

# Synthesis and Characterization of New Polyamides Derived from 1,3-(4-Carboxy phenoxy) propane and Aromatic Diamines

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**ABSTRACT:** Six new polyamides **5a-f** containing flexible trimethylene segments in the main chain were synthesized through the direct polycondensation reaction of 1,3-(4-carboxy phenoxy) propane **3** with six derivatives of aromatic diamines **4a-f** in a medium consisting of *N*-methyl-2-pyrrolidone, triphenyl phosphite, calcium chloride, and pyridine. The polycondensation reaction produced a series of novel polyamides containing flexible trimethylene segments in the main chain in high yield with inherent viscosities between 0.32 and 0.68 dL/g. The resulted polymers were fully characterized by means of FTIR spectroscopy, elemental analyses, inherent viscosity, and solubility tests. Thermal properties of these polymers were

investigated by using thermal gravimetric analysis (TGA) and differential thermal gravimetric (DTG). The glass-transition temperatures of these polyamides were recorded between 165 and 190°C by differential scanning calorimetry, and the 10% weight loss temperatures were ranging from 360 to 430°C under nitrogen. 1,3-(4-Carboxy phenoxy) propane **3** was prepared from the reaction of 4-hydroxy benzoic acid **1** with 1,3-dibromo propane **2** in the presence of NaOH solution. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1769–1774, 2009

**Key words:** polyamides; 1,3-bis(4-benzoyl chloride phenoxy) propane; aromatic diamines

## INTRODUCTION

Aromatic polyamides have received considerable attention with regard to the production of high-performance materials because of their outstanding thermal stability, chemical resistance, and electrical and mechanical properties.<sup>1–3</sup> However, their applications are restricted because of their poor solubility in organic solvents and too high glass transition temperatures that make them very difficult to be processed by spin coating or thermoforming techniques.<sup>4,5</sup> Much effort has been made to create structurally-modified aromatic polymers having increased solubility and processability with retention of their high thermal stability. It is known that the solubility of polymers is often increased when flexible bonds such as [–O–, –SO<sub>2</sub>–, –CH<sub>2</sub>–, –C(CF<sub>3</sub>)<sub>2</sub>], bulky pendent groups (such as *t*-butyl and adamantyle), large pendent groups or polar constituents are incorporated into the polymer backbone due to the altering crystallinity and intermolecular interactions.<sup>6–8</sup> If the flexible segments are carefully chosen, it is possible to promote solubility without

affecting thermal and mechanical properties to any great extent.<sup>9–12</sup> In our pervious articles, we described synthesis of different polyamides and poly (amide-imide)s containing heterocyclic moieties in the main chain such as hydantoin derivatives with improved solubility and thermal properties.<sup>13–20</sup>

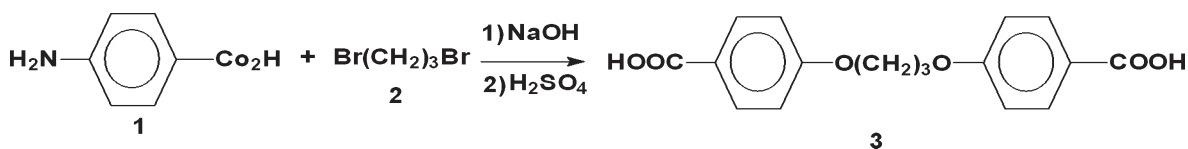
In this article, we describe synthesis and characterization of a series of novel polyamides **5a-f** containing trimethylene segments from the direct polycondensation reaction of 1,3-(4-carboxy phenoxy) propane **3** with six aromatic diamines such as 1,4-diamino benzene **4a**; 1,5-diamino naphthalene **4b**; 4,4'-diamino diphenyl ether **4c**; 2,6-diamino pyridine **4d**; 4,4'-diamino diphenyl sulfone **4e**; and 3,3'-diamino diphenyl sulfone **4f** in a medium consisting of *N*-methyl-2-pyrrolidone, triphenyl phosphite, calcium chloride, and pyridine. Results showed that these novel polymers with a flexible segment in the main chain have better solubility in organic solvents when compared to aromatic polyamides.

## EXPERIMENTAL

### Materials

All chemicals were purchased from Merck Chemical Co. (Germany) and Aldrich (USA).

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Scheme 1 Synthesis route of diacid 3.

### Techniques

$^1\text{H-NMR}$  spectra were recorded on a Bruker 500 MHz instrument. Fourier transform infrared (FTIR) spectra were recorded on Galaxy series FTIR 5000 spectrophotometer (England). Spectra of solids were performed by using KBr pellets. Vibrational transition frequencies are reported in wave number ( $\text{cm}^{-1}$ ). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s), and broad (br). Inherent viscosities were measured by a standard procedure using a Technico Regd Trad Merk Viscometer. Thermal gravimetric analysis (TGA and DTG) data for polymers were taken on a Mettler TA4000 system under  $\text{N}_2$  atmosphere at a rate of  $10^\circ\text{C}/\text{min}$ . Differential scanning calorimetric analysis was performed on differential scanning calorimeter (Du Pont 910) at a heating rate of  $10^\circ\text{C}/\text{min}$ . Elemental analyses were performed by the Arak Petrochemical Company, Arak, Iran.

### Monomer synthesis

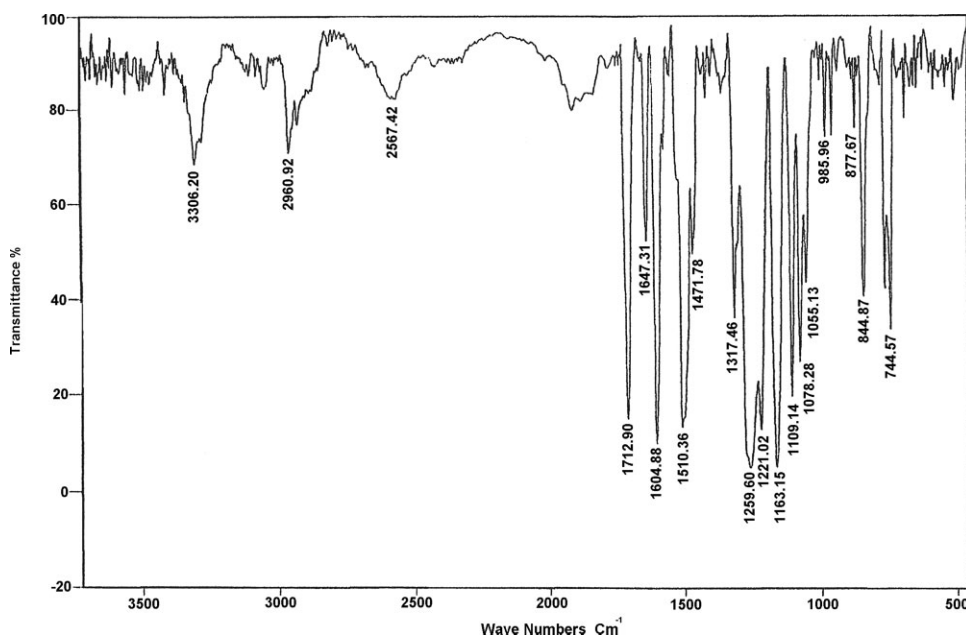
#### 1,3-bis (4-carboxy phenoxy) propane 3

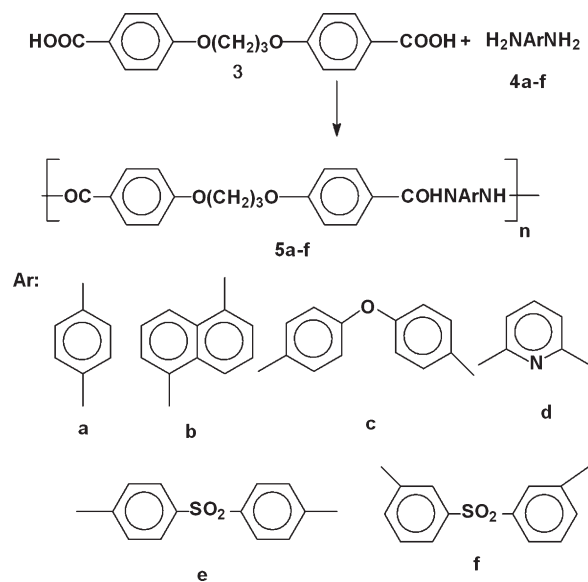
Diacid 3 was prepared according to a typical procedure that was shown is Scheme 1. Into a 250 mL round bottomed flask with dropping funnel fitted

with a stirring bar were placed (4.60 g, 33.3 mmol) 4-hydroxy benzoic acid 1 and (2.60 g, 65.0 mmol) sodium hydroxide in 14.0 mL  $\text{H}_2\text{O}$ . Then (3.40 g, 16.8 mmol), 1,3-dibromo propane 2 was added into the reaction mixture slowly with stirring, and the reaction mixture was refluxed for 3.5 h. After that (0.66 g, 16.5 mmol) NaOH was added and refluxing continued for 2 h. Then, the heat was removed, and the stirring continued at room temperature for over night. After that the white precipitate was filtered and washed with 10 mL methanol, the solid was dissolved in 34 mL  $\text{H}_2\text{O}$ . By adding a solution of  $\text{H}_2\text{SO}_4$  (6N), a white solid was precipitate, washed with the cold water, and filtered at room temperature until 6.32 g (60%) white product was obtained. m.p:  $318\text{--}320^\circ\text{C}$ , FTIR (KBr): 2511–3016 (s, br), 1678 (s), 1606 (s), 1431 (s), 1303 (s), 1249 (s), 1170 (s), 1055 (m), 1514 (m), 999 (m), 848 (m), 766 (s), 542 (w), 549 (w)  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (DMSO- $d_6$ ), TMS)  $\delta$ : 2.18–2.23 (q, 2H), 4.18–4.22 (t, 4H), 7.01–7.04 (d, 4H), 7.86–7.89 (d, 4H), 12.62 (s, br, 2H) ppm. Elem. Anal. Calcd for  $\text{C}_{17}\text{H}_{16}\text{O}_6$ : C, 64.58; H, 5.06; Found: C, 64.2; H, 5.0.

### Polymer synthesis

The PAs 5a-f were prepared by the following general procedure (using polymer 5b as an example).

Figure 1  $^1\text{H-NMR}$  Spectrum of diacid 3.



Scheme 2 Synthesis of polyamides 5a-f.

Into a 25 mL round-bottomed flask, which was fitted with a stirring bar were placed 1,5-diamino naphthalene **4b** (0.101 g, 0.64 mmol), diacid **3** (0.202 g, 0.64 mmol), calcium chloride (0.20 g, 1.80 mmol), triphenyl phosphite (1.68 mL, 6.00 mmol), pyridine (0.36 mL), and *N*-methyl-2-pyrrolidone (1.6 mL). The reaction mixture was heated under reflux on an oil bath at 60°C for 1h, then 90°C for 2h, and 130°C for 8 h. Then, the reaction mixture was poured into 25 mL of methanol, and the precipitated polymer was collected by filtration and washed thoroughly with methanol and dried at 60°C for 12 h under vacuum to leave 0.25 g (86%) of yellow solid polymer **5b**. The PAs **5a-f** were analyzed by using FTIR spectroscopy.

Polymer 5a, FTIR (KBr)

3325 (m), 3078 (w), 1670 (m), 1593 (m), 1518 (s), 1479 (m), 1413 (m), 1300 (s), 1242 (m), 1182 (w), 1149 (m),

TABLE I  
Synthesis and Some Physical Properties of  
Polyamides 5a-f

Aromatic diamine	Polymer	Yield (%)	$\eta_{inh}$ (dL/g) <sup>a</sup>
<b>4a</b>	<b>5a</b>	87	0.59
<b>4b</b>	<b>5b</b>	86	0.40
<b>4c</b>	<b>5c</b>	80	0.68
<b>4d</b>	<b>5d</b>	71	0.32
<b>4e</b>	<b>5e</b>	89	0.34
<b>4f</b>	<b>5f</b>	94	0.37

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

1033 (w), 896 (w), 761 (w), 723 (w), 682 (m), 611 (m), 526 (m).

Polymer 5b, FTIR (KBr)

3325 (m), 1674 (m), 1589 (s), 1512 (s), 1400 (m), 1317 (s), 1242 (m), 1182 (w), 1147 (m), 1107 (m), 1049 (w), 727 (w), 688 (w), 580 (w).

Polymer 5c, FTIR (KBr)

3308 (m), 3055 (w), 1651 (m), 1604 (m), 1500 (s), 1408 (m), 1319 (m), 1257 (m), 1221 (m), 1103 (w), 1022 (w), 846 (w), 761 (w), 686 (w), 518 (w).

Polymer 5d, FTIR (KBr)

3335 (m), 3055 (w), 1662 (m), 1606 (m), 1516 (s), 1408 (m), 1319 (m), 1265 (m), 1184 (w), 1116 (w), 993 (w), 895 (w), 844 (w), 792 (w), 761 (w), 688 (w).

Polymer 5e, FTIR (KBr)

3310 (m), 1658 (s), 1601 (m), 1521 (s), 1489 (s), 1408 (m), 1325 (m), 1269 (m), 1184 (w), 1072 (w), 966 (w), 848 (w), 783 (w), 688 (w), 582 (w), 518 (w).

TABLE II  
Elemental Analysis of Polyamides 5a

Polymer	Formula		C%	H%	N%
<b>5a</b>	C <sub>23</sub> H <sub>20</sub> N <sub>2</sub> O <sub>4</sub> (388.25) <sub>n</sub>	Calcd	71.14	5.15	7.21
		Found	70.60	4.70	6.90
<b>5b</b>	C <sub>27</sub> H <sub>22</sub> N <sub>2</sub> O <sub>4</sub> (438.29) <sub>n</sub>	Calcd	73.98	5.01	6.39
		Found	72.60	4.65	5.10
<b>5c</b>	C <sub>29</sub> H <sub>24</sub> N <sub>2</sub> O <sub>5</sub> (480.31) <sub>n</sub>	Calcd	72.51	4.99	5.83
		Found	71.60	5.30	4.70
<b>5d</b>	C <sub>22</sub> H <sub>19</sub> N <sub>3</sub> O <sub>4</sub> (389.22) <sub>n</sub>	Calcd	67.88	4.88	10.79
		Found	66.50	3.90	9.60
<b>5e</b>	C <sub>29</sub> H <sub>24</sub> N <sub>2</sub> O <sub>6</sub> S (528.37) <sub>n</sub>	Calcd	65.91	4.54	5.30
		Found	64.80	4.00	6.00
<b>5f</b>	C <sub>29</sub> H <sub>24</sub> N <sub>2</sub> O <sub>6</sub> S (528.37) <sub>n</sub>	Calcd	65.91	4.54	5.30
		Found	64.70	4.00	6.10

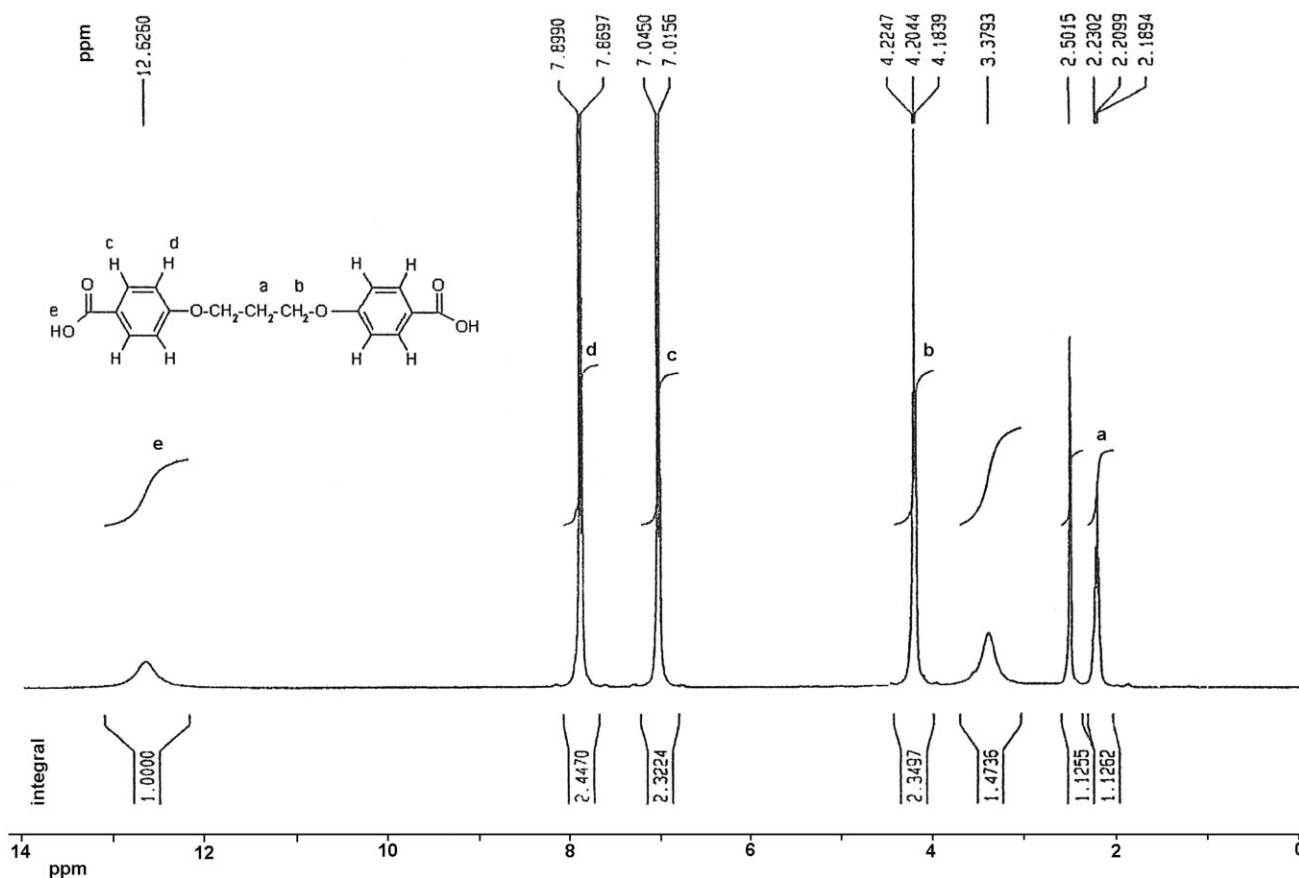


Figure 2 FTIR Spectrum of polyamide 5d.

#### Polymer 5f, FTIR (KBr)

3331 (m), 3076 (w), 1680 (s), 1606 (s), 1523 (s), 1411 (s), 1321 (s), 1267 (s), 1178 (s), 1076 (w), 1024 (w), 947 (w), 854 (m), 769 (m), 688 (m).

## RESULTS AND DISCUSSION

### Monomer synthesis

1,3-(4-Carboxy phenoxy) propane **3** was prepared from the reaction of 4-hydroxy benzoic acid **1** with 1,3-dibromo propane **2** in presence of NaOH solution (Scheme 1). The chemical structure and purity of diacid **3** were proved with elemental analysis,  $^1\text{H-NMR}$ , and FTIR spectroscopy. The measured results in elemental analyses of compound **3** closely corresponded to the calculated ones, demonstrating that the expected compound was obtained. The FTIR spectrum of compound **3** showed a broad peak between 2500 and 3100  $\text{cm}^{-1}$ , which was assigned to the COOH groups, and absorption band appeared at 3331  $\text{cm}^{-1}$ , which was assigned to the NH groups.

The  $^1\text{H-NMR}$  spectrum of compound **3** showed a broad singlet peak at 12.62 ppm, which was assigned to the  $\text{H}_e$  protons of the COOH groups. Two doublet peaks between 7.01 and 7.04 ppm and 7.86 and 7.89 ppm were assigned to the  $\text{H}_c$  and  $\text{H}_d$

protons of the phenyl ring. Furthermore, a multiple peak between 2.18–2.23 ppm was assigned to the  $\text{H}_a$ , and a peak as triplet was assigned to the  $\text{H}_b$  (Fig. 1).

### Polymer synthesis

PAs **5a-f** were synthesized by the direct polycondensation reaction of an equimolar mixture of diacid **3** with six aromatic diamines **5a-f** in a medium consisting of *N*-methyl-2-pyrrolidone, triphenyl

TABLE III  
Solubility of PAs 5a-f

Solvents	5a	5b	5c	5d	5e	5f
DMAc	+	+	+	+	+	+
DMSO	+	+	+	+	+	+
DMF	+	+	+	+	+	+
NMP	+	+	+	+	+	+
THF	+	+	+	+	+	+
Acetone	+	+	+	+	+	+
$\text{CHCl}_3$	-	-	-	-	-	-
EtOH	-	-	-	-	-	-
MeOH	-	-	-	-	-	-
$\text{CH}_2\text{Cl}_2$	-	-	-	-	-	-
$\text{H}_2\text{O}$	-	-	-	-	-	-

+: Soluble at room temperature; -: Insoluble at room temperature.

**TABLE IV**  
Thermal Behavior of PAs 5c, d, e

Polymer	$T_g$	$T_5$ ( $^{\circ}\text{C}$ ) <sup>a</sup>	$T_{10}$ ( $^{\circ}\text{C}$ ) <sup>b</sup>	Char yield <sup>c</sup> (%)
5c	165	245–250	360–370	62
5d	175	235–240	395–400	48
5e	190	365–370	430–435	65

<sup>a,b</sup> Temperature at which 5 and 10% weight loss was recorded by TGA at heating rate of  $10^{\circ}\text{C}/\text{min}$  in  $\text{N}_2$  respectively.

<sup>c</sup> Percentage weight of material left undecomposed after TGA analysis  $600^{\circ}\text{C}$ .

phosphite, calcium chloride, and pyridine (Scheme 2). The syntheses and some physical properties of these new PAs 5a-f are given in Table I. The entire polycondensation reaction readily proceeded in a homogeneous solution; tough and stringy precipitates formed when the viscous PAs solution was obtained in moderate to good yields (Table I).

### Polymer characterization

The syntheses and some physical properties of PAs 6a-f are summarized in Table I. These polymers had inherent viscosities around 0.32–0.68 dL/g and were yellow crystals. These polymers were confirmed to be PAs with FTIR spectroscopy and elemental analyses (Table II). A representative FTIR spectrum of polymer 5d is shown in Figure 2. FTIR spectrum shows that the carbonyl peak of polymer shift to

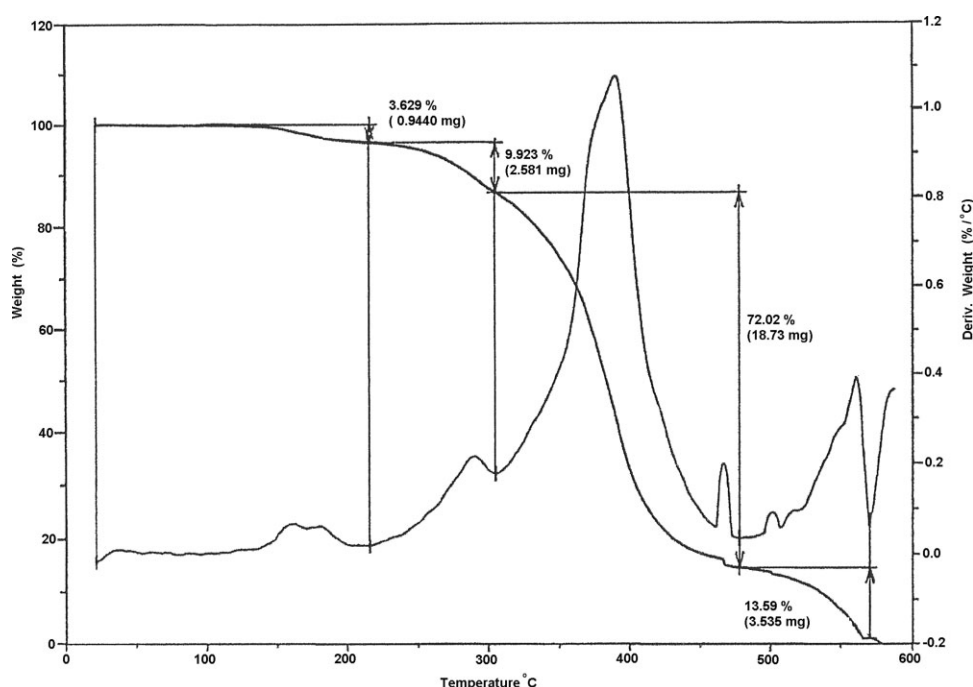
lower frequency in comparison with diacid 4, and OH peak at  $2500\text{--}3100\text{ cm}^{-1}$  of diacid disappeared.

The elemental analysis of the resulting polymers is in good agreement with the calculated values for the proposed structures (Table II).

The solubility of PAs 5a-f was investigated with 0.01 g polymeric samples in 2 mL of solvent. All polymers are dissolved in organic solvents such as DMF, DMAC, DMSO, NMP, THF, and acetone at room temperature and are insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol, and water (Table III).

### Thermal properties

The thermal properties of PAs 5a-f were investigated with TGA and DTG in a nitrogen atmosphere at a rate of heating of  $10^{\circ}\text{C}/\text{min}^{-1}$ , and the thermal data are summarized in Table IV (Fig. 3). The initial decomposition temperatures of 5 and 10% weight losses ( $T_5$  and  $T_{10}$ ) and the char yield at  $600^{\circ}\text{C}$  for 5c, 5d, and 5e are summarized in Table IV. These polymers exhibited good resistance to thermal decomposition, up to  $235\text{--}365^{\circ}\text{C}$  in nitrogen, and began to decompose gradually above that temperature.  $T_5$  for polymers 5c, 5d, and 5e ranged from 235 to  $265^{\circ}\text{C}$ , and  $T_{10}$  for all polymers ranged from 360 to  $430^{\circ}\text{C}$ , and the residual weight for these polymers at  $600^{\circ}\text{C}$  ranged from 48 to 65% in nitrogen. In the DSC experiments, there is no melting endotherm in the DSC thermograms. Glass transition temperatures



**Figure 3** TGA- and DTG-thermogram of polyamide 5c.



of these polymers were found to be in the range of 165–190°C. Polyamide **5e** containing sulfone group exhibited higher  $T_g$  value than polyamides **5c** and **5d**.

### CONCLUSIONS

This work involved the syntheses of several new PAs **5a-f** through direct polycondensation reaction of diacid **3** with six aromatic diamines **4a-f** by using triphenyl phosphite, NMP, calcium chloride, and pyridine as condensing agents. These new PAs were soluble in various organic solvents and had good thermal stability. The presence of trimethylene as a flexible segment into the backbone increased the solubility of these polymers in comparison to aromatic polyamides. These properties could make these PAs attractive for practical applications, such as processable high-performance engineering plastics.

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