

Preparation and Characterization of New Photoactive Polyamides Containing 4-(4-Dimethylaminophenyl)urazole Units

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ABSTRACT: 4-(4-dimethylaminophenyl)-1,2,4-triazolidine-3,5-dione (DAPTD) was prepared from 4-dimethylamino-benzoic acid in five steps. The compound DAPTD was reacted with excess acetyl chloride in *N,N*-dimethylacetamide (DMAc) solution and gave 1,2-bisacetyl-4-[4-(dimethylaminophenyl)]-1,2,4-triazolidine-3,5-dione as a model compound. Solution polycondensation reactions of monomer with succinyl chloride (SucC), suberoyl chloride (SubC), and sebacoyl chloride (SebC) were performed under conventional solution polymerization techniques in the presence of triethylamine and pyridine as a catalyst in *N*-meth-

ylpyrrolidone (NMP) and led to the formation of novel aliphatic polyamides. These novel polyamides have inherent viscosities in the range of 0.09–0.21 dL/g in *N,N*-dimethylformamide (DMF) at 25°C. Fluorimetric studies of the model compound as well as polymers were performed. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 947–954, 2007

Key words: polyamides; step-growth polymerization; inherent viscosity; 4-(4-dimethylaminophenyl)-1,2,4-triazolidine-3,5-dione; thermal gravimetric analysis (TGA); fluorimetric

INTRODUCTION

Urazole derivatives are very interesting five-membered heterocyclic compounds, which at position four can provide a wide variety of aliphatic as well as aromatic substituents. Urazoles are unusual because they possess two pyramidal nitrogen atoms (sp^3) and a planar nitrogen atom (sp^2) in the same molecule. They are also unusual as the two pyramidal nitrogen atoms are bonded to one another. Because optically active forms of urazole do not appear to exist, it has always been assumed that nitrogen inversion takes place in urazole that is similar to nitrogen inversions in other amines.¹

Urazole is an important chemical reagent in the laboratory and in industry. Industrially, urazole is used in the manufacture of automobile air bags, as a blowing agent in plastics, in the production of herbicides,² in the production of antifungal compounds, and in polymeric materials.^{3,4} It is also used in the production of antitumor drugs^{5,6} and as a stabilizer

in milk. Urazole is used as a laboratory reagent for synthesizing novel heterocyclic^{7–10} and organometallic compounds. Urazole has also been used in studies of the origin of life due to its chemical similarity to uracil.

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 heterocyclic polymers.¹¹ The investigation of thermally stable linear polymer systems has received great emphasis because of the requests for heat-resistant materials such as laminates, films, and fibers. The introduction of heterocycle units into the polymer backbone has been explored as a convenient way to obtain thermally stable materials.¹² Polyamides containing heterocyclic units in the main chain possess excellent thermal stabilities. So, to prepare novel processible polyamides with enhanced thermal stabilities, new diamine monomers containing urazole heterocyclic group and bearing bulky aromatic pendant groups in the fourth 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.

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Recently we have been able to take advantage of these acidic N-H in urazoles and synthesis novel polymers.^{13–17} A major objective was to study the effect of the flexible linkages and urazole heterocyclic moieties.

The purpose of this investigation was to examine the step-growth polymerization reactions of DAPTD as a heterocyclic monomer with aliphatic diacid chlorides. In the present article, we report on the successful polycondensation reaction where DAPTD 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 Chemical (Buchs, Switzerland), Aldrich Chemical (Milwaukee, WI), and Riedel-deHaen AG (Seelze, Germany). DMAc (*N,N*-dimethylacetamide) was dried over BaO and then was distilled under reduced pressure. Proton nuclear magnetic resonance ¹H NMR (500 MHz) spectra were recorded in DMSO-*d*₆ on a Bruker (Germany), Avance 500 instrument. Multiplicities of proton resonance were designated as singlet (s), doublet (d), doublet of doublet (dd), triplet (t), and multiplet (m). FTIR spectra were recorded on a Nicolet Impact 400D IR spectrophotometer. Spectra of solids were carried out using KBr pellets. Vibrational transition frequencies are reported in wavenumber (cm⁻¹). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s), and broad (br). All melting points were taken with a Gallenham melting point apparatus. Inherent viscosities were measured by standard procedure using a Cannon Fenske Routine viscometer. Elemental analyses were performed by Research institute of petroleum industry, Tehran, Islamic Republic of Iran. Fluorescence and UV-vis spectra were recorded in DMF on a JASCO, FP-750, and UV/VIS/NIR, JASCO, V-570, spectrophotometer, respectively. Mass spectra were recorded on a Fisons (Trio 1000) spectrometer. Thermal gravimetric analysis (TGA) data for polymers were taken on a TGA Perkin-Elmer (Jugesheim, Germany) Thermal analyzer under a nitrogen atmosphere at a rate of 10°C/min, and differential scanning calorimetry (DSC) data were recorded on a DSC-PL-1200 instrument (London, England) under a nitrogen atmosphere at a rate of 10°C/min.

Preparation of 4-dimethylaminobenzoyl azide

Into a 25-mL round-bottom flask, the suspension of 4-dimethylaminobenzoic acid (1.00 g, 6.05 × 10⁻³ mol) in acetone (10 mL) was cooled to 0°C and triethylamine (0.61 g, 6.05 × 10⁻³ mol) was added over a

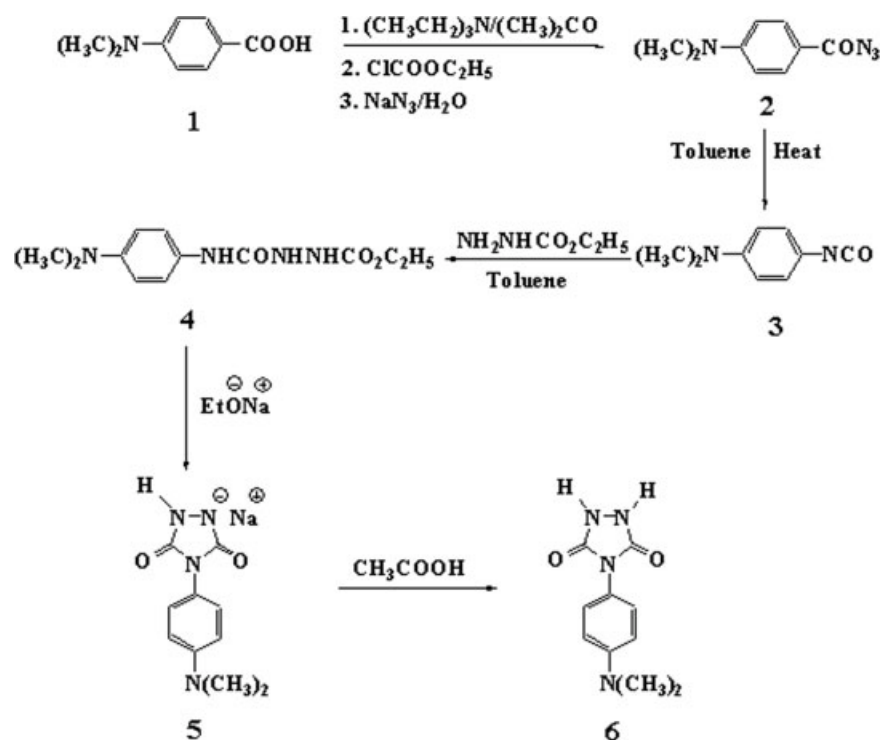
period of 10 min. The reaction mixture was stirred for further 1 h and then a solution of ethylchloroformate (0.66 g, 6.05 × 10⁻³ mol) in acetone (3 mL) was added at -10°C over a period of 10 min. The resulting reaction mixture was stirred for 3 h at the same temperature and then a solution of sodium azide (0.79 g, 1.21 × 10⁻² mol) in distilled water (5 mL) was added dropwise. Finally, the reaction mixture was stirred for 2 h at the same temperature, 2 h at 0°C and 4 h at room temperature and then poured into 50 mL of ice-cold water. The solid was filtered off, and dried to give 0.84 g (76%) of white solid. Recrystallization from acetone-water mixture gave white crystals. mp = 90–92°C; IR (KBr): 3103 (m, C–H Aromatic), 2913 (m, C–H aliphatic), 2125 (s, N₃), 1666 (s, C=O), 1597 (s, C=C) cm⁻¹.

Preparation of 1-ethoxycarbonyl-4-(4-dimethylaminophenyl) semicarbazide

Into a 100-mL round-bottom flask, 4-dimethylaminobenzoyl azide (3.00 g, 1.58 × 10⁻² mol) and 45 mL of dry toluene were added. The stirrer was started and the reaction mixture was refluxed under nitrogen atmosphere for 11 h. At the end of refluxing the reaction mixture was cooled, then filtered off immediately. The clear solution was transferred into a 100 mL two-necked round-bottom flask. The solution was cooled in an ice bath and a solution of ethyl carbazate (1.64 g, 1.58 × 10⁻² mol) in 20 mL of dry toluene was added dropwise for a period of 15 min. The suspension was stirred for 2 h in ice bath, then for 8 h at room temperature. The solid was filtered off, and dried to give 4.12 g (98%) of white solid. mp = 168–170°C; IR (KBr): 3307 (m, N–H), 2988 (m, C–H), 1759 (s, C=O), 1655 (s, C=O) cm⁻¹.

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

Into a 100-mL round-bottom flask, sodium metal (0.27 g, 1.17 × 10⁻² mol) was dissolved in 25 mL of absolute ethanol. Nitrogen gas bubbled through the solution and 1-ethoxycarbonyl-4-(4-dimethylaminophenyl) semicarbazide (3.00 g, 1.13 × 10⁻² mol) was added at once. The solution was refluxed under nitrogen atmosphere for 7.5 h, and then cooled in ice bath. The solution was neutralized with acetic acid to pH of 6. The product was isolated and dried to give 2.28 g (92%) of white solid. Recrystallization from hot water gave crystals. mp = 248–250°C; IR (KBr): 3195 (s, br, N–H), 3051 (s, C–H Aromatic), 2988 (m, C–H Aliphatic), 1767 (w, C=O Urazole ring), 1676 (s, C=O, Urazole ring) cm⁻¹; ¹H NMR (500 MHz, DMSO-*d*₆): δ 2.91 (s, 6H), 6.74–6.76 (d, 2H, *J* = 8.3 Hz), 7.16–7.18 (d, 2H, *J* = 8.3 Hz), 10.63 (s, 2H) ppm. Anal. Calcd for C₁₀H₁₂N₄O₂: C, 54.5%;



Scheme 1 Synthesis of monomer 6.

H, 5.5%; N, 25.4%. Found: C, 54.7%; H, 5.3%; N, 25.2%. Mass (EI), m/z : 220 ($[M^+]$, 100%), 219 (65%), 162 (46%), 161 (60%), 135 (40%).

Preparation of 1,2-bisacetyl-4-(4-dimethylamino-phenyl)-1,2,4-triazolidine-3,5-dione (model compound 7)

Into a 25-mL round-bottom flask, acetyl chloride (0.855 g, 1.09×10^{-2} mol) was added to a solution of DAPTD (0.200 g, 9.08×10^{-4} mol) in 1.0 mL of dry DMAc. The solution was stirred for 18 h at room temperature. The excess acetyl chloride was removed by aspirator and the residue was precipitated in 30 mL of water. The resulting solid was filtered off, dried to give 0.22 g (81%) of white solid 7. This solid was recrystallized from ethanol, mp = 192–194°C; IR(KBr): 3080 (m, C–H Aromatic), 2903 (m, C–H Aliphatic), 2817 (w, C–H Aliphatic), 1752 (s, C=O, Urazole ring), 1725 (s, C=O, Urazole ring and Acetyl) cm^{-1} ; $^1\text{H NMR}$ (500 MHz, DMSO- d_6): δ 2.46 (s, 6H), 2.95 (s, 6H), 6.78–6.80 (d, 2H, $J = 10.0$ Hz), 7.25–7.27 (d, 2H, $J = 10.0$ Hz) ppm. Anal. Calcd for $\text{C}_{14}\text{H}_{16}\text{N}_4\text{O}_4$: C, 55.3%; H, 5.3%; N, 18.4%. Found: C, 55.8%; H, 5.4%; N, 18.7%. Mass (EI), m/z : 304 ($[M^+]$, 27%), 262 (46%), 220 (40%), 162 (100%), 161 (35%).

Polymer synthesis

All the polymers were synthesized by three different methods.

Polymerization of DAPTD with SucC

Method I. Into a 25-mL round-bottom flask, DAPTD (0.1121 g, 5.09×10^{-4} mol) and pyridine (0.04 mL, 5.09×10^{-4} mol) were added to a solution of SucC (8) (0.0789 g, 5.09×10^{-4} mol) in 0.7 mL of *N*-methyl-2-pyrrolidone (NMP). The solution was stirred for 3 h at -5°C , then for 24 h at room temperature. The viscous solution was precipitated in 30 mL of methanol–water mixture (50 : 50). The solid was filtered off, dried to give 0.147 g (77%) of polyamide PA1A. mp = 234–241°C. The above polymerization was repeated, in the presence of triethylamine as a catalyst.

Method II. The above polymerization was repeated, but the reaction mixture was stirred at -5°C for 3 h, 12 h at room temperature, 6 h at 60°C , and then 10 h at 85°C in the presence of different catalysts.

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

IR(KBr): 3093 (w, C–H Aromatic), 2931 (m, C–H Aliphatic), 2860 (m, C–H Aliphatic), 1778 (s, C=O, Urazole ring), 1712 (s, C=O, Urazole ring and amide) cm^{-1} . $^1\text{H NMR}$ (500 MHz, DMSO- d_6): δ 2.87 (s, 4H), 2.95 (s, 6H), 6.80–6.82 (d, 2H, $J = 9.0$ Hz), 7.16–7.18 (distorted d, 2H) ppm. Anal. Calcd for $\text{C}_{14}\text{H}_{14}\text{N}_4\text{O}_4$: C, 55.6%; H, 4.7%; N, 18.5%. Found: C, 54.7%; H, 4.8%; N, 18.8%.

The PA2 and PA3 were prepared by similar procedures.

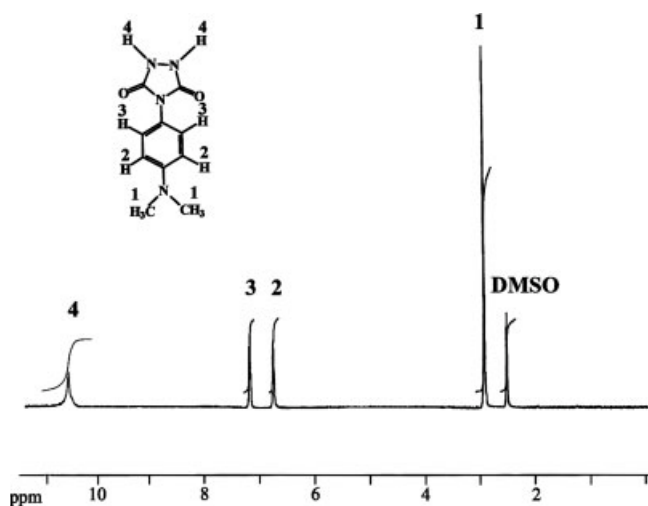


Figure 1 ^1H NMR (500 MHz) Spectrum of monomer compound **6** in $\text{DMSO}-d_6$ at room temperature.

Polymer PA2

IR(KBr): 3073 (w, C—H Aromatic), 2934 (m, C—H Aliphatic), 2808 (w, C—H Aliphatic), 1749 (s, C=O, Urazole ring), 1708 (s, C=O, Urazole ring and amide) cm^{-1} . ^1H NMR (500 MHz, $\text{DMSO}-d_6$): δ 1.15–1.78 (s, br, 8H), 2.42 (s, 4H), 2.73 (s, 6H), 6.79–6.81 (d, 2H), 7.16–7.22 (distorted d, 2H) ppm.

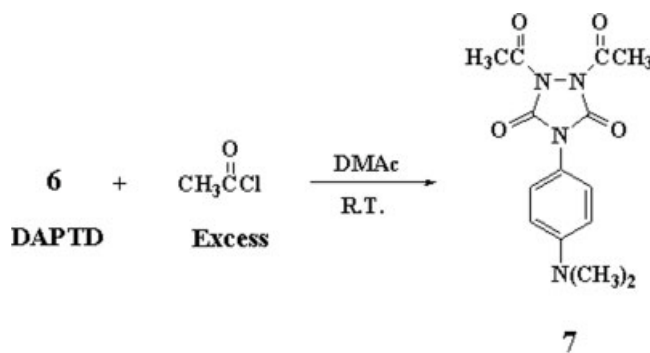
Polymer PA3

IR(KBr): 3027 (m, C—H Aromatic), 2927 (s, C—H Aliphatic), 2857 (m, C—H Aliphatic), 1749 (s, C=O, Urazole ring), 1698 (s, C=O, Urazole ring and amide) cm^{-1} .

RESULTS AND DISCUSSION

Monomer synthesis

In our continuous study on the preparation of polymers containing urazole ring in the backbone, a new monomer 4-(4-dimethylaminophenyl)-1,2,4-triazolidine-3,5-dione (**DAPTD**) was synthesized. **DAPTD** was prepared in five steps starting from 4-dimethylaminobenzoic acid. The synthesis of acyl azide was accomplished by “one-pot” Weinstock modification of the Curtius reaction.¹⁸ Here, the isolation of intermediate is not involved and the acyl azide was obtained in comparatively purer form and in good yield. The acyl azide was subjected to thermal decomposition in dry toluene at reflux temperature to yield isocyanate. Isocyanate subsequently was reacted with ethyl carbazate, and 1-ethoxycarbonyl-4-(4-dimethylaminophenyl) semicarbazide was obtained in quantitative yield (Scheme 1). Cyclization of compound 1-ethoxycarbonyl-4-(4-dimethylaminophenyl)



Scheme 2 Synthesis of model compound **7**.

semicarbazide with sodium ethoxide gave urazole. The purity of monomer **6** was checked by TLC. The ^1H NMR spectrum of **6** showed all peaks which are in agreement with the structure of compound **6** (Fig. 1). The structure of urazole was also confirmed by IR, UV-vis, fluorimetric, mass spectra, and elemental analysis.

Model compounds studies

DAPTD was allowed to react with excess acetyl chloride in DMAc solution at room temperature for 18 h and gave 1,2-bis(acetyl)-4-(4-dimethylaminophenyl)-1,2,4-triazolidine-3,5-dione (**7**) in high yield (Scheme 2). The compound **7** was characterized by IR, ^1H NMR, UV-vis, fluorimetric, mass spectra, and elemental analysis. The IR spectrum of **7** does not show any peaks around 3200 cm^{-1} for the N—H bond, this indicates that both N—H's have been reacted with acetyl chloride. It also shows peaks at

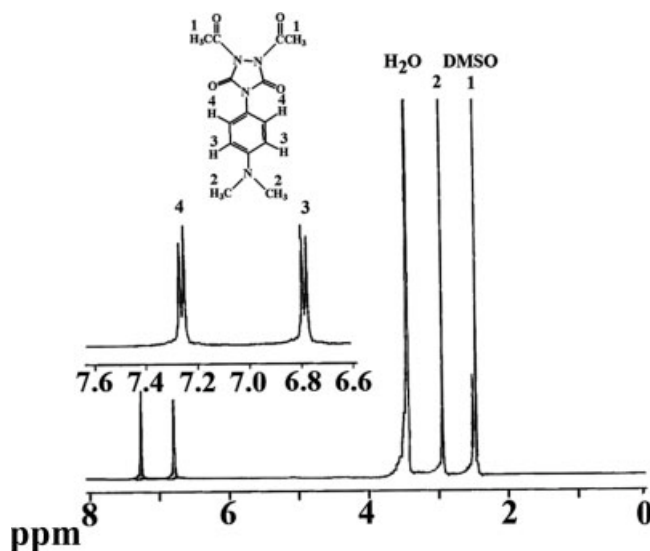
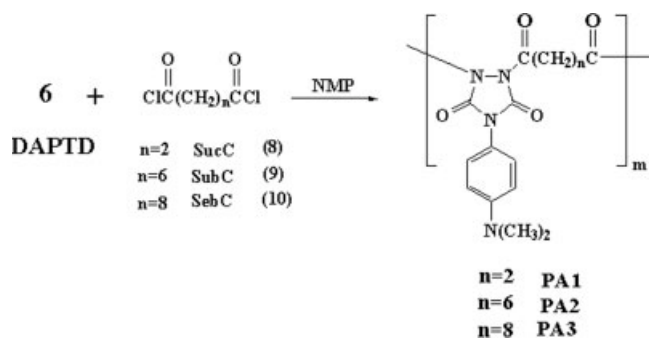


Figure 2 ^1H NMR (500 MHz) Spectrum of model compound **7** in $\text{DMSO}-d_6$ at room temperature.



Scheme 3 Polycondensation reactions of monomer 6 with aliphatic diacid chlorides.

1752 and 1725 cm^{-1} for the carbonyl groups which are related to the urazole moiety and acetyl groups. The ^1H NMR spectrum of 7 showed all peaks which are in agreement with the structure of compound 7 (Fig. 2). The purity of this model compound 7 was checked by TLC.

Polymerization reactions

Because 1,2-bisacetyl-4-(4-dimethylaminophenyl)-1,2,4-triazolidine-3,5-dione (7) as a model compound 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 (8), SubC (9), and SebC (10) were selected as diacid chlorides. The polymerization reaction of monomer 6 with these diacid chlorides were performed under conventional solution polymerization techniques at low as well as high temperature in the presence of different catalysts PA1-PA3 (Scheme 3). The polymerization reaction of monomer 6 with SucC was carried out by three different methods. In Method I, the reaction mixture was kept at -5°C , and then it was allowed to come to room temperature in the

TABLE I
Reaction Conditions for the Polymerization of Monomer DAPTD (6) with SucC (8) by Different Methods and Some Physical Properties for PA1A-PA1F

Polymer	Method ^a	Catalyst	Yield (%)	η_{inh} (dL/g) ^d
PA1A	I	Py ^b	77	0.16
PA1B	I	TEA ^c	68	0.19
PA1C	II	Py	68	0.15
PA1D	II	TEA	65	0.21
PA1E	III	Py	78	0.16
PA1F	III	TEA	85	0.19

^a Method I: reaction time: 3 h, -5°C , 24 h, room temperature; Method II: 3 h, -5°C , 12 h, room temperature, 6 h, 60°C , 10 h, 85°C ; Method III: refluxing at 1 min.

^b Pyridine.

^c Triethylamine.

^d Measured at a concentration of 0.5 g/dL in DMF at 25°C .

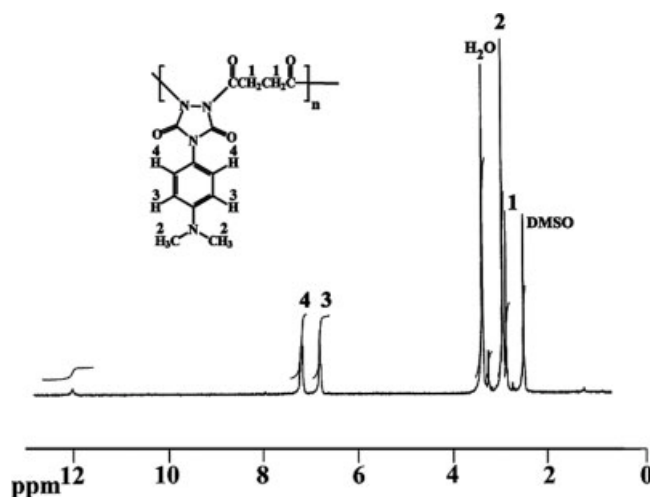


Figure 3 ^1H NMR (500 MHz) Spectrum of PA1 in $\text{DMSO}-d_6$ at room temperature. Peak at 12 ppm is related to COOH end group.

presence of pyridine and triethylamine, respectively. The resulting polyamides PA1A and PA1B have moderate inherent viscosity, and yield. In Method II, the reaction mixture was kept at -5°C and was allowed to come to room temperature and then was heated gradually at 60 and at 85°C in the presence of pyridine and triethylamine, respectively. The resulting polyamides PA1C and PA1D have moderate inherent viscosity and yield. In Method III, the reaction mixture was refluxed up for 1 min in NMP. The resulting polyamides PA1E and PA1F have high yield and good inherent viscosity. Reaction conditions and some physical properties for PA1A-PA1F are summarized in Table I. The resulting polymers were characterized by IR, ^1H NMR, elemental analysis, UV-vis, and TGA. The IR spectrum of polymer PA1 showed two peaks at 1778 and 1712 cm^{-1} for the carbonyl groups. The ^1H NMR spectrum (Fig. 3)

TABLE II
Reaction Conditions for the Polymerization of Monomer DAPTD (6) with SubC (9) by Different Methods and Some Physical Properties for PA2A-PA2F

Polymer	Method ^a	Catalyst	Yield (%)	η_{inh} (dL/g) ^d
PA2A	I	Py ^b	73	0.13
PA2B	I	TEA ^c	72	0.14
PA2C	II	Py	71	0.14
PA2D	II	TEA	79	0.15
PA2E	III	Py	74	0.12
PA2F	III	TEA	79	0.15

^a Method I: reaction time: 3 h, -5°C , 24 h, room temperature; Method II: 3 h, -5°C , 12 h, room temperature, 6 h, 60°C , 10 h, 85°C ; Method III: refluxing at 1 min.

^b Pyridine.

^c Triethylamine.

^d Measured at a concentration of 0.5 g/dL in DMF at 25°C .

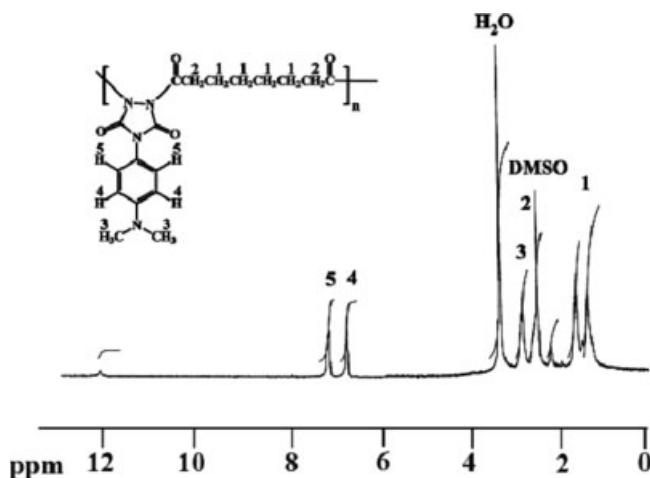


Figure 4 ^1H NMR (500 MHz) Spectrum of PA2 in $\text{DMSO-}d_6$ at room temperature. Peak at 12 ppm is related to COOH end group.

of polymer PA1 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 6 with SubC was also carried out by three different methods (Table II). We obtained comparable results of three methods.

The IR spectrum of polymer PA2 showed two strong peaks at 1749 and 1708 cm^{-1} for the carbonyl groups, which are related to the urazole moiety and amide groups. The ^1H NMR spectrum (Fig. 4) of polymer PA2 showed peaks that confirmed its chemical structure.

The polymerization reaction of monomer 6 with SebC was also performed by three different methods (Table III). Here also we obtained comparable results of three methods.

TABLE III
Reaction Conditions for the Polymerization of Monomer DAPTD (6) with SebC (10) by Different Methods and Some Physical Properties for PA3A-PA3F

Polymer	Method ^a	Catalyst	Yield (%)	η_{inh} (dL/g) ^d
PA3A	I	Py ^b	71	0.10
PA3B	I	TEA ^c	71	0.11
PA3C	II	Py	75	0.12
PA3D	II	TEA	65	0.10
PA3E	III	Py	75	0.09
PA3F	III	TEA	76	0.12

^a Method I: reaction time: 3 h, -5°C , 24 h, room temperature; Method II: 3 h, -5°C , 12 h, room temperature, 6 h, 60°C , 10 h, 85°C ; Method III: refluxing at 1 min.

^b Pyridine.

^c Triethylamine.

^d Measured at a concentration of 0.5 g/dL in DMF at 25°C .

TABLE IV
UV-vis Spectra of Monomer 6, Model Compound 7, and Polymers PA1-PA3 in DMF

Code	Color	λ_{max} (nm)	A	ϵ ($\text{M}^{-1} \text{cm}^{-1}$)
Compound 6	White	262	0.729	251,551
		310	0.100	34,565
Compound 7	White	268	0.459	153,113
		309	0.085	28,373
PA1	White	264	0.499	124,997
		307	0.049	12,192
PA2	White	263	0.399	199,520
		304	0.068	33,830
PA3	White	269	0.256	155,212
		314	0.054	25,534

The IR spectrum of polymer PA3 showed two strong peaks at 1749 and 1698 cm^{-1} for the carbonyl groups which are related to the urazole moiety and amide groups.

The UV-vis spectra of the monomer 6, model compound 7, polyamides PA1, PA2, and PA3 were recorded in DMF and the data are shown in Table IV. It is apparent that the wavelength of maximum absorption is related to the dimethylaminophenyl group in the compounds. All of these compounds showed almost similar UV-vis spectra pattern.

Fluorescence spectra of the monomer 6, model compound 7, and PA1 were recorded in DMF and the data are presented in Table V. All of these compounds showed almost similar fluorescence spectra pattern. For example, the sample was excited at 260 nm and emission fluorescence wavelengths were observed at 361 and 427 nm. The fluorescent intensity of these compounds is almost medium. These fluorescent characteristic of monomer, model compound, and polymers are due to *N,N*-dimethylaminophenyl chromophore.¹⁹

The polymers PA1, PA2, and PA3 are soluble in organic solvents such as NMP, DMF, DMSO, DMAc, and in H_2SO_4 , partially soluble in methanol and

TABLE V
Fluorescence Spectra of Monomer 6, Model Compound 7, and Polymer PA1 in DMF

Code	C (10^{-6} M)	λ_{Ex} (nm)	λ_{Em} (nm)
Compound 6	2.90	269, 322 ^a	361, 427 ^c
		299, 324, 360 ^b	467, 499, 547 ^d
Compound 7	4.40	269, 322 ^a	357, 427 ^c
		294, 322, 357 ^b	465, 500, 530 ^d
PA1	2.90	266, 283 ^a	355, 427 ^c
		274, 319, 357 ^b	463, 496, 530 ^d

^a λ_{Em} for scanning excitation spectra = 260 nm.

^b λ_{Em} for scanning excitation spectra = 358 nm.

^c λ_{Ex} for scanning emission spectra = 260 nm.

^d λ_{Ex} for scanning emission spectra = 437 nm.

TABLE VI
Solubility of PA1–PA3^a

Solvent	PA1	PA2	PA3
DMAc	+	+	+
DMF	+	+	+
NMP	+	+	+
DMSO	+	+	+
H ₂ SO ₄	+	+	+
Pyridine	+	+	+
HOAc	±	±	±
EtOAc	–	–	–
CH ₃ CN	–	–	–
Toluene	–	–	–
MeOH	±	±	±
THF	–	–	–
EtOH	±	±	±
CHCl ₃	–	–	–
CH ₂ Cl ₂	–	–	–
H ₂ O	–	–	–
Acetone	–	–	–
Cyclohexane	–	–	–

(+) soluble at room temperature; (–) insoluble at room temperature; and (±) partially soluble.

^a Concentration: 5 mg mL⁻¹.

ethanol and are insoluble in solvents such as water, acetone, cyclohexane, and chloroform (Table VI).

Thermal properties

The thermal stability of the PA1, PA2, and PA3 were evaluated with TGA and DSC under a nitrogen atmosphere (Table VII). Thermal properties of the 5 and 10% weight loss (T₅, T₁₀) of the polymers and residue at 600°C (char yield) were used as criterions for their thermal stability. An examination of the data reveals that PAs are thermally stable up to 200°C. According to Table VII, it is clear that the PA1 (based on SucC) has higher thermal stability than the other PAs. DSC of these polymers was also run under a nitrogen atmosphere and we did not observe any *T_g* transitions. Typical TGA curves of PA1 are shown in Figure 5.

TABLE VII
Thermal Properties of PAs

Polymer	T ₅ (°C) ^a	T ₁₀ (°C) ^b	Char yield (%) ^c
PA1	291	306	24
PA2	210	280	12
PA3	230	250	–

^a Temperature at which 5% weight loss was recorded by TGA at heating rate of 10°C/min in N₂.

^b Temperature at which 10% weight loss was recorded by TGA at heating rate of 10°C/min in N₂.

^c Percentage weight of material left undecomposed after TGA analysis at a temperature of 600°C in N₂.

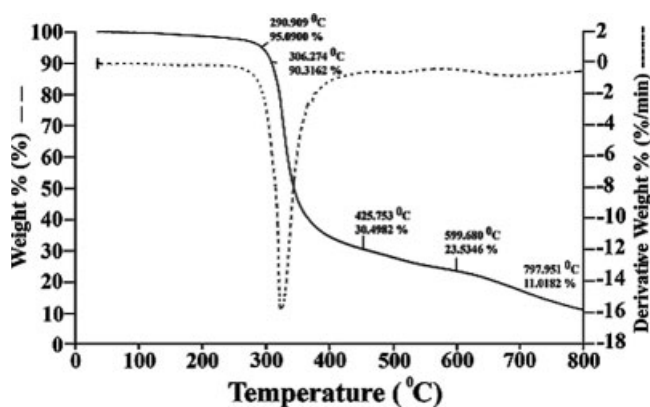


Figure 5 TGA/DTG of PA1 with a heating rate of 10°C/min in nitrogen atmosphere.

CONCLUSIONS

This investigation has shown that DAPTD (6) 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 6 can act as a bifunctional monomer and its polymerization reaction with aliphatic diacid chlorides gave novel polyamides with dimethylaminophenyl containing urazole linkages having inherent viscosities of 0.09–0.21 dL/g, which roughly correspond to molecular weight of 4000–15,000 g/mol. The resulting PAs have low molecular weight, this could be because of the cyclization reactions.^{20,21} On the other hand, the presence of NH and COOH end groups by ¹H NMR indicate the formation of linear polymer, then it could be concluded that both cyclic as well as linear structures are formed in this polymerization process. Although all catalysts used in these polymerization reactions are useful, triethylamine seems to be more effective. We are currently using this method for the synthesis of novel polymers and modification of polymers. The resulting polyamides exhibit moderate fluorescent activity and can be used as photoactive tracers.

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