

Synthesis and characterization of new soluble polyamides from Acenaphthohydrazinomercaptotriazole diamine

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Abstract

A diamine Acenaphthohydrazinomercaptotriazole (AHTD) was synthesized in one step from acenaphthoquinone and 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole. The diamine was characterized by FTIR, ¹HNMR, ¹³CNMR and melting point. Diamine was used to prepare novel polyamides. The low temperature solution polycondensation of diamine with terephthaloyl and terephthalic acid chlorides afforded diamine-containing polyamides with inherent viscosities of 0.38–0.47 dl/g in DMF at 25 °C. The polyamides were generally soluble in a wide range of solvents such as dimethylformamide (DMF), N-Methylpyrrolidone (NMP), tetrachloroethane (TCE), dimethylsulfoxide (DMSO) and H₂SO₄. Thermal analysis showed that these polyamides were practically crystalline and with T_g under 100 °C.

Keywords: polyamides, thermal stability, polycondensation, acenaphthoquinone.

1. Introduction

Acenaphthoquinone is a quinone derived from acenaphthene. It is insoluble in water, but soluble in alcohol. It is used as an intermediate for the manufacturing of dyes, pharmaceuticals and pesticides. It is also used in chemical research as a drug and therapeutic agent. Triazole derivatives have been reported as a class of useful heterocyclic compounds, and have found widespread applications in the fields of agrochemicals and pharmaceuticals^[1,2]. We have synthesized a diamine that produced of reaction of acenaphthoquinone with triazole derivatives and is used for production of thermally stable polyamides. Polyamides are characterized as high temperature resistant materials with a favorable balance of other physical and chemical properties^[3]. Aromatic polyamides have the poor process ability due to their insolubility in common organic solvents and extremely high glass transition or melt temperature. The synthesis of soluble polyamides without deteriorating their excellent properties^[4-10]. DSC studies of some polyamides^[11,12] were reported in literature. We successfully prepared aromatic polyamides^[13], polyimides^[14], polyesters, polyquinoxalines, from a number of new functional monomers^[15]. Thermally stable polymers have received extensive interest due to the increasing demands for high temperature polymers as replacements for ceramics and metals in the automotive, aerospace, and microelectronics industries. Aromatic polyamides are one of the most important classes of high performance polymers, because they possess excellent mechanical properties, thermal stability, chemical resistance, and low flammability. However, they encounter processing difficulties due to limited solubility in organic solvents and high glass transition or melting temperatures. It is a result of chain stiffness and intermolecular hydrogen bonding between amide groups. In this article, we report the synthesis of polyamides by low temperature solution polycondensation of diamine with terephthaloyl and terephthalic acid chlorides such as terephthaloyldichloride

(TP), isophthaloyldichloride (IP), adipoylchloride (AP) and sebacoyldichloride (SC). Physical properties of polymers including characterization, inherent viscosity, solubility, and thermal properties are also reported.

2. Experimental

2.1 Materials and instruments

Acenaphthoquinone, 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole and other reagents and solvents were purchased from Fluka and used without purification. ¹HNMR and ¹³CNMR spectra were recorded on a 500 MHz Bruker Avance DRX instrument using DMSO-d₆ as solvent and tetramethyl silane as an internal standard. FTIR spectra were recorded using a Bruker Vector 22 spectrometer on KBr pellets. The CHN- 600 Leco analyzer was used for elemental analysis. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis were performed using Perkin-Elmer Pyris and Metler Toledo 822^o, respectively. Inherent viscosity ($\eta_{inh} = Lm_{rel}/C$) of polymers were determined for solution of 0.5 g/dl in NMP at 25 °C using an Ubbelohde viscometer. Total sulfur was measured using Tanaka Model RX-360 SH.

3. Preparation of Monomers

3.1 Acenaphthohydrazinomercaptotriazoldiamine (AHTD)

The 1,2-dihydro-acenaphthylene-1,2-dione (1.82 g, 10 mmol) was dissolved in 25 ml of ethanol and 1 ml of conc. HCl and then added to a suspension of 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole (2.92 g, 20 mmol) in 25 ml of ethanol and 5 ml water. The mixture was stirred for 10 h at reflux temperature. The orange solid was filtered off, washed with ethanol and water and dried in a vacuum

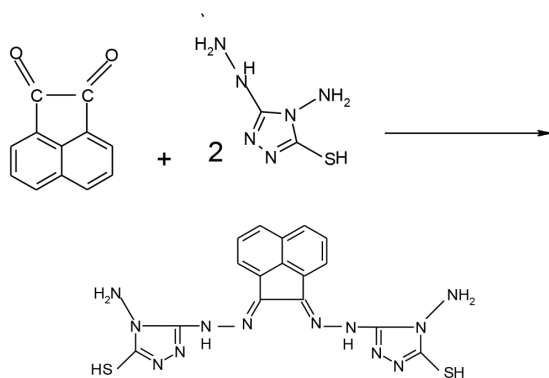
oven at 70 °C. A orange solid product was obtained in a 65% yield which starts to melt at 260 °C.

The chemical structure of diamine and its procedure is shown in Scheme 1.

4. Preparation of Polyamides

4.1 Polyacenaphthohydrazinomercaptotriazolerephthalate (PA1)

A typical procedure for the preparation of polyamides is given in Scheme 2. A 100 ml two-necked flask equipped with a dropping funnel and gas inlet tube was charged with a mixture of AHTD (0.656 g, 2 mmol), 30 ml dimethylformamide



Scheme 1. The procedure for the preparation of Diamine.

(DMF) and triethylamine (0.8 ml). 2 mmol Diacidchloride (DC) (such as terephthaloyl chloride, isophthaloyl chloride, adipoyl chloride and sebacyl chloride) dissolved in 20 ml DMF was added dropwise to the stirred solution at 0 °C under N₂. The mixture was subsequently stirred at ambient temperature for 5 h under N₂, and then it was poured into cold water. The orange solid product was separated by filtration and washed with NaHCO₃ solution. Then the solid product dried in vacuum oven at 70 °C. An orange solid product was obtained in a 86% yield which starts to melt at 280 °C.

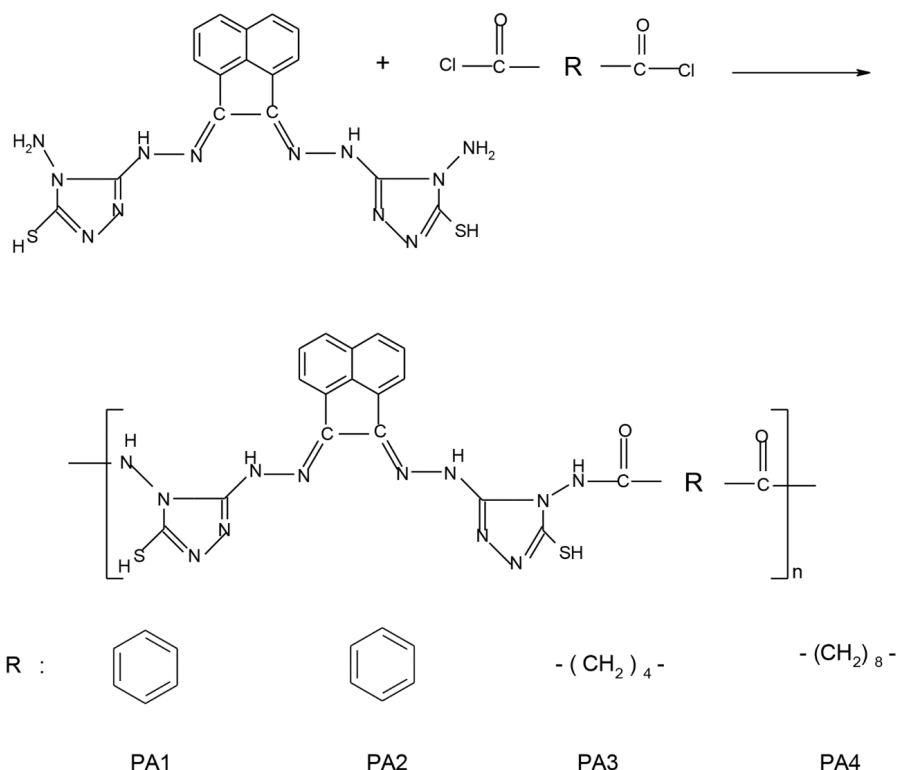
5. Result and Discussion

5.1 IR, ¹HNMR and Elemental Analysis of diamine(AHTD)

The monomer, AHTD, was prepared according to the procedures which are given in the Scheme 1. IR, ¹HNMR and the results of elemental analysis are given in Table 1.

These regions of the IR spectra in Figure 1 are of particular interest, the 3150-3446 cm⁻¹ (NH and NH₂ asymmetric and symmetric stretch), 2980 (C-H aromatic ring) 1638(C=N), 1590(C=C), 1585 cm⁻¹ (NH₂) and 908(C-S) and ¹HNMR, ¹³CNMR data in Figure 2 and Figure 3 with ¹HNMR (CDCl₃): δ(ppm) 12.7-12.9(NH), 7.78-8.3(CH aromatic), 5.7(NH₂) and 1.1(SH) and ¹³CNMR(400, DMSO, d₆, TMS) δ ppm: 118.87 (C_{Ar}), 125.24(C_{Ar}), 127.22 (C_{Ar}), 129.49 (C_{Ar}), 130.95 (C_{Ar}), 136.66 (C_{Ar}), 133.27(C=N) and 179.23(C-S)

The polyamides were synthesized by direct polycondensation of aromatic and aliphatic diacidchlorides (Scheme 2) with



Scheme 2. The typical procedure for the preparation of polyamides.

AHTD using triethylamine as catalyst. The reactions were carried out in DMF solution of the diacidchloride and AHTD in a nitrogen atmosphere and at room temperature. The polymerizations proceeded in homogeneous solution

and the yields of the polyamides were quantitative. The elemental analysis values of all the polyamides, Table 1, were generally in good agreement with the calculated values of proposed structures. As representative example,

Table 1. Spectra data, elemental analysis results and the yield of polyamides.

Substrate	IR (KBr, cm ⁻¹)	NMR (DMSO-d ₆ , δ, ppm)	Elemental analysis					
			Calc.			Found		
			C	H	N	C	H	N
AHTD	3150-3446 cm ⁻¹ (NH and NH ₂ asymmetric and symmetric stretch), 2980 (C-H aromatic ring), 1638(C=N), 1590 (C=C), 908(C-S)	12.7-12.9(NH), 7.78, 8.3(CH,Aromatic), 5.7(NH2), 1.1(SH)	43.84	3.19	38.35	44.12	3.25	37.92
PA1	3430(N-H), 3100 (C-H aromatic), 1790 (C=O), 1631 (C=N), 1527(C=C aromatic), 910(C-S)	12.7(NH), 7.8 - 8.8 (CH Aromatic), 1.1(SH)	50.70	2.82	29.57	51.02	2.98	28.98
PA2	3300(N-H), 3117 (N-H), 2965 (C-H aromatic), 1636 (C=O), 1560 (C=N), 1508(C=C aromatic), 910(C-S)	12.7(NH), 7.8 - 8.8 (CH Aromatic), 1.1(SH)	50.70	2.82	29.57	51.32	3.02	28.83
PA3	3210(N-H), 3000 (C-H aromatic), 2800(C-H aliphatic) 1638 (C=O), 1590 (C=N), 1476(C=C aromatic), 910(C-S)	12.8(NH), 7.1 - 8.4 (CH Aromatic), 1.9 - 2.1(CH ₂), 1.1(SH)	48.17	3.65	30.65	47.92	3.56	31.03
PA4	3430(N-H), 2900 (C-H aliphatic) 1636 (C=O), 1570(C=N), 1505(C=C aromatic), 910(C-S)	12.8(NH), 7.1 - 8.4 (CH Aromatic), 1.9 - 2.8(CH ₂), 1.1(SH)	51.65	4.64	27.81	51.89	4.35	28.12

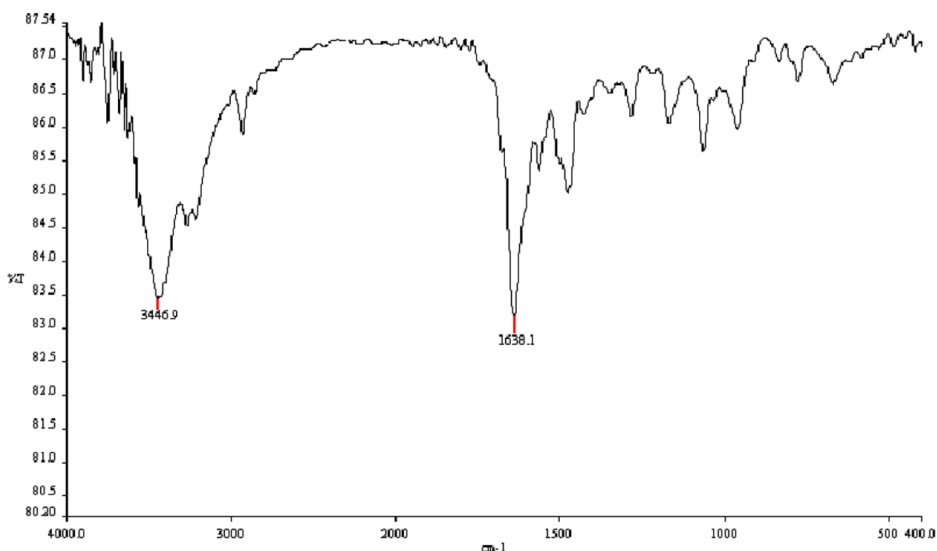


Figure 1. IR spectra of diamine.

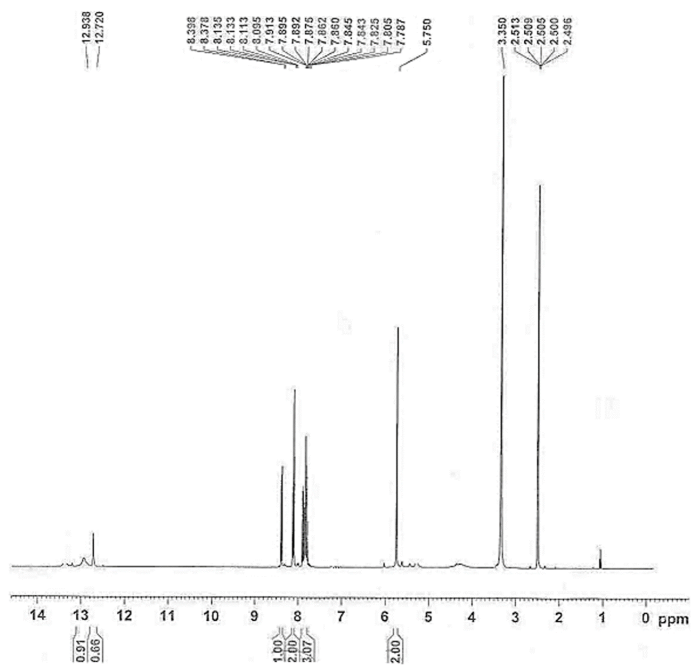


Figure 2. ¹H NMR spectra of diamine.

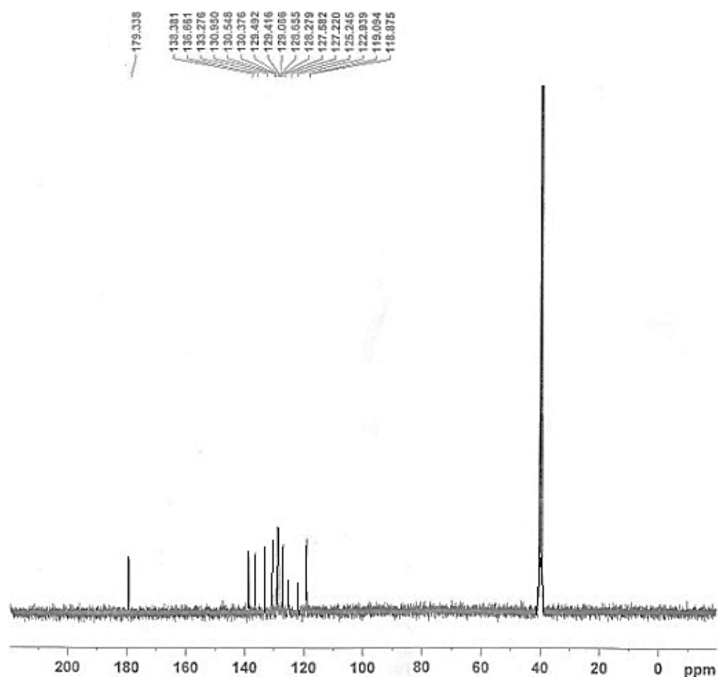


Figure 3. ¹³C NMR spectra of diamine.

the complete elemental analysis of PA1 was as follows: C, 50.70% (51.02% calculated); H, 2.82% (3.21%); N, 29.57% (28.58%). The polyamides were also characterized by IR and NMR spectrometers. The presence of amide bands at ca. 3430 cm^{-1} (N-H stretching), 1790 cm^{-1} (C=O stretching), 1631 cm^{-1} (N-H bending and C-N stretching) and 910 cm^{-1} (C-S), in the IR spectra in Figure 4 for PA1 and amidic proton

at ca. 12.5 ppm in the NMR spectra of PA1 in Figure 5 confirmed the amidic structure of polymers.

The limiting viscosity number $[\eta]$ of polyamides was determined for extracted and dried polymers in DMF, depending on the solubility of the polyamide. For the same or similar type of linear polymers the $[\eta]$ value is proportional to the molecular mass. The inherent viscosities of polyamides (PA1-PA4), obtained in DMF were in the

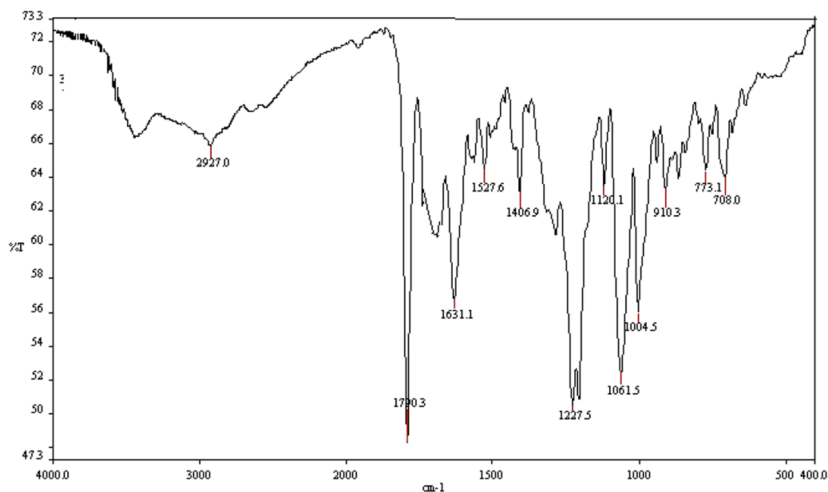


Figure 4. FTIR spectra of PA1.

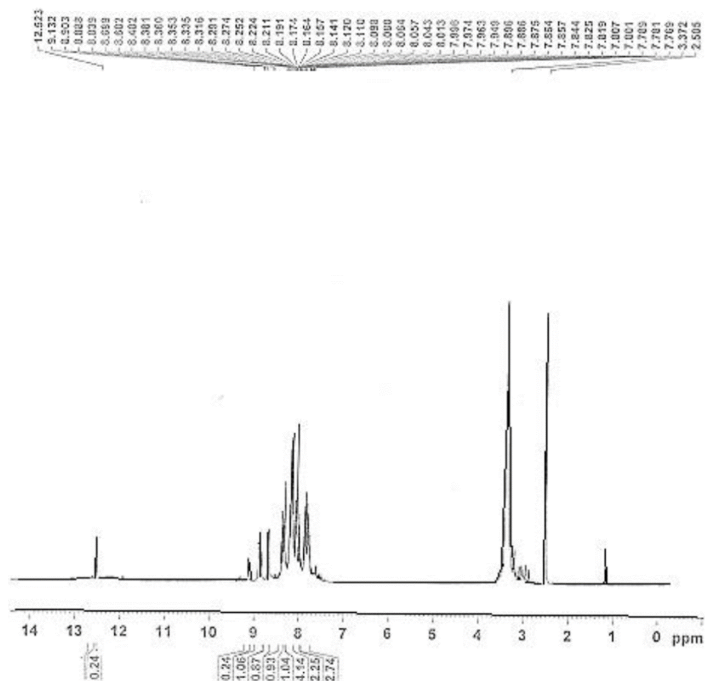


Figure 5. ^1H NMR spectra of PA1.

range of 0.38–0.47 dl/g that revealed reasonable molecular weights. The limiting viscosity number $[\eta]$ of aromatic polyamides is less than aliphatic polyamides.

One of the major objectives of this study was producing modified polyamides with improved solubility. The solubility of these polyamides was determined for the powdery samples in excess solvents and the results are listed in Table 2.

All the polyamides were readily soluble in common polar aprotic solvents without need for heating. Also, by heating they were soluble in a less efficient solvent such as THF. The good solubility behavior of most prepared polyamides can be explained through the enhancement of solubility induced by the side biphenyl groups of the diamine moiety. The thermal behavior of polyamides was studied by DSC and TGA. Thermal properties of the prepared polyamides were evaluated by means of DSC and TGA. Representative DSC

and TGA thermograms are shown in Figures 6, 7, 8 and 9 for two aromatic and aliphatic polyamides (PA2, PA3).

The DSC curves of Polyamides (PA2, PA3) were shown the glass transition temperature of these polymers at 65 °C and 55 °C and crystallinity temperature of both polymers at 251 °C and the melt temperature of polymers at 330 °C and 310 °C respectively. The DSC curves showed that the aliphatic polyamides have lower glass transition temperature such as aromatic polyamides and they have certainly melt temperature less than aromatic polyamides.

The thermal stability of polyamides was also evaluated by TGA. The temperatures of the 10%, 25% and 50% weight loss and the remained polyamides at 600 °C in nitrogen atmosphere were given in Table 3.

Table 2. Solubility of polyamides.

Polym. code	NMP	DMF	DMSO	TCE	THF	H ₂ SO ₄	HMPA	DMAC	Aceton	Ethanol	Methanol	CHCl ₃
AHTD	+	+	+	+	+	+	+	+	+	+	+	±
PA1	+	+	+	±	+	+	+	+	-	±	-	±
PA2	+	+	+	±	+	+	+	+	-	±	-	±
PA3	+	+	+	±	+	+	±	+	-	±	-	±
PA4	+	+	+	±	+	+	±	+	-	±	-	±

Soluble (+), partially soluble (±), insoluble (-) Solubility tested with 0.5 g of polymer in 100 ml of solvent. NMP=N-methylpyrrolidone, DMF=dimethylformamide, DMSO=dimethylsulfoxide, TCE=tetrachloroethane, Py=pyridine, THF=tetrahydrofuran, HMPA=hexamethylphosphoramide, DMAC=dimethylacetamide.

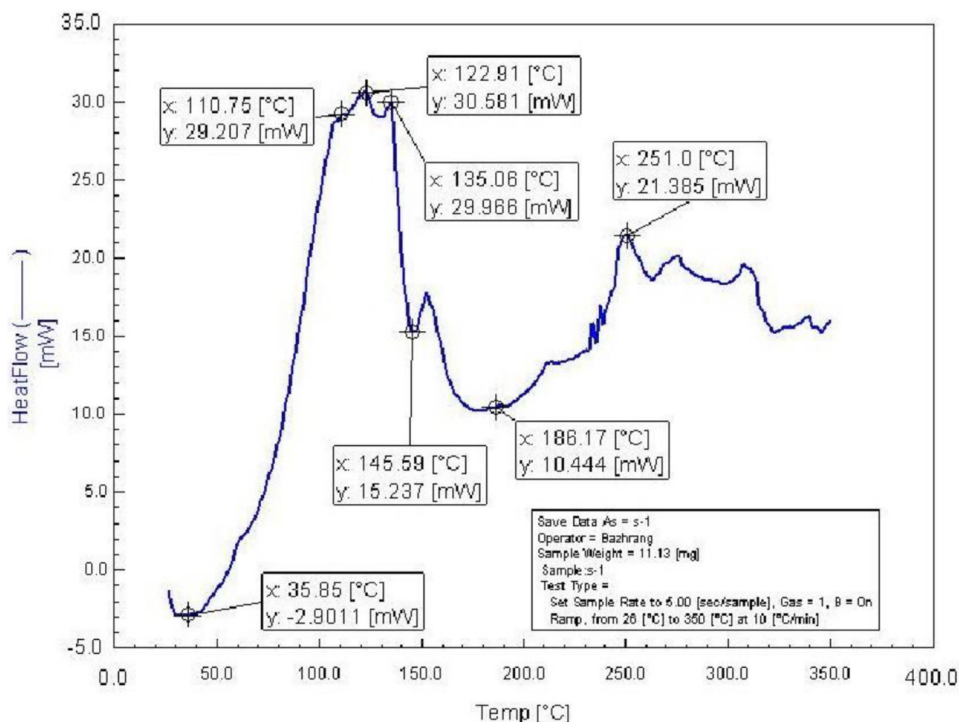


Figure 6. DSC of PA2.

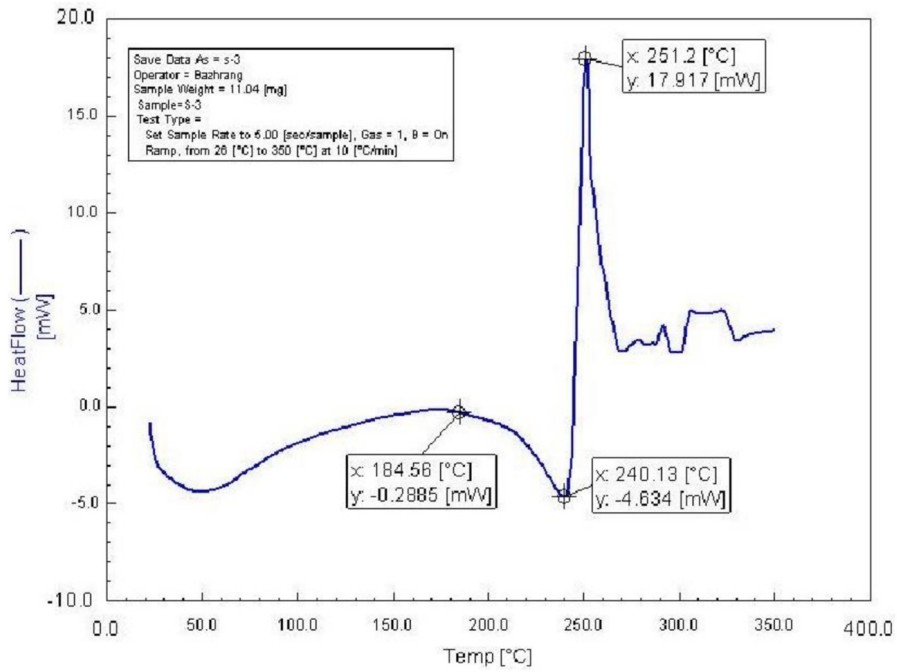


Figure 7 . DSC of PA3.

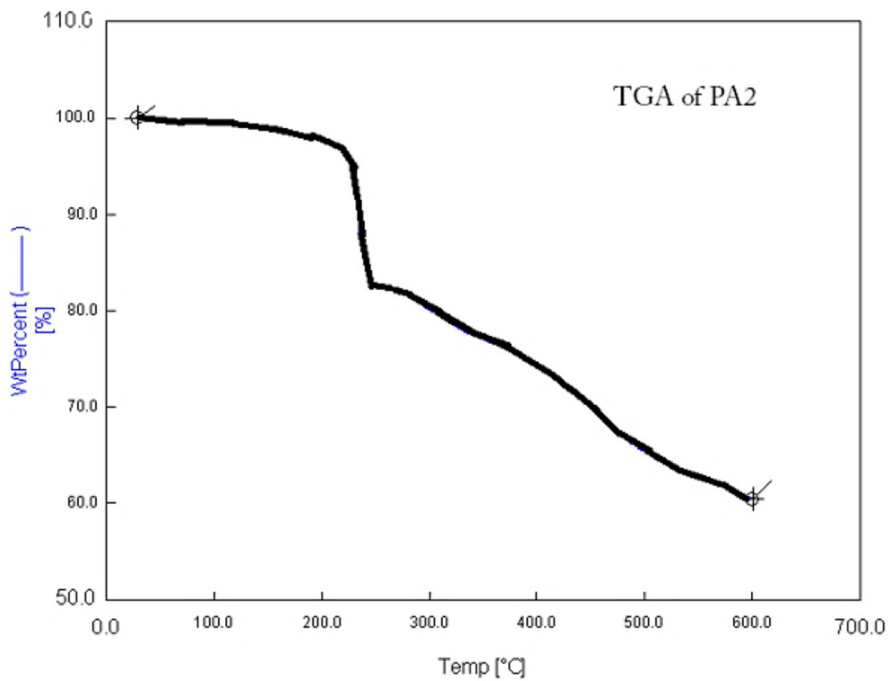


Figure 8 . TGA of PA2.

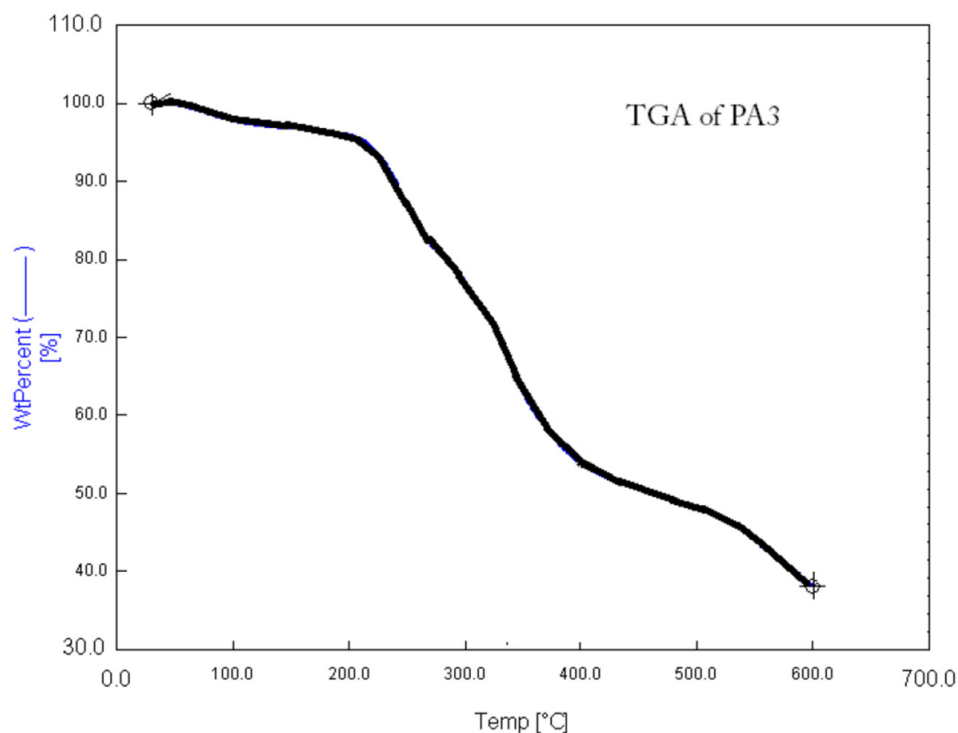


Figure 9. TGA of PA3.

Table 3. Thermal analysis, viscosity and yield of the polyamides.

Compound code	T_g	T_c	T_m	$T_{10}(^{\circ}\text{C})^a$	$T_{25}(^{\circ}\text{C})^b$	$T_{50}(^{\circ}\text{C})^c$	%Ch. Y. ^d	η_{inh} (dl/g) ^e
AHTD	-	-	260	-	-	-	-	0.04
PA1	90	251	320	230	320	420	42	0.38
PA2	65	251	330	230	400	-	60	0.42
PA3	55	251	310	220	310	450	38	0.45
PA4	50	240	310	180	290	340	16	0.47

T_g : Glasstransition Temperature. T_c : crystallinity Temperature. T_m : Melting temperature. ^a10% weight loss. ^b25% weight loss. ^c50% weight loss. ^dChar yield percent at 600 °C, obtained from TGA. ^eMeasured in DMF at 25 °C ($c=0.5$ g/dl).

All the polymers were stable up to 200 °C in nitrogen and show almost the same stability. We found that these polyamides did not show obvious weight losses until the temperature reached 200 °C in nitrogen, implying that no thermal decomposition occurred. However, as the temperature over 200 °C, the polymers showed a rapid thermal decomposition. The 10% weight loss of all polymers was in temperature range of 180-230 °C. The 25% weight loss of all polymers was in temperature range of 290-320 °C. The 50% weight loss of all polymers was in temperature range of 340-450 °C. The polyamides (PA1,PA2) remained 42-60% of the original weight at 600 °C in nitrogen and the polyamides (PA3,PA4) remained over 16-38% of the original weight at 600 °C in nitrogen. Two of the polyamides(aliphatic) exhibited a more

weight loss at the same temperature and they have a short char yield against aromatic polyamides.

6. Conclusion

A series of polyamides were prepared from the reaction of two aromatic and two aliphatic diacid chlorides with a diamine AHTD. The molar ratio of diacid chloride to the AHTD was 2:2 and the reaction was carried out at ambient temperature for 5 h under N_2 atmosphere. The polyamides were fully characterized and their thermal properties were studied. Two of the polyamides(aliphatic) exhibited a more weight loss at the same temperature and they have a short char yield against aromatic polyamides. The introduction of aromatic side groups in structure of the diamine resulted

in crystalline polyamides that the degree of crystallinity has a big influence on hardness, density, transparency and diffusion. The polyamides have very good solubility in aprotic solvents such as DMF and generally, the solubility of aromatic polyamides were better in selected solvents. Aliphatic polyester hopes of higher inherent viscosity and thus had a higher molecular weight. The glass temperature of the aliphatic polyamides was lower than aromatic polyamides but unlike crystalline temperature and melting temperature are close together and the differences were not significant.

7. References

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