



# SYNTHESIS AND CHARACTERIZATION OF POLYIMIDES BASED ON A FLEXIBLE DIAMINE

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The diamine 1,4-phenylenedi(oxy-4,4'-aniline) was prepared via the nucleophilic substitution reaction and polymerized with different dianhydrides either by a one step solution polymerization reaction or a two steps procedure. These polymers had inherent viscosities ranging from 0.64-0.83 dL g<sup>-1</sup>. Few of the polymers were soluble in most of the organic solvents such as DMSO, DMF, DMAc, NMP and m-cresol even at room temperature and some were soluble on heating. The degradation temperature of the resultant polymers falls in the ranges from 300-450 °C in nitrogen (with only 10% weight loss). The specific heat capacity at 200 °C ranges -4.0322-2.4059 J g<sup>-1</sup> K<sup>-1</sup>. The maximum degradation temperature ranges from 550-600 °C. T<sub>g</sub> values of the polyimides were found from 207 to 228 °C. The activation energy and enthalpy of the polyimides were found in the range of 36.6-94.5 and 34.8-92.5 kJ mole<sup>-1</sup> and the moisture absorption from 0.24-0.75%.

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## Introduction

Aromatic polyimides have excellent reputation as high performance materials based on their excellent thermal stability, chemical resistance and mechanical properties. Because of above mentioned properties polyimides can be used in a wide variety of applications such as polymer matrices for high temperature advanced composites, membranes for the low temperature energy separation of industrial gases, interlayer dielectrics, high temperature adhesive and coatings.<sup>1-4</sup> Despite their widespread use, most of them have high melting or softening temperatures and limited solubility in most of the organic solvents because of their rigid backbones and strong intermolecular interactions which may restrict their use in some fields. For such difficulties to be overcome, polymer structure modifications become necessary. Considerable research efforts have been done in designing and synthesizing new dianhydrides<sup>5</sup> and diamines<sup>6-11</sup> thus producing a great variety of soluble and processable polyimides for various purposes. Since 1960, essentially the beginning of the search for high temperature polymers, more attention was focused on the polyimides than any other high performance/high temperature polymers. This is primarily due to the availability of the polyimide monomers (particularly aromatic diamines and dianhydrides), the ease of polymer synthesis, and their unique combination of physical and mechanical properties. However, most fully aromatic polyimides are insoluble in any organic solvent, and they have very high glass transition temperatures, often higher than their decomposition temperatures, which greatly limits their usefulness for many applications. Therefore, much work has been done to

improve the processability of aromatic polyimides while maintaining their excellent level of thermal and mechanical properties.<sup>12,13</sup> To meet these aims, by balancing processability and performance, a number of approaches for structural modifications have been pursued such as incorporation of additional ether, ester, urethane, or amide linkages onto the polymer backbone.<sup>14-17</sup> Incorporation of aryl ether unit is particularly successful method for improving solubility with slight reduction in thermal properties.<sup>18,19</sup> In the present study the diamine 1,4-phenylenedi(oxy-4,4'-aniline) was synthesized and used to prepare a series of polyimides using various dianhydrides. Due to the presence of flexible moiety in the polyimide backbone, a decrease in the rigidity of the polymer chain would be expected which could improve the solubility of the polymers.

## Experimental

### Materials

Hydroquinone, p-fluoronitrobenzene, potassium carbonate, 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride (BP), 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (HF), 3,4,9,10-perylenetetracarboxylic acid dianhydride (PD) and pyromellitic dianhydrides (PMDA) of analytical grade from Aldrich were used as received. All the other reagents and solvents were of analytical grade and used without further purification.

### Measurements

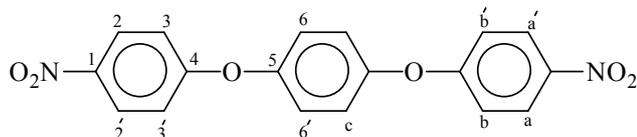
<sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on instrument Jeol 270 spectrophotometer in DMSO using tetramethylsilane as an internal reference. Infrared measurements (KBr pellets) were recorded in the range of 400-4000 cm<sup>-1</sup> on Bio-Rad Excalibur FTIR Model FTS 3000 MX. Melting points were recorded on Electrothermal IA 9000 series digital melting

point apparatus. Inherent viscosities were obtained using Gilmount falling ball viscometer at  $0.2 \text{ g dL}^{-1}$  in DMSO and  $\text{H}_2\text{SO}_4$ . Thermal and DSC analysis were carried out using Perkin Elmer TGA-7 and DSC 404C Netzsch under nitrogen atmosphere. Elemental analysis was carried out using Perkin Elmer CHNS/O 2400. Wide-angle diffractograms were obtained using 3040/60 X'Pert PRO diffractometer. Moisture absorption was determined by weighing the changes of the dried pellets before and after immersion in distilled water at  $25^\circ\text{C}$  for 24 hours. Activation energy, entropy and enthalpy were calculated using Horowitz and Metzger method.<sup>20</sup>

## Monomer Synthesis

### 1,4-Phenylenedi(oxy-4,4'-nitrobenzene) PONB (1)

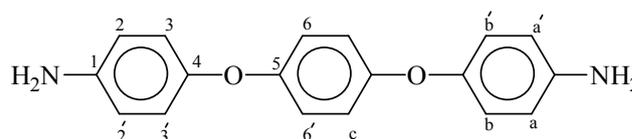
A mixture of 2.0g (0.018 mol) of hydroquinone, 5.0g (0.036 mol) of anhydrous  $\text{K}_2\text{CO}_3$  and 3.81 ml (0.036 mol) of 4-fluoronitrobenzene in a two neck round bottom flask having 70 ml of DMAc was heated at  $100^\circ\text{C}$  for 20 h under nitrogen atmosphere. The colour of the solution changes from yellow to dark brown as the reaction proceeded. After cooling to room temperature, the reaction mixture was poured in 800 ml of water to form yellow solid which was washed thoroughly with water and then separated by filtration. The crude product was recrystallized from ethanol. Yield 87 %, m.p.  $238^\circ\text{C}$ . Elemental analysis calculated for  $\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_6$  (352): C = 61.36%, H = 3.409%, N = 7.95% and found C = 61.02%, H = 3.69%, N = 7.45%. FTIR (KBr pellet) in  $\text{cm}^{-1}$ : 1589 (aromatic C=C), 1506 and 1340 ( $\text{NO}_2$ ), 1235 (C–O–C).  $^1\text{H-NMR}$  (DMSO- $d_6$ ) in  $\delta$ (ppm) and  $J(\text{Hz})$ : 7.22 (4H, d,  $J_{ab}=J_{a'b'}=9.30$ ), 7.3(4H, s), 8.31 (4H, d,  $J_{ba}=J_{b'a'}=9.30$ ).  $^{13}\text{C-NMR}$  (DMSO- $d_6$ ) in  $\delta$  (ppm): 116.093 (2C, C5), 125.82 (4C, C3, 3'), 127.31 (4C, C6, 6'), 145.469 (4C, C2, 2'), 149.625 (2C, C4), 163.24 (2C, C1). Yield 87 %, m.p.  $238^\circ\text{C}$ . Crystal data: almost colorless crystal grown during slow crystallization in ethanol/water (4:1) v/v,  $0.38 \text{ mm} \times 0.11 \text{ mm} \times 0.10 \text{ mm}$ , triclinic, P1 with  $a=7.2861(6)$ ,  $b=10.1381(9)$ ,  $c=12.0838(11) \text{ \AA}$ ,  $\alpha=91.973(7)$ ,  $\beta=106.497(7)$ ,  $\gamma=110.152(6)^\circ$  where  $D_x=1.472 \text{ Mg m}^{-3}$  for  $Z=2$  and volume ( $V$ ) =  $794.74 (12) \text{ \AA}^3$ .<sup>22</sup>



### 1,4-Phenylenedi(oxy-4,4'-aniline) POA (2)

A 250 ml two neck flask was charged with 1.0g (2.84 mmol) of (1), 10 ml of hydrazine monohydrate, 80 ml of ethanol and 0.06g of 5% palladium on carbon (Pd–C). The mixture was refluxed for 16 hours and then filtered to remove Pd–C and the solvent was evaporated and the crude solid was recrystallized from ethanol to yield 85% of the theoretically calculated yield, m.p.  $182^\circ\text{C}$ . Elemental analysis calculated for  $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_6$  (MW=292): C = 73.97%, H = 5.47%, N = 9.58 and found C = 73.75%, H = 5.12%, N = 9.79%. FTIR (KBr pellet) in  $\text{cm}^{-1}$ : 3400 and 3312 ( $\text{NH}_2$ ), 1639 (N–H bending), 1213 (C–O–C), 1495 (NH

deformation).  $^1\text{H NMR}$  (DMSO- $d_6$ ) in  $\delta$  (ppm) and  $J$  (Hz): 5.08 (4H, s), 6.51 (4H, d,  $J_{ab}=J_{a'b'}=8.27$ ), 6.82 (4H, d,  $J_{ba}=J_{b'a'}=8.28$ ), 6.91 (4H, s).  $^{13}\text{C NMR}$  (DMSO- $d_6$ ) in  $\delta$  (ppm): 115.885 (4C, C3, 3'), 118.856 (4C, C6, 6'), 126.328 (4C, C2, 2'), 145.49 (2C, C1) 147.55 (2C, C5), 156.58 (2C, C4). Yield 85%, m.p.  $182^\circ\text{C}$ . Crystal data: almost colorless crystal grown during slow crystallization in ethanol/water (4:1) v/v,  $0.42\text{mm} \times 0.40\text{mm} \times 0.20 \text{ mm}$ , monoclinic,  $\text{P}2_1/\text{c}$  with  $a=6.9579(9)$ ,  $b=22.664(3)$ ,  $c=5.1202(7) \text{ \AA}$ ,  $\beta=111.287 (2)^\circ$  where  $D_x=1.290 \text{ Mg/m}^3$  for  $Z=2$  and volume ( $V$ ) =  $752.34 (7) \text{ \AA}^3$ .<sup>23</sup>



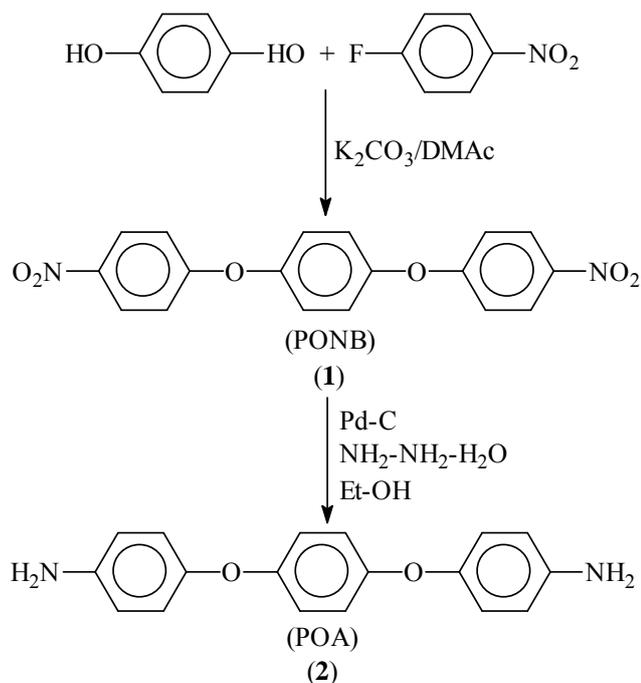
## Polymer Synthesis

To a stirred solution of POA (0.36 g, 1.238 mmol) in 8 ml of DMAc was added 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride (BP) (0.4 g, 1.238 mmol). The mixture was stirred at room temperature for 2 hours under argon atmosphere to form a polyamic acid (precursor). The film was casted onto a glass plate by heating polyamic acid solution for 18 hours at  $80^\circ\text{C}$ , 2 hours at  $150^\circ\text{C}$ , 2 hours at  $200^\circ\text{C}$ , 2 hours at  $250^\circ\text{C}$  and 2 hours at  $280^\circ\text{C}$  which converted polyamic acid into polyimide films. The same procedure was adopted for the polymerization of POA with 4,4'-hexafluoroisopropylidene diphthalic anhydride (HF) and pyromellitic dianhydride (PMDA) however, the polymerization with perylene dianhydride (PD) was carried out by following procedure. In a 250 ml two neck round bottom flask fitted with nitrogen inlet and outlet the diamine POA [(0.37g, 1.27 mmol), dianhydride (0.5g, 1.27 mmol)], m-cresol (20 ml) and isoquinoline (1 ml) were added. The mixture was heated to  $180\text{--}200^\circ\text{C}$  under nitrogen for 6 hours and then cooled to room temperature. The resulting dark red solution was poured into 300 ml of acetone and the resulting solid was washed with (1 N) sodium hydroxide followed by water. After drying at  $150^\circ\text{C}$  overnight, polyimide was obtained as dark red solid. The inherent viscosities of the polymers were subsequently determined at concentration  $0.2 \text{ g dL}^{-1}$  at  $25^\circ\text{C}$  in DMSO and  $\text{H}_2\text{SO}_4$ .

## Results and Discussion

### Monomer Synthesis

The diamine POA was synthesized according to the well developed method (Scheme-1) The first step is Williamsons etherification<sup>21</sup> reaction of 1,4-dihydroxybenzene and p-fluoronitrobenzene in the presence of potassium carbonate in DMAc, followed by stirring of the mixture at  $100^\circ\text{C}$  for 20 h. The diamine POA was readily obtained in good yield by the catalytic reduction of the intermediate dinitro compound with hydrazine hydrate and Pd–C catalyst in refluxing ethanol. The schematic diagram of diamine



**Figure 1.** Schematic diagram for the synthesis of 1,4-phenylenedi(oxy-4,4'-aniline)

synthesis is shown in the Fig. 1. Elemental, FTIR and NMR analysis were carried out to confirm the structures of intermediate and diamine. The nitro group of intermediate compound gave two absorption band at  $1506$  and  $1340\text{ cm}^{-1}$  ( $\text{NO}_2$  a symmetric and symmetric stretching). The PONB crystallizes with two half-molecules in the asymmetric unit. All molecules lie on a centre of inversion. The dihedral angles between the central and terminal benzene rings are  $74.75(4)$  and  $85.25(5)^\circ$  for the two molecules in the asymmetric unit.<sup>22</sup> After reduction the characteristic absorption of the nitro compound disappeared, and the amino group showed a pair of N–H stretching bands in the region of  $3300\text{--}3500\text{ cm}^{-1}$ . The diamine POA is located on a crystallographic inversion center and the terminal aminophenoxy rings are almost perpendicular to the central benzene ring with a dihedral angle of  $85.40(4)^\circ$ . The molecular conformation is stabilized by N–H---O and N–H---N intermolecular hydrogen-bonding interactions.<sup>23</sup> All the spectroscopic data obtained was in good agreement with the expected structure.

### Polymer Synthesis

The diamine monomers were polymerized with four different aromatic dianhydrides namely 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride (BP), 4,4'-hexafluoroisopropylidene)diphthalic anhydride (HF), 3,4,9,10-perylene tetracarboxylic acid dianhydride (PD) and pyromellitic dianhydride (PMDA) as shown in Fig. 2. The polyimides of BP, HF and PMDA were prepared by following a conventional two step procedure which includes the ring-opening polyaddition at room temperature to poly(amic acid), followed by sequential heating to  $280\text{ }^\circ\text{C}$ . The polyimide of perylene dianhydride was prepared by a different method. The polyamic acid precursors were prepared by the addition of dianhydride to the diamine solution gradually. The molecular weights were high enough

to cast tough and transparent polyimide films. A rapid temperature elevation resulted in cracked or brittle films. The inherent viscosities determined for some polymer films give values in the range of  $0.64\text{--}0.83\text{ dL g}^{-1}$  at concentration of  $0.2\text{ g dL}^{-1}$  at  $25\text{ }^\circ\text{C}$  which indicates high molecular weights of the polymers as shown in Table-2. The polyimides obtained were subjected to solubility and thermal studies. Some of the thermally cured polyimides exhibited excellent solubility in polar solvents such as DMSO, DMF and DMAc. The formation of polyimides was confirmed by IR and elemental analysis (Table-1). All the polyimides exhibited the characteristic imide group absorption around  $1780$  and  $1725\text{ cm}^{-1}$  (typical of imide carbonyl (symmetric and asymmetric stretching),  $1380\text{ cm}^{-1}$  (C–N stretch) and  $1100$  and  $730\text{ cm}^{-1}$  (imide ring deformation). The disappearance of the amide and carboxyl bands indicated a virtually complete conversion of the poly(amic acid) precursor into polyimides. The results of the elemental analysis of all the synthesized polyimides are listed in Table 1. The values found were in good agreement with the calculated one.

	BP=3,3',4,4'-Benzophenone-tetracarboxylic acid dianhydride
	HF=4,4'-(Hexafluoroisopropylidene)diphthalic anhydride
	PD= 3,4,9,10-Perylenetetracarboxylic acid dianhydride
	PMDA=Pyromellitic dianhydride

**Figure 2.** Four different acid dianhydrides used for polymerization.

### Organo Solubility and Moisture Absorption.

The inherent viscosities determined for polymer films except POA-BP gave values in the range of  $0.64\text{--}0.83\text{ dLg}^{-1}$ , reflecting high molecular weight of the polymers. The solubility of the polyimides was determined qualitatively and the results are listed in Table 2. The solvents like DMSO, DMF, DMAc, m-cresol and THF were tested. Some polymers are found soluble on heating while others are slightly soluble and some are insoluble. The organo solubility behaviour of the polymers is generally depended on their chain packing ability and intermolecular interactions that was affected by the rigidity, symmetry and the regularity of the backbone. From the Table 2 it was noticed that the introduction of fluorinated dianhydride component (HF) is especially effective for the high solubility, irrespective of the diamine component. This increase in solubility might be attributed to the molecular asymmetry and the presence of bulky trifluoromethyl groups,

**Table 1.** Elemental Analysis of the polymers

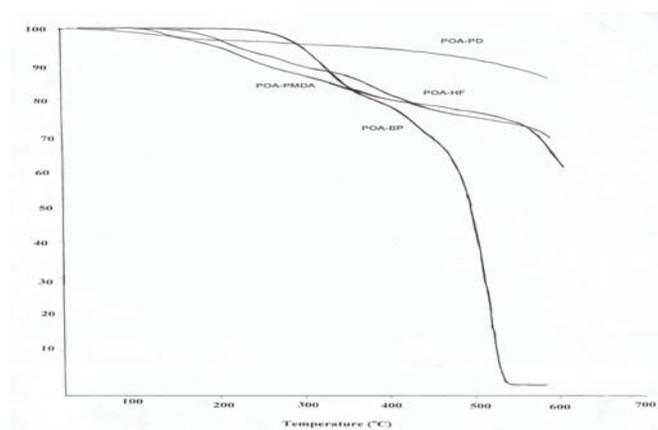
Polyimide	Formula of the Repeat Unit (Formula Wt.)	C%	H%	N%
		Calc.(Found)	Calc. (Found)	Calc. (Found)
POA-BP	C <sub>35</sub> H <sub>18</sub> N <sub>2</sub> O <sub>7</sub> (578)	72.66 (71.95)	3.11 (3.20)	4.84 (4.48)
POA-HF	C <sub>37</sub> H <sub>18</sub> N <sub>2</sub> O <sub>6</sub> F <sub>6</sub> (700)	63.42 (63.14)	2.57 (2.61)	4.00 (3.79)
POA-PD	C <sub>42</sub> H <sub>20</sub> N <sub>2</sub> O <sub>6</sub> (648)	77.77 (77.01)	3.08 (3.29)	4.32 (4.10)
POA-PMDA	C <sub>28</sub> H <sub>14</sub> N <sub>2</sub> O <sub>6</sub> (474)	70.88 (71.83)	2.95 (3.10)	5.90 (6.58)

**Table 2.** Inherent Viscosity, solubility and moisture absorption of polymers

Polymer	DMSO	DMF	DMAc	m-cresol	THF	H <sub>2</sub> SO <sub>4</sub>	$\eta_{\text{inn}}$ , dL g <sup>-1</sup>	Moisture absorption <sup>c</sup> , %
POA-BP	-	-	-	-	-	+	-	0.61
POA-HF	+++	+++	+++	+++	-	+++	0.83 <sup>a</sup>	0.24
POA-PD	+	+	+	+	-	++	0.64 <sup>b</sup>	0.75
POA-PMDA	-	-	-	-	-	++	0.71 <sup>b</sup>	0.51

+++ = soluble at room temperature, ++ = soluble on heating, + = slightly soluble on heating, - = insoluble; a) measured from 0.2 g dL<sup>-1</sup> at 25 °C in DMSO; b) measured from 0.2 g dL<sup>-1</sup> at 25 °C in H<sub>2</sub>SO<sub>4</sub>; c) moisture absorption was measured at 25±1 °C for 24 hours

which increase the disorder in the chains and hinders the dense chain stacking, thereby reducing the interchain interactions and so enhancing solubility. The poor solubility of the remaining polyimides might be attributed to crosslinking within polymer chain or the tight chain packing and aggregation during imidization at elevated temperature. The moisture absorption of the synthesized polyimides was found in the range of 0.24-0.61 %. The fluorinated polyimide was found to absorb lowest absorption as compared to other polyimides because the trifluoromethyl group possesses the amphiprotic feature, which inhibits the absorption of moisture molecules on the surface of the fluorinated polyimides.<sup>24</sup>

**Figure 3.** TGA curves of the synthesized polyimides

### X-ray Diffraction Data

All the polyimides were characterized with WAXD studies. The WAXD pattern is shown in Figure 4. All polyimides except POA-HF, displayed a semicrystalline pattern where as POA-HF displayed nearly completely amorphous pattern because of the bulky CF<sub>3</sub> group which disrupted the symmetry or dense chain packing leading to highly ordered regions. The bulky CF<sub>3</sub> also induces looser chain packing and reveals a large decrease in crystallinity leading to highly ordered regions.<sup>24</sup>

### Thermal Properties

Thermal properties of the polyimides were investigated by the thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) at heating rate of 10 °C min<sup>-1</sup>. Table 3 presents the thermal properties of the polyimides. The results of the TGA analysis showed no significant weight loss below 300 °C in nitrogen. The maximum degradation temperature ( $T_{\text{max}}$ ) for most of the polymers lies between 550-600 °C.

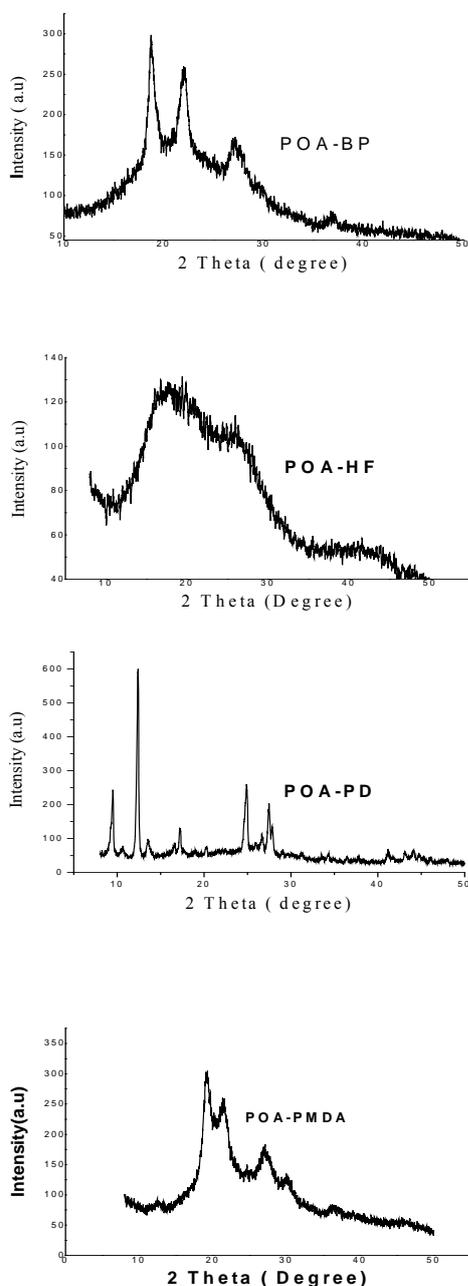
The thermal stability of the polymers was also evaluated in term of 10 % weight loss ( $T_{10}$ ), maximum degradation temperature ( $T_{\text{max}}$ ) and residual weight at 600 °C as listed in Table 3. It has been seen by comparing  $T_{10}$  of the polymers that the introduction of the diacid PD is especially effective to improve the thermal stability of the polyimides regardless of the diamine component. This increase in thermal stability is attributed to rigid and bulky PD unit which inhibit the rotation of bonds, resulting in an increase in chain stiffness while the polyimides having HF unit are less thermally stable than PD unit which is probably due to the different packing density of the polymer aggregation and the interaction of the polymer chain. The presence of bulky CF<sub>3</sub> group reduces the chain interactions and causes the poor packing of the polymer chain and lowers the thermal stability. This thermal behaviour is in agreement with the literature.<sup>25</sup>

The thermal degradation kinetics for the polymers was calculated from TGA curves and the activation energy of the pyrolysis was obtained using the Horowitz and Metzger method which is an integral method for the determination of kinetic parameters. In this method, double logarithm of the reciprocal of the weight fraction of the reactant was plotted against the temperature difference and the kinetic parameters were calculated by some mathematical calculations using battery programme based on Horowitz and Metzger method. The thermal degradation of the polyimides in the absence of the oxygen was believed to involve the direct cleavage of the C-N bond. The specific heat capacity ranges from -4.0322 to 2.4059 J g<sup>-1</sup> K<sup>-1</sup> at

**Table 3.** Thermal behaviour of pPolymers in nitrogen flow.

Polymer	Specific heat capacity <sup>a</sup> at 200 °C, J g <sup>-1</sup> K <sup>-1</sup>	Thermal Stability <sup>b</sup>		R <sub>600</sub> (%) <sup>e</sup>	T <sub>g</sub> (°C) <sup>f</sup>	Activation energy, kJ mol <sup>-1</sup>	Entropy, kJ mol <sup>-1</sup> .K	Enthalpy kJ mol <sup>-1</sup>
		T <sub>10</sub> (°C) <sup>c</sup>	T <sub>max</sub> (°C) <sup>d</sup>					
POA-BP	2.4059	350	550	80.5	228	53.8	0.265	52.0
POA-HF	0.5162	300	580	66.0	225	48.8	0.213	40
POA-PD	-4.0322	450	600	85.6	-	94.5	0.672	92.5
POA-PMDA	2.3949	300	600	62.8	207	36.6	0.093	34.8

a) Measured from DSC under nitrogen at heating rate of 10 °C min<sup>-1</sup>; b) Measured from TGA under nitrogen at heating rate of 10 °C min<sup>-1</sup>; c) Temperature at 10% weight loss; d) Maximum degradation temperature obtained from differential curves; e) Residual weight at 600°C; f) T<sub>g</sub> (glass transition temperature)

**Figure 4.** Wide-angle X-ray diffractograms of the prepared polymers

200 °C. T<sub>g</sub> values of the polyimides ranged from 207 to 228 °C. The activation energy and enthalpy of the polyimides are in the range of 36.6-94.5<sup>26</sup> and 34.8-92.5 kJ mol<sup>-1</sup>, respectively, and are comparable with the literature.

## Conclusions

The diamine POA was successfully prepared in high purity and high yield and was polymerized with four different aromatic dianhydrides to obtain moderate to high molecular weight polyimides. Polyimides with 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride, 4,4'-(hexafluoroisopropylidene) diphthalic anhydride and pyromellitic dianhydrides could be thermally converted into tough and flexible polyimide films. Few polyimides synthesized were soluble in most of the organic solvents such as DMSO, DMF, DMAc and m-cresol. The degradation for 10% weight loss ranges from 300-450°C. The maximum degradation temperature ranges from 550-600 °C and specific heat capacity -4.0322 to 2.2.4059 J g<sup>-1</sup> K<sup>-1</sup> at 200 °C. T<sub>g</sub> values of the polyimides ranged from 207 to 257 °C. All polyimides show semicrystalline pattern except POA-HF which shows completely amorphous pattern. The moisture absorption of the polyimides is in the range of 0.24-0.75%. Activation energy and enthalpy of the polyimides is in the range of 36.6-94.5 kJ mol<sup>-1</sup> and 34.8-92.5 kJ mol<sup>-1</sup>, respectively. These polyimides could be considered as processable high performance polymeric materials.

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