

Aromatic Polyamide–Imides as Materials for Membranes.

I. Synthesis and Characterization

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SYNOPSIS

Diamine amic acids were synthesized by reacting aromatic diamines with pyromellitic dianhydride in dimethylacetamide/dioxane. High molecular weight polyamide–amic acids were prepared by low-temperature solution polymerization of diamine amic acids with isophthaloyl chloride in dimethylacetamide. The cyclodehydration of polyamide–amic acids to the corresponding polyamide–imides was accomplished by heating the cast films at 175°C for 3 h. The polyamide–imides were soluble in polar aprotic solvents like dimethylformamide, dimethylacetamide, dimethyl sulfoxide, and *N*-methyl-2-pyrrolidone and could be cast into tough and flexible films. They were characterized by elemental analyses, inherent viscosities, IR, and ¹H-NMR spectra. The glass transition temperatures of polyamide–imides were determined by differential scanning calorimetry. The thermal stabilities of the polymers were measured by thermogravimetric analyses in air. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Recently, synthetic polymeric membranes have achieved tremendous importance for desalination, for the resolution of gaseous and aqueous liquid mixtures, for the purification of chemical and biological products, etc. The salient features of polymers suitable as barrier materials are the inherent chemical, mechanical, and thermal properties and their processability. The appropriate chemical structure combines polar and nonpolar functional groups with a polymeric network. The family of nitrogen-containing polymers are considered as suitable polymeric materials for a broad spectrum of membrane applications. This class of polymers is characterized by amide and imide linkages between aromatic/heterocyclic structural units.^{1–5} Aromatic polyamides,^{6–9} polyamide–imides,^{10,11} polyamide–hydrazides,^{12,13} etc., are reported to be the most versatile class of membrane polymers for high-pressure and high-temperature service conditions. Membranes of these polymers are, usually, prepared according to a phase-inversion technique.¹⁴ The resulting membrane contains a solute separating bar-

rier layer supported on a porous substructure. These membranes are called “asymmetric membranes or integrally skinned membranes,” in which both the solute separating layer and its porous support are formed simultaneously from the same polymer. The relations between preparative factors and structure and performances of integrally skinned membranes have been described by many researchers.^{8,15–17}

The present article reports the synthesis and characterization of aromatic alternating polyamide–imides having tricomponent structures. The main objective of the present study was to obtain soluble polyamide–imides that can be used for the development of membranes for various separation applications.

EXPERIMENTAL

Materials

m-Phenylenediamine (MPD), *p*-phenylenediamine (PPD), 4,4'-diaminodiphenyl ether (DPE), 4,4'-diaminodiphenyl sulfone (DPS), and isophthaloyl chloride (IPC) from Aldrich and pyromellitic dianhydride (PMDA) from BDH Chemicals were used as received. All other reagents and solvents were of analytical grade and used without further purification.

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Synthesis

N,N'-Bis(3-aminophenyl)terephthalamido-2,5-dicarboxylic Acid (B3APTA)

In a 250 mL three-neck flask, 10.81 g of *m*-phenylenediamine was dissolved in 100 mL dioxane and cooled to 10°C. Then, 10.91 g of pyromellitic dianhydride was added and stirred for 1 h at 10°C. The reaction temperature was then raised to 50°C and stirred for another 2 h. The solvent was then evaporated under vacuum. The solid product was purified by recrystallization from ethanol. Yield: 79% (17.1 g); mp 254–256°C.

ANAL: Calcd for C₂₂H₁₈N₄O₆: C, 60.83%; H, 4.17%; N, 12.90%.

Found: C, 60.74%; H, 4.13%; N, 12.85%.

IR (KBr, cm⁻¹). 3300 (N—H and acid O—H stretch), 1715 (acid C=O stretch), 1665 (amide C=O stretch). The ¹H-NMR spectral data of B3APTA are presented in Table I.

N,N'-Bis(4-aminophenyl)terephthalamido-2,5-dicarboxylic Acid (B4APTA)

This compound was prepared by reacting *p*-phenylenediamine (10.81 g) with pyromellitic dianhydride

(10.91 g) in dioxane by following the exact same procedure described in the preparation of B3APTA. The crude product after recrystallization from ethanol gave 84% (18.2 g) of B4APTA. Mp 268–270°C.

ANAL: Calcd for C₂₂H₁₈N₄O₆: C, 60.83%; H, 4.17%; N, 12.90%.

Found: C, 60.78%; H, 4.13%; N, 12.83%.

IR (KBr, cm⁻¹). 3300 (N—H and acid O—H stretch), 1710 (acid C=O stretch), 1665 (amide C=O stretch).

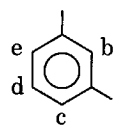
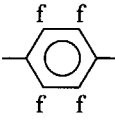
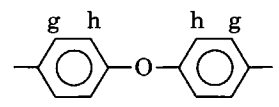
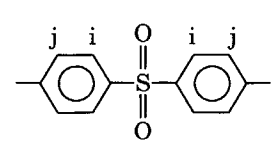
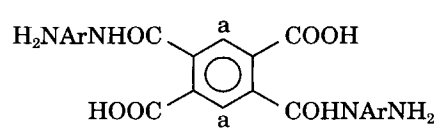
N,N'-Bis[4-(4-aminophenoxy)phenyl]terephthalamido-2,5-dicarboxylic Acid (BAPOPTA)

This compound was obtained by reacting 4,4'-diaminodiphenyl ether (20.02 g) with pyromellitic dianhydride (10.91 g) in dimethylacetamide under the similar conditions described in the preparation of B3APTA. The product was isolated in water and recrystallized from ethanol. The yield was 85% (26.3 g). Mp 263–265°C.

ANAL: Calcd for C₃₄H₂₆N₄O₈: C, 66.01%; H, 4.37%; N, 9.06%.

Found: C, 65.94%; H, 4.33%; N, 8.98%.

Table I ¹H-NMR Chemical Shift Data of Diamine Amic Acids

Diamine Amic Acid	Ar	Chemical Shift (ppm)	
B3APTA		10.15	(s, 2 H, NHCO)
		8.37	(s, 2 H, a)
		6.85–6.12	(m, 8 H, b–e)
		3.55	(s, 4 H, NH ₂)
B4APTA		10.21	(s, 2 H, NHCO)
		8.49	(s, 2 H, a)
		6.52	(s, 8 H, f)
		3.57	(s, 4 H, NH ₂)
BAPOPTA		10.33	(s, 2 H, NHCO)
		8.52	(s, 2 H, a)
		7.94–7.58	(m, 8 H, g)
		7.06–6.64	(m, 8 H, h)
		3.84	(s, 4 H, NH ₂)
BAPSPTA		10.43	(s, 2 H, NHCO)
		8.16	(s, 2 H, a)
		7.49–7.41	(d, 8 H, i)
		6.62–6.54	(d, 8 H, j)
		4.03	(s, 4 H, NH ₂)
			

IR (KBr, cm^{-1}). 3350 (N—H and acid O—H stretch), 1715 (acid C=O stretch), 1665 (amide C=O stretch).

***N,N'*-Bis[4-(4-aminophenylsulfonyl)phenyl]terephthalamido-2,5-dicarboxylic Acid (BAPSPTA)**

This compound was prepared from 4,4'-diaminodiphenyl sulfone (24.83 g) and PMDA (10.91 g) in dimethylacetamide according to the similar procedure described in the preparation of B3APTA. The crude product on recrystallization from ethanol gave 80% of BAPSPTA. Mp 279–281°C.

ANAL: Calcd for $\text{C}_{34}\text{H}_{26}\text{N}_4\text{O}_{10}\text{S}_2$: C, 57.14%; H, 3.67%; N, 7.84%.

Found: C, 57.08%; H, 3.65%; N, 7.79%.

IR (KBr, cm^{-1}) 3300 (N—H and acid O—H stretch), 1715 (acid C=O stretch), 1665 (amide C=O stretch).

Polymer Synthesis

The polyamide-amic acids were prepared by low-temperature solution polymerization of diamine amic acids with isophthaloyl chloride in dimethylacetamide containing LiCl. As an illustration, the preparation of polyamide-amic acid of B3APTA with IPC is described here. B3APTA (8.68 g, 0.02 mol) was dissolved in 75 mL of DMAc containing 1.55 g of LiCl and cooled to 0–5°C. To this solution at 5°C, with stirring, IPC (3.38 g, 0.02 mol) was added in small portions for a period of 30 min. After stirring at 5°C for 1 h, the temperature of the reaction was increased to 30°C and further stirred for 8 h. The polymer was isolated in excess methanol and further purified by reprecipitation in methanol from the NMP solution and finally dried in vacuum.

Polyamide-Imides

Polyamide-imides were prepared by thermal cyclodehydration of polyamide-amic acids. A solution of polyamide-amic acid in dimethylformamide was prepared and cast on a glass plate and the solvent was removed under vacuum. The dried film was thermally imidized in a forced-air oven at 175°C for 3 h.

Measurements

The elemental analyses of diamine amic acids and polymers were performed by a Carlo Erba 1013 C—H—N analyzer. Infrared spectra were recorded

on a Biorad FT 40 IR spectrophotometer. NMR spectra were obtained with a JEOL JNX 100 FT NMR spectrometer. The spectra were recorded in $\text{DMSO-}d_6$ and the chemical shifts were measured using tetramethylsilane (TMS) as an internal reference. The inherent viscosities of the polyamide-imides were determined in dimethylacetamide containing 2 wt % of LiCl using a Ubbelohde viscometer at 30°C. Glass transition temperatures of the polyamide-imide films were determined by a Perkin-Elmer D7 differential scanning calorimeter at the heating rate of 10°C. The thermal stabilities of the polymers were measured using a Mettler TA 3000 thermal analyzer at a heating rate of 15°C/min in air.

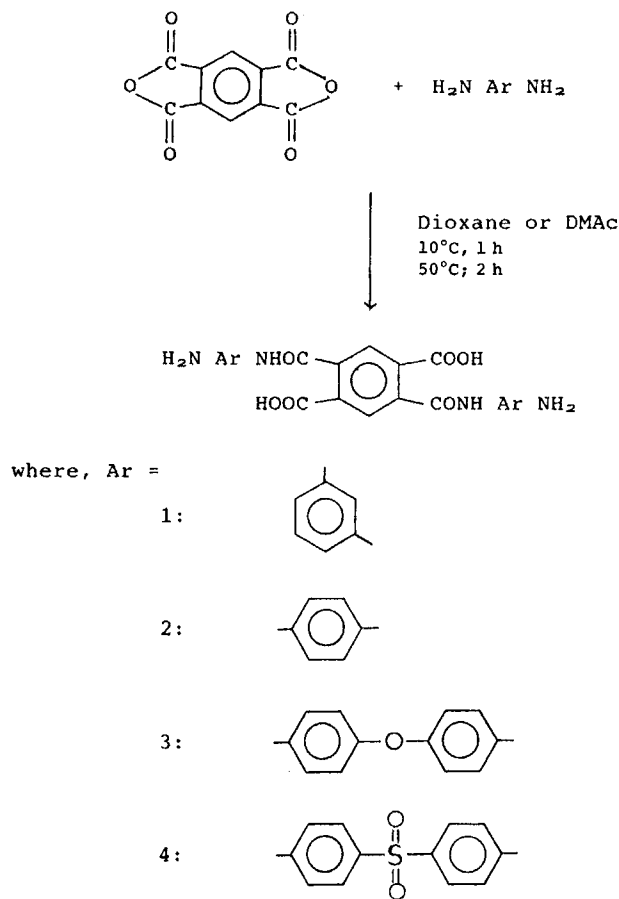
RESULTS AND DISCUSSION

Synthesis of Diamine Amic Acids

Four diamine amic acids such as B3APTA, B4APTA, BAPOPTA, and BAPSPTA, which contain free primary amine (NH_2), carboxylic acid (COOH), and amide ($\text{C}=\text{O NH}$) groups, were prepared quantitatively by reacting *m*-phenylenediamine, *p*-phenylenediamine, 4,4'-diaminodiphenyl ether, and 4,4'-diaminodiphenyl sulfone, respectively, with pyromellitic dianhydride in dioxane/dimethylacetamide. Scheme 1 illustrates the preparation of diamine amic acids.

The elemental analyses data of the diamine amic acids were in good agreement with the calculated values for the assigned structures. The infrared spectra of diamine amic acids are characterized by strong absorptions at about 1710 and 1665 cm^{-1} , which correspond to the carbonyl ($\text{C}=\text{O}$) stretching vibrations of carboxylic acid and amide linkage, respectively. The broad absorptions at 3300 cm^{-1} are due to the acid O—H and N—H stretchings.

In the $^1\text{H-NMR}$ spectra, all the diamine amic acids show distinct resonance absorptions for both the dianhydride and diamine structural components in the aromatic region. Figure 1 shows the aromatic region of the proton NMR spectra of diamine amic acids. The complete chemical-shift assignment data of the diamine amic acids are presented in Table I. The diamine amic acids show a singlet between 8.52 and 8.16 ppm, which corresponds to the two aromatic protons of the PMDA structural unit. The $^1\text{H-NMR}$ spectrum of B4APTA shows a singlet at 6.52 ppm due to the aromatic protons of the PPD structural component. Since MPD contains three nonequivalent aromatic protons, the proton NMR



Scheme 1: Preparation of Diamine amic acids.

spectrum of B3APTA exhibits a multiplet at 6.85–6.12 ppm due to the coupling to each other of these nonequivalent protons. The two doublets in the BAPSPTA spectrum at 7.49–7.41 and 6.62–6.54 ppm with their intensities corresponding to eight protons each are assignable to the aromatic protons at *ortho*- and *meta*-positions, respectively, to the sulfone (SO_2) group of the diaminodiphenyl sulfone unit. These doublets arise due to the coupling of two non-equivalent protons at an *ortho*-position to each other. BAPOPTA exhibits multiplets at 7.94–7.58 and 7.06–6.64 ppm corresponding to the protons at *meta*- and *ortho*-positions to the ether linkage of diaminodiphenyl ether. All the diamine amic acids show a singlet between 4.03 and 3.55 ppm due to amine protons of the diamine units and at 10.43–10.15 ppm due to amide protons.

Polyamide-Imides

The preparation of polyamide-imides, usually, consists of two steps: (1) preparation of polyamide-amic acid and (2) chemical/thermal cyclodehydration of

polyamide-amic acid to polyamide-imide. Polyamide-amic acids can be prepared in a number of ways: (1) by the 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, e.g., trimellitoyl chloride; and (3) polymerization of a diamine containing amide linkages with dianhydride. A number of polyamide-imides have been reported, and these polymers are reckoned to possess good thermal stability, toughness, and ease of processability and to be intermediate between polyamides and polyimides in properties.¹⁸⁻²²

We prepared polyamide-amic acids (5–8) by low-temperature solution polymerization of diamine amic acids with isophthaloyl chloride in dimethylacetamide. Polyamide-imides (9–12) having tri-component structures were obtained by thermal cyclodehydration of polyamide-amic acids (5–8) in a forced air oven at 175°C for 3 h. In the tri-component polymer structures such as diamine, diacid chloride, and dianhydride, one of the amino group of the diamine has been linked as an amide (reaction with IPC) and the other one attached as an imide (reaction with anhydride). Scheme 2 illustrates the

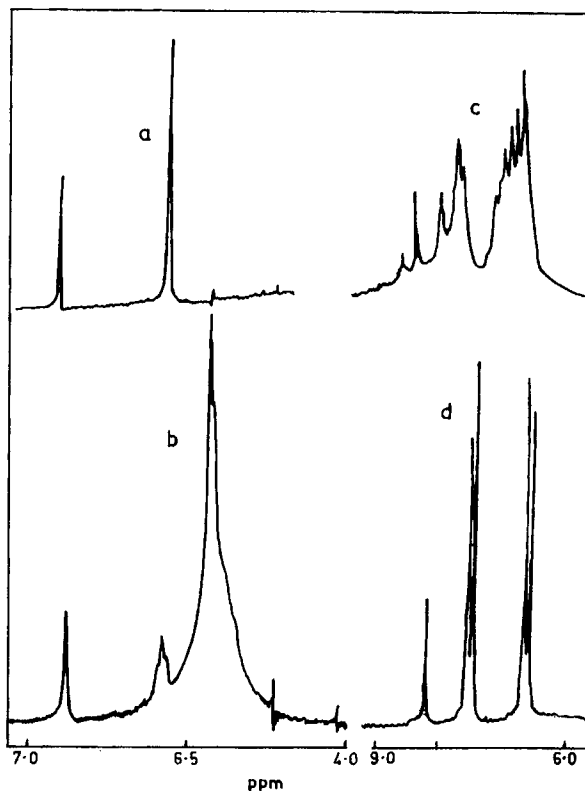
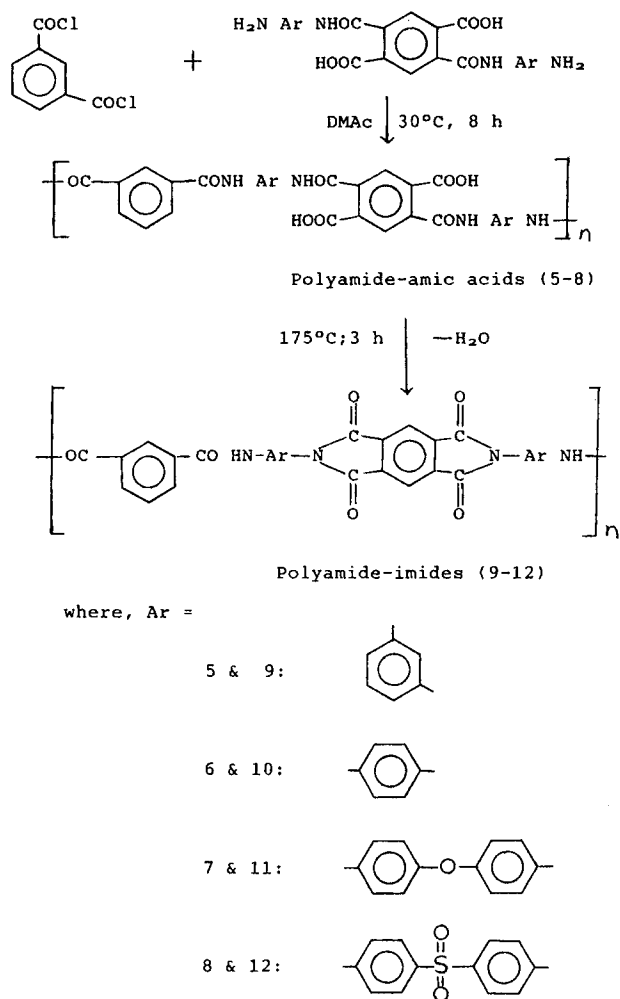


Figure 1 $^1\text{H-NMR}$ spectra of diamineamic acids: (a) B4APTA; (b) B3APTA; (c) BAPOPTA; (d) BAPSPTA.



Scheme 2: Preparation of Polyamide-imides.

synthesis of tricomponent polyamide-imides. The elemental analyses data of polymers were in good agreement with the calculated values for the proposed structures.

Characterization of Polymers

Processability of the polymer in terms of solubility and tractability is one of the major requirements for membranes and also for any other application. Table II shows the qualitative solubility characteristics of polyamide-imides in various organic solvents. The polyamide-imides (**9**, **11**, **12**) were soluble in polar aprotic solvents like DMF, DMAc, NMP, and DMSO, which are common solvents for the preparation of asymmetric membranes. However, polymer 10 was insoluble in the same solvents even in the presence of LiCl. The difference in solubility between *meta* and *para* isomers is characteristic of many types of polyamides, polyamide-imides, po-

lyimides, etc., and is probably due to the fact that *meta* geometry tends to hinder packing of polymer molecules to decrease interchain interactions.²³ The presence of ether or sulfone linkages at an appropriate position of the polyimide backbone results in remarkable improvement in solubility and processability of the resin without appreciable sacrifice of high-temperature stability.²⁴ The soluble nature of the polyamide-imides (**9**, **11**, **12**) facilitates to use them for membrane separations, spray coating, etc. The inherent viscosities (Table III) of the polyamide-imides in dimethylacetamide are in the range of 0.68–0.84 dL/g (Table III).

The IR spectra of polyamide-amic acids show a broad absorption band at around 3300 cm^{-1} , corresponding to carboxylic acid O—H and amide N—H stretchings. Strong peaks at about 1705 and 1665 cm^{-1} are due to C=O stretchings of acid and amide groups, respectively. Polyamide-imides show characteristic absorption bands at 1780–1765 cm^{-1} and 1720–1705 cm^{-1} due to imide carbonyl stretchings. In addition, polyamide-imides show a broad absorption band at about 3350 cm^{-1} due to amide N—H stretchings and at 1675–1660 cm^{-1} due to amide C=O stretching vibrations.

Figure 2 represents the $^1\text{H-NMR}$ spectrum of polymer **8** in $\text{DMSO-}d_6$. Polymers **5–8** exhibit a singlet between 10.89 and 10.43 ppm, which may be assigned to amide (CON—H) protons. The two aromatic protons of the PMDA unit are observed as a singlet between 8.64 and 8.52 ppm. The multiplet resonance absorptions at 8.15–6.13 ppm correspond

Table II Solubility of Alternating Polyamide-Imides

Solvent	Polyamide-Imide			
	9	10	11	12
NMP	S+	I	S+	S+
DMF	S+	I	S+	S+
DMAc	S+	I	S+	S+
DMSO	S+	I	S+	S+
THF	I	I	I	I
MeOEtOH	I	I	I	I
Dioxane	I	I	I	I
CH_3CN	I	I	I	I
EAc	I	I	I	I
DCM	I	I	I	I
DCE	I	I	I	I
CHCl_3	I	I	I	I
$\text{C}_6\text{H}_5\text{Cl}$	I	I	I	I

S+ = soluble on heating in presence of LiCl; I = insoluble.

Table III Properties of Polyamide-Imides

Polymer	n_{inh} (dL/g) ^a	T_g (°C) ^b	T_{id}	T_{d10}
9	0.84	265	389	471
10	—	296	430	519
11	0.80	282	419	494
12	0.68	286	405	477

^a Measured with 0.5 g/dL DMAc at 30°C.

^b Determined by DSC in air at a heating rate of 10°C/min.

T_{id} Initial decomposition temperature (°C).

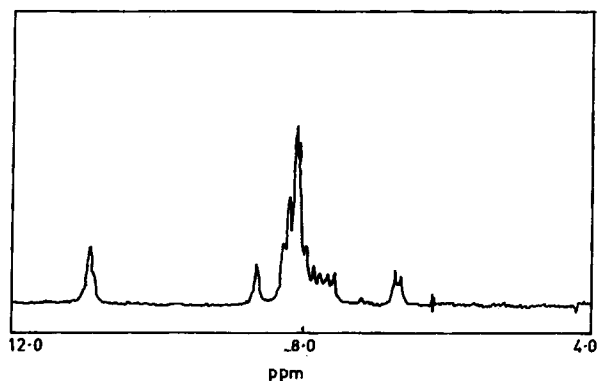
T_{d10} Temperature (°C) at which 10% weight loss was recorded by TG.

to the aromatic protons of IPC and diamine structural components.

Thermal Properties

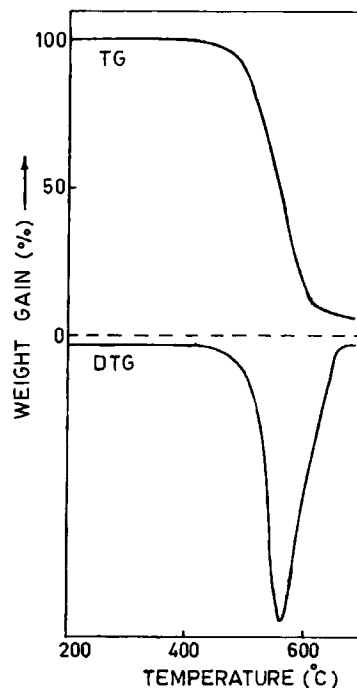
The chain stiffness of the polymers is characterized by the glass transition temperature (T_g) and is an additional requirement for barrier applications. Table III gives the T_g values of polyamide-imides determined by DSC. The polyamide-imides have relatively high glass transition temperatures between 265 and 296°C. Polymer **10** has a higher T_g value of 296°C, whereas polymer **9** has a lower T_g value of 265°C. Poly(BAPSPTA-IPC) and poly(BAPOPT-IPC), **12**, **18** which have flexible ether and sulfone linkages, respectively, in the polymer backbone, have somewhat lower T_g 's than does polymer **10**. Generally, the glass transition temperature of polyamide-imides and polyimides depends on imidization reaction conditions, e.g., curing time and temperature, of the precursors, namely, polyamic acids. Hence, different T_g values have been reported for the polymers derived from the same monomer pairs depending upon the method and conditions of imidization.²⁵

The thermal stabilities of polyamide-imides have been studied by thermogravimetric analyses in air.

**Figure 2** ¹H-NMR spectrum of poly(BAPSPTA-IPC).

The polymers undergo decomposition in a single stage. Figure 3 shows the TGA curve of polymer **11**. The IDT and temperatures of 10 wt % loss of the polymers **9–12** are presented in Table III. The initial decomposition of polyamide-imides starts above 375°C. The temperature at which 10% weight loss is observed is in the range of 471–519°C, depending upon the precursor diamine. The results clearly indicate that polymers **11** and **12** have good thermal stabilities with enhanced solubility in various organic solvents. The asymmetric membranes of polyamide-imides are under investigation and these studies will be reported elsewhere.

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**Figure 3** TGA curve of polyamide-imide (**11**) in air.

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