proteins, etc. because these membranes contain highly hydrophilic skin layer of amide

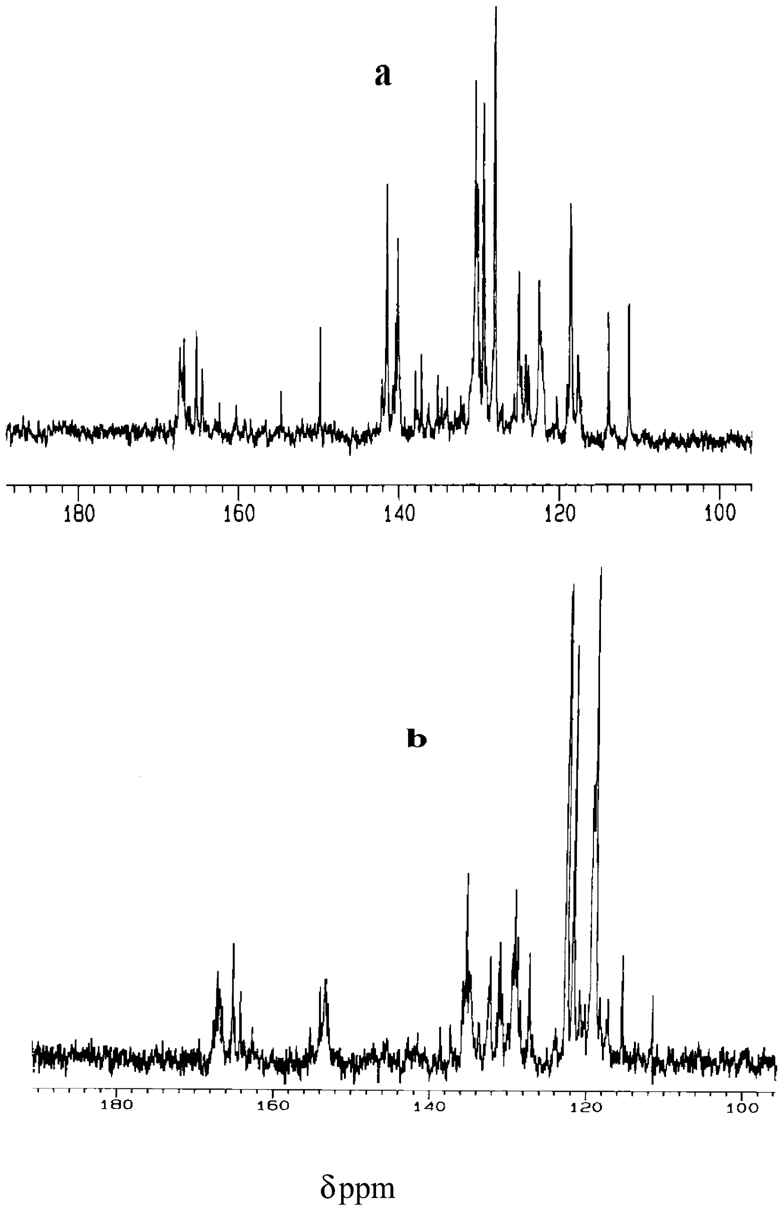


Fig. 4. ^{13}C NMR spectra of: (a) polymer **14** and (b) polymer **15**.

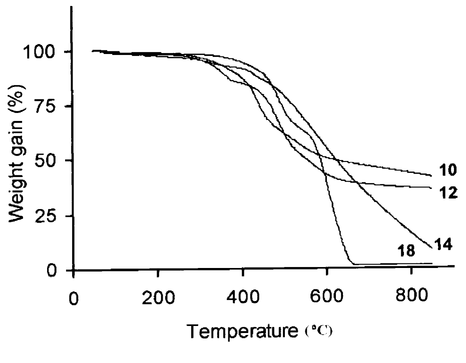


Fig. 5. TGA curves of polymers **10**, **12**, **14** and **18** in air.

and charged carboxylic acid functional groups which greatly minimizes membrane fouling by the adsorption of solutes. Membrane **1**, which has all *meta*-substituted benzene rings, exhibits a compromise between water flux and salt rejection. These membranes are expected to be useful for nanofiltration applications such as treatment of dye effluents, separation of low molecular organic solutes, etc. It may be appropriate to mention here that composite membranes containing poly(MPD–TMC) skin layer are well known to exhibit very high salt rejections with considerable good water fluxes.

The performance (permeate flux and solute rejection) of the composite membranes is generally determined by chemical nature and preparation conditions of the ultrathin skin layer [21]. The chemical nature is an inherent property

Table 3
TGA and DSC data for poly(amide imide)s

Polymer no.	T_g (°C)	IDT (°C)	T_{d10}	DTR (°C)		wt% Loss at 800 °C
				Stage 1	Stage 2	
7	247	275	415	275–402 (12)	402–650 (36)	54
8	260	290	394	290–490 (29)	490–800 (28)	57
9	–	250	330	250–615 (50)	615–848 (12)	60
10	–	230	240	230–390 (60)	390–600 (38)	98
11	199	270	342	270–344 (12)	344–442 (18)	65
12	207	275	370	275–410 (16)	410–695 (46)	64
13	230	293	411	295–800 (82)	–	82
14	270	294	464	294–410 (10)	410–800 (75)	85
15	224	266	447	266–420 (15)	420–800 (80)	95
16	227	256	463	256–438 (17)	438–840 (87)	95
17	220	252	436	252–482 (33)	482–800 (59)	92
18	240	320	458	320–544 (37)	544–666 (61)	98

Figures in parenthesis indicate polymer weight loss (%) in the temperature range. IDT, initial decomposition temperature; DTR, decomposition temperature range. T_g values were obtained from DSC 2nd heating curves.

Table 4
Performances of composite membranes

Memb. no.	PWP (L/m^2 h)	Permeate flux (L/m^2 h)	Rejections (%)		
			NaCl	Na_2SO_4	$CaCl_2$
M-1	76.5	75.0	76.6	81.2	68.0
M-2	190.0	172.0	24.4	45.9	6.6
M-3	42.5	37.0	42.6	52.6	36.5
M-4	4.2	4.0	68.5	72.6	40.0

Feed concentration: 2000 ppm, applied pressure: 20 kg/cm^2. PWP, pure water permeation rate.

of the reactants taken to form the barrier layer. The preparation conditions that are decisive in determining the performances of the composite membranes are the concentrations of the reactants, reaction temperature, curing time and curing temperature. For any given pair of reactants taken to form the skin layer the preparation conditions have to be optimized to obtain membrane with optimum performance characteristics. Because these composite membranes contain poly(amide amic acid) skin layer, it is expected that both curing time and curing temperature would have a profound effect on the chemical nature and physical structure (morphology of the resultant skin layer) and thereby on the performance characteristics of the membrane. The detailed investigations on the preparation of PSF–PAA and PSF–PAA–PAI composite membranes for possible applications in the separation of organic–organic and organic–aqueous liquid mixtures such as ethanol–water, acetic acid–water, MEK–toluene, etc. are under investigation and these results will be reported elsewhere.

Acknowledgements

Financial support from Department of Science and Technology, New Delhi (Ref No. SP/S1/H-21/2001) is greatly acknowledged. Also thanks are due to Analytical Science Division, CSMCRI, for providing spectra.

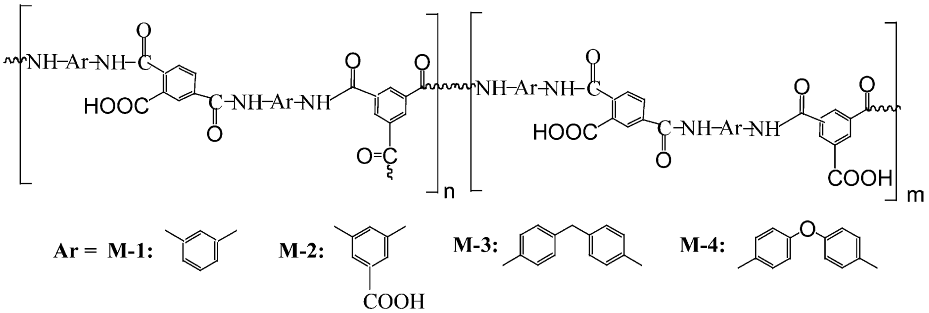


Fig. 6. Structure of poly(amide amic acid) thin film of the membranes.

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