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Novel organosoluble polyamides with phthalimide pendant group: Synthesis, physical and thermal characterization

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ABSTRACT

A diamine, 4-(4-phthalimidophenyl)-1,2,4-triazolidyne-3,5-diamine (UD) as urazolediamine was synthesized in 8 steps from 4-nitrobenzoic acid. The diamine was characterized using FTIR, ^{1}HNMR and melting point. Then it was used to prepare novel polyamides. Two novel phthalimide-containing aromatic–aliphatic polyamides, polyurazolterephtaloyl (PUT) and polyurazolsebacoyl (PUS), were prepared from the new diamine. The low temperature solution polycondensation of diamine with two aromatic and aliphatic diacid chlorides afforded diamine-containing polyamides with inherent viscosities of 0.32 and 0.36 dl/g in H_2SO_4 at 25 °C. Polyamides were generally soluble in a wide variety of different solvents such as dimethyformamide (DMF), N-Methylpyrolidone (NMP), tetrachloroethane (TCE), dimthylsulfoxide (DMSO) and H_2SO_4. Thermal analysis showed that these polyamides were practically amorphous and exhibited 10% weight loss at about 250 °C. The glass transition temperatures (T_g) of the polymers were in the range of 144–183 °C. The temperatures at 10% weight loss ($T_{10\%}$) from their thermogravimetric analysis curves were found to be in the range of 251–275 °C in nitrogen atmosphere.

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KEYWORDS

Urazolediamine;
Diacid chlorides;
Phthalimide;
Polyamides;
Thermalstability.

INTRODUCTION

Phthalimide-containing compounds have attracted attention of scientists in different fields[1-8]. In recent years, the need for novel polyamides which have aromatic groups with improved specific properties such as high thermal stability and good mechanical properties, has strongly affected the production strategy of composite materials[9-14]. Introduction of bulky alkyl and aryl substituents reduce the hydrogen bonding at the amide linkage, flexible linkage[15,16], asymmetric/symmetric bulky units in the aromatic rings, pendent phenyl group into the polyamide backbone[17,18], and etc. Aromatic and aliphatic polyamides are well known as high performance engineering thermoplastics and have been widely used in various industries because of their good thermal stability, chemical resistance, and mechanical properties[19]. Thermally stable polymers have attracted extensive interests due to 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[20]. However, they have encountered difficulties in processing due to limited solubility in organic solvents and high glass transition or melting temperatures. These can be as a result of chain stiffness and intermolecular hydrogen bonding between amide groups[21].

In this article, we report the synthesis of polyamides containing phthalimide group by low temperature solution polycondensation of diacid chlorides such as terephthaloyldichloride (TPDC) and sebacoyldichloride (SCDC) with diamine 4-(4-phthalimidophenyl)-1,2,4-triazolidyne-3,5-diamine as UD. Physical properties of polymers including inherent viscosity and solubility, thermal properties and elemental analysis are also reported. The objective of this paper is to achieve thermally stable polymers which benefits advantages of many physical properties compared to conventional synthesized thermally stable polymers.

EXPERIMENTAL

Materials and instruments

4-nitrobenzoic acid, thionylchloride and other reagents and solvents were purchased from Fluka and used without purification. ^{1}HNMR spectra were recorded on a 500 MHz Bruker Advance DRX instrument using DMSO-d_6 as solvent and tetramehyl silane as an internal standard. FTIR spectra were recorded using a Bruker Vector 22 specterometer on KBr pellets. The CHN- 600 Leco analyzer was used for elemental analysis. Thermal gravimetric analysis (TGA) and differential scanning alorimeter (DSC) analysis were performed using Perkin-Elmer Pyris and Metler Tolledo 822^e, respectively. Inherent viscosity ($\eta_{inh}=Ln\eta_{rel}/C$) of polymers were determined for solution of 0.5 g/dl in NMP at 25 °C using an ubbelohde viscometer.

Preparation of monomers

4-Nitrobenzoylchloride[22]

A 100 ml flask was charged with a mixture of 4-nitrobenzoic acid (5.00 g, 29.9 mmol), 5 ml thionyl chloride and 20 ml ethylacetate. Subsequently the mixture was stirred at reflux temperature for 2 hours to obtain a transparent solution. Next, the additional content of thionyl chloride and solvent was extracted out of solution by using distillation and was poured into cold water. The yellow powder produced was separated by filtration. Then the product dried in vacuum oven at 50 ^{o}C. A purified sample was obtained by recrystallization from carbontetrachloride and obtained in a 95% yield (5.43 g.) with the melting point of 71-72 ^{o}C.

IR (KBr): 3100 (m), 1950(m), 1755(s), 1600(s), 1520(s), 1395(s), 1345(s), 1310(s), 1190(s), 1105(s), 1005(m), 890(s), 865(s),830 (s), 755(m), 690(s), 630(s), 550(s) cm^{-1}.

4-Nitrobenzoylazide[22]

A 100 ml flask was charged with 4-nitrobenzoylchloride (5.43 g, 29.2 mmol) and 10 ml acetone. The mixture was subsequently stirred at 5 ^{o}C temperature and then added dropwise a solution with sodiumazide (1.96 g, 30.1 mmol) in 7 ml water for 30 minutes. The solution was stirred for 1 hour and the white precipitate was filtered and dried at air. A purified sample was obtained in a 90% yield (4.95 g) with the melting point of 73-75 ^{o}C.

IR (KBr): 3100 (m), 2330 (w), 2190 (s), 2110 (s), 1960 (w), 1820 (w), 1690 (s), 1600 (s), 1535 (s), 1410 (m), 1350 (s), 1320 (m), 1330 (s), 1280 (s), 1105 (s), 990 (s), 870 (m), 840 (s), 705 (s) cm^{-1}.

1-Ethoxycarbonyl-4-(4-nitrophenyl) semicarbazide[22]

A 250 ml flask was charged with 4-nitrobenzoylazide (4.00 g, 21 mmol) and 75 ml dried toluene. The mixture was subsequently stirred under N_2 at reflux temperature for 6 hours. The solution was cooled and filtered. The solution put In Balloon that cooled and stirred. The solution was cooled at 5 ^{o}C and then charged dropwise with a mixture of ethylhydrazin carboxilate (ethyl carbazate)(2.70 g, 21 mmol) and 40 ml dried toluene in 15 minutes. The solution was stirred for 30 minutes in ice bed and for 1 hour at room temperature. The solution refluxed for 3 hours and cooled and then filtered and dried at 70 ^{o}C for one day. A purified sample was obtained in a 93% yield (4.8 g) with the melting point of 219-220 ^{o}C.

IR (KBr): 3300 (s, sh), 3150 (m), 3100 (m), 3000 (w), 1700 (s), 1670 (s), 1625 (s), 1580 (s), 1510 (s, sh), 1410 (m), 1370 (m), 1340 (s), 1300 (s), 1240 (s), 1175 (m),1110 (m), 1050 (w), 1010 (m), 890 (w), 850 (m), 830 (m), 750 (m), 700 (m), 630 (m) cm^{-1}.

1-Ethoxycarbonyl-4-(4-aminophenyl) semicarbazide[22]

A 250 ml flask was charged with 1-ethoxycarbonyl-4-(4-nitrophenyl)semicarbazide (3.04 g, 11.3 mmol), $SnCl_2.2H_2O$ (9.73 g, 4.3 mmol) and 15 ml ethanol. The mixture was subsequently stirred under N_2 at reflux temperature for 4.5 hours to obtain a transparent solution. The solution was cooled with ice bed and water and stirred for 15 minutes. The PH of solution was raised to 10 with a solution of sodium hydroxide 30%. The mixture was put in 30 ml ethylacetate. Afterward the white powder was filtered and dried at 70 °C for one day. A purified sample was obtained in a 82% yield (2.2 g) with the m.p. > 340 °C.

IR (KBr): 3350 (m), 3250 (m), 3130 (w), 2980 (m), 2900 (m), 1720 (s), 1650 (s), 1600 (m), 1560 (s), 1505 (s), 1305 (m), 1230 (s), 1170 (w), 1090 (w), 1030 (m), 930 (w), 875 (m), 855 (m), 825 (m), 785 (w), 770 (w), 750 (w), 700 (w), 665 (m) cm^{-1}.

4-(4-aminophenyl)-1,2,4-triazolidyne-3.5-dione (Urazole)[22]

A 100 ml round flask was charged with pure sodium (0.23 g, 10 mmol) dissolved in 14 ml absolute ethanol. The solution was under N_2 and added 1-ethoxycarbonyl-4-(4-aminophenyl)semicarbazide (2 g, 8.4 mmol). The mixture was subsequently stirred under N_2 at reflux temperature for 4.5 hours and cooled with ice bed. The solution was neutralized with HCl 30%. The white product was filtered (1.38 g., 86%) and recrystallized with hot water and dried. A purified sample was obtained in a 86% yield (1.38 g) with the melting point 270 - 273 °C.

IR (KBr): 3430 (m), 3350 (m), 3000-3200 (s, br), 2800 (w), 1770 (m), 1720-1640 (s, br), 1615 (s), 1515 (s), 1460 (s), 1280 (m), 1220 (m), 1170 (m), 1110 (m), 1030 (w), 925 (w), 820 (m), 780 (s), 760 (s), 660-680 (m, br) cm^{-1}.

4-(4-phthalimidophenyl)-1,2,4-triazolidyne-3,5-dione[22]

A 25 ml round flask was charged with 4-(4-aminophenyl)urazole (0.2 g, 1.04 mmol) and a mixture of solvents, acetic acid / pyridine (3/2), and anhydride phthalic (0.15 g, 1.04 mmol). The mixture was subsequently stirred at room temperature for 2 days till the amic acid was produced as a white precipitate. The solution was stirred at reflux temperature for 8 hours and then filtered and the white precipitate washed with ethanol and filtered and dried. The white purified sample (1.38 g) was obtained in a 76% yield (0.46 g) with the melting point of 363 - 365 °C.

IR (KBr): 3200 (w), 3100 (m), 2800 (w), 1760 (w), 1700 (s, br), 1520 (s), 1460 (s), 1380(s), 1290 (m), 1220 (m, sh), 1160 (w), 1120(s),1080 (s), 880 (s), 840 (s), 790 (m, sh), 770 (m), 720 (s), 680 (s), 660(m), 530 (s) cm^{-1}.

^{1}H-NMR (DMSO-d6, TMS): δ 10.57 (s, 2H, br), 8.00 (m, 2H, J=10 Hz), 7.93 (m, 2H, J=10 Hz), 7.63 (d, 2H, J=10 Hz), 7.58 (d, 2H, J=10 Hz).

4-(4-phthalimidophenyl)-1,2,4-triazolidyne-3,5-diamine

A 10 ml round flask was charged with *4-(4-phthalimidophenyl)-1,2,4-triazolidyne-3,5dione* (2.5 g, 7.7737 mmol), and hexamethylenediisocyanate (0.2615 g, 1.555 mmol) and 3 ml dimethlformamide. The mixture was subsequently stirred at room temperature for 2 days and the precipitate was obtained in a Solution with low concentration of water/ acid and filtered and dried. The purified sample was obtained in a 85% yield with the melting point 124 - 125 °C.

IR (KBr): 3480 (w NH), 3150-3100 (s, br NH2), 1720 (s, br, C=O), 1577(w), 1520 (s), 1500(m, br),1423 (s), 1250 (m), 1145 (m), 764(m), 737(m), 715 – 686 (s, sh), 639 (w), 432 (m) cm^{-1}.

Preparation of polyamides

Polyurazoleterephthalte (PUT)

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 4-(4-phthalimidophenyl)-1,2,4-triazolidyne-3,5-diamine (1.012 g, 2 mmol), 20 ml dimethylformamide (DMF) and triethylamine (0.8ml). Terephthaloyledichloride (TPDC) (0.406gr, 2 mmol) dissolved in 20 ml DMF was added dropwise to the stirred solution at 0 ^{o}C under N_2. The mixture was subsequently stirred at ambient temperature for 5 hours under N_2 and then poured into cold water. The yellow solid product was separated by filtration and washed with $NaHCO_3$ solution. Then the red solid product dried in vacuum oven at 70 ^{o}C. A purified sample was obtained by soxhlet from methanol for 24hours.

IR(cm^{-1}) 3247(NH), 1655(C=O), 1608(C=N), and ^{1}HNMR (DMSO-d$_6$): δ(ppm), 10.45-11.52(4H, NH), 7.2-7.9(12H, phenyl), 1.1-1.3(24H, aliphatic).

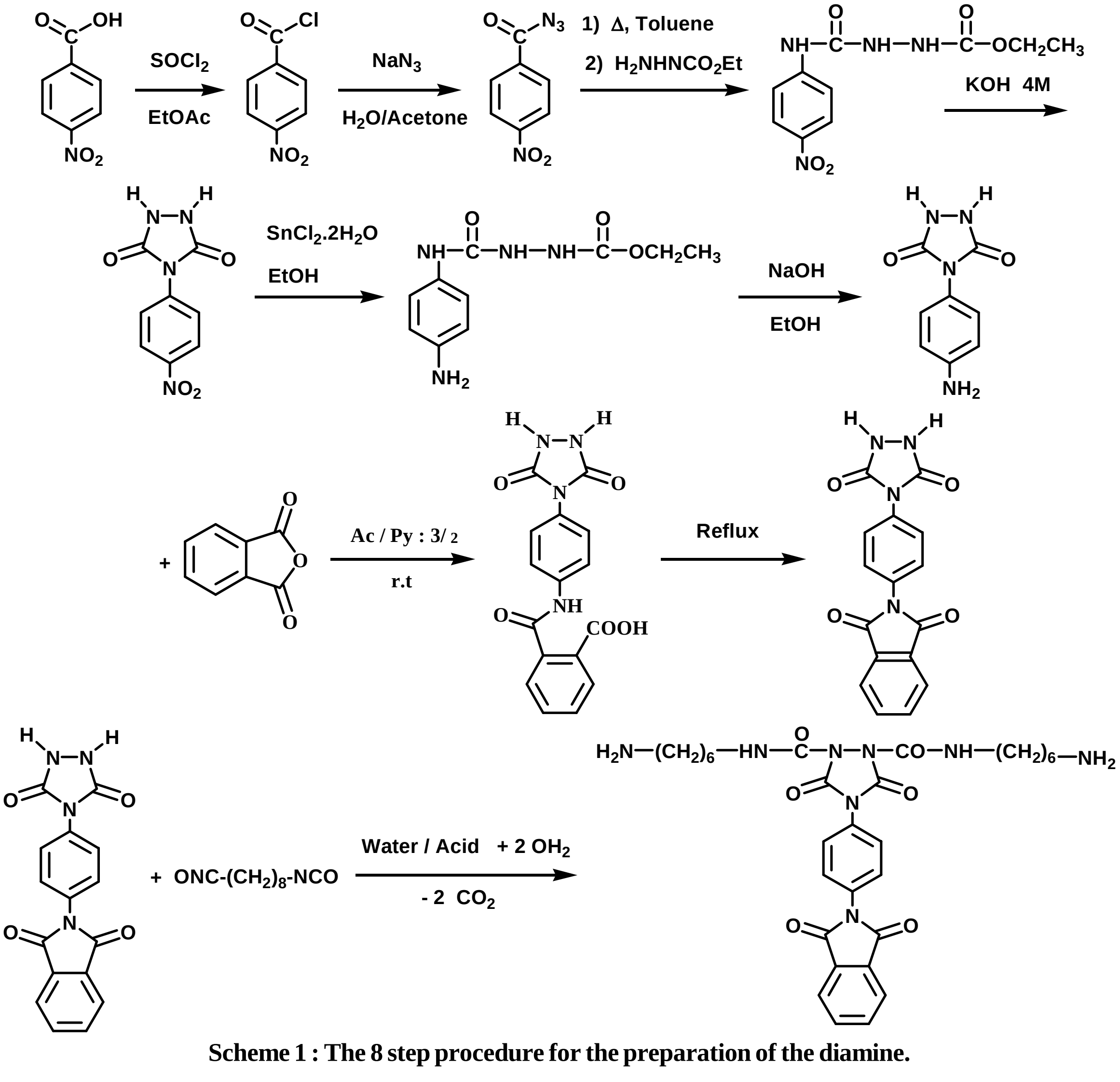
The polyurazolesebasate (PUS)

This was also prepared by the same mentioned procedure using different acid chlorides such as sebacoyledichloride.

IR(cm^{-1}) 3242(NH), 1686(C=O), 1608(C=N), and ^{1}HNMR (DMSO-d$_6$): δ(ppm), 11.95(2H, NH), 10.45(2H, NH), 7.3-7.5(8H, phenyl), 2.8-2.9(16H, aliphatic), 1.2-1.6(24H, aliphatic).

RESULTS AND DISCUSSION

The monomer, urazolediamine (UD), was prepared according to the procedures given in the literature. The chemical structure of UD is shown in Scheme 1.



Scheme 1 : The 8 step procedure for the preparation of the diamine.

The regions of the IR spectra of dione(ref.22) are of particular interest, the 3200 (w), 3100 (m), 2800 (w), 1760 (w), 1700 (s, br), 1520 (s), 1460 (s), 1380(s), 1290 (m), 1220 (m, sh), 1160 (w), 1120(s),1080 (s), 880 (s), 840 (s), 790 (m, sh), 770 (m), 720 (s), 680 (s), 660(m), 530 (s) cm^{-1} and NMR data of dione in Figure 1 with ^{1}H-NMR (DMSO-d6, TMS): δ 57/10 (s, 2H, br), 00/8 (m, 2H, J=10 Hz), 93/7 (m, 2H, J=10

Hz), 63/7 (d, 2H, J=10 Hz), 58/7 (d, 2H, J=10 Hz).

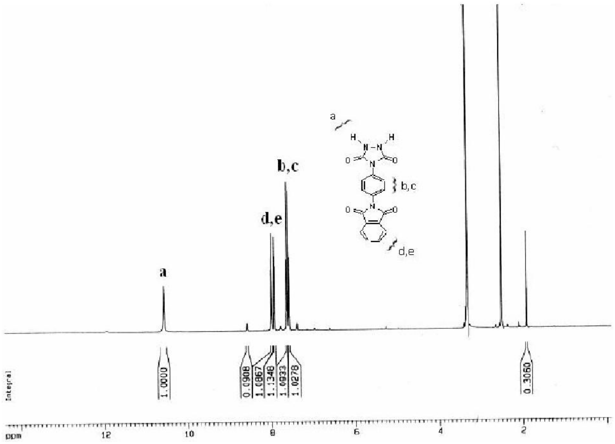


Figure 1 : ^{1}HNMR of dione[22]

The regions of the IR spectra of UD in Figure 2 are of particular interest, IR (KBr): 3480 (w NH), 3150-3100 (s, br NH2), 1720 (s, br, C=O), 1577(w), 1520 (s), 1500(m, br),1423 (s), 1250 (m), 1145 (m), 764(m), 737(m), 715 - 686 (s, sh), 639 (w), 432 (m) cm^{-1}.

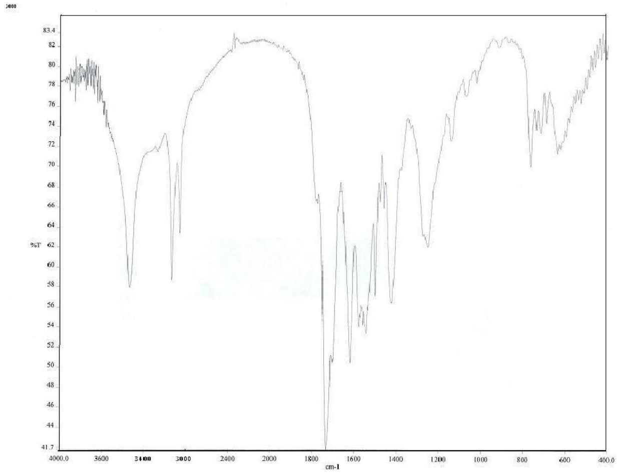
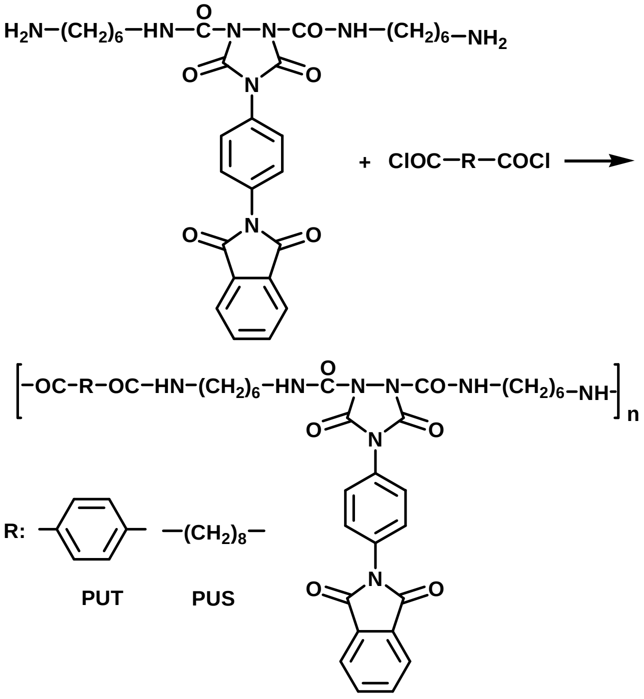


Figure 2 : IR of diamine

The polyamides (PUT, PUS) were synthesized by direct polycondensation of aromatic and aliphatic diacidchlorides in Scheme 2 with UD using triethylamine as catalyst. The reactions were carried out in DMF solution of the diacidchloride and UD in a nitrogen atmosphere at room temperature.

The polymerizations proceeded in homogeneous solution and the yields of the polyamides were quantitative. The elemental analysis values of the polyamides, TABLE 1, were generally in good agreement with the calculated values of proposed structures. As representative example, the complete elemental analysis of PUT was as follows: C, 62.7% (62.1% calculated); H, 5.6% (6.1%); N, 15.8% (15.5%). The polyamides were also characterized by IR and NMR spectrometers.



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

The amidic proton at ca. 11.95 and 10.45 ppm in the ^{1}HNMR spectra of PUS in Figure 3 confirmed the amidic structure of polymers.

The limiting viscosity number $[\eta]$ of polyamides was determined for extracted and dried polymers in H_2SO_4, 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 (PUT, PUS), obtained in H_2SO_4 were in the range of 0.32–0.36 dl/g that revealed reasonable molecular weights.

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 phthalimide groups of the diamine moiety. The ther-

TABLE 1 : Spectra data, elemental analysis results of polyamides.

Substrate	IR (KBr, cm_1)	NMR (DMSO-d6, δ, ppm)	Elemental analysis					
			Calc.			Found		
			C	H	N	C	H	N
PUT	3247(NH), 1655(C=O), 1608(C=N)	11.52(2H, NH), 10.45(2H, NH), 7.2-7.9(12H, phenyl), 1.1-1.3(24H, aliphatic)	62.1	6.1	15.5	62.7	5.6	15.8
PUS	IR(cm^{-1}) 3242(NH), 1686(C=O), 1608(C=N)	11.95(2H, NH), 10.45(2H, NH), 7.3-7.5(8H, phenyl), 2.8-2.9(16H, aliphatic), 1.2-1.6(24H, aliphatic).	63.2	6.5	14.9	62.9	6.9	15.1

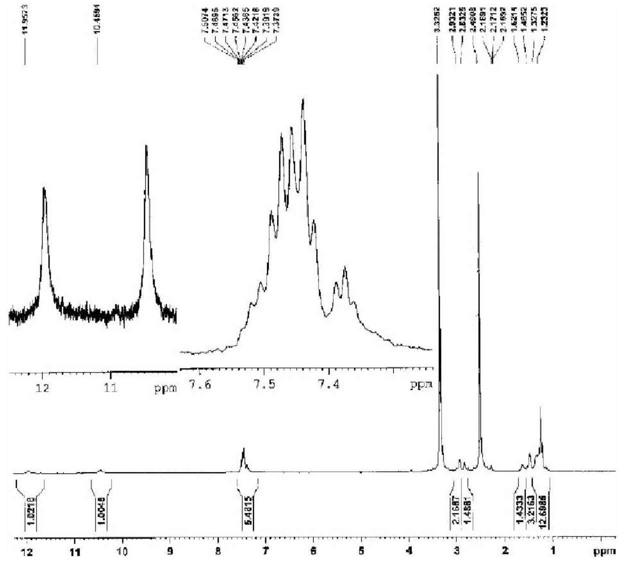


Figure 3 : ^{1}HNMR of PUS

mal 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 thermograms are shown in Figures 4, 5 for polyamides.

The first DSC scan up to 300 ºC showed exothermic peak at 144 °C and 183 °C as glass transition temperature for PUT and PUS respectively which disappeared completely in the second DSC scan. The DSC curves of Polyamides (PUT, PUS) were shown the melting point of these polymers at 242 °C and 259 °C respectively which appeared in the second DSC scan.

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 ºC in nitrogen atmosphere were given in TABLE 3.

TABLE 2 : Solubility of polyamides.

Polym. code	NMP	DMF	DMSO	TCE	THF	$H2SO_4$	HMPA	DMAC	Aceton	Ethanol	Methanol	$CHCl_3$
PUT	+	+	+	±	±	+	+	+	±	-	-	±
PUS	+	+	+	±	±	+	+	+	±	-	-	±

(1) Soluble (+), partially soluble (±), insoluble (-); (2) Solubility tested with 0.5 g of polymer in 100 ml of solvent; (3) NMP = N-methylpyrolidone, DMF = dimethylformamide, DMSO = dimetylsolfoxide, TCE = tetrachloroethane, Py = pyridine, THF = tetrahydrofurane, HMPA = hexamethylenphosphoramide, DMAC = dimethylacetamide

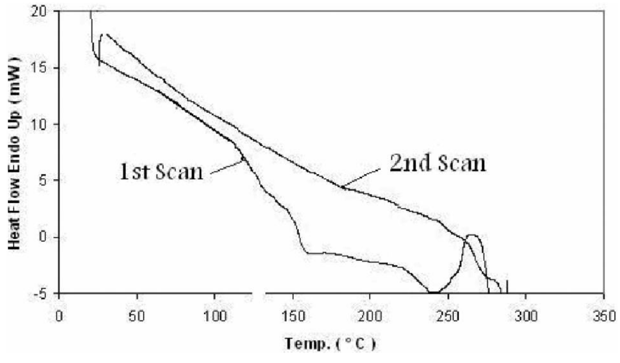


Figure 4 : DSC of PUT (Run 1,2)

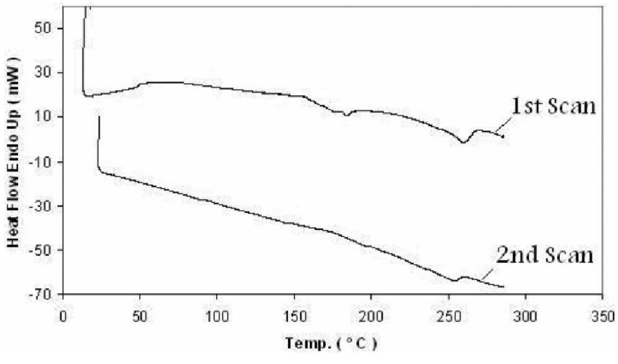


Figure 5 : DSC of PUS (Run 1,2)

The representative TGA curves of two PAs are shown in Figure 6.

The polymers were stable up to 200 °C in nitrogen and show almost the same stability. The 50% weight loss of polymers was in temperature range up to 380 °C. The polyamides (PUT, PUS) remained 14.5% and 6.5% of the original weight at 600 °C in nitrogen in comparison with their aromatic and aliphatic structures.

TABLE 3 : Thermal analysis, viscosity and yield of the polyamides.

Compound code	T_g [a]	T_m [a]	$T_{10\%}$ (°C) [b]	$T_{50\%}$ (°C) [c]	%Ch. Y. [d]	η_{inh} (dl/g) [e]	Yield (%)
PUT	144	242	275	380	14.5	0.32	94
PUS	183	259	251	415	6.5	0.36	95

[a] from DSC curves; [b] 10% weight loss; [c] 50% weight loss; [d] Char yield percent at 600 °C, obtained from TGA; [e] Measured in H_2SO_4 at 25 °C (C=0.5 g/dl).

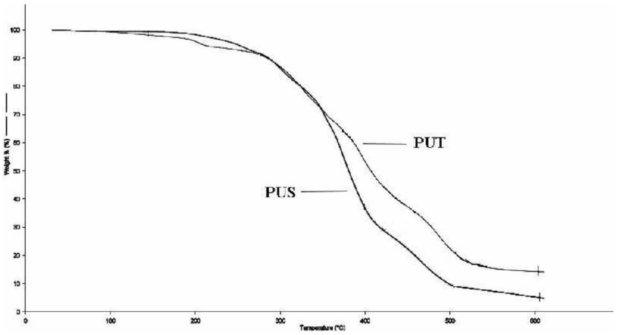


Figure 6 : TGA of PAs

CONCLUSION

Two polyamides, containing phthalimide group were prepared from the reaction of two diacid chlorides with a diamine as urazolediamine (UD). The molar ratio of diacid chloride to the diamine was 2:2 and the reaction was carried out at ambient temperature for 5 hours under N_2 atmosphere. The polyamides were fully characterized and their thermal properties were studied. The introduction of phthalimide pendant groups in structure of the diamine resulted in amorphous polyamides with very good solubility in aprotic solvents such as DMF (due to presence of these groups in polymer structure).

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