

Synthesis of Some Polyamides from Bis(thiosemicarbazone)acenaphthenequinone

NAVABEH NAMI^{a*}, HOSSEIN MIGHANI^{b*},
NAJMEH KIA^a and HAMED SADATFARAJI^b

^aDepartment of Chemistry, Qaemshahr Branch, Islamic Azad University, Qaemshahr, Mazandaran Iran

^bDepartment of Chemistry, University of Golestan, Gorgan, Iran

Navabehnami@yahoo.com

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Abstract: Bis(thiosemicarbazone)acenaphthenequinone (LH₆) was synthesized in one step from acenaphthoquinone and thiosemicarbazone. The diamine (LH₆) was characterized by FT-IR, ¹H NMR and melting point. diamine was used to prepare novel polyamides. The low temperature solution polycondensation of ligand with aromatic ring. Diacid chlorides and high temperature polycondensation with dicarboxylic acid afforded ligand-containing polyamides with inherent viscosities of 0.31–0.38 dL/g in *N*-methylpyrrolidone at 25 °C. The polyamides were generally soluble in a wide range of solvents such as dimethylformamide(DMF), *N*-Methylpyrrolidone(NMP), dimethylsulfoxide (DMSO) and H₂SO₄. Thermal analysis showed that these polyamides were practically amorphous and exhibited 10% weight loss at and above 220 °C.

Keywords: Polyamides, Thermalstability, Bisthiosemicarbazone, Acenaphthoquinone, Diacide

Introduction

Polyamides, the most versatile class of engineering polymers, display a wide range of properties. Aliphatic polyamides find many industrial and textile applications due to their high mechanical strength and durability. Many studies on polyamides have been reported previously¹⁻⁶. Aromatic polyamides (aramids) are being used in industry because of their outstanding properties. However, poor solubility in common organic solvents and high melting temperatures are the limiting factors for the processing of these materials. A lot of attempts have been made to solubilize these polymers in order to prepare their composites using different techniques⁷⁻¹¹. Aliphatic–aromatic polyamides (glass clear nylons) offer a wide range of properties including transparency, thermal stability, good barrier and solvent resistant properties. These commercial polyamides have been reinforced with various ceramic phases¹²⁻¹⁵. There are numerous references to polyamides from aliphatic diamines and aromatic diacids and a far lesser number to polyamides from aromatic diamines and aliphatic diacids¹⁶⁻²⁴. Probably the reason that aliphatic–aromatic polyamides have been studied

in greater detail than the aromatic–aliphatic is that many of the former group can be made by melt and plasticized melt methods^{18,19,25} or by standard interfacial procedures^{21,23,26}. The aromatic–aliphatic polyamides, on the other hand are difficult to prepare by interfacial and solution methods^{16,27} and when prepared by melt methods, frequently are discolored and may have branched or network structures. In the other hand, polymers with a system of conjugated -C=C- and -C=N- bonds in their main chain have been drawing the attention of researchers because of their importance in many areas^{28–32}. Among these polymers, polyamides, which are characterized by the presence of HC=N linkages, are of considerable interest and are produced by the polycondensation of diamines with various dicarbonyl compounds. They have thermal stability similar to that of polyamides and have been used as solid stationary phases for gas chromatography³³. The high thermal stability of fully aromatic polyamides is due to the great number of aromatic rings and the extent of electronic conjugation over the entire molecule, which lead to polymers with high conducting properties. To lower the transition temperatures and to improve the solubility, several methods are used, such as copolymerization and the introduction of bulky alkyl, alkoxy, or aryl groups into the aromatic rings or into the polymer backbone^{32,34}. In this article, we report the synthesis of new polyamides with pendant bulky aryl groups containing by the low-temperature polycondensation reaction of diacid chlorides such as terephthaloyl dichloride, isophthaloyl dichloride, sebacoyl dichloride, adipoyl dichloride, and succinoyl dichloride with a new diamine, bis(thiosemicarbazone)acenaphthenequinone(LH₆). The physical properties of the polymers, including the characterization, inherent viscosity (η_{inh}), solubility and thermal properties, are also reported. We will also report other properties of these polyamides in a future publication.

Experimental

acenaphthoquinone, thiosemicarbazide and other reagents and solvents were purchased from Fluka and used without purification. ¹H NMR spectra were recorded on a 500 MHz Bruker Advance DRX instrument using DMSO-d₆ as solvent and tetramethylsilane as an internal standard. FT-IR 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°, respectively. Inherent viscosity ($\eta_{inh} = Lm\eta_{rel}/C$) 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.

Preparation of monomers

Bis(thiosemicarbazone)acenaphthenequinone (LH₆)

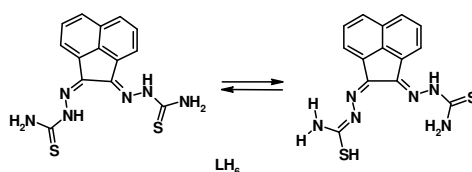
The thiosemicarbazide (3.64 g, 40.30 mmol) and acenaphthoquinone (3.64 g, 20.20 mmol) were added in 40 mL of ethanol, 40 mL of 2 N HCl and 1 mL of conc. HCl. The mixture was stirred for 10 h under reflux condition. After cooling the reaction, the yellow solid was filtered off, washed with ethanol and dried in a vacuum oven at 70 °C for 2 h. A yellow solid product was obtained in a 70% yield which starts to melt and decompose at 250 °C.

IR (KBr) (ν_{max} cm⁻¹): 3440 (NH), 3250(NH₂), 3050 (C-H aromatic ring), 1598(CN), 1479 (C=C_{Ar}), 823 (CS). ¹H NMR (400, DMSO, d₆, TMS) δ ppm: 4.2(1H, S, NH), 5.28(1H, S, SH), 5.75(2H, S, NH₂), 7.8-7.9 (3H, m, CH_{Ar}), 8.0 (2H, t, CH_{Ar}), 8.38 (1H, d, CH_{Ar}), 12.93 (1H, S, NH), 13.38 (1H, S, NH). ¹³C NMR (400, DMSO, d₆, TMS) δ ppm: 118.13(C_{Ar}), 122.91(C_{Ar}), 127.28(C_{Ar}), 129.08(C_{Ar}), 133.39(C_{Ar}), 140.18(C_{Ar}), 55.07(C=N), 165.94 (C=S). Anal. Calcd. For [C₁₄H₁₂N₆S₂]: C, 51.22; H, 3.65; N, 25.6. Found: C, 50.87; H, 3.87; N, 26.23.

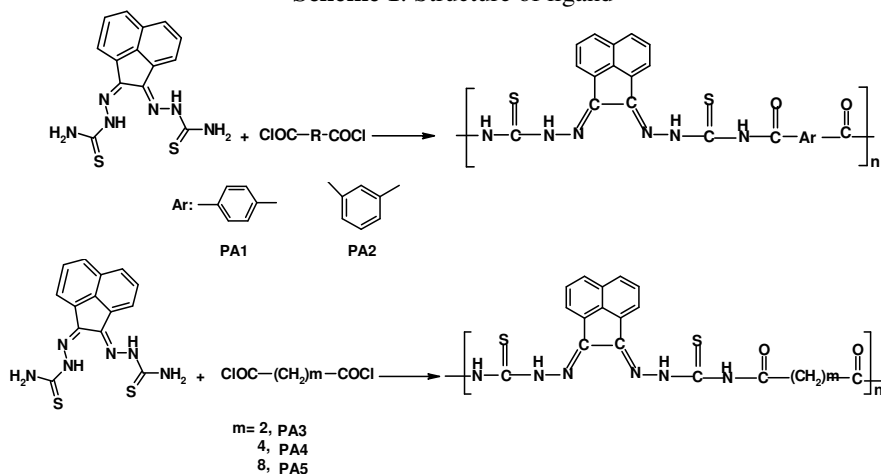
Preparation of polyamides

General procedure

A typical procedure for the preparation of polyamides is given in Scheme 2. A two-necked flask equipped with a dropping funnel and gas inlet tube was charged with a mixture of LH₆ (0.712 g, 2 mmol), 20 mL dimethylformamide (DMF) and triethylamine (0.8 mL). Diacid chloride (DC) (2 mmol) dissolved in 20 mL DMF was added drop wise to the stirred solution at 0 °C under N₂. The mixture was subsequently stirred at ambient temperature for 3 h under N₂ and then it was poured into cold water. The yellow solid product was separated by filtration and washed with NaHCO₃ solution. Then the red solid product dried in vacuum oven at 70 °C. A purified sample was obtained by using a Soxhlet extraction system from methanol for 24 h.



Scheme 1. Structure of ligand



Scheme 2. The typical procedure for the preparation of polyamides

Poly [acenaphthenequinone bis(thiosemicarbazone)terephthalate] (PA1)

Yield 92%, mp 262 °C, IR (KBr) (ν_{\max} cm⁻¹): 3423 (N-H), 3300 (N-H), 3000 (C-H aromatic), 1684 (C=O), 1630 (C=N), 1596 (C=C_{Ar}), ¹H NMR (400, DMSO, d₆, TMS) δ ppm : 7.84, 7.89 (2H, m, CH_{Ar}), 8, 8.11 (2H, m, CH_{Ar}), 8.1, 8.29 (4H, m, CH_{Ar}), 8.31, 8.38 (1H, m, CH_{Ar}), 8.4 (1H, CH_{Ar}), 8.69 (1H, S, NH), 8.9 (1H, S, NH), 12.26 (1H, S, NH), 12.91 (1H, S, NH). Anal. Cald. For [C₂₂H₁₄N₆O₂]: C, 57.64; H, 3.05; N, 18.34. Found: C, 56.89; H, 3.25; N, 18.67.

Poly [acenaphthenequinone bis(thiosemicarbazone)isophthalate] (PA2)

Yield 90%, mp 265 °C, IR (KBr) (ν_{\max} cm⁻¹): 3246(N-H), 3153(N-H), 1640(C=O), 1593 (C=N), 1476(C=C aromatic). Anal. Cald. For [C₂₂H₁₄N₆O₂]: C, 57.64; H, 3.05; N, 18.34. Found: C, 56.89; H, 3.25; N, 18.67.

Poly [acenaphthenequinone bis(thiosemicarbazone)succinate] (PA3)

Yield 91%, mp 255 °C, IR (KBr) (ν_{\max} cm^{-1}): 3253(N-H), 3175 (N-H), 2900 (C-H_{Aliphatic}), 1717 (C=O), 1595 (C=N), 1478(C=C_{Ar}), ¹H NMR (400, DMSO, d₆, TMS) δ ppm :3.06, 3.09 (2H, t, CH₂), 3.13, 3.14 (2H, t, CH₂), 7.91, 7.99 (3H, m, CH_{Ar}), 8, 8.11(1H, m, CH_{Ar}), 8.15, 816 (1H, d, CH_{Ar}), 10.4, 12.4 (4H, S, NH). Anal. Calcd. for [C₁₈H₁₄N₆O₂]: C, 52.68; H, 3.41; N, 20.48. Found: C, 53.23; H, 3.25; N, 20.27.

Poly [acenaphthenequinone bis(thiosemicarbazone)adipoate] (PA4)

Yield 94%, mp 252 °C, IR (KBr) (ν_{\max} cm^{-1}): 3257(N-H), 3100 (N-H), 2800 (C-H_{Aliphatic}), 1685 (C=O), 1601 (C=N), 1489 (C=C_{Ar}). Anal. Calcd. for [C₂₀H₁₈N₆O₂]: C, 54.79; H, 4.11; N, 19.17. Found: C, 55.27; H, 3.87; N, 19.93.

Poly [acenaphthenequinone bis(thiosemicarbazone)sebacoilate] (PA5)

Yield 85%, mp 250 °C, IR (KBr) (ν_{\max} cm^{-1}): 3430(N-H), 3248 (N-H), 2926 (C-H aliphatic), 1685 (C=O), 1599 (C=N), 1488(C=C_{Ar}), ¹H NMR (400, DMSO, d₆, TMS) δ ppm : 1.65, 1.68(3H, t, CH₂), 2.16, 2.19 (2H, t, CH₂), 2.56 (1H, S, CH₂), 2.81 (2H, CH₂), 7.74, 7.77 (3H, m, CH_{Ar}), 7.85, 7.87(1H, d, CH_{Ar}), 7.99, 8.01(2H, t, CH_{Ar}), 8.59(1H, S, NH), 11.23(1H, S, NH), 12.51 (1H, S, NH). Anal. Calcd. for [C₂₀H₂₆N₆O₂]: C, 58.29; H, 5.26; N, 17. Found: C, 57.89; H, 5.62; N, 17.41.

Results and Discussion

The monomer, LH₆, was prepared according to the procedures given in the literature. The chemical structure of LH₆ is shown in Scheme 1. IR, ¹H NMR and elemental analysis data for the LH₆ of the present study are in good agreement with the structure. The IR spectra of this compound showed the NH and NH₂ asymmetric and symmetric stretching in 3250-3440 cm^{-1} , C=N in 1598 cm^{-1} and C=C in 1479 cm^{-1} . ¹H NMR showed NH₂ protons in 5.75 ppm and three exchangeable protons of NH in 4.2, 12.93 and 13.38 ppm, one SH proton in 5.28 ppm.

The polyamides (PA1- PA5) were synthesized by direct polycondensation of aromatic and aliphatic diacid chlorides (Scheme 2) with LH₆ using triethylamine as catalyst. The reactions were carried out in dimethyl formamide solution of the diacid chloride and LH₆ 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 were generally in good agreement with the calculated values of proposed structures. As representative example, the complete elemental analysis of PA1 was as follows: C, 57.89% (57.64% calculated); H, 3.25% (3.05%); N, 18.67% (18.34%).

The polyamides were also characterized by IR and NMR spectrometers. The IR Spectra of PA1 showed amide bands at ca. 3423 cm^{-1} (N-H stretching), 1684 cm^{-1} (C=O stretching) and ca. 1630 cm^{-1} (C=N stretching).

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 *N*-methylpyrrolidone were in the range of 0.25–0.34 dL/g that revealed reasonable molecular weights (Table 1).

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 phenylene groups of the diacid chlorides moiety.

Table 1. Thermal analysis, viscosity and yield of the polyamides

Compd code	T _g	T _{10%} , °C ^a	T _{50%} , °C ^b	%Ch. Y. ^c	η _{inh} dL/g ^d	Yield, %
LH ₆	-	-	--	--	0.04	70
PA1	92	250	430	38	0.32	92
PA2	-	-	-	-	0.31	91
PA3	120	240	560	42.5	0.34	95
PA4	-	-	-	-	0.25	94
PA5	-	240	430	42.5		

^a10% weight loss, ^b50% weight loss, ^cChar yield percent at 600 °C, obtained from TGA, ^dMeasured in N-methylpyrrolidone at 25 °C (c=0.5 g/dL)

Table 2. Solubility of polyamides

Polym. Code	NMP	DMF	DMSO	TCE	THF	H ₂ SO ₄	HMPA	DMAC	Aceton	Ethanol	CHCl ₃
LH ₆	+	+	+	±	+	+	+	+	-	±	±
PA1	+	+	+	±	+	+	+	+	-	±	±
PA2	+	+	+	±	+	+	+	+	-	±	±
PA3	+	+	+	±	+	+	+	+	-	±	±
PA4	+	+	+	±	+	+	+	+	-	±	±
PA5	+	+	+	±	+	+	+	+	-	±	±

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=hexamethylenphosphoramidate, DMAC=dimethylacetamide

Thermal properties of the prepared polyamides were evaluated by means of DSC and TGA. Representative DSC thermograms of PA1, PA3 and PA5 are shown in Figures 1-3. The DSC scan up to 300 °C of PA1 and PA3 showed strong exothermic peaks at 251 °C with glass transition of these polymers at 186 °C and 240 °C, respectively.

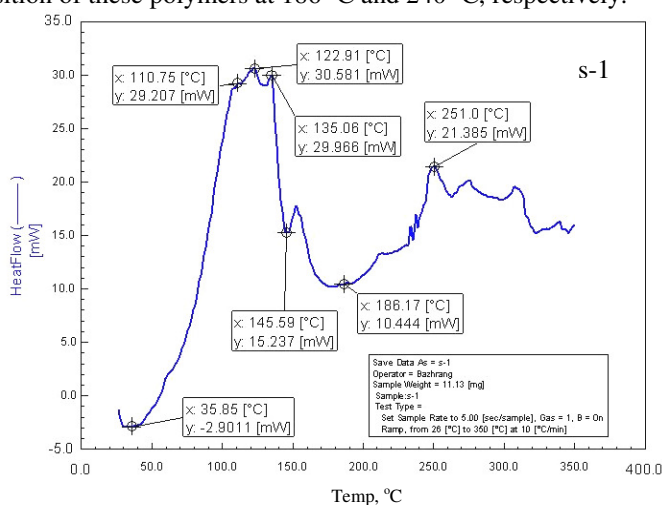


Figure 1. DSC of PA1

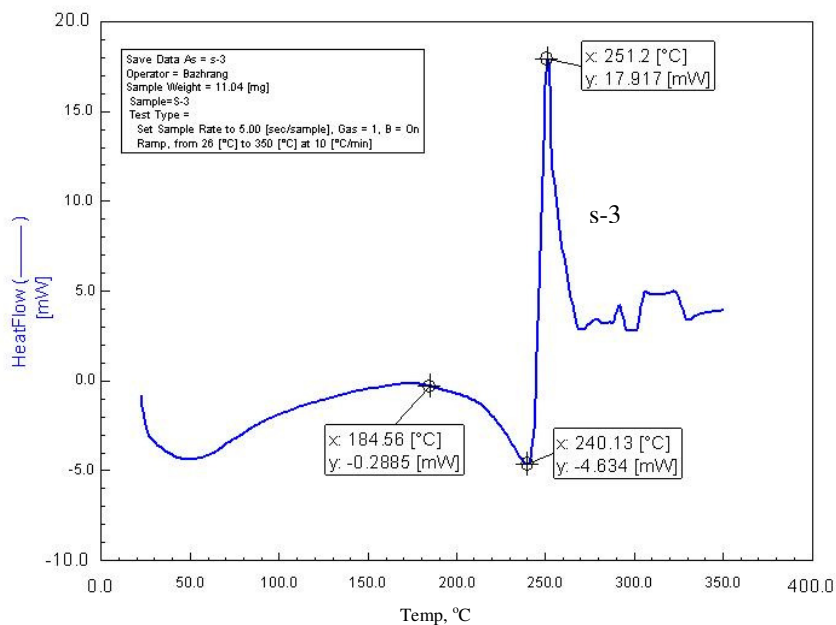


Figure 2. DSC of PA3

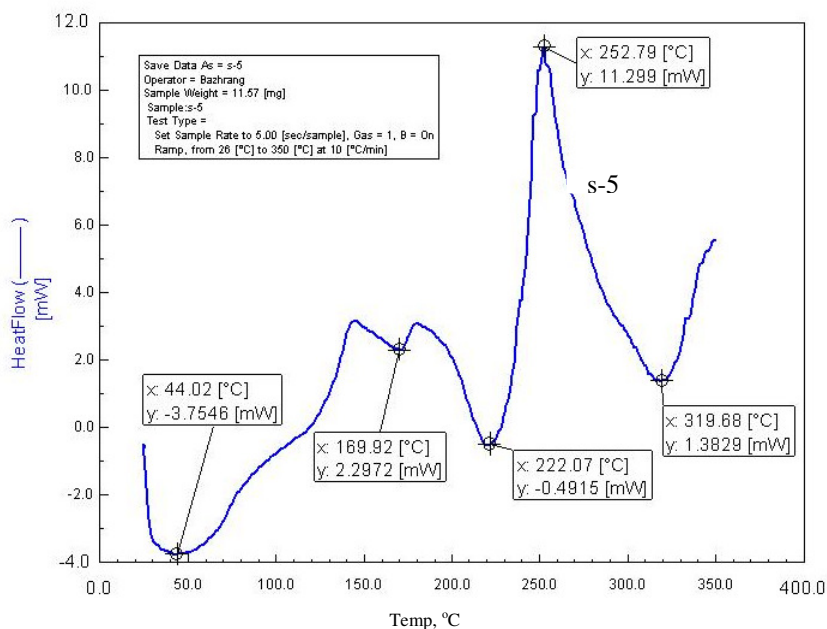


Figure 3. DSC of PA5

The thermal stability of polyamides was also evaluated by TGA. The temperatures of the 10% and 50% weight loss and the remained polyamides at 600 °C in nitrogen atmosphere were given in Table 1.

The representative TGA curves are shown in Figures 4-6. 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 50% weight losses of PA1 and PA5 were in temperature range of 430 °C. It was 560 °C in PA3. The polyamides (PA3, PA5) remained 42.5% of the original weight at 600 °C in nitrogen; the polyamide (PA1) remained 38% of the original weight at 600 °C in nitrogen.

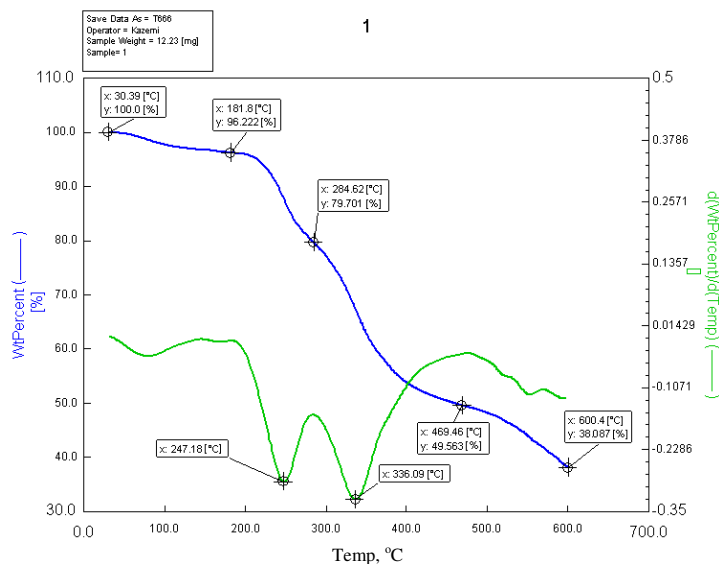


Figure 4. TGA of PA1

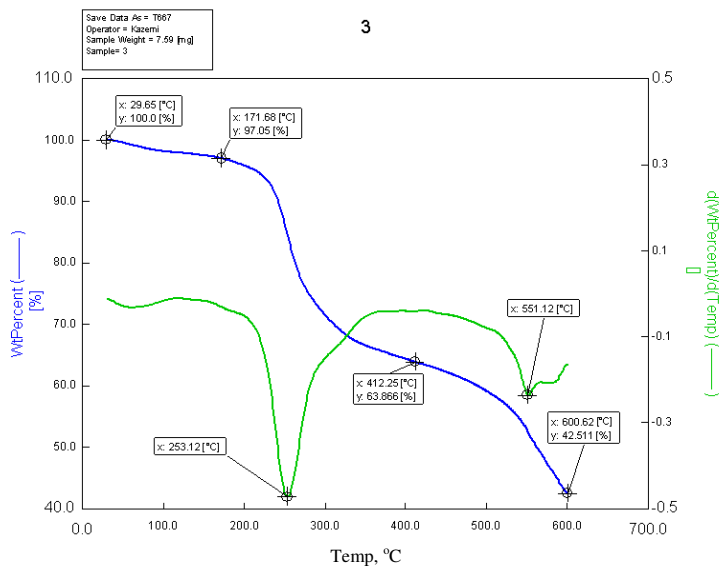


Figure 5. TGA of PA3

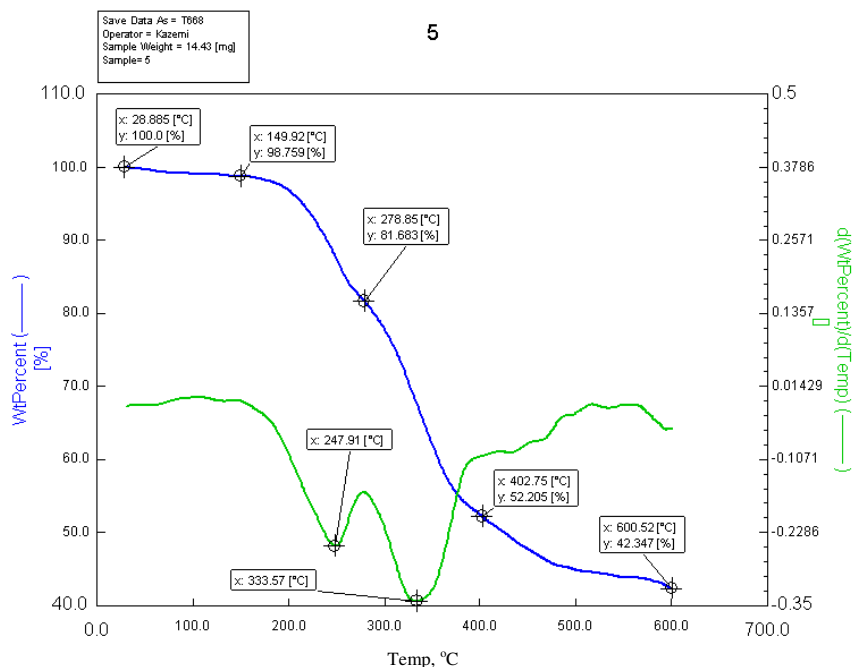


Figure 6. TGA of PA5

Conclusion

A series of polyamides were prepared from the reaction of diacid chlorides with a diamine LH₆. The molar ratio of diacid chloride to the LH₆ was 2:2 and the reaction was carried out at ambient temperature for 3 h under N₂ atmosphere. The polyamides were fully characterized and their thermal properties were studied. The introduction of phenyl side groups in structure of the diamine resulted in amorphous polyamides with very good solubility in aprotic solvents such as DMF.

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