

# New Polyamides Based on 2,5-Bis[(4-carboxyanilino) carbonyl] pyridine and Aromatic Diamines: Synthesis and Characterization

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**ABSTRACT:** Seven new polyamides **6a–g** were synthesized through the direct polycondensation reaction of 2,5-bis[(4-carboxyanilino) carbonyl] pyridine **4** with seven derivatives of aromatic diamines **5a–g** 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 pyridyl moiety in the main chain in high yield with inherent viscosities between 0.32–0.72 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 and differential thermal gravimetric. All the poly-

mers were soluble at room temperature in polar solvents, such as *N,N*-dimethyl acetamide, *N,N*-dimethyl formamide, dimethyl sulfoxide, and *N*-methyl-2-pyrrolidone. 2,5-Bis[(4-carboxyanilino) carbonyl] pyridine **4** as a new monomer containing pyridyl moiety was synthesized by using a two-step reaction. At first 2,5-pyridine dicarboxylic acid **1** was converted to 2,5-pyridine dicarbonyl dichloride **2**. Then diacid **4** was prepared by condensation reaction of diacid chloride **2** with *p*-aminobenzoic acid **3**. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1152–1157, 2008

**Key words:** high performance polymers; polyamides; pyridyl moiety; aromatic diamines

## INTRODUCTION

Aromatic polyamides have received considerable attention with regard to the production of high performance materials due to their outstanding thermal stability, chemical resistance and electrical and mechanical properties.<sup>1–3</sup> However, their application is 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> Many efforts have been made to create structurally modified aromatic polymers having increased solubility and process ability with retention of their high thermal stability. It is known that the solubility of polymers often increases when flexible bonds, large pendent groups or polar constituents incorporated into the polymer backbone.<sup>6–8</sup> If the pendent groups are carefully chosen, it will be possible to promote solubility without affecting thermal and mechanical properties to any great extent. Furthermore in many cases, the introduction of various heterocyclic aromatic rings into the main chain of polyamides leads

to polymers with improved solubility and superior thermal stability.<sup>9–12</sup> In our previous studies, 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 of a series of novel polyamides **6a–g** containing pyridyl ring from the direct polycondensation reaction of 2,5-bis[(4-carboxyanilino) carbonyl] pyridine **4** with seven aromatic diamines, such as 3,3'-diamino diphenyl sulfone **5a**, 4,4'-diamino diphenyl sulfone **5b**, 4,4'-diamino diphenyl ether **5c**, 1,4-diamino benzene **5d**, 1,5-diamino naphthalene **5e**, 6-chloro-2,4-diamino-1,3-diazine **5f**, 6-phenyl-2,4-diamino-1,3,5-triazine **5g** by using *N*-methyl-2-pyrrolidone (NMP), triphenylphosphite, and pyridine as condensing agents. These polymers have a heterocyclic aromatic ring such as pyridyl moiety in the main chain for improving solubility in organic solvents in comparison with aromatic polyamides.

## EXPERIMENTAL

### Materials

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

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## 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 by using a Technico Regd Trad Merk Viscometer. Thermal gravimetric analysis and differential thermal gravimetric (TGA and DTG) data for polymers were taken on a Mettler TA4000 System under  $\text{N}_2$  atmosphere at a rate of  $10^\circ\text{C}/\text{min}$ . Elemental analyses were performed by the Arak Petrochemical Company, Arak, Iran.

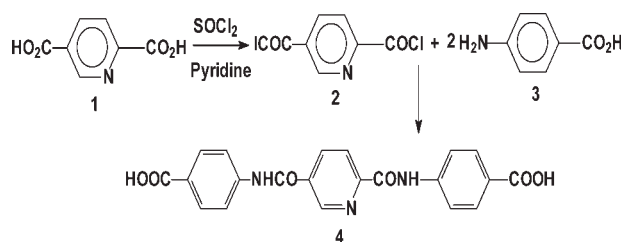
## Monomer synthesis

### 2,5-Pyridine dicarbonyl dichloride 2

Into a 100 mL round-bottomed flask were placed 2.00 g (11.90 mmol) of 2,5-pyridine dicarboxylic acid **1**, 20 mL of thionyl chloride and 0.1 mL pyridine as a base. Reaction mixture was heated on an oil bath at  $70^\circ\text{C}$ , until the suspension mixture was converted into a clear solution. Then unreacted thionyl chloride was removed by distillation and then residue was placed under vacuum to leave 2.00 g (83%) of 2,5-pyridine dicarbonyl dichloride **2**. FTIR (KBr): 1726 (s), 1602 (w, sh), 1402 (s), 1234 (s, sh), 1128 (s), 748 (s), 491 (m), 277 (m)  $\text{cm}^{-1}$ .

### 2,5-Bis[(4-carboxyanilino) carbonyl] pyridine 4

Into a 100 mL round-bottomed flask were added (2.04 g, 10.00 mmol) 2,5-pyridine dicarbonyl dichloride **2**, 20 mL of dry THF and the reaction mixture was cooled into an ice-water bath and after that, a solution of 4-amino benzoic acid **3** (2.68 g, 20.00 mmol) in 20 mL of dry THF was added slowly at 10 min. The reaction mixture was stirred overnight at room temperature and after cooling the solvent excess was removed by distillation and the residue was washed twice with hot water to give the pure diacid **4** (3.72 g, 92% yield); m.p  $380^\circ\text{C}$  (dec) 3331 (m), 2500–3100 (s, br), 1687 (s, br), 1593 (s), 1523 (s), 1441 (s), 1294 (s, br), 1178 (s), 1022 (m), 947 (w), 856 (m), 771 (m), 678 (m), 551 (m).  $^1\text{H}$  NMR (DMSO- $d_6$ , TMS),  $\delta$ : 7.91–7.96 (m, 4H), 8.04–8.12 (m, 5H), 8.33–8.35 (d, 2H), 9.09 (s, 2H), 10.94 (s, 2H). Analysis: Calculated for  $\text{C}_{21}\text{H}_{15}\text{N}_3\text{O}_6$ : C, 62.24; H, 3.70; N, 10.36; found: C, 62.0; H, 3.6; N, 10.0.



**Scheme 1** Synthesis of 2,5-bis[(4-carboxyanilino) carbonyl] pyridine **4**.

## Polymer synthesis

The PAs **6a–g** were prepared by the following general procedure (using polymer **6a** as an example). Into a 25 mL round-bottomed flask, which was fitted with a stirring bar were placed 3,3'-diamino diphenyl sulfone **5a** (0.08 g, 0.32 mmol), diacid **4** (0.13 g, 0.32 mmol), calcium chloride (0.10 g, 0.90 mmol), triphenyl phosphite (0.84 mL, 3.00 mmol), pyridine (0.18 mL), and *N*-methyl-2-pyrrolidone (0.8 mL). The reaction mixture was heated under reflux on an oil bath at  $60^\circ\text{C}$  for 1 h, then  $90^\circ\text{C}$  for 2 h, and  $130^\circ\text{C}$  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  $60^\circ\text{C}$  for 12 h under vacuum to leave 0.15 g (86%) of yellow solid polymer **6a**. The PAs **6a–g** were analyzed by using FTIR spectroscopy.

## RESULTS AND DISCUSSION

### Monomer synthesis

2,5-Bis[(4-carboxyanilino) carbonyl] pyridine **4** was synthesized through the condensation reaction of one equivalent of 2,5-pyridine dicarbonyl dichloride **2** with two equivalent of 4-amino benzoic acid **3** in extra pure THF, as shown in Scheme 1. Then diacid **4** was washed with hot water and then purified by recrystallization from DMF.

The chemical structure and purity of this compound were proved with elemental analysis,  $^1\text{H}$  NMR, and FTIR spectroscopy. The measured results in elemental analyses of diacid **4** closely corresponded to the calculated ones, demonstrating that the expected compound was obtained. The FTIR spectrum of compound **4** showed a broad peak between 2500 and  $3100\text{ cm}^{-1}$ , which was assigned to the COOH group and absorption band appeared at  $3321\text{ cm}^{-1}$  was assigned to the NH groups (Fig. 1).

The  $^1\text{H}$  NMR spectrum of compound **4** showed a broad singlet peak at 10.94 ppm, which was assigned to the  $\text{H}_a$  proton of the COOH groups. The broad singlet peak at 9.09 ppm was assigned to  $\text{H}_b$  and  $\text{H}_c$  protons of the NH groups. Peak between

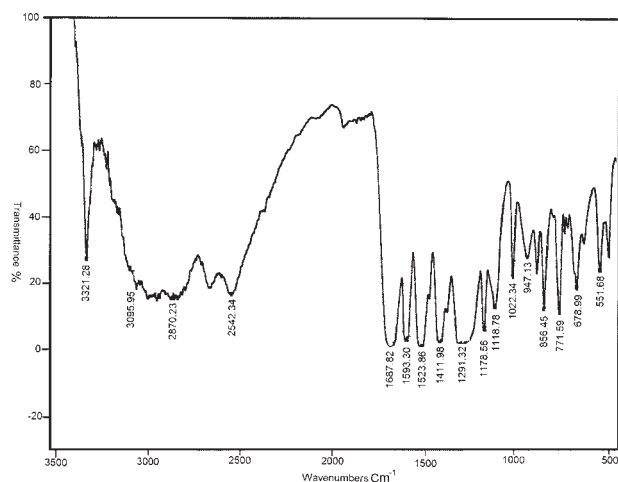
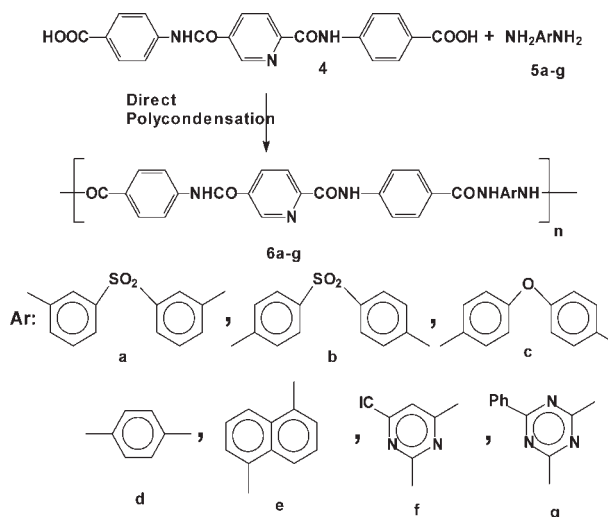


Figure 1 FTIR Spectrum of diacid **4**.

8.33–8.35 ppm was assigned to the H<sub>d</sub> and H<sub>e</sub> protons of the pyridine ring. Peaks between 8.04–8.12 ppm were assigned to the H<sub>f</sub> proton of the pyridine ring and H<sub>g</sub>, H<sub>h</sub>, protons of the phenyl rings. Finally a peak between 7.91–7.94 ppm was assigned to the H<sub>i</sub> and H<sub>j</sub> protons of the phenyl ring (Fig. 2).

### Polymer synthesis

PAs **6a–g** were synthesized by the direct polycondensation reaction of an equimolar mixture of diacid **4** with seven aromatic diamines **5a–g** in a medium consisting of NMP, triphenyl phosphite, calcium chloride, and pyridine (Scheme 2).



Scheme 2 Synthesis of polyamides **6a–g**.

The syntheses and some physical properties of these new PAs **6a–g** are given in Table I. The entire polycondensation reaction readily proceeded in a homogeneous solution while tough and stringy precipitates formed as the viscous PAs solution was obtained in moderate to good yields.

### Polymer characterization

The syntheses and some physical properties of PAs **6a–g** are summarized in Table I. These polymers had inherent viscosities around 0.32–0.72 dL/g and showed yellow crystal. These polymers confirmed

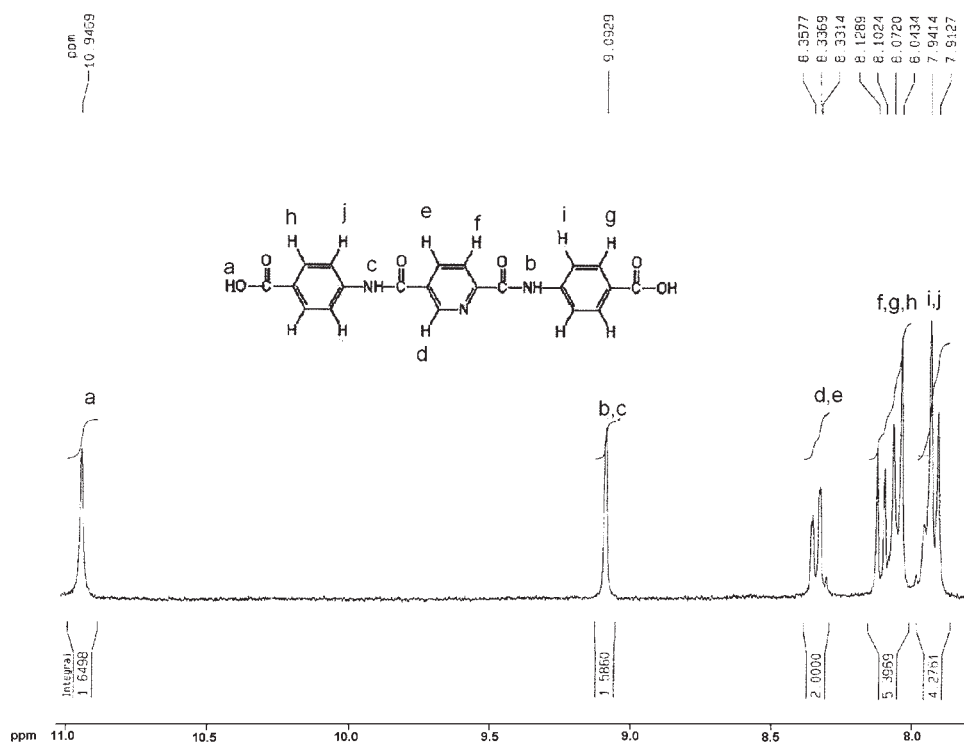


Figure 2 <sup>1</sup>H NMR Spectrum of diacid **4**.

**TABLE I**  
Synthesis and Some Physical Properties  
of Polyamide 6a–g

Aromatic diamines	Polymer	Yield (%)	$\eta_{inh}$ (dL/g) <sup>a</sup>
5a	6a	86	0.32
5b	6b	89	0.72
5c	6c	91	0.52
5d	6d	89	0.43
5e	6e	90	0.41
5f	6f	77	0.43
5g	6g	76	0.48

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

to be PAs with FTIR spectroscopy and elemental analyses (Table II). A representative FTIR spectrum of polymer **6d** is shown in Figure 3. FTIR spectra shows that the carbonyl peak of polymer shift to lower frequency in comparison with diacid **4** and OH peak at 2500–3100  $\text{cm}^{-1}$  of diacid disappeared.

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

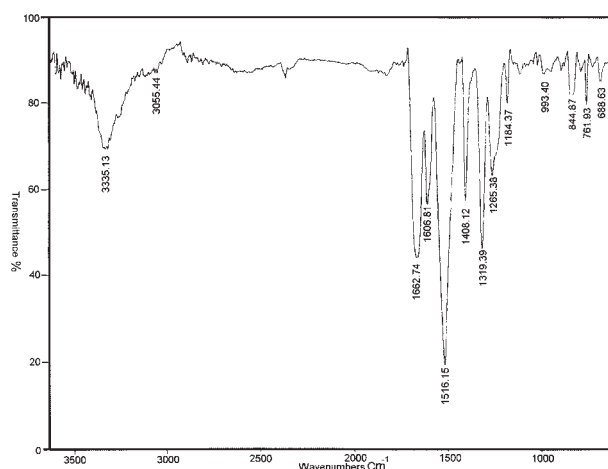
The solubility of PAs **6a–g** was investigated with 0.01 g polymeric samples in 2 mL of solvent (Table III). All polymers were dissolved in organic solvent, such as DMF, DMAC, DMSO, and NMP at room temperature and are insoluble in solvent, such as chloroform, methylene chloride, methanol, ethanol, and water.

### Thermal properties

The thermal properties of PAs **6a–g** were investigated with TGA and DTG in a nitrogen atmosphere at a heating rate of 10°C/min and the thermal data are summarized in Table IV (Figs. 4 and 5). The

**TABLE II**  
Elemental Analysis of Polyamides 6a–g

Polymer	Formula		C%	H%	N%
<b>6a</b>	$\text{C}_{33}\text{H}_{23}\text{N}_5\text{SO}_6$	Calcd	64.17	3.75	11.34
	$(617.64)_n$	Found	63.50	3.00	10.80
<b>6b</b>	$\text{C}_{33}\text{H}_{23}\text{N}_5\text{SO}_6$	Calcd	64.17	3.75	11.34
	$(617.64)_n$	Found	65.10	4.10	10.50
<b>6c</b>	$\text{C}_{33}\text{H}_{23}\text{N}_5\text{O}_5$	Calcd	73.05	4.27	12.91
	$(542.57)_n$	Found	72.50	3.50	11.30
<b>6d</b>	$\text{C}_{27}\text{H}_{19}\text{N}_5\text{O}_4$	Calcd	67.92	4.01	14.67
	$(477.48)_n$	Found	66.70	3.10	13.50
<b>6e</b>	$\text{C}_{31}\text{H}_{21}\text{N}_5\text{O}_4$	Calcd	70.58	4.01	13.27
	$(527.54)_n$	Found	69.80	5.20	12.60
<b>6f</b>	$\text{C}_{25}\text{H}_{16}\text{N}_7\text{O}_4\text{Cl}$	Calcd	58.43	3.14	19.08
	$(513.90)_n$	Found	57.30	3.80	20.20
<b>6g</b>	$\text{C}_{30}\text{H}_{20}\text{N}_8\text{O}_4$	Calcd	64.74	3.62	20.13
	$(556.54)_n$	Found	63.40	3.00	18.90



**Figure 3** FTIR Spectrum of polyamide **6d**.

initial decomposition temperatures of 5 and 10% weight losses ( $T_5$  and  $T_{10}$ ) and the char yield at 600°C are summarized in Table IV. These polymers exhibited good resistance to thermal decomposition, up to 330–405°C in nitrogen, and began to decompose gradually above that temperature.  $T_5$  for these polymers from 330 to 405°C and  $T_{10}$  for all polymers ranged from 345 to 490°C, and the residual weight for these polymers at 600°C ranged from 43 to 66% in nitrogen.

### CONCLUSIONS

This work involved the syntheses of several new PAs **6a–g** through direct polycondensation reaction of diacid **4** with seven aromatic diamines **5a–g** 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 pyridyl segments as a heterocyclic ring into the backbone

**TABLE III**  
Solubility of PAs 6a–g

Solvents	6a	6b	6c	6d	6e	6f	6g
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 6c–e

Polymer	$T_5$ (°C) <sup>a</sup>	$T_{10}$ (°C) <sup>b</sup>	Char yield <sup>c</sup> (%)
6a	405–410	490–495	58
6b	400–405	440–450	47
6c	330–335	345–350	52
6d	375–380	435–440	63
6e	360–365	420–425	66
6f	380–385	400–405	43
6g	405–410	445–450	52

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

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

increased the solubility of these polymers. These properties could make these PAs attractive for practical applications, such as processable high-performance engineering plastics.

## APPENDIX

### Polymer 6a

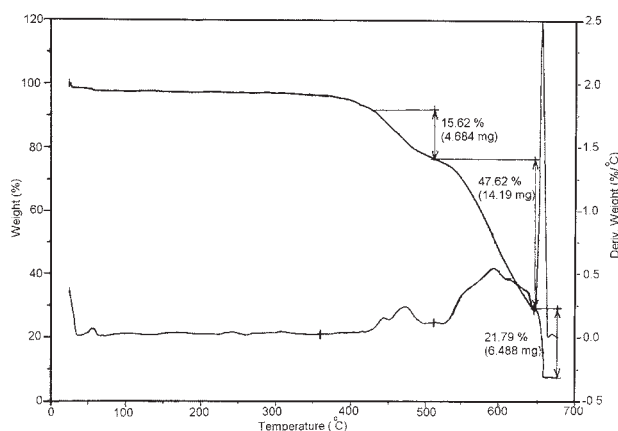
FTIR (KBr): 3325 (m), 3078 (w), 1670 (m), 1593 (m), 1518 (s), 1479 (m), 1413 (m), 1300 (s), 1242 (m), 1182 (w), 1149 (m), 1033 (w), 896 (w), 761 (w), 723 (w), 682 (m), 611 (m), 526 (m).

### Polymer 6b

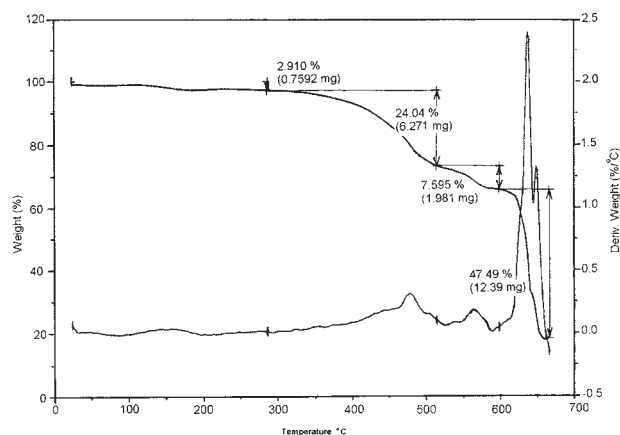
FTIR (KBr): 3325 (m), 1674 (m), 1589 (s), 1512 (s), 1400 (m), 1317 (s), 1242 (m), 1182 (w), 1147 (m), 1107 (m), 1049 (w), 727 (w), 688 (w), 580 (w).

### Polymer 6c

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).



**Figure 4** TGA and DTG thermogram of Polyamide 6b.



**Figure 5** TGA and DTG thermogram of Polyamide 6g.

### Polymer 6d

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 6e

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).

### Polymer 6f

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).

### Polymer 6g

FTIR (KBr): 3025 (m), 3076 (w), 1730 (m), 1680 (s), 1593 (m), 1523 (s), 1491 (m), 1411 (m), 1321 (m), 1269 (s), 1197 (m), 1176 (s), 1074 (m), 1026 (w), 941 (w), 854 (w), 763 (m), 688 (m).

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