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## Synthesis and characterization of new heat-resistance polymers based on N-(4-carboxy phenyl) trimellitimide and aromatic diamines

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### Abstract

Five new aromatic poly(amide-imide)s (**5a-e**) were synthesized by direct polycondensation reaction of N-(4-carboxy phenyl) trimellitimide (**3**) with five aromatic diamines (**4a-e**) by using triphenyl phosphite in N-methyl-2-pyrrolidone (NMP) and pyridine at solution containing dissolved CaCl<sub>2</sub>. All of the polymers were obtained in quantitative yields with inherent viscosities between 0.29-0.40 dL/g. The resulting poly(amide-imide)s were characterized with elemental analysis, viscosity measurements, solubility test, FT-IR spectroscopy, thermo gravimetric analysis (TGA) and differential thermal gravimetry (DTG). All of the polymers were soluble in N-methyl-2-pyrrolidone (NMP), N,N-dimethylacetamide (DMAC), N,N-dimethyl formamide (DMF), dimethyl sulfoxide (DMSO) at room temperature. N-(4-carboxy phenyl)trimellitimide (**3**) was prepared from the reaction of trimellitic anhydride (**1**) with 4-aminobenzoic acid (**2**) at room temperature and refluxing at 100-110°C in acetic acid as a solvent with a quantitative yield.

**Keywords:** Poly(amide-imide)s, Polycondensation reaction, Trimellitic moieties

### 1. Introduction

Wholly aromatic polyamides (PAs) have been noted for their high thermal and chemical resistance as well as their high strength and high modulus as fibers [1, 2]. Kevlar [poly(*p*-phenylene terephthalamide)] and Nomex [poly(*m*-phenylene isophthalamide)] are commercially marketed as high-performance polymers, usually in fiber form. Rigid-rod-like aromatic polymers are usually difficult to process because of their high softening or melting temperatures and their insoluble nature in most organic solvents [3, 4]. Current or previous attempts at the solubilization and processing of rigid-chain polymers have been made through synthetic modification by the addition of flexible linkages [5] (e.g., -O- and -SO<sub>2</sub>-), molecular asymmetry [6] and bulky side groups [7] into the back-bone.

Also aromatic polyimides (PIs) are well known for their excellent thermal stabilities, electric insulation properties, and chemical resistance. However, their applications are limited because of their high softening or melting temperatures and insoluble nature in most organic solvents [8]. To overcome these drawbacks, PI structures are often modified. One method uses copolymerization to synthesize copolymers to improve the processing ability, such as

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poly(amide-imide)s (PAIs). PAIs have the advantages of both PAs and PIs and possess thermal stability balanced with processability [9, 10]. These polymers can be synthesized from various aromatic monomers containing anhydrides, carboxylic acids, aromatic diamines and amino acids by condensation [11-13]. Poly(amide-imide)s (PAIs) show a variety of applications as they retain good mechanical properties at high temperatures and show easier process ability when compared with other aromatic thermostable polymers such as polyamides and polyimides [14]. They are finding numerous applications in adhesives, electronic wire enamel, injection-molding, extrusion products and membranes [15].

In our previous works, we used this method for the synthesis of a series of new PAIs with needed properties [16-22]. In this study, we prepared a series of novel PAIs containing trimellitic rings and aromatic diamine through the polycondensation reaction of N-(4-carboxy phenyl) trimellitimide (**3**) with five aromatic diamines (**4a-e**). Resulting polymers show thermal stability in high temperatures and have good solubility in common organic solvents such as N-methyl-2-pyrrolidone (NMP), N,N-dimethylacetamide (DMAC), N,N-dimethyl formamide (DMF), dimethyl sulfoxide (DMSO) at room temperature.

## 2. Experimental

### 2.1. Materials

All chemicals were purchased from Fluka chemical Co. (Switzerland), Aldrich chemical Co. (Milwaukee, WI), and Merck chemical Co. (Germany).

### 2.2. Techniques

Fourier transform infrared (FTIR) spectra were recorded a Galaxy series FTIR 5000 spectrophotometer (England). Spectra of the solids were obtained with KBr pellets. The vibrational transition frequencies are reported as wave numbers ( $\text{cm}^{-1}$ ). The band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br). Inherent viscosity ( $\eta_{\text{inh}}$ ) values were measured with a standard procedure with a technico Regd Trad Merk viscometer. Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) data for the polymers were obtained on a Mettler TA4000 system under  $\text{N}_2$  atmosphere at a rate of  $10^\circ\text{C}/\text{min}$ . Elemental analyses were performed by Arak petrochemical Co. (Arack, Iran).

### 2.3. Monomer synthesis

N-(4-carboxy phenyl) trimellitimide (**3**): This compound was prepared according to a typical procedure shown in Scheme 1. Into a 250-ml round bottom flask 2.00 g (10 mmol) trimellitic anhydride (**1**), 1.43 g (10 mmol) 4-aminobenzoic acid (**2**), 25 ml of glacial acetic acid and a stirring bar were placed. The mixture was stirred at room temperature overnight and then refluxed for 4 hrs. Then solvent was removed under reduced pressure, and the residue was dissolved in 100 ml of cold water. The solution was stirred until a white precipitate was formed and then the precipitate was filtered off and dried to produce 2.85 g (91%) of compound (**3**) as white crystals. Mp  $275\text{-}300^\circ\text{C}$ . FTIR (KBr,  $\text{cm}^{-1}$ ): 3200-2900 (m, br), 1725 (s, sh), 1601 (m), 1425 (m), 1377 (s, sh), 1298 (s, sh), 1091 (m), 723 (m, br), 507 (w).  $^1\text{H-NMR}$  [(DMSO- $d_6$ ), tetramethylsilane,  $\delta$ ]: 7.60-7.63 (d, 2H), 8.08-8.09 (d, 2H), 8.11-8.12 (d, 1H), 8.32(s, 1H), 8.41-8.45 (dd, 1H) ppm.

### 2.4. Polymer synthesis

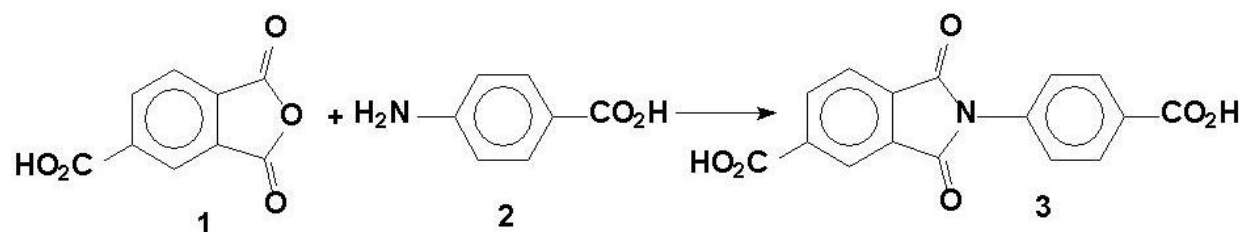
Into a 250 ml round bottomed flask were placed an equimolar mixture of 0.108 g (1.0 mmol) of diamine (**4a**), 0.311 g (1.0 mmol) of N-(4-carboxy phenyl) trimellitimide (**3**), 0.110 g of

calcium chloride, 0.26 ml of triphenyl phosphite, 1.2 ml of pyridine and the reaction mixture was refluxed for 7 hrs. After cooling, the reaction mixture was poured into a large amount of methanol with constant stirring, producing a stringy precipitate that was washed thoroughly with methanol, collected on a filter, and dried at 60 °C for 12 hrs under vacuum to leave 0.33 g (86 %) of solid polymer (**5a**). All of the PAIs (**5b-e**) were prepared similarly.

### 3. Result and discussion

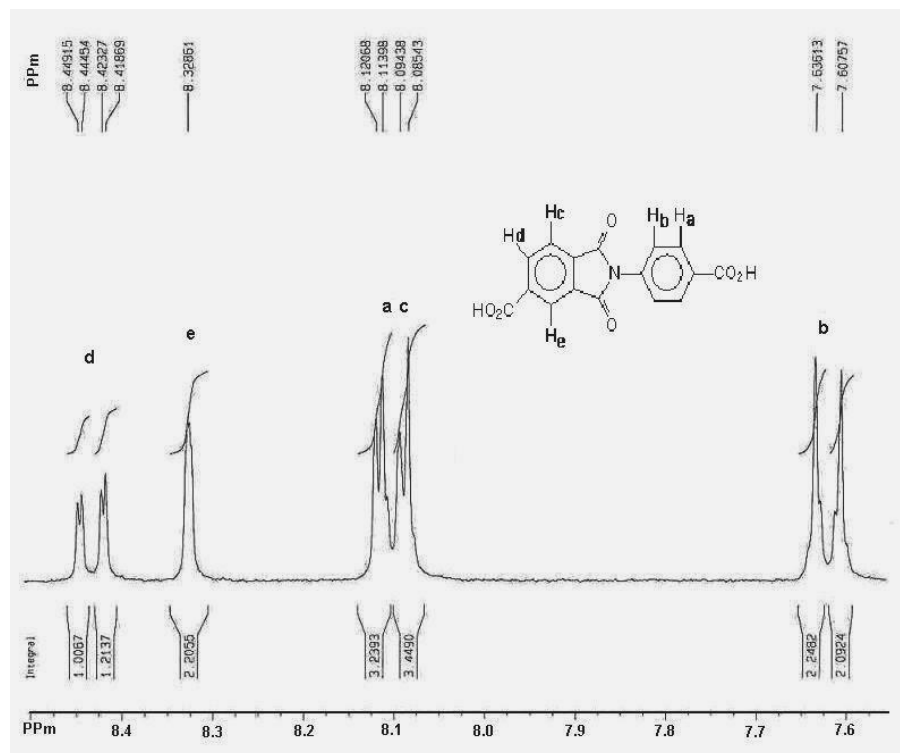
#### 3.1. Monomer synthesis

N-(4-carboxy phenyl) trimellitimide (**3**) was prepared in a one pot reaction sequence, as shown in Scheme 1. Diacid (**3**) was synthesized through the condensation reaction of one equivalent trimellitic anhydride (**1**) with one equivalent of 4-aminobenzoic acid (**2**) in glacial acetic acid as solvent (Scheme 1). After cooling the reaction mixture, the residue was dissolved in cold water until a gummy solid was provided a white solid with the addition of excess water.



**Scheme 1** Synthetic route of N-(4-carboxy phenyl) trimellitimide (**3**)

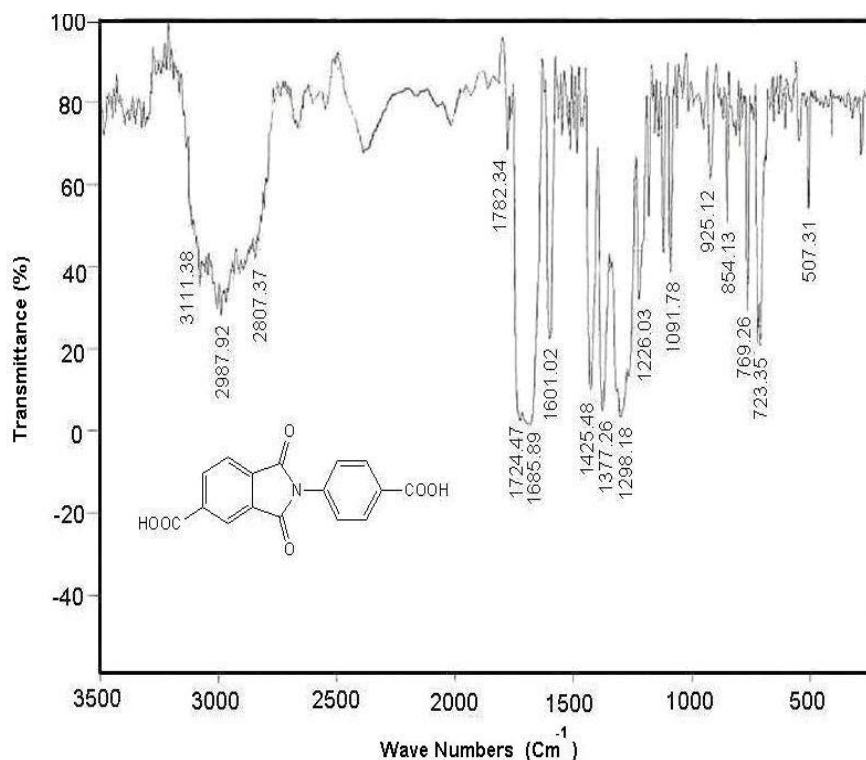
The chemical structure of diacid (**3**) was confirmed by FTIR and <sup>1</sup>H-NMR spectroscopy. The <sup>1</sup>H-NMR spectrum of compound (**3**) showed two doublet peaks between 7.60-7.63 and 8.11-8.12 ppm, which were assigned to the H<sub>b</sub> and H<sub>a</sub> protons of the carboxylic acid ring respectively.



**Fig. 1** <sup>1</sup>H-NMR spectrum of N-(4-carboxy phenyl) trimellitimide (**3**)

One doublet peak between 8.08-8.09 ppm was assigned to H<sub>c</sub> proton of the imide ring. The singlet peak at 8.32 ppm was assigned to H<sub>e</sub> proton of the imide ring. Finally, two doublet peaks between 8.14-8.45 ppm which were assigned to the H<sub>d</sub> proton of the imide ring (Fig. 1).

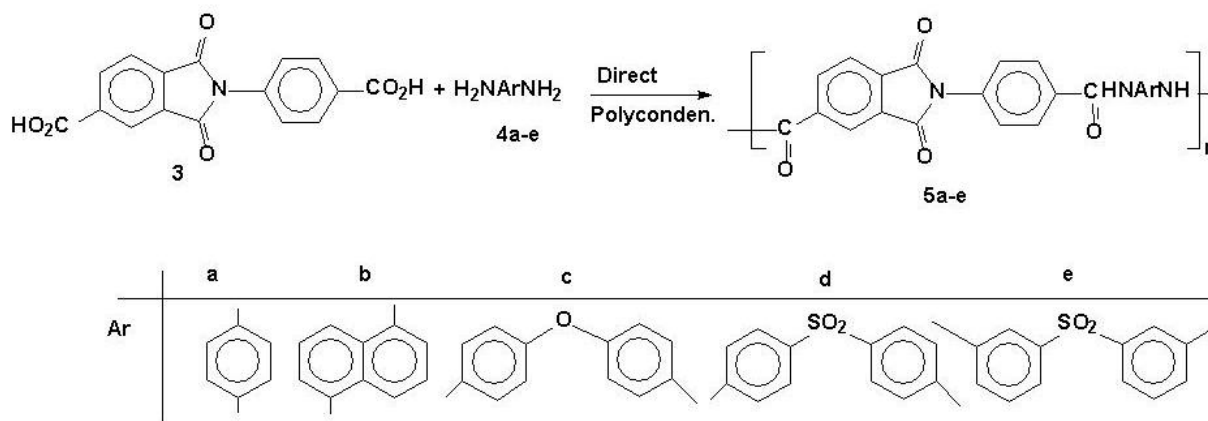
The FTIR spectrum of compound (3) showed a broad peak between 2800, 3100 cm<sup>-1</sup>, which was assigned to the COOH groups. Several absorption bands appeared at 1782, 1724, 1377, 769 and 723 cm<sup>-1</sup>, which were characteristic peaks for the imide ring (Fig.2).



**Fig. 2** FT-IR spectrum of N-(4-carboxy phenyl) trimellitimide (3)

### 3.2. Polymer synthesis

PAIs (5a-e) were synthesized by the direct solution polycondensation reaction of an equimolar mixture of diacid (3) with five different aromatic diamines (4a-e) by using triphenyl phosphate (TPP) and pyridine as condensing agents (Scheme 2). The synthesis and some physical properties of these PAIs (5a-e) are given in Table 1. All the polymers were obtained in moderate to good yields and had inherent viscosities between 0.29-0.40 dLg<sup>-1</sup>.



**Scheme 2** Synthetic route of poly(amide-imide)s (5a-e)

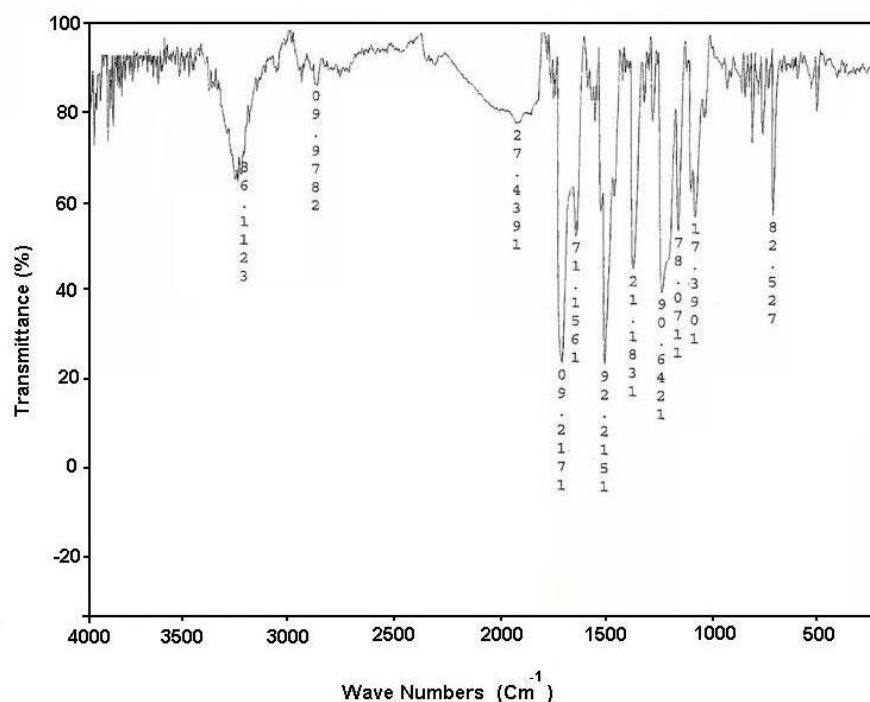
**Table 1**  
Synthesis and Some Physical Properties of PAIs (**5a-e**)

Polymer	Diamine	Yield (%)	$\eta_{inh}$ (dl/g) <sup>a</sup>
<b>5a</b>	<b>4a</b>	86	0.32
<b>5b</b>	<b>4b</b>	83	0.35
<b>5c</b>	<b>4c</b>	90	0.40
<b>5d</b>	<b>4d</b>	80	0.29
<b>5e</b>	<b>4e</b>	78	0.31

<sup>a</sup> Measured at a concentration of 0.5 g/dL in DMF at 25°C

### 3.3. Polymer characterization

The synthesis and some physical properties of PAIs (**5a-e**) are summarized in Table 1. These polymers were confirmed to be PAIs by using FTIR spectroscopy and elemental analyses (Table 2). A representative FTIR spectrum of PAIs **5a** is shown in Fig. 3.



**Fig. 3** FT-IR spectrum of PAIs **5a**

This polymer had absorption band between 1712 and 1660  $\text{cm}^{-1}$  due to imide and amide carbonyl groups. Absorption bands around 1380  $\text{cm}^{-1}$  and 730-710  $\text{cm}^{-1}$  demonstrated the presence of the imide heterocyclic absorption in this polymer. The other spectra showed similar patterns (see the appendix). The elemental analysis values of the resulting polymers were in good agreement with the calculated values for the proposed structures (Table 2).

The solubility of PAIs (**5a-e**) was investigated with 0.01g polymeric samples in 2 ml of a solvent. All these PAIs were soluble in organic solvents such as N, N-dimethylformamide (DMF), N, N-dimethylacetamide (DMAC), DMSO, NMP and chloroform at room temperature and were insoluble in solvents such as ethanol, MeOH, acetone, methylene chloride and water (Table 3).

**Table 2**  
Elemental Analysis of PAIs (**5a-e**)

Polymer	Formula		C (%)	H (%)	N (%)
<b>5a</b>	$C_{22}H_{13}N_3O_4$	Calcd	68.9	3.4	10.9
	$(383.22)_n$	Found	68.0	3.7	10.0
<b>5b</b>	$C_{26}H_{15}N_3O_4$	Calcd	72.0	3.4	9.7
	$(433.26)_n$	Found	73.0	4.0	10.0
<b>5c</b>	$C_{28}H_{17}N_3O_5$	Calcd	70.7	3.5	8.8
	$(475.28)_n$	Found	71.0	3.9	9.1
<b>5d</b>	$C_{28}H_{17}N_3O_6S$	Calcd	64.2	3.2	8.0
	$(523.28)_n$	Found	65.0	3.6	8.5
<b>5e</b>	$C_{28}H_{17}N_3O_6S$	Calcd	64.2	3.2	8.0
	$(523.28)_n$	Found	65.2	3.9	8.1

**Table 3**  
Solubility of PAIs (**5a-e**)

Solvent	5a	5b	5c	5d	5e
DMF	+	+	+	+	+
DMSO	+	+	+	+	+
DMAc	+	+	+	+	+
NMP	+	+	+	+	+
CHCl <sub>3</sub>	+	+	+	+	+
EtOH	-	-	-	-	-
MeOH	-	-	-	-	-
Acetone	-	-	-	-	-
CH <sub>2</sub> Cl <sub>2</sub>	-	-	-	-	-
H <sub>2</sub> O	-	-	-	-	-

+ = soluble at room temperature; - = insoluble at Room temperature

### 3.4. Thermal properties

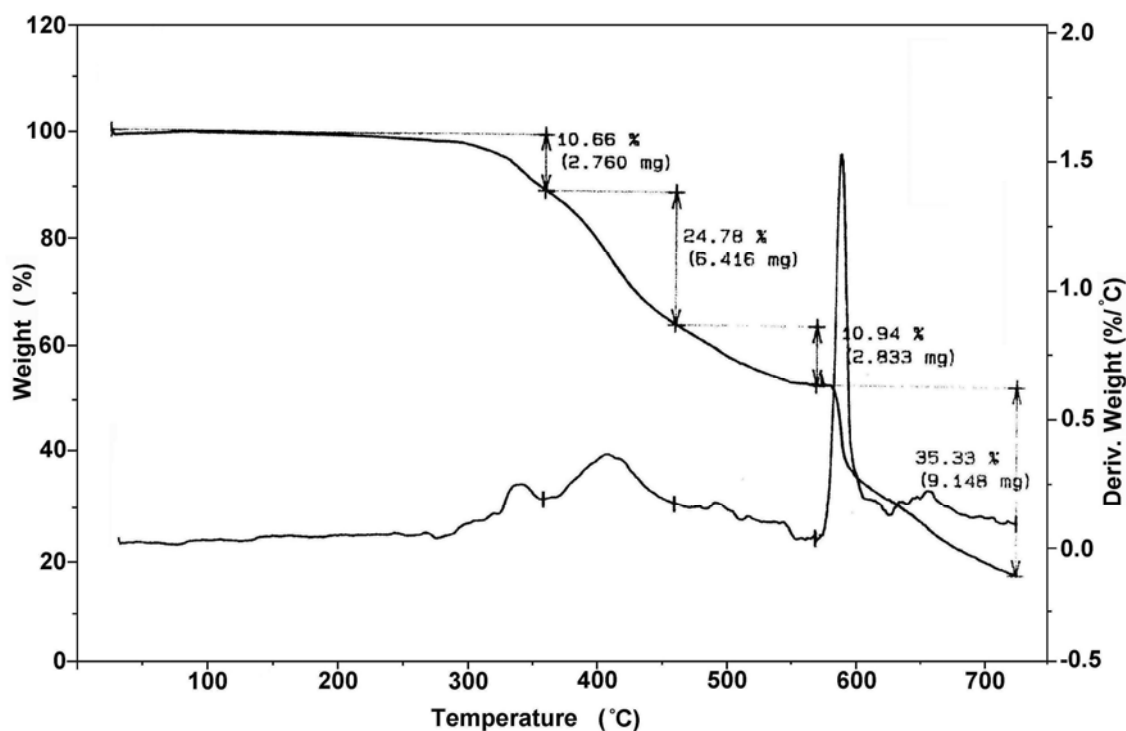
The thermal properties of two samples of resulting polymers (**5a**, **e**) were investigated with TGA and DTG in nitrogen atmosphere at a rate of heating of 10 °C per minute, and thermal data are summarized in Table 4 (Fig. 4). The initial decomposition temperatures of 5 and 10 % weight losses ( $T_5$  and  $T_{10}$ ) and the char yields at 600 °C for **5a** and **5e** are summarized in Table 4. These polymers exhibited good resistance to thermal decomposition, up to 330-340 °C in nitrogen, and began to decompose gradually that temperature.  $T_5$  for polymers **5a** and **5e** ranged from 340-345 and 330-335 °C, and residual weight for these polymers at 600 °C ranged from 35 and 25% in nitrogen respectively.

**Table 4**  
Thermal Behavior of **5a** and **5e**

Polymer	T <sub>5</sub> (C) <sup>a</sup>	T <sub>10</sub> (C) <sup>b</sup>	Char yield <sup>c</sup>
5a	340-345	350-355	35%
5e	330-335	340-345	25%

<sup>a,b</sup> Temperature at which 5% and 10% weight loss was recorded by TGA at heating rate of 10 °C min<sup>-1</sup> in N<sub>2</sub> respectively

<sup>c</sup> Percentage weight of material left undecomposed after TGA analysis 600 °C



**Fig. 4** TGA & DTG thermograms of PAIs **5a**

#### 4. Conclusions

This work involved the syntheses of several new PAIs (**5a-e**) through the direct polycondensation reactions of diacid **3** with five aromatic diamines **4a-e** with triphenyl phosphite (TPP) and pyridine as condensing agents. These PAIs were soluble in various organic solvents and have good thermal stability. The introduction of trimellitic moieties into the backbone increased the thermal properties and easier processability when compared with other aromatic thermostable polymers such as polyamides and polyimides.

#### Appendix

*Polymer 5a*: FTIR (KBr, cm<sup>-1</sup>): 3211 (m, br), 2879 (w), 1934 (m, br), 1712 (s, sh), 1651 (m, sh), 1512 (s), 1381 (m), 1246 (m, sh), 1170 (m, sh), 1093 (m), 725 (m).

*Polymer 5b*: FTIR (KBr, cm<sup>-1</sup>): 3115 (w), 2957 (m, sh), 1709 (s, sh), 1656 (s, sh), 1604 (m), 1512 (s, br), 1402 (s), 1234 (s, br), 827 (m), 727 (m).

*Polymer 5c*: FTIR (KBr,  $\text{cm}^{-1}$ ): 3100 (m), 2966 (w, br), 1722 (s), 1610 (m), 1512 (s, sh), 1384 (s), 1246 (s, br), 1097 (m, sh), 937 (m), 727 (m).

*Polymer 5d*: FTIR (KBr,  $\text{cm}^{-1}$ ): 3300 (m, br), 2872 (w), 1714 (s), 1591 (m), 1512 (s), 1384 (m), 1315 (m), 1248 (m), 1107 (m), 827 (m), 725 (m, sh), 596 (w).

*Polymer 5e*: FTIR (KBr,  $\text{cm}^{-1}$ ): 3329 (m, br), 2872 (w), 1720 (s, sh), 1656 (s, sh), 1512 (s, sh), 1384 (s), 1315 (m), 1244 (s, sh), 1120 (m, sh), 821 (m), 742 (s).

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