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Step-growth Polymerization Reaction of 4-(4-Acetamidophenyl)-1,2,4-triazolidine-3,5-dione with Aliphatic Diacid Chlorides

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ABSTRACT

4-(4-aminophenyl)-1,2,4-triazolidine-3,5-dione **(1)** was reacted with one mole of acetyl chloride in dry N,N-dimethylacetamide (DMAc) at low temperature and 4-(4-acetamidophenyl)-1,2,4-triazolidine-3,5-dione **APTD (3)** was obtained in high yield. The compound **APTD** was reacted with excess acetyl chloride in DMAc solution and gave 1,2-bis-acetyl-4-(4-acetamidophenyl)-1,2,4-triazolidine-3,5-dione **(4)** as a model compound. Solution polycondensation reactions of monomer **3** with succinyl chloride **(SucC)**, suberoyl chloride **(SubC)** and sebacoyl chloride **(SebC)**, were performed under conventional solution polymerization techniques in the presence of different catalysts and lead to the formation of novel aliphatic polyamides. These novel polyamides have inherent viscosities in a range of 0.08-0.24 dLg^{-1} in *N,N*-dimethylformamide (DMF) at 25°C. Some structural characterization and physical properties of these novel polymers are reported.

Key Words:
polyamides;
step-growth polymerization;
inherent viscosity;
4-(4-acetamidophenyl)-1,2,4-triazolidine-3,5-dione;
thermogravimetric analysis.

INTRODUCTION

The incorporation of heterocyclic rings in the backbone of the synthetic polymer is to impart certain properties to the polymer [1]. Polyamides and polyureas containing urazole derivatives nuclei have been reported [2-5]. Polyamides are well recognized as a class of commercially important thermostable polymers. The ordering and varying of backbone functions have profound effects on the final properties such as solubility and thermal characteristics of the resulting heterocyclic macromol-

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ecules [6]. The investigation of thermally stable linear polymer systems has received great emphasis due to requests for heat-resistant materials such as laminates, films, and fibres. The introduction of heterocycle units into the polymer backbone has been explored as a convenient way to obtain thermally stable materials [7].

Polyamides containing heterocyclic units in the main chain possess excellent thermal stabilities. Thus, in order to prepare novel processible polyamides with enhanced thermal stabilities, new diamine monomers containing urazole heterocyclic group and bearing bulky aromatic pendant groups in the 4-position of the urazole ring are introduced and used for preparation of polyamides. The incorporation of heterocyclic units and flexible linkages can provide beneficial effects for solubility because this approach produces a separation of chains, a weakening of hydrogen bonding and a lowering of chain packing with a gain of free volume.

Previous results have validated this approach [8-16] and the work reported in this article was designed synthesis of a new monomer containing urazole heterocyclic group and aromatic pendant groups in the 4-position of urazole ring and its polycondensation with a set of aliphatic diacid chlorides. A major objective was to study the effects of the flexible linkages and urazole heterocyclic moieties.

Urazole derivatives are very interesting five-membered heterocyclic compounds, which at position 4 can provide a wide variety of aliphatic as well as aromatic substituents. Some urazole derivatives were found to be potent cytotoxic agents in murrain and human cancer cell lines and also reduce DNA synthesis significantly with moderate reduction in RNA synthesis. Kinetic studies suggest that the inhibitation of rate limiting enzymes is responsible for its cytotoxicity. Other pharmaseuotical properties of urazole derivatives are hypolipidemic activity via lowering both serum cholesterol and triglyceride levels, herbicides [17], pesticides [18] and insecticides also these compositions are useful as additives for functional fluids [19] and as anti-inflammatory agents [20]. Synthesis of thermoplastics, manufacture of heat resistant coatings, tire rubbers with high gripability and melamine resins are among the works were done in the field of polymerization of urazole derivatives.

Aromatic and aliphatic polyamides have been widely prepared and used. The purpose of this investigation was to examine the step-growth polymerization reactions of **APTD** as a heterocyclic monomer with aliphatic diacid chlorides. In the present work we have reported the successful polycondensation reaction where **APTD** as a novel monomer is used for the synthesis of new aliphatic polyamides containing heterocyclic moieties.

EXPERIMENTAL

Materials and Equipments

Reagents were purchased from Fluka (Buchs, Switzerland), Aldrich (Milwaukee, WI) and Riedel-deHaen AG (Seelze, Germany). 4-(4-aminophenyl)-1,2,4-triazolidine-3,5-dione **(1)** was prepared in 6 steps according to our previous work [21]. DMAc (*N,N*-dimethylacetamide) was dried over BaO and then was distilled under reduced pressure. Proton nuclear magnetic resonance (500 MHz) spectra were recorded on a Bruker (Germany), Avance 500 instrument. IR Spectra were recorded on a Shimadzu 435 IR spectrophotometer. IR Spectra of solids were carried out using KBr pellets.

All melting points were taken with a Gallenham melting point apparatus. Inherent viscosities were measured by standard procedure using a Cannon Fensk Routine viscometer. Thermal gravimetric analysis (TGA) data for polymers were taken on a Mettler TGA-50. Elemental analyses were performed by Malek Ashter University, Tehran, I. R. Iran.

Monomer Synthesis

Preparation of 4-(4-Acetamidophenyl)-1,2,4-triazolidine-3,5-dione (APTD) (3)

In a 25 mL round bottom flask, 4-(4-aminophenyl)-1,2,4-triazolidine-3,5-dione **(1)** (3.00 g, 1.56×10^{-3} mol) was dissolved in 3 mL of dry DMAc. The solution was cooled to -15°C in an ice-salt bath. Then a solution of 1.22 g (1.56×10^{-3} mol, 1.11 mL) of acetyl chloride **(2)** in 0.5 mL of dry DMAc was added dropwise and the mixture was kept at -15°C for 8 h. Then it was stirred at room temperature for overnight. The reaction mixture was poured into 50 mL of water. The white solid was filtered off, and dried to give 3.33 g (91%) of white solid. Recrystallization from hot water gave white crystals. mp = 292-293°C; IR (KBr): 3340 (s), 3150 (s), 3070 (s), 2900 (m), 2800 (m), 1780 (m), 1710 (s), 1673 (s), 1610 (s), 1550 (s), 1520 (s), 1447 (s), 1416 (s),

1377 (s), 1325 (s), 1268 (m), 1250 (w), 1215 (m), 1180 (w), 1120 (m), 1095 (m), 1038 (w), 1010 (w), 965 (w), 830 (s), 790 (s), 758 (w), 735 (w), 702 (m), 650 (s), 630 (m, sh), 598 (w), 520 (m) cm^{-1}; ^1H NMR (500 MHz, MDSO-d_6): 2.09 (s, 3H, CH_3), 7.34-7.36 (d, 2H, Ar-H, J = 8.8 Hz), 7.65-7.67 (d, 2H, Ar-H, J = 8.8 Hz), 10.09 (s, 1H, N-H), 10.41 (s, br, 2H, N-H). Anal. calcd. for $C_{10}H_{10}N_4O_3$: 51.28 % C; 4.30 % H; 23.92 % N. Found: 51.60 % C; 4.61 % H; 24.65% N.

Model Compound Synthesis

Preparation of 1,2-bis-Acetyl-4-(4-acetamidophenyl)-1,2,4-triazolidine-3,5-dione (Model Compound 4)

In a 25 mL round-bottom flask, acetyl chloride (0.6703 g, 8.54×10^{-3} mol) was added to a solution of **APTD (3)** (0.200 g, 8.54×10^{-4} mol) in 1.0 mL of dry DMAc. The solution was stirred for 36 h at room temperature. The excess acetyl chloride was removed by aspirator and the residue was percipitated in 50 mL of water. The resulting solid was filtered off, dried to give 0.2473 g (91.0%) of white solid **(4)**. This solid was recrystallized from acetone and water, mp = 195-196°C; IR (KBr): 3350 (s), 3100 (w), 2850 (w), 1810 (m, sh), 1760 (s), 1725 (s), 1690 (s), 1680 (s), 1600 (s), 1530 (s), 1600 (m), 1515 (s), 1470 (w), 1407 (s), 1370 (s), 1310 (s), 1245 (s), 1225 (s), 1167 (s), 1040 (s), 1010 (s), 965 (s), 875 (m), 840 (s), 800 (s), 750 (s), 720 (m, sh), 700 (m), 670 (w), 650 (w), 610 (m), 580 (s), 520 (w) cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ 2.08 (s, 3H), 2.48 (s, 6H), 7.41-7.43 (d, 2H, J = 8.8 Hz), 7.71-7.73 (d, 2H, J = 8.8 Hz), 10.17 (s, 1H). Anal. calcd. for $C_{14}H_{14}N_4O_5$: 52.83 % C; 4.43 % H; 17.60 % N. Found: 52.72 % C; 4.59 % H; 17.72 % N.

Polymerization of APTD with SucC

Method I

In a 25 mL round-bottom flask **APTD (3)** (0.1230 g, 5.25×10^{-4} mol) and pyridine (0.085 mL, 1.05×10^{-3} mol) were added to a solution of **SucC (5)** (0.0814 g, 5.25×10^{-4} mol) in 0.6 mL of N-methyl-2-pyrrolidone (NMP). The solution was stirred for 3 h at -5°C, then for 18 h at room temperature. During of this period 0.5 mL of NMP was added. The viscous solution was precipitated in 50 mL of methanol. The solid was filtered off, dried to give 0.1799 g (88.0%) of polyamide **PA1A**; mp = 288-298°C. The above polymerization was repeated, in the presence of triethylamine and dibutyltin dilurate as catalyst, respectively.

Method II

The above polymerization was repeated, but the reaction mixture was refluxed in NMP for 1 min. in the presence of different catalysts.

IR(KBr): 3330 (m), 3100 (w), 2900 (w), 1790 (s), 1720 (s), 1670 (s), 1608 (w), 1530 (s), 1410 (s), 1373 (m), 1320 (m), 1285 (m), 1240 (m), 1180 (m), 1160 (m, sh), 1120 (w), 1090 (w), 1040 (w), 1020 (w), 970 (w), 950 (w), 830 (m), 760 (w), 670 (w), 590 (w), 530 (w) cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): 2.08 (s, br, CH_3), 2.90 (s, br, CH_2), 7.35-7.38 (d, Ar-H, J = 16.8 Hz), 7.73-7.84 (distorted d, Ar-H), 10.09-10.19 (m, br, N-H). Anal. calcd. for $C_{14}H_{12}N_4O_5$: 53.17 % C; 3.82 % H; 17.71 % N. Found: 52.31 % C; 3.98 % H; 17.58 % N.

Polymerization of APTD with SucC

Method I

In a 25 mL round-bottom flask, **APTD (3)** (0.1096 g, 4.68×10^{-4} mol) and pyridine (0.075 mL, 9.36×10^{-4} mol) was added to a solution of **SubC (6)** (0.0987 g, 4.68×10^{-4} mol) in 0.5 mL of NMP. The solution was stirred for 3 h at -5°C, then for 12 h at room temperature. During of this period 0.6 mL of NMP was added. The viscous solution was precipitated in 50 mL of methanol. The solid was filtered off, dried to give 0.1286 g (69.5%) of white polyamide **PA2A**; mp = 256-262°C. The above polymerization was repeated, in the presence of triethylamine and dibutyltin dilurate as catalyst, respectively.

Method II

The above polymerization was repeated, but the reaction mixture was refluxed in NMP for 1 min in the presence of different catalysts.

IR(KBr): 3310 (m), 3130 (m), 2930 (m), 1790 (m), 1710 (s, br), 1670 (s), 1608 (m), 1525 (s), 1410 (s), 1315 (s), 1260 (s), 1153 (m), 1070 (m), 1017 (w), 836 (m), 750 (m), 720 (m), 670 (w) cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): 1.38 (s, br, CH_2), 1.64 (s, br, CH_2), 2.07 (s, CH_3), 2.79-2.85 (s, br, CH_2), 7.37-7.41 (distorted d, Ar-H), 7.69 (distorded d, Ar-H), 10.15 (s, N-H). Anal. calcd. for $C_{18}H_{20}N_4O_5$: (58.06 % C; 5.41 % H; 15.04

% N). Found: (57.42 % C; 5.79 % H; 14.31 % N).

Polymerization of APTD with SucC

Method I

In a 25 mL round bottom flask, **APTD** (0.200 g, 8.54 × 10^{-4} mol) and pyridine (0.138 mL, 1.71 × 10^{-3} mol) was added to a solution of **SebC (7)** (0.2042 g, 8.54 × 10^{-4} mol) in 0.75 mL of NMP. The reaction mixture was stirred for 3 h at -5°C, then for 12 h at room temperature. During of this period 0.5 mL of NMP was added. The viscous solution was precipitated in 50 mL of methanol. The solid was filtered off, dried to give 0.3274 g (81.0%) of white polyamide **PA3A**; mp = 178-182°C. The above polymerization was repeated, in the presence of triethylamine and dibutyltin dilurate as a catalyst, respectively.

Method II

The above polymerization was repeated, but the reaction mixture was refluxed in NMP for 1 min in the presence of different catalysts.

IR(KBr): 3300 (m), 3230 (m), 2920 (m), 1746 (s, br), 1608 (m), 1540 (m, sh), 1520 (s), 1410 (s), 1370 (s), 1312 (s), 1230 (s), 1165 (m), 1060 (m), 1010 (m), 833 (w), 800 (w), 748 (w), 665 (w) cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 1.29-1.34 (m, br, CH_2), 1.62 (s, br, CH2), 2.07 (s, CH_3), 2.84 (s, br, CH_2), 7.37-7.40 (distorted d, Ar-H), 7.69 (s, Ar-H), 10.14 (s, N-H). Anal. calcd. for $C_{20}H_{24}N_4O_5$: (59.99 % C; 6.04 % H; 13.99 % N). Found: (59.24 % C; 6.45 % H; 12.68 % N).

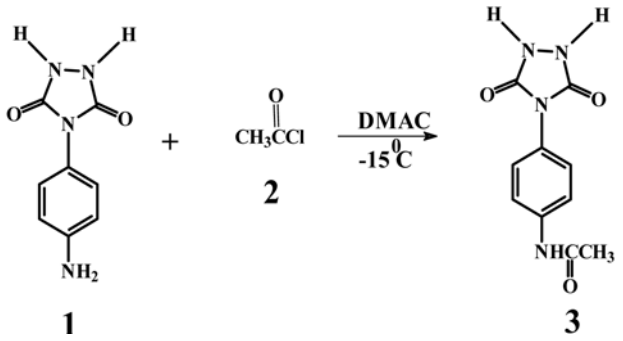
RESULTS AND DISCUSSION

Monomer Synthesis

The monomer 4-(4-acetamidophenyl)-1,2,4-triazolidine-3,5-dione **(APTD) (3)** was synthesized from the reaction of 4-(4-aminophenyl)-1,2,4-triazolidine-3,5-dione **(1)** with acetyl chloride **(2)** in dry DMAc in an ice-salt bath at -15°C (Scheme I). The purity of monomer **3** was checked by TLC. The structure of this monomer was confirmed by IR, ^1H NMR spectra and elemental analysis.

Model Compound Studies

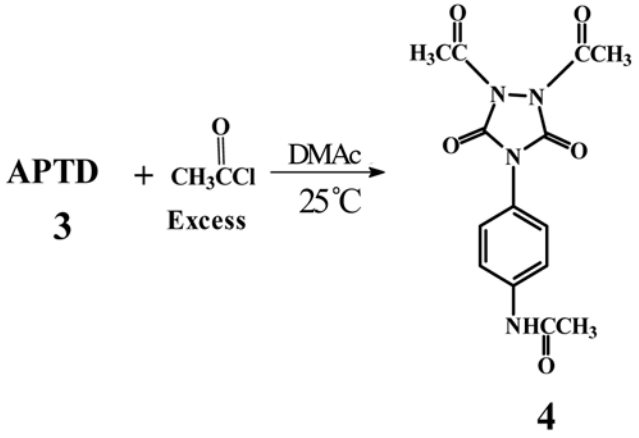
APTD (3) was allowed to react with excess acetyl chloride in DMAc solution at room temperature for 36 h and gave 1,2-bis-Acetyl-4-(4-Acetamidophenyl)-1,2,4-triazolidine-3,5-dione **(4)** in high yield (Scheme II). The compound **4** was characterized by IR, ^1H NMR and elemental analysis. The IR spectrum of **4** show a peak around 3350 cm^{-1} for the N-H bond acetamide substitute. It also shows three peaks at 1760, 1725 and 1690 cm^{-1} for the carbonyl groups. The first two peaks are characteristic pattern for the urazole moiety. The ^1H NMR spectrum of **4** showed all peaks which are in agreement with the structure of compound **4** (Figure 1). The purity of this model compound was checked by TLC.



Scheme I. Synthesis of monomer 3.

Polymerization Reactions

Since 1,2-bis-Acetyl-4-(4-acetamidophenyl)-1,2,4-triazolidine-3,5-dione **(4)** as a model compounds was synthesized in high yield and purity, we became interested to perform this type of the reaction for the formation of the novel polyamides. Thus **SucC (5)**, **SubC (6)** and **SebC (7)** were selected as diacid chlorides. The polymerization reaction of monomer **3** with these diacid



Scheme II. Synthesis of model compound 4.

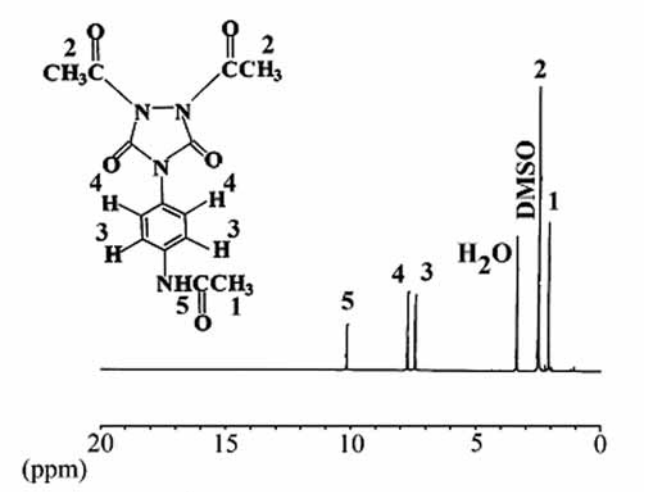


Figure 1. ^{1}H NMR (500 MHz) Spectrum of model compound **4** in DMSO-d_6 at room temperature.

chlorides were performed under conventional solution polymerization techniques at low as well as high temperture in the presence of different catalysts **PA1-PA3** (Scheme III). The polymerization reaction of monomer **3** with **SucC** was carried out with two different methods. In method **I** the reaction mixtures were kept at-5°C then was allowed to increase to room temperture in the presence of either of pyridine, dibutyltin dilaurate, and triethylamine. The resulting polyamides **PA1A-PA1C** have high inherent viscosity and high yeild. In method **II** the reaction mixture was refluxed up for 1 min in NMP. The resulting polyamides **PA1D-PA1F** have lower yield and inherent viscosity. Thus, method **I** is better reaction condition for the polymerization reaction of monomer **3** with **SucC**. Reaction conditions and some physical properties of **PA1A-PA1F** are summerized in Table 1. The resulting polymers were characterized by IR, ^{1}H NMR, elemental analysis and TGA.

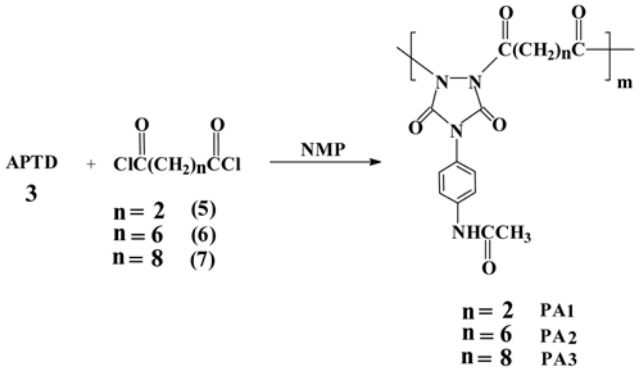
Table 1. Reaction conditions for the polymerization of monomer **APTD (3)** with **SucC (5)** by different methods and some physical properties of **PA1A-PA1F**.

Polymer	Method[a]	Catalyst	Yield (%)	Inherent viscosity (dL/g)[e]
PA1A	**I**	Py	81.0	0.24
PA1B	**I**	TEA	92.0	0.12
PA1C	**I**	DBTDL	79.0	0.11
PA1D	**II**	Py	73.0	0.15
PA1E	**II**	TEA	68.5	0.11
PA1F	**II**	DBTDL	73.0	0.12

[(a)] Method I: 3 h at -5°C; 18 h at 25°C, Method II: Refluxing at 1 min; [(b)] pyridine; [(c)] triethylamine; [(d)] dibutyltin dilaurate; [(e)] Measured at a concentration of 0.5 g/dL in DMF at 25°C.

The IR spectrum of polymer **PA1** showed three peaks at 1790, 1720, and 1670 cm^{-1} for the carbonyl groups. The ^{1}H NMR spectrum of polymer **PA1** (Figure 2) showed all peaks for aliphatic and aromatic as well as end group N-H protons. The elemental analysis result is also in good agreement with calculated percentages for carbon, hydrogen and nitrogen contents in polymer repeating unit.

The polymerization reaction of monomer **3** with **SubC** was also carried out with two different methods (Table 2). We obtained comparable results of two methods.



Scheme III. Ploycondensation reactions of monomer 3 with aliphatic diacid chlorides.

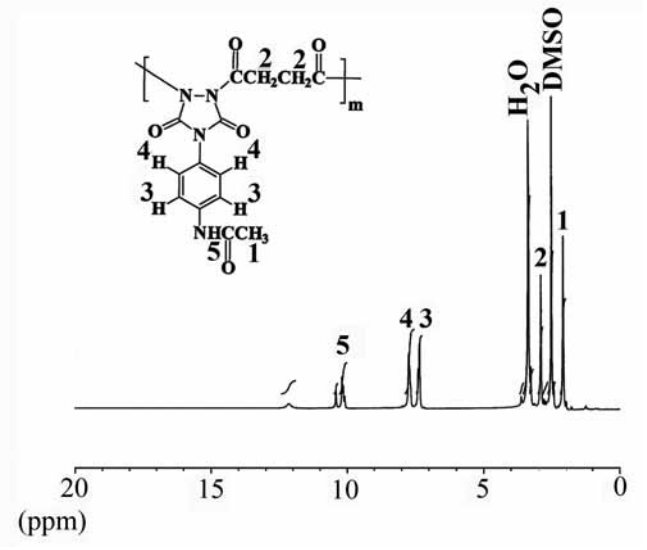


Figure 2. ^{1}H NMR (500 MHz) Spectrum of **PA1** in DMSO-d_6 at room temperature.

Table 2. Reaction conditions for the polymerization of monomer **APTD (3)** with **SucC (6)** by different methods and some physical properties of **PA2A-PA2F**.

Polymer	Method[a]	Catalyst	Yield (%)	Inherent viscosity (dL/g)[e]
PA2A	**I**	Py[b]	69.5	0.13
PA2B	**I**	TEA[c]	62.0	0.10
PA2C	**I**	DBTDL[d]	76.0	0.12
PA2D	**II**	Py	70.5	0.11
PA2E	**II**	TEA	85.0	0.12
PA2F	**II**	DBTDL	81.5	0.08

[a] Method I: 3 h at -5°C; 18 h at 25°C, Method II: Refluxing at 1 mi; [b] pyridine; [c] triethylamine; [d] dibutyltin dilaurate; [e] Measured at a concentration of 0.5 g/dL in DMF at 25°C.

The IR spectrum of polymer **PA2** showed two strong peaks at 1710 and 1670 cm^{-1} for the carbonyl groups. The ^1H NMR spectrum of polymer **PA2** (Figure 3) showed peaks that confirm its chemical structure. The elemental analysis are also in good agreement with calculated percentages of carbon, hydrogen, and nitrogen contents in polymer repeating unit of **PA2**.

The polymerization reaction of monomer **3** with **SebC** was also performed with two different methods (Table 3). Here method **I** with pyridine as catalyst is the best method for the polymerization reaction.

The IR spectrum of polymer **PA3** showed two strong peaks at 1746 and 1670 cm^{-1} for the carbonyl groups. The ^1H NMR spectrum of polymer **PA3** (Figure 4) showed peaks that confirm its chemical structure. The elemental analysis are also in good agreement with calculated percentages of carbon, hydrogen and nitrogen contents in polymer repeating unit of **PA3**.

The polymers **PA1**, **PA2**, and **PA3** are soluble in organic solvents such as NMP and H_2SO_4, partial soluble in DMF, DMSO, DMAc and insoluble in solvents such as water, methanol, acetone, cyclohexane, and chloroform.

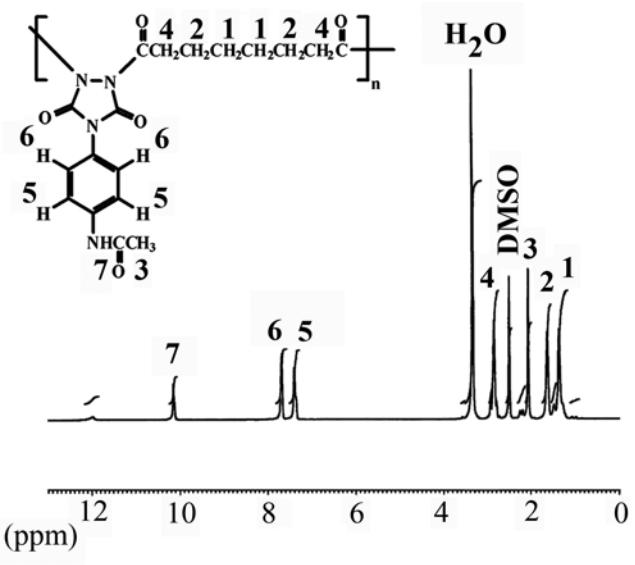


Figure 3. ^1H NMR (500 MHz) Spectrum of **PA2** in DMSO-d_6 at room temperature.

Table 3. Reaction conditions for the polymerization of monomer **APTD (3)** with **SucC (7)** by different methods and some physical properties of **PA3A-PA3F**.

Polymer	Method[a]	Catalyst	Yield (%)	Inherent viscosity (dL/g)[e]
PA3A	**I**	Py[b]	81.0	0.16
PA3B	**I**	TEA[c]	78.0	0.12
PA3C	**I**	DBTDL[d]	81.0	0.08
PA3D	**II**	Py	69.0	0.12
PA3E	**II**	TEA	75.0	0.11
PA3F	**II**	DBTDL	73.0	0.10

[a] Method I: 3 h at -5°C; 18 h at 25°C, Method II: Refluxing at 1 mi; [b] pyridine; [c] triethylamine; [d] dibutyltin dilaurate; [e] Measured at a concentration of 0.5 g/dL in DMF at 25°C.

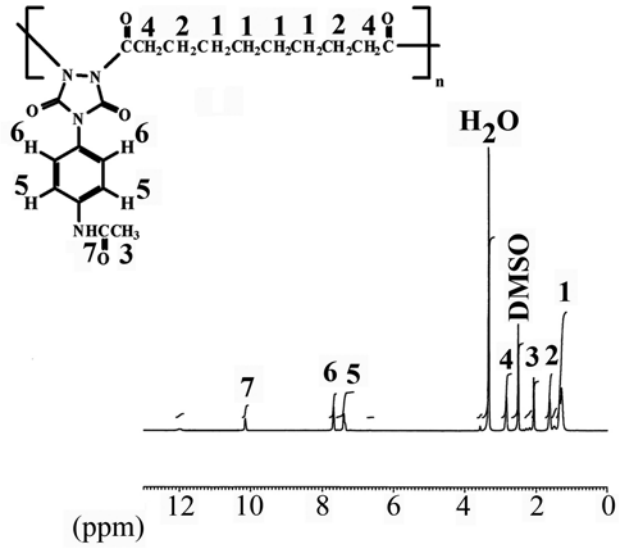


Figure 4. ^1H NMR (500 MHz) Spectrum of **PA3** in DMSO-d_6 at room temperature.

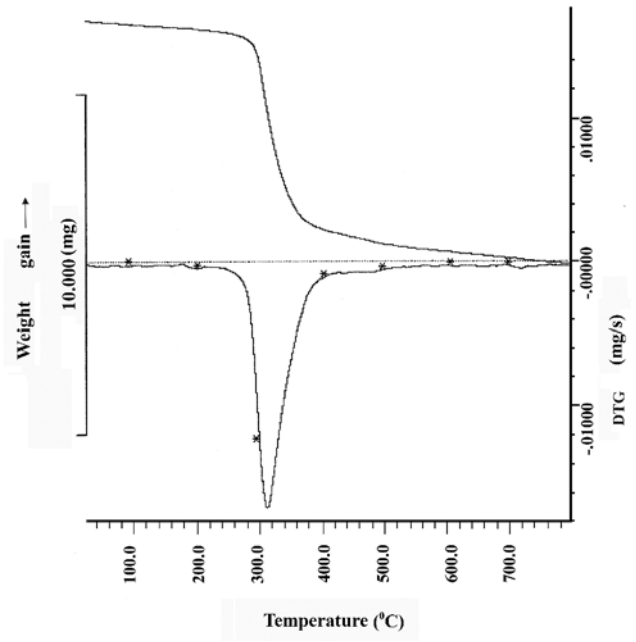


Figure 5. TGA/DTG of **PA1** with heating rate of 10°C/min, in nitrogen atmosphere.

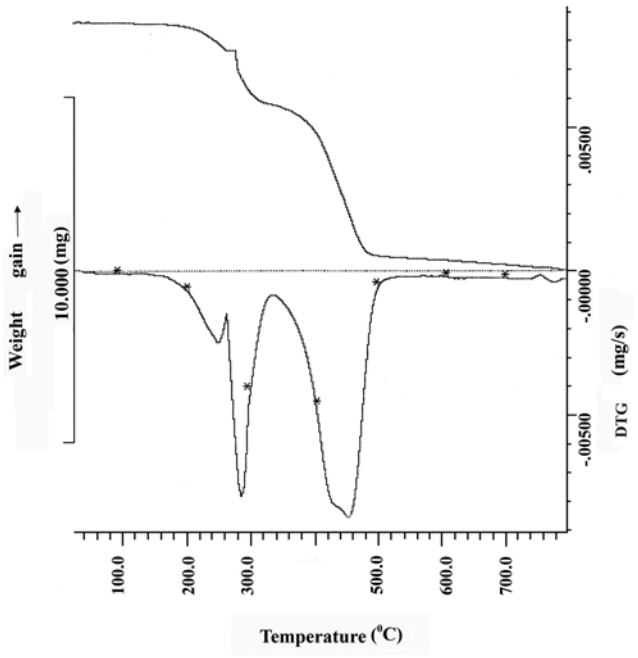


Figure 7. TGA/DTG of **PA3** with heating rate of 10°C/min, in nitrogen atmosphere.

Thermal Properties

The thermal behaviour of polyamides **PA1**, **PA2**, and **PA3** were measured by thermaogravimetric analysis (TGA) at a rate of 10°C/min in nitrogen atmosphere. An examination of the data reveals that all of the above polyamides are thermally stable up to 200°C. The temperatures of 5% and 10% weight loss together with char yield at 600°C for PAI, PA2, and PA3 are 280, 260°C, and 16.6%; 300, 243°C, and 17.8 %; and 251, 280°C, and 15.6%, respectively. Figures 5-7 show thermograms of these polyamids.

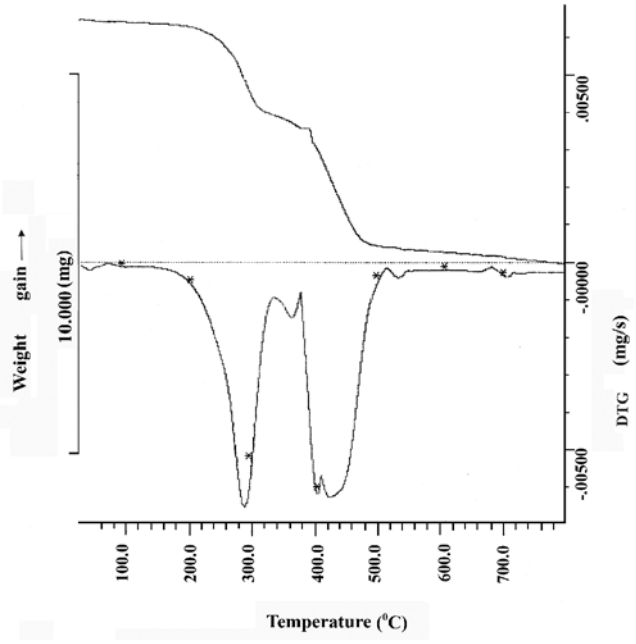


Figure 6. TGA/DTG of **PA2** with heating rate of 10°C/min, in nitrogen atmosphere.

CONCLUSION

This investigation has shown that **APTD (3)** is an interesting monomer for the polycondensation reactions. This compound has two acidic N-H groups and it can be readily reacted with acetyl chloride. Thus compound **3** can act as a bifunctional monomer and its polymerization reaction with aliphatic diacid chlorides gave novel polyamides with urazole linkages having inherent viscosities of 0.08-0.24 dL/g, which roughly correspond to molecular weight of 4000 to 15000 g/mol.

Although all catalysts used in these polymerization reactions are usefull, but pyridine seems to be more effective. Diacid chloride with lower CH_2s gives higher viscosity. This could be due to the formation of cyclic structure from long alkyl chain. We are interested in using this method for the synthesis of novel polymers and modification of macromolecules.

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