

# SYNTHESIS AND CHARACTERIZATION OF NEW THERMALLY STABLE POLYAMIDES BASED ON 2,5-PYRIDINE DICARBOXYLIC ACID AND AROMATIC DIAMINES

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## ABSTRACT

Six new thermally stable polyamides **3a-f** were synthesized through the polycondensation reaction of 2,5-pyridine dicarboxylic acid **1** with six different derivatives of aromatic diamines **2a-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 pyridyl moieties in the main chain in high yield with inherent viscosities between 0.50-0.82 dL/g. The resulting polymers were fully characterized by means of FT-IR spectroscopy, elemental analyses, inherent viscosimetry, and solubility tests. Thermal properties of these polymers were investigated by using thermal gravimetric analysis (TGA) and differential thermal gravimetry (DTG). All of the polymers 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.

## INTRODUCTION

Aromatic polyamides have received considerable attention with regard to the production of high performance materials due to their outstanding thermal stability, chemical resistance, electrical and mechanical properties.<sup>1-3</sup> However their applications are restricted because of their poor solubility in organic solvents and extremely 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 process ability 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, adamantyl and naphthyl), large pendent groups or polar constituents such as heterocyclic segments are incorporated into the polymer backbone due to the altering crystallinity and intermolecular interactions.<sup>6-8</sup> If the heterocyclic moiety is carefully chosen, it is possible to promote solubility without affecting thermal and mechanical properties to any great extent.<sup>9-16</sup> In our previous papers 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>17-25</sup>

In this article, synthesis and characterization of six new polyamides **3a-f** containing pyridyl moieties in the main chain was reported from the polycondensation reaction of 2,5-pyridine dicarboxylic acid **1** and 1,4-phenylene diamine **2a**, 1,5-naphthalene diamine **2b**, 4,4'-diamino diphenyl ether **2c**, 2,6-diamino pyridine **2d**, 4,4'-diamino diphenyl sulfone **2e**, 3,3'-diamino diphenyl sulfone **2f** 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 compared to aromatic polyamides.

## EXPERIMENTAL

### Materials

2,5-pyridine dicarboxylic acid **1**, 1,4-phenylene diamine **2a**, 1,5-naphthalene diamine **2b**, 4,4'-diamino diphenylether **2c**, 2,6-diamino pyridine **2d**, 4,4'-diaminodiphenyl sulfone **2e**, 3,3'-diaminodiphenyl sulfone **2f**, triphenyl phosphate, N-methyl-2-pyrrolidone (NMP), pyridine were purchased from Merck Chemical Company and were used as received. Commercially available calcium chloride (CaCl<sub>2</sub>; from Merck) was dried under vacuum at 150°C for 6 h.

### Techniques

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 (cm<sup>-1</sup>). 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 (TGA and DTG) data for polymers were taken on a Mettler TA4000 System under N<sub>2</sub> atmosphere at a rate of 10°C/min. Elemental analyses were performed by the Arak Petrochemical Company, Arak, Iran.

### Polymer synthesis

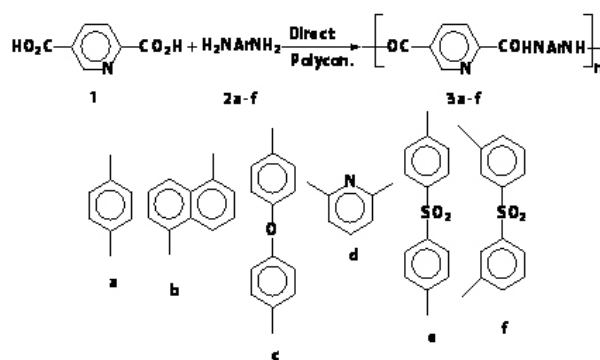
The PAs **3a-f** were prepared by the following general procedure (using

polymer **3a** as an example). Into a 25 mL round-bottomed flask which was fitted with a stirring bar were placed 1,4-phenylene diamine **2a** (0.069 g, 0.64 mmol), diacid **1** (0.106 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 1 h, then at 90°C for 2 h, and at 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 0.14 g (91.5 %) of white solid polymer **3a**. The PAs **3a-f** were analyzed by using FT-IR spectroscopy.

## RESULTS AND DISCUSSION

### Polymer synthesis

PAs **3a-f** were synthesized by the direct polycondensation reaction of an equimolar mixture of diacid **1** with six aromatic diamines **2a-f** in a medium consisting of N-methyl-2-pyrrolidone, triphenyl phosphite, calcium chloride and pyridine (Scheme 1).



Scheme 1 Synthesis of polyamides **3a-f**

The syntheses and some physical properties of these new PAs **3a-f** are given in Table 1. The entire polycondensation reaction readily proceeded in a homogeneous solution while tough and stringy precipitates formed as the viscous PAs solution was obtained in good yields.

Table 1.- Some physical properties of PAs **3a-f**

Diamines	Polymer	Yield (%)	$\eta_{inh}$ (dL/g) <sup>a</sup>	Colors
<b>2a</b>	<b>3a</b>	91	0.70	White
<b>2b</b>	<b>3b</b>	92	0.65	Off-white
<b>2c</b>	<b>3c</b>	89	0.50	White
<b>2d</b>	<b>3d</b>	85	0.70	Off-White
<b>2e</b>	<b>3e</b>	90	0.82	Yellow
<b>2f</b>	<b>3f</b>	87	0.72	Yellow

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

### Polymer characterization

The syntheses and some physical properties of PAs **3a-f** are summarized in Table 1. These polymers had inherent viscosities around 0.50-0.82 dL/g and showed white to yellow crystals. These polymers were confirmed to be PAs with FT-IR spectroscopy and elemental analyses (Table 2). A representative FT-IR spectrum of polymer **3a** shows that the carbonyl peak of polymer shift to lower frequency in comparison with diacid **1** and OH peak at 2500-3100  $\text{cm}^{-1}$  of diacid disappeared. The polymer exhibited characteristic absorption bands at 1709  $\text{cm}^{-1}$  for the amide carbonyl group and absorption bands of amide groups appeared at 3308  $\text{cm}^{-1}$  (N-H stretching). Also spectral data of resulting PA **3a-f** were showed in Table 2. All of the polymers show similar FT-IR spectrum.

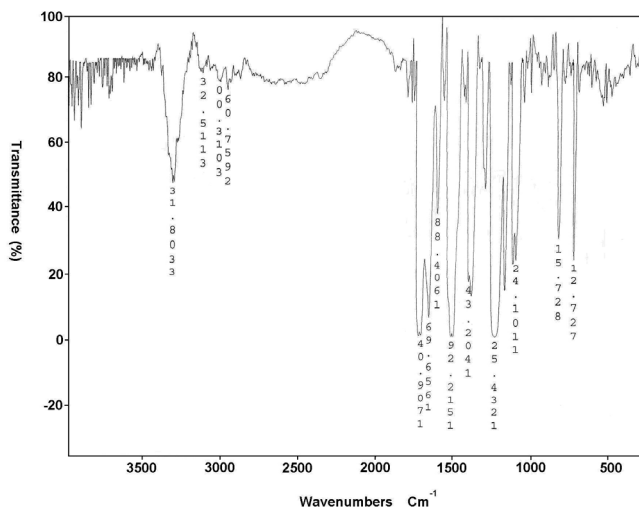


Fig. 1 FTIR Spectrum of PA **3a**

Table 2.- FTIR Characterization of PAIs **3a-f**

Polymer	Spectral data
<b>3a</b>	<b>FT-IR (KBr):</b> 3308 (m), 3115 (w), 3013 (w), 2957 (w), 1709 (s), 1656 (s), 1604 (m), 1512 (s), 1402 (s), 1234 (s), 1101 (m), 827 (m), 727 (m) $\text{Cm}^{-1}$ .
<b>3b</b>	<b>FT-IR (KBr):</b> 3325 (m), 1698 (m), 1589 (s), 1512 (s), 1400 (m), 1317 (s), 1242 (m), 1182 (w), 1147 (m), 1107 (m), 1049 (w), 727 (w) $\text{Cm}^{-1}$ .
<b>3c</b>	<b>FT-IR (KBr):</b> 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) $\text{Cm}^{-1}$ .
<b>3d</b>	<b>FT-IR (KBr):</b> 3335 (m), 3055 (w), 1705 (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) $\text{Cm}^{-1}$ .
<b>3e</b>	<b>FT-IR (KBr):</b> 3310 (m), 1700 (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) $\text{Cm}^{-1}$ .
<b>3f</b>	<b>FT-IR (KBr):</b> 3331 (m), 3076 (w), 1699 (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) $\text{Cm}^{-1}$ .

The elemental analysis of the resulting polymers is in good agreement with the calculated values for the proposed structures (Table 3).

Table 3.- Elemental Analysis of PAs **3a-f**.

Polymer	Formula		C%	H%	N%
<b>3a</b>	$\text{C}_{13}\text{H}_9\text{N}_3\text{O}_2$	Calcd	65.29	3.76	17.56
	$(239.13)_n$	Found	64.90	3.10	17.00
<b>3b</b>	$\text{C}_{17}\text{H}_{11}\text{N}_3\text{O}_2$	Calcd	70.60	3.80	14.52
	$(289.17)_n$	found	70.00	3.40	13.80
<b>3c</b>	$\text{C}_{17}\text{H}_{13}\text{N}_3\text{O}_3$	Calcd	66.24	4.23	13.67
	$(307.17)_n$	found	65.90	4.00	13.10
<b>3d</b>	$\text{C}_{12}\text{H}_8\text{N}_4\text{O}_2$	Calcd	60.01	3.33	23.32
	$(240.12)_n$	found	59.20	2.90	22.80
<b>3e</b>	$\text{C}_{19}\text{H}_{13}\text{N}_3\text{O}_4\text{S}$	Calcd	60.17	3.42	11.07
	$(379.19)_n$	found	59.80	3.00	10.60
<b>3f</b>	$\text{C}_{19}\text{H}_{13}\text{N}_3\text{O}_4\text{S}$	Calcd	60.17	3.42	11.07
	$(379.19)_n$	found	59.60	2.90	10.70

The solubility of PAs **3a-f** was investigated with 0.01g polymeric samples in 2 mL of solvent. All of the polymers are dissolved in organic solvents such as DMF, DMAc, DMSO and NMP at room temperature and are insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol and water (Table 4).

Table 4.- Solubility behavior PAs **3a-f**

Solvents	<b>3a</b>	<b>3b</b>	<b>3c</b>	<b>3d</b>	<b>3e</b>
DMAc	+	+	+	+	+
DMSO	+	+	+	+	+
DMF	+	+	+	+	+
NMP	+	+	+	+	+
THF	+	+	+	+	+
$\text{CHCl}_3$	-	-	-	-	-
Acetone	-	-	-	-	-
EtOH	-	-	-	-	-
MeOH	-	-	-	-	-
$\text{CH}_2\text{Cl}_2$	-	-	-	-	-
$\text{H}_2\text{O}$	-	-	-	-	-

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

### Thermal properties

The thermal properties of PAs **3a-f** were investigated with TGA and DTG in a nitrogen atmosphere at a heating rate of  $10^\circ\text{C}/\text{min}^1$  and the thermal data

are summarized in Table 5. The initial decomposition temperatures of 5 and 10% weight losses ( $T_5$  and  $T_{10}$ ) and the char yield at 600°C for these polymers are summarized in Table 5. These polymers exhibited good resistance to thermal decomposition, up to 295-315 °C in nitrogen, and began to decompose gradually above that temperature.  $T_5$  for these polymers ranged from 295 to 315 °C and  $T_{10}$  for all polymers ranged from 325 to 365 °C, and the residual weight for these polymers at 600 °C ranged from 10 to 58 % in nitrogen. Results show that two PAs **3e** and **3f** with sulfone moiety in the main chain have higher thermal stability in comparing to other PAs **3a-d** because they have a rigid structure such as sulfone moiety in the main chain. These results show PAs **3a-f** have thermal resistance and they can be used as engineering plastic in many applications.

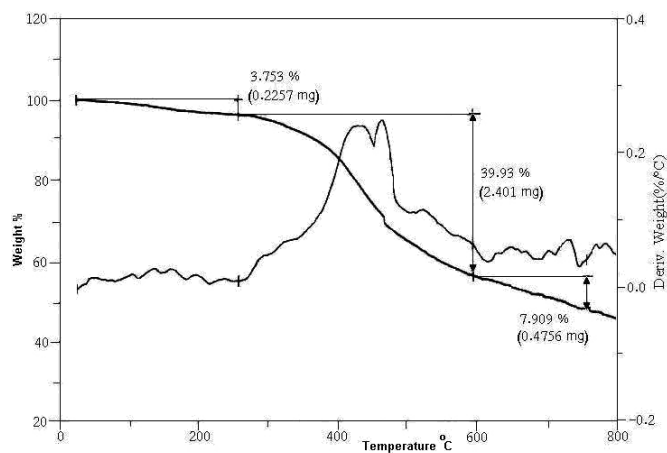


Fig. 2 TGA & DTG thermogram of PA 3e

Table 5.- Thermal behavior of PAs 3a-f

Polymer	$T_5$ (°C) <sup>a</sup>	$T_{10}$ (°C) <sup>b</sup>	Char Yield <sup>c</sup>
<b>3a</b>	305-310	325-330	10 %
<b>3b</b>	295-300	350-355	33 %
<b>3c</b>	305-310	330-335	17 %
<b>3d</b>	305-310	360-365	55 %
<b>3e</b>	315-320	365-370	58 %
<b>3f</b>	300-305	345-350	48 %

<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.

## CONCLUSION

This work involved the syntheses of several new PAs **3a-f** through the direct polycondensation reaction of diacid **1** with six aromatic diamines **2a-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 pridyl segments as a hetrocyclic ring into the backbone increased the solubility of these polymers. These properties could make these PAs attractive for practical applications, such as processable high-performance engineering plastics.

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