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Synthesis and Characterization of Organosoluble Polyimides Containing Pyridyl Moiety with Ether Linkages

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Two novel diamine monomers, bis(4-amino-3,5-dimethylphenyl)-3-pyridyl methane and bis(4-aminophenoxy-3,5-dimethylphenyl)-3-pyridyl methane were synthesized. A series of pyridine containing aromatic polyimides derived from the diamines were synthesized through a typical two-step polymerization method. Most of the polymers show good solubility in NMP, DMAc, DMF, DMSO and $CHCl_3$ at room temperature. These polyimides exhibit T_g in the range of 249–317°C and 10% wt loss (T_{10}) takes place in the range of 474–564°C in N_2 and 469–558°C in air. The polymers have tensile strength in the range of 88–96 MPa, elongation at break in the range of 8.5–12.5% and tensile modulus in the range of 1.5–2.1 GPa. These polyimides also have low dielectric constant (3.26–3.64 at 1 KHz and 3.24–3.61 at 10 KHz) and low moisture absorption (0.42–0.89%).

Keywords: polyimides; diamine; pyridine moiety; solubility; thermal stability

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1 Introduction

Polyimides are of great interest in engineering and microelectronics for a number of applications as a result of their unique property combinations (1–3). However, most of them have high melting or softening temperatures, strong inter-chain interactions and are insoluble in most organic solvents because of the rigidity of the backbone, and hence have limited use for many applications (4). Extensive efforts have been made to improve the solubility of polyimides without apparent sacrifices in their thermal, mechanical and other required properties.

The heterocyclic rings in the main chain of a polymer impart certain properties to the polymer. Some of the heterocyclic groups such as 2,6-pyridine (5–7), 1,3,4-oxadiazole (8), 2,3-quinoxaline (9) and 2,5-thiophene (10) have been incorporated into diamines, which were used to synthesize polyimides. The effect of the heterocyclic units on the T_g of the polyimides is variable. Recently, many reports describing polyimides containing heterocyclic units on their backbone with improved solubility have appeared in the literature. Their solubility enhancement is achieved either by incorporating flexible linkages or by introducing bulky substituents on the heterocyclic unit (11–13).

In this present study, diamine monomers with pyridine pendant group and flexible ether linkages were synthesized and used to produce a series of novel polyimides. In this respect, it is known that the incorporation of ether linkages into the main chain of the polymer greatly enhances molecular mobility and provides solubility, but it decreases thermal transitions and stability (14–16). On the other hand, the incorporation of bulky pendant group can give rise to restricted molecular mobility, so that the overall observable effect is a rising of the T_g and an improvement of solubility simultaneously (17–19).

2 Experimental

2.1 Materials

Pyridine-3-aldehyde (E. Merck), 2,6-dimethylaniline (Aldrich), 2,6-dimethylphenol (E. Merck), hydrochloric acid (HCl, Spectrochem), p-chloronitrobenzene (Spectrochem), hydrazine monohydrate (Lancaster) and p-toluenesulphonic acid (SRL) were used as received. Pyromellitic dianhydride (PMDA, E. Merck) was purified by sublimation at 200–220°C in vacuum, 3,3′,4,4′-benzophenonetetracarboxylicacid dianhydride (BPDA, Sigma), oxydiphthalic anhydride (ODPA, E. Merck) and hexafluoroisopropylidine dianhydride (HFIDA, E. Merck) were recrystallized from acetic anhydride. All the reaction solvents such as N,N-dimethylacetamide (DMAc, spectrochem), N-methyl-2-pyrrolidone (NMP, Aldrich) and N,N-dimethylformamide (DMF, E. Merck), tetrahydrofuran (THF, SRL) were purified by refluxing with calcium hydride, distilled under reduced pressure and stored over 4 Å molecular sieves.

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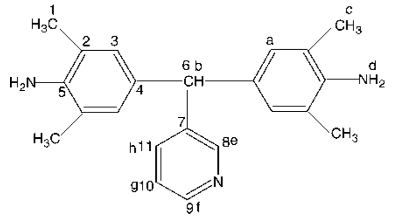
2.2 Monomer Synthesis

2.2.1 Synthesis of bis(4-amino-3,5-dimethylphenyl)-3-pyridyl methane (BAPM)

A three-necked flask equipped with an addition funnel, nitrogen inlet, reflux condenser and a bent inlet for dry HCl was charged with 2,6-dimethylaniline (24.2 g, 0.2 mol). Dry HCl gas (23 mL) was passed into the reaction vessel for 90 min. The solid obtained was dissolved in 12 mL of DMF. To this solution, pyridine-3-aldehyde (10.7 g, 0.1 mol) in DMF was added dropwise. After the completion of the addition, the reaction mixture was maintained at 120°C for 6–7 h. The reaction mixture was cooled and the pH was brought to seven using NaOH. The product obtained was filtered, washed repeatedly with methanol and dried in vacuum oven for 12 h at 70°C. Yield: 89%, m.p. (189–190°C). IR (KBr, cm^{-1}); 3434 and 3395 cm^{-1} (asymmetric and symmetric stretching of N-H group), 1624 cm^{-1} (N-H bending vibration), 2965 and 2924 cm^{-1} (C-H stretching of CH_3 group). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm); $\delta - 6.63$ (s, 4H, a), 5.3 (s, 1H,b), 2.10 (s, 12H, c), 3.88 (s, 4H, d), 8.43 (s, 1H, e), 8.37 (d, 1H, f), 7.28–7.31 (t, 1H, g), 7.57–7.58 (d, 1H, h). ^{13}C-NMR (400 MHz, $CDCl_3$, ppm); $\delta - C^1$-17.8, C^2-121.9, C^3-129.0, C^4-132.8, C^5-146.5, C^6-54.6, C^7-132.8, C^8-154.1, C^9-141.4, C^{10}-122.8, C^{11}-139.0. Elemental analysis; calculated for $C_{22}H_{25}N_3$: C-79.72%; H-7.60%; N-12.68%. Found: C-78.78%; H-7.62 %; N-12.71%.



2.2.2 Synthesis of bis(4-hydroxy-3,5-dimethylphenyl)-3-pyridyl methane (BHPM)

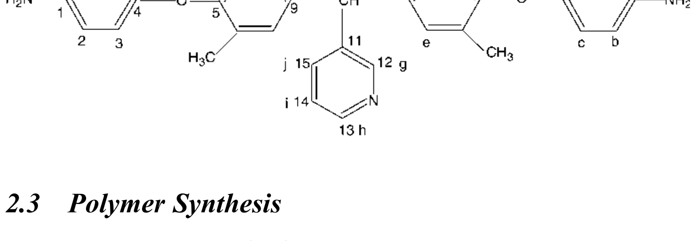
18.3 g (0.15 mol) of 2,6-dimethylphenol was charged in to a three-necked flask, equipped with a reflux condenser, Dean-Stark apparatus and nitrogen inlet. To this, 6.42 g (0.06 mol) of pyridine-3-aldehyde, 1.17 g (0.006 mol) of p-toluenesulphonic acid monohydrate and 60 mL of toluene were added. The reaction mixture was refluxed at 132–134°C for 5 h under nitrogen atmosphere. Water produced by the reaction was removed as azeotrope with toluene. The reaction mixture was cooled and 10% aqueous solution of NaOH was added to the resulting solution. The product obtained was filtered, washed with methanol and dried. The resulting solid was recrystallized from methanol/water (3:1,v/v). Yield: 91%. M.p. (154–155°C). IR (KBr, cm^{-1}); 3539 and 3438 cm^{-1} (asymmetric and symmetric stretching of O-H group), 2955 and 2911 cm^{-1} (C-H stretching of CH_3 group), the absence of peak around 1660 cm^{-1} due to carbonyl stretch of pyridine-3-aldehyde shows the completion of the reaction. Elemental analysis; calculated for $C_{22}H_{23}NO_2$; C-79.26%; H-6.95%; N-4.20%. Found: C-78.84%; H-7.03%; N-4.28%.

2.2.3 Synthesis of bis(4-nitrophenoxy-3,5-dimethylphenyl)-3-pyridyl methane (BNPPM)

BNPPM was synthesized by the reaction of 14.65 g (0.044 mol) of bis(4-hydroxy-3,5-dimethylphenyl)-3-pyridyl methane, 13.97 g (0.089 mol) of p-chloronitrobenzene, 12.14 g (0.088 mol) of K_2CO_3 and 25 mL of DMAc at 158–160°C for 10 h under nitrogen atmosphere. After completion of the reaction, the solution was cooled and poured into cold water. The crude dinitro product was recrystallized from ethanol: water (1:1, v/v). Yield:83%. M.p. (169–170°C). IR (KBr, cm^{-1}); 1518 and 1359 cm^{-1} (asymmetric and symmetric stretching of $-NO_2$ group), 1258 cm^{-1} (C-O-C stretching). Elemental analysis; calculated for $C_{34}H_{29}N_3O_6$; C-70.95%; H-5.07%; N-7.30%. Found: C-70.01%; H-5.11%; N-7.33%.

2.2.4 Synthesis of bis(4-aminophenoxy-3,5-dimethylphenyl)-3-pyridyl methane (BAPPM)

17.25 g (0.03 mol) of the dinitro compound (BNPPM) in 65 mL of 2-methoxy ethanol was charged into a three-necked round bottom flask and 0.1 g of 10% palladium on carbon (Pd/C) was added. To this, 75 mL of 80% hydrazine monohydrate was added dropwise at 90°C for one hour. After the addition was complete, the reaction mixture was refluxed for 12 h under N_2 atmosphere. After the removal of Pd/C, the excess solvent was distilled off and poured into distilled water. The obtained product was filtered and dried. The product was recrystallized from 2-methoxyethanol/water (3:1, v/v). Yield: 79%. M.p. (177–178°C). IR (KBr, cm^{-1}); 3416 and 3356 cm^{-1} (asymmetric and symmetric stretching of $-NH_2$ group), 1215 cm^{-1} (C-O-C stretching). ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm); 4.01 (s, 4H, a), 6.42 (d, 4H, b), 6.67 (d, 4H, c), 2.35 (s, 12H, d), 6.59 (s, 4H, e), 5.34 (s, 1H, f), 8.47 (s, 1H, g), 8.39 (d, 1H, h). 7.29–7.31 (t, 1H, i), 7.60–7.62 (d, 1H, j). ^{13}C-NMR (400 MHz, $CDCl_3$, ppm); δ-C^1-139.8, C^2-118.1, C^3-114.8, C^4-146.1, C^5-135.9, C^6-18.1, C^7-126.9, C^8-125.8, C^9-133.5, C^{10}-54.2, C^{11}-132.6, C^{12}-153.6, C^{13}-142.1, C^{14}-122.5, C^{15}-138.6. Elemental analysis; calculated for $C_{34}H_{33}N_3O_2$; C-79.20%; H-6.45%; N-8.15%. Found: C-78.76%; H-6.51%; N-8.24%.



2.3 Polymer Synthesis

2.3.1 Two-step Method

9.93 g (0.03 mol) of BAPM was dissolved in 20 mL of dried DMAc. After the diamine was completely dissolved, 6.54 g (0.03 mol) of pyromellitic dianhydride was added in one portion. The reaction mixture was stirred at room temperature in a nitrogen atmosphere for 16–18 h. Then, one part of the obtained poly(amic acid) solution was spread on a glass plate using doctors knife, which was placed in an oven at 80°C for 1 hr to remove the solvent. The semi-dried poly(amic acid) film was sequentially heated from 120°C to 210°C at a heating rate of 30°C/20 min. and finally 250°C for 30 min. By soaking in hot water, a flexible film was self stripped off from the glass plate.

For the chemical imidization method, 5 mL of acetic anhydride and 2 mL of pyridine were added to the remaining poly(amic acid) solution, and the mixture was heated at 100°C for 3 h to achieve a complete imidization. The resultant solution was poured into methanol. The precipitated polymer was collected by filtration and dried in vacuum at 150°C for 8 h.

2.4 Measurements

Fourier Transform Infra Red (FT-IR) spectra were recorded on a Nicolet spectrometer with KBr pellet. ^{1}H-NMR spectra were recorded using a Jeol Ex-400 spectrometer with $CDCl_3$ as solvent and tetramethylsilane (TMS) as reference. Elemental analysis was performed on a Carlo Erba EA 1108 micro analyzer; DSC and TGA were performed with a Q10 and Q100 series of TA instruments at a heating rate of 10°C/min. The inherent viscosities were measured with an Ubbelohde viscometer with a 0.5 g/dL solution in NMP at 30°C. The solubility was determined by dissolving 0.5 g of the sample in 8 mL of the solvent at room temperature. The solubility was determined visually. Mechanical properties of the films were measured with an Instron model 1130 tensile tester using a 5 Kg load cell at a crosshead speed of 0.5 mm/min on strips of approximately 30–40 mm thick and 0.5 cm wide with a 2 cm gauge length. Wide-angle X-ray diffraction measurements were performed at room temperature (about 25°C) on a X-pert PAN analytical X-ray diffractometer using Ni-filtered Cu Kα radiation. The scanning rate was 20°/min over a range of $2\theta = 5-40°$. Dielectric properties were studied on polymer films by the parallel plate capacitor method using HP-4194A impedance/Gain phase analyzer at a frequency of 1 KHz. Gold electrodes were vacuum deposited on both the surfaces of the dried films. Moisture absorption was measured by immersing the specimens in water at room temperature for three days and the weight difference before and after immersion was determined.

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3 Results and Discussion

3.1 Monomer Synthesis

The pyridine containing monomers BAPM and BAPPM were prepared according to the developed method (20, 21) (Scheme 1). The diamine BAPM was synthesized from 2,6-dimethylaniline and pyridine-3-aldehyde using HCl as catalyst. The FT-IR spectrum exhibits the characteristic absorption bands at 3395 and 3415 cm^{-1} of amino groups. ^{1}H-NMR and ^{13}C-NMR spectrum of BAPM are given in Figures 1 and 2. The signals at 2.10 and 3.88 ppm in the ^{1}H-NMR spectrum are due to the CH_3 and NH_2 protons of the diamine.

The diamine BAPPM was synthesized from 2,6-dimethylphenol in three steps. The bisphenol compound BHPM was synthesized from the reaction of pyridine-3-aldehyde with an excess of 2,6-dimethylphenol in the presence of p-toluenesulphonic acid as catalyst. The dinitro compound BNPPM was prepared by a nucleophilic substitution reaction of BHPM with p-chloronitrobenzene in the presence of K_2CO_3. The catalytic dehydrogenation of BNPPM to the diamine BAPPM was accomplished by means of hydrazine monohydrate and a catalytic amount of Pd/C. The IR spectrum of BNPPM shows characteristic absorptions due to nitro group at 1518 and 1359 cm^{-1}. After dehydrogenation, the characteristic absorptions of the nitro group, disappeared and new absorptions at 3416, 3356 cm^{-1} (asymmetric and symmetric stretching) and 1626 cm^{-1}(N-H deformation) due to NH_2 group appeared.

3.2 Polymer Synthesis

All the PI-Ia-d and PI-IIa-d series polyimides containing the pyridyl pendant group were synthesized by the conventional one-step and two-step polymerization methods as shown in Scheme 2. In the two-step procedure, transformation from poly(amic acid) to polyimide is possible via the thermal or chemical cyclo-dehydration; merits of the former are easy to handle and to cast into thin films. The formation of polyimides was confirmed with FT-IR, ^{1}H-NMR and elemental analysis. All the polyimides exhibited characteristic imide group absorptions around 1780, 1725 cm^{-1} (asymmetric and symmetric stretching of carbonyl groups), 1380 cm^{-1} (C-N-C stretching), 1100 and 720 cm^{-1} (imide ring deformation). Figure 3 shows the typical ^{1}H-NMR spectrum of PI-Ia in $CDCl_3$. Table 1 shows the results of the elemental analysis of all the polyimides. The values are generally in good agreement with the calculated values of the proposed structures.

3.3 Polymer Solubility

The solubility of polyimides via both thermal and chemical imidization was tested in various organic solvents and the results are summarized in Table 2. Most of the polyimides are soluble in polar aprotic solvents such as NMP, DMAc, DMF and DMSO. They are also soluble in low boiling solvents such as $CHCl_3$ and THF. It was observed that the polyimides obtained by chemical imidization are more soluble compared with those obtained by thermal imidization. The less solubility of the thermal imidized polyimides is possibly due to the presence of partial intermolecular cross-linking during the solid state thermal imidization or denser chain packing and aggregation during imidization at elevated temperature, while chemical imidization gives a loosely packed polyimide solid (22, 23). PI-IIa-d series

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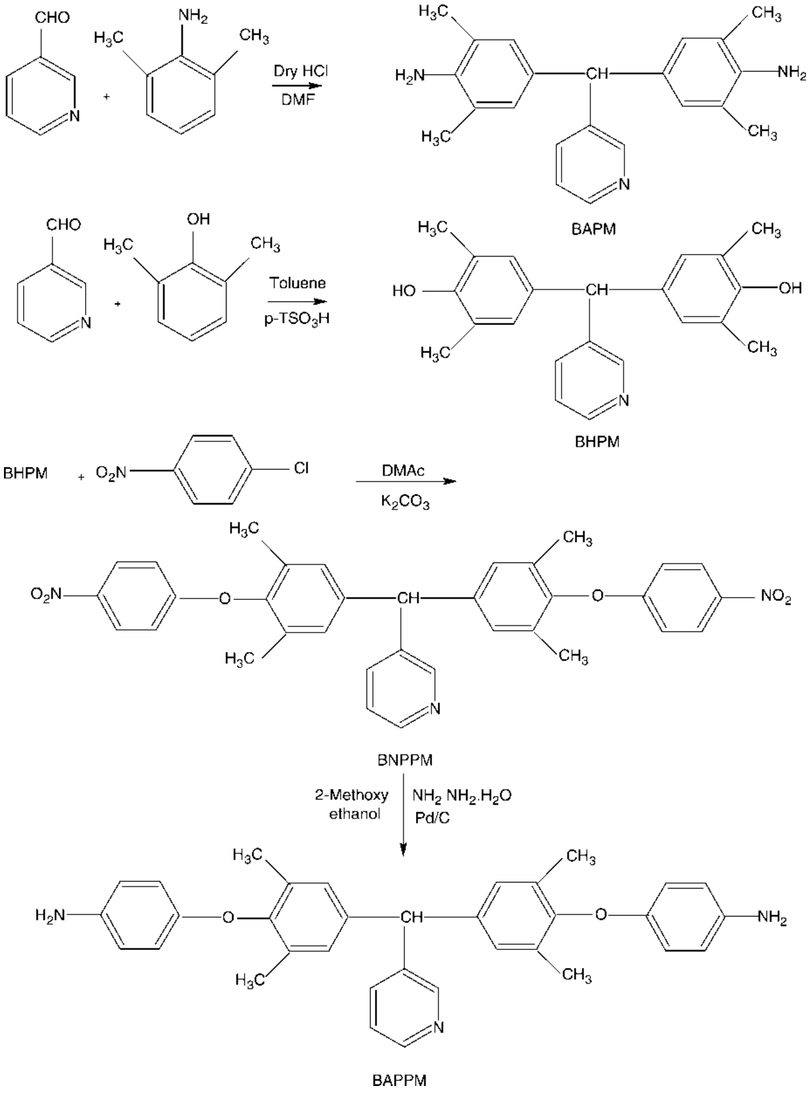

Sch. 1. Synthesis of monomers.

polyimides have shown better solubility compared to the PI-Ia-d series. This may be attributed to the combined effect of bulky pendant group (which decreases polymer inter and intra chain interactions and disturbs the co-planarity of aromatic units to reduce the packing efficiency and the crystallinity) (24) and flexible ether-bridged segments (which enhance the rotational freedom thereby enhancing the solubility).

PMDA based polyimides show less solubility than the others due to the inherent rigidity and strong intermolecular interactions. In the HFIDA derived polyimides, the low cohesive energy provided by the fluorinated group may also be attributed to the enhanced solubility. The relatively higher solubility of the BPDA and ODPA based polyimides may be due to the presence of >C=O and -O- linking groups/atom between phthalimide groups, which reduce the electron affinity of the dianhydride, causing a reduction in the over all inter-chain interaction (24).

Inherent Viscosity

The inherent viscosity of the polyimides was measured at a concentration of 0.5 g/dL in NMP at 30°C, and the results are presented in Table 5. The inherent viscosity values of polyimides are in the 0.61–1.02 dL/g range. The values are lower than those of general polyimides, which may be due to higher polymer chain flexibility because of the presence of a pyridine substituent dangling from the main chain of the polymer, but the presence of CH_3 group in the benzene ring increases the segmental rigidity of the polymer backbone resulting in increased solution viscosity. The inherent viscosity of all the polyimides is sufficient to permit the casting of flexible and tough film.

3.4 Thermal Properties

The thermal properties of the polyimides were measured by thermogravimetry (TGA) and differential scanning

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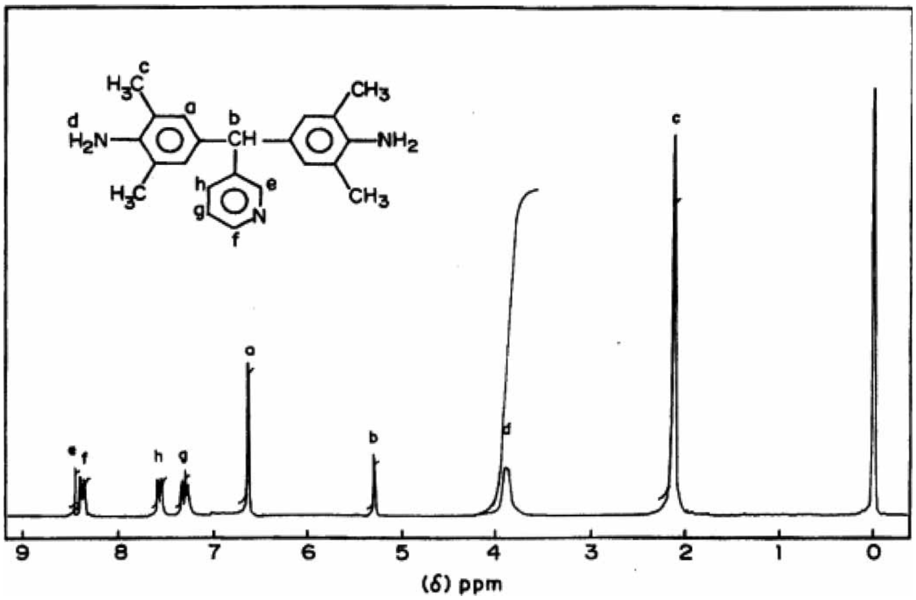


Fig. 1. ^{1}H-NMR spectrum of BAPM.

calorimetry (DSC). The thermal behavior data of all polymers are listed in Table 3. DSC experiments were conducted at a heating rate of 10°C/min in N_2. The T_g values of these polyimides are in the 249–317°C range. In the PI-IIa-d series polyimides, the presence of flexible ether unit should increase the overall flexibility of the polymer chain and thus, T_g of the polymer are expected to decrease. But the insertion of alkyl substitution at ortho positions to the ether linkage

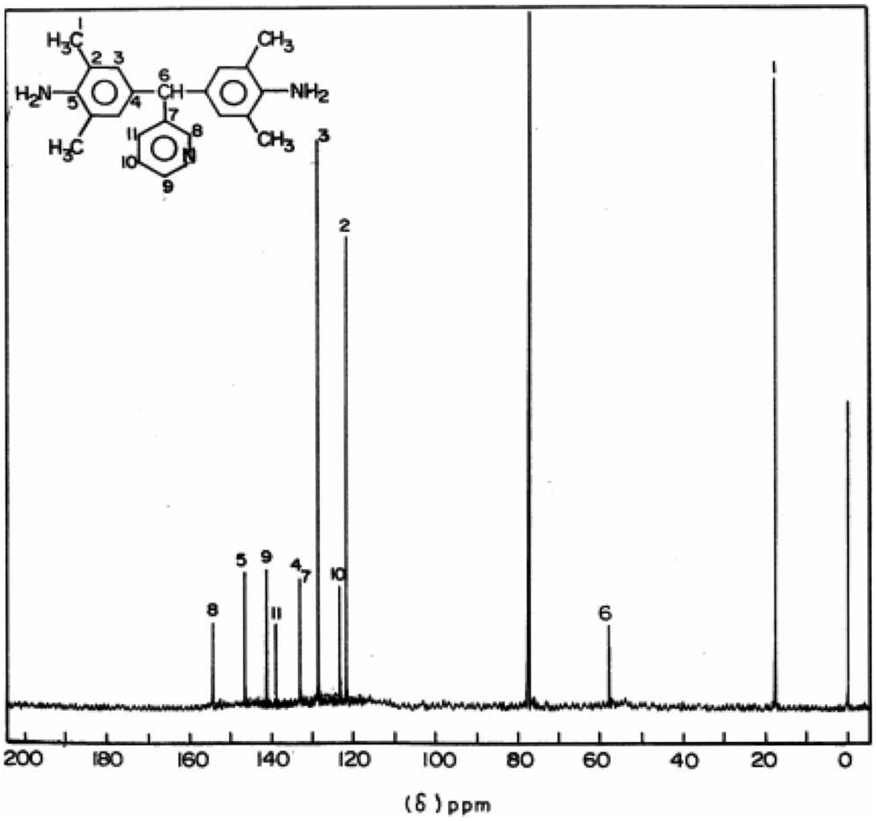
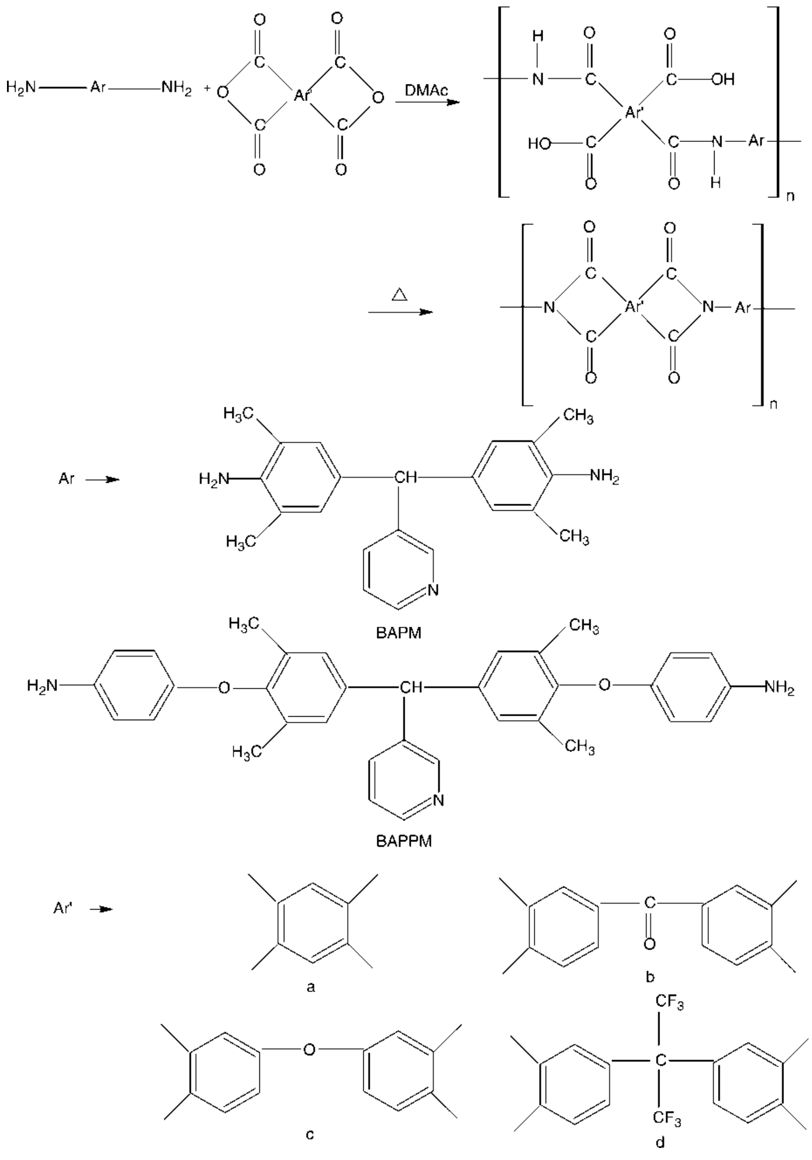


Fig. 2. ^{13}C-NMR spectrum of BAPM.



Sch. 2. Synthesis of polymers.

generally increases the T_g of the polymers, due to the hindrance of the chain rotation. The ODPA derived polyimides show the lowest T_g because of the presence of a flexible ether bridge between the phthalimide units, and the polyimide from PMDA exhibited the highest T_g, since the presence of pyromellitic unit increases the rigidity of the chain.

The thermal stability of the polyimides was evaluated by TGA in both air and N_2 atmosphere. Figure 4 shows the typical TGA curves (N_2 atm) for polyimide PI-Ia-b and PI-IIc-d. 10% (T_{10}) weight loss temperature is found to be in the range of 474–564°C in N_2, and 469–558°C in air. They left more than 40% char yield at 800°C in N_2. The T_{10} values for the PI-IIa-d series were slightly lower than the PI-Ia-d series, possibly because of the ether linkage present in the main chain of PI-IIa-d. The TGA data indicates that these polyimides have fairly high thermal stability.

3.5 Crystallinity

The crystallinity of the prepared polymers was evaluated by wide-angle X-ray diffraction experiments. Typical diffraction patterns for some representative polymers are presented in Figure 5. For all the polymers the reflection patterns are featureless, showing only broad amorphous halos. These results could be explained by the presence of the bulky pendant group inhibited close packing of the polymer chains, leading to a decrease in crystallinity.

3.6 Mechanical Properties

Mechanical properties of polyimide films were measured at room temperature by stress-strain analysis and are summarized in Table 4. The polymers have tensile strength in the range of 88–96 MPa, elongation at break in the range

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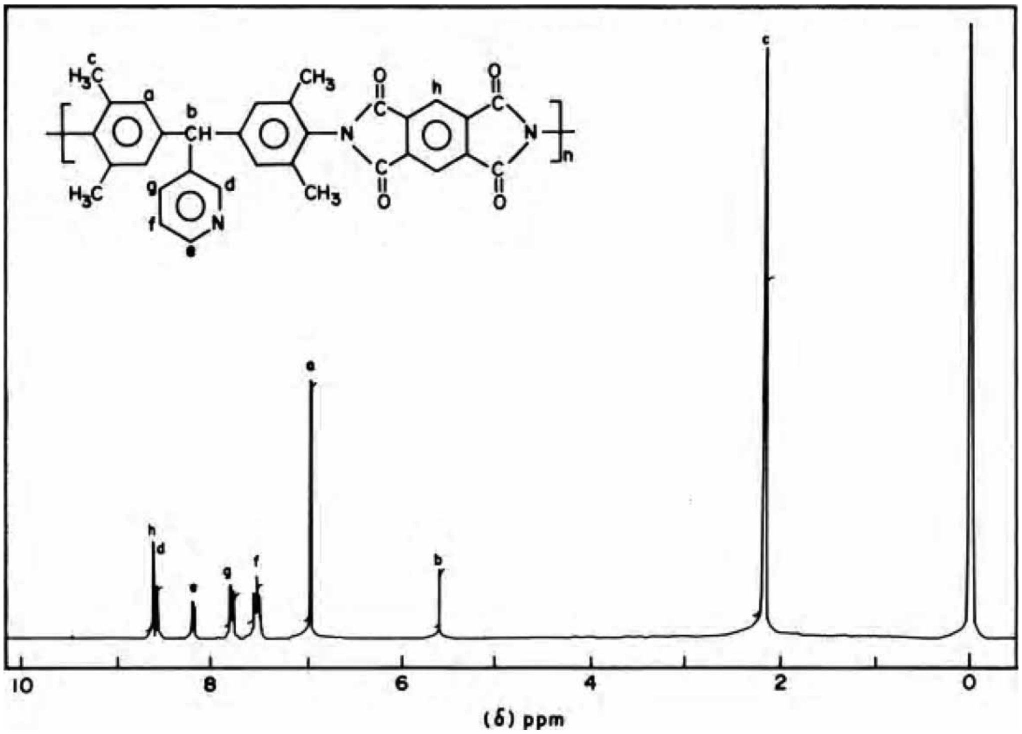

Fig. 3. ^{1}H-NMR spectrum of PI-Ia.

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of 8.5–12.5% and tensile modulus in the range 1.5–2.1 GPa. The PI-IIb-d series showed higher % elongation to break than the PI-Ib-d series, indicating elevated toughness. It may be due to the effective uncoiling of the long chain diamine units at their ether linkages providing a mechanism for considerable chain extension under stress (24).

3.7 Dielectric Properties and Moisture Absorption

The dielectric constant and moisture absorption of the thermally imidized polyimide films were studied and the results are given in Table 5. The measurement of dielectric constants was performed between gold layers. Dielectric constant is in the 3.26–3.64 range at 1 KHz and 3.24–3.61 at 10 KHz.

Table 1. Elemental analysis of the polyimides

			Elemental analysis (%)		
S. no.	Polymer	Molcular formula	C	H	N
1	PI-Ia	$(C_{32}H_{23}N_3O_4)n$	C = 74.85	C = 4.51	C = 8.18
			F = 73.52	F = 4.53	F = 8.32
2	PI-Ib	$(C_{39}H_{27}N_3O_5)n$	C = 75.85	C = 4.40	C = 6.80
			F = 74.60	F = 4.43	F = 6.82
3	PI-Ic	$(C_{38}H_{27}N_3O_5)n$	C = 75.37	C = 4.49	C = 6.94
			F = 74.12	F = 4.52	F = 6.98
4	PI-Id	$(C_{41}H_{27}N_3O_4F_6)n$	C = 66.59	C = 3.68	C = 5.68
			F = 65.59	F = 3.71	F = 5.73
5	PI-IIa	$(C_{44}H_{31}N_3O6)n$	C = 75.75	C = 4.48	C = 6.02
			F = 74.40	F = 4.49	F = 6.16
6	PI-IIb	$(C_{51}H_{35}N_3O_7)n$	C = 76.40	C = 4.40	C = 5.24
			F = 75.15	F = 4.42	F = 5.27
7	PI-II$_C$	$(C_{50}H_{35}N_3O_7)n$	C = 76.04	C = 4.46	C = 5.32
			F = 77.18	F = 4.62	F = 5.34
8	PI-IId	$(C_{53}H_{35}N_3O_6F_6)n$	C = 68.91	C = 3.82	C = 4.55
			F = 68.13	F = 3.85	F = 4.58

Table 2. Solubility of chemically/thermally imidized polyimides

S. no	Polyimide	NMP	DMF	DMSO	DMAc	THF	$CHCl_3$
1	PI-Ia	++/(±)	++/+	++/(±)	++/+	−/−	++/−
2	PI-Ib	++/(±)	++/+	++/(±)	++/+	−/−	++/−
3	PI-Ic	++/(±)	++/(±)	++/(±)	++/(±)	−/−	++/−
4	PI-Id	++/(±)	++/(±)	++/(±)	++/(±)	−/−	++/−
5	PI-IIa	++/(±)	++/+	++/(±)	++/+	+/−	++/−
6	PI-IIb	++/(±)	++/(±)	++/(±)	++/+	+/−	++/−
7	PI-II$_C$	++/(±)	++/(±)	++/(±)	++/(±)	+/−	++/−
8	PI-IId	++/(±)	++/(±)	++/(±)	++/(±)	+/−	++/−

++ - Completely soluble at room temperature.
+ - Sparingly soluble on heating.
(±) - Soluble on heating.
- Insoluble on heating.

Table 3. Thermal properties of polyimides

			T_{10} in °C^b		
S. no.	Polymer	T_g in °C^a	In air	In N_2	Char yield^c (%)
1	PI-Ia	317	558	564	52
2	PI-Ib	279	536	543	54
3	PI-Ic	265	518	520	48
4	PI-Id	277	509	515	44
5	PI-IIa	287	498	503	46
6	PI-IIb	268	483	485	49
7	PI-II$_C$	249	472	479	42
8	PI-IId	259	469	474	40

[a] Mid point temperature base line shift on the second DSC heating trace (scan rate = 10°C/min) of the sample after quenching from 400°C.
[b] Temperature at which 10% weight loss was recorded by TGA at a heating rate of 10°C/min in air and nitrogen atmosphere.
[c] Residual weight % at 800°C in N_2.

Compared with Kapton (3.89 at 1 KHz), these polyimides have a lower dielectric constant. This may be due to the addition of pendant groups and flexible bridging units, which limit chain-packing density and enhance the free volume. Introduction of free volume in a polymer chain reduces the number of polarizable groups per unit volume resulting in lower dielectric constant. The decreased dielectric constant of HFIDA derived polyimides could be attributed to the presence of the bulky CF_3 groups, which results in less efficient chain packing and increased free volume. The strong electro negativity of fluorine atom results in very low polarizability of C-F bonds, thereby decreasing the dielectric constant (25, 26). They also exhibit lower moisture absorptions as a result of the hydrophobicity of the CF_3 group (27). The moisture absorption of the polyimides is in the range of 0.42–0.89%.

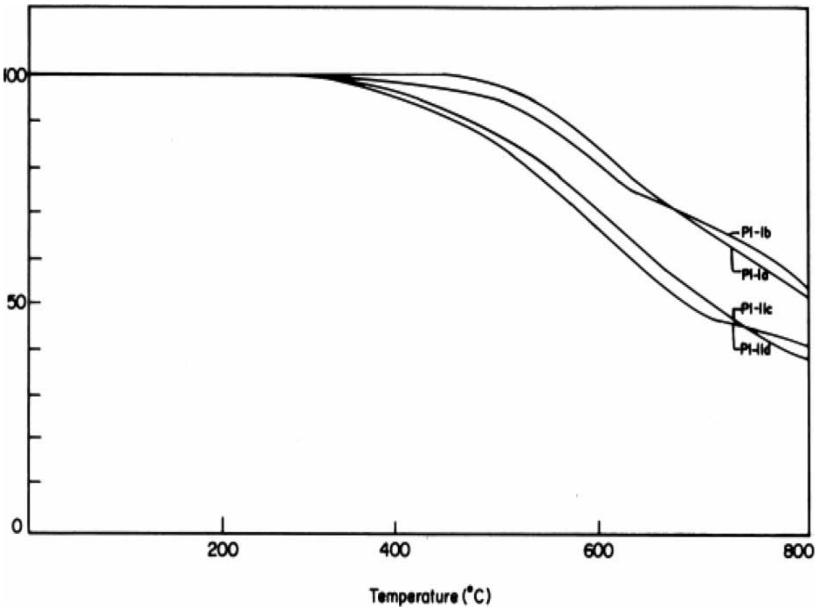

Fig. 4. TGA thermograms of polymers in N_2 atmosphere.

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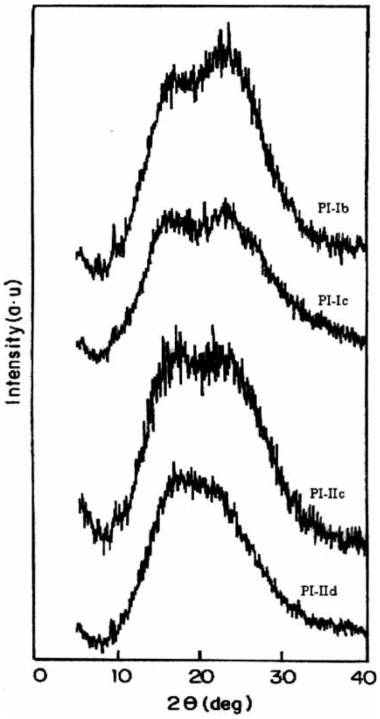

Fig. 5. Wide-angle X-ray diffractograms of polymers.

Table 4. Mechanical properties of polyimide films

S. no.	Polymer	Tensile strength MPa	Tensile elongation (%)	Tensile modulus GPa
1	PI-Ia	—	—	—
2	PI-Ib	96	11.25	2.1
3	PI-Ic	95	10.51	1.9
4	PI-Id	90	8.00	1.6
5	PI-IIa	—	—	—
6	PI-IIb	93	12.5	1.9
7	PI-II$_C$	92	11.5	1.7
8	PI-IId	88	8.5	1.5

Table 5. Inherent viscosity, moisture absorption and dielectric constant

S. no.	Polymer	Inherent viscosity η_{inh}	Moisture absorption (%)	Dielectric constant	
				1 KHz	10 KHz
1	PI-Ia	1.02	—	—	—
2	PI-Ib	0.94	0.75	3.34	3.33
3	PI-Ic	0.87	0.65	3.51	3.49
4	PI-Id	0.68	0.42	3.26	3.24
5	PI-IIa	0.91	—	—	—
6	PI-IIb	0.88	0.89	3.48	3.46
7	PI-II$_C$	0.79	0.78	3.64	3.61
8	PI-IId	0.61	0.51	3.38	3.32

4 Conclusions

Novel diamine monomers containing pyridine heterocyclic ring as pendant group along with ether linkages were prepared and used for the synthesis of novel polyimides. These polyimides exhibit excellent solubility, relatively high glass transition temperature, and exhibit good thermal stability in air and N_2 atmosphere. It seems that using a pyridine ring as a pendant moiety in the diamine monomer causes improvement in the solubility of the resulting polyimides. However, a slight decrease in thermal stability can be observed compared to that of reported polyimides containing heterocyclic moiety in the main chain itself. Thus, this series of polyimides demonstrates a good combination of properties and processability (ignoring the small decrease in thermal properties).

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