

# Microwave-Assisted Rapid Polycondensation Reaction of 4-(4'-Acetamidophenyl)-1,2,4-triazolidine-3,5-dione with Diisocyanates

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**ABSTRACT:** 4-(4'-Aminophenyl)-1,2,4-triazolidine-3,5-dione was reacted with 1 mol of acetyl chloride in dry *N,N*-dimethylacetamide (DMAc) at  $-15^{\circ}\text{C}$  and 4-(4'-acetamidophenyl)-1,2,4-triazolidine-3,5-dione [4-(4'-acetanilido)-1,2,4-triazolidine-3,5-dione] (APTD) was obtained in high yield. The reaction of the APTD monomer with excess *n*-isopropylisocyanate was performed at room temperature in DMAc solution. The resulting bis-urea derivative was obtained in high yield and was finally used as a model for the polymerization reaction. The step-growth polymerization reactions of monomer APTD with hexamethylene diisocyanate, isophorone diisocyanate, and tolylene-2,4-diisocyanate were performed under microwave irradiation and solution polymerization in the presence of pyridine, triethylamine, or

dibutyltin dilaurate as a catalyst. Polycondensation proceeded rapidly, compared with conventional solution polycondensation; it was almost completed within 8 min. The resulting novel polyureas had an inherent viscosity in the range of 0.07–0.17 dL/g in dimethylformamide or sulfuric acid at  $25^{\circ}\text{C}$ . These polyureas were characterized by IR,  $^1\text{H-NMR}$ , elemental analysis, and thermogravimetric analysis. The physical properties and structural characterization of these novel polyureas are reported. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2103–2113, 2004

**Key words:** 4-(4'-aminophenyl)-1,2,4-triazolidine-3,5-dione; polyureas; inherent viscosity; step-growth polymerization; thermal properties; thermogravimetric analysis

## INTRODUCTION

The synthesis, characterization, and applications of polyesters, polyamides, polyurethane, and polyimide have been widely studied; but few works have been reported on the synthesis of polyureas. This could be due to their high melting points and low solubility. Because polyureas have a  $-\text{NH}-\text{CO}-\text{NH}-$  functional group, they can make hydrogen bonds from different sides. Polyureas are polyamides of carbonic acid; they are tough, high melting, and suitable for fiber applications.<sup>1</sup> A number of methods have been used to prepare polyureas, but the best method is to react diamine with diisocyanates. This reaction is a step-growth addition reaction of amine across the carbon–nitrogen double bond and there is no by-product. Polyureas have been used for many applications including encapsulation of pharmaceuticals, ink, dyes, and modification of wool fibers by interfacial grafting techniques.<sup>2</sup>

4-Substituted urazoles are five-member heterocyclic compounds, which have two N—H protons. These protons are rather acidic. The urazole derived from the ene reaction of triazolinediones with alkenes and polydienes has one N—H proton. The acidity of this proton has been measured and it is quite acidic with a  $\text{p}K_a$  of 4.71, which is almost the same as that of acetic acid.<sup>3</sup> Urazole compounds have the potential to undergo N-acylation. 4-Substituted urazoles were converted to 1-acyl derivatives by acylation reactions with a series of carboxylic acid anhydrides.<sup>4</sup> A simplified procedure for the N-acylation of oxazolidin-2-one chiral auxiliaries has also been reported.<sup>5</sup>

We recently took advantage of these acidic N—H protons in a compound, 1-methyl-2,5-bis(4-phenylurazoyl)pyrrole, and synthesized novel polymers via N-alkylation and N-acylation reactions.<sup>6,7</sup> Polymerization of the compound 4-phenylurazole (PHU) with phosgene, terephthaloyl chloride, and epichlorohydrin reportedly produces insoluble polymers.<sup>8</sup> In contrast, polymerization of PHU with aliphatic diacid chlorides gave soluble polyamides with an inherent viscosity of 0.39 dL/g.<sup>9</sup> Copolymerization of 4-cyclohexylurazole (CHU) with aliphatic diacid chlorides yielded soluble polyamides.<sup>10</sup>

In a previous article we reported the reaction of PHU and CHU and other urazole derivatives with diisocyanates.<sup>11–16</sup> The resulting novel polyureas had

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inherent viscosities in the range of 0.04–0.23 dL/g. Some of them are photoactive materials as well as polymeric dyes.

Here we wish to report the successful microwave-assisted step-growth polymerization reactions in which as the novel monomer 4-(4'-acetamidophenyl)-1,2,4-triazolidine-3,5-dione [4-(4'-acetanilido)-1,2,4-triazolidine-3,5-dione] (APTD) is used for the synthesis of soluble polyureas.

## EXPERIMENTAL

### Materials and methods

The reagents were purchased from Fluka Chemical (Buchs, Switzerland), Aldrich Chemical (Milwaukee, WI), and Riedel-deHaen AG (Seelze, Germany). 4-(4'-Aminophenyl)-1,2,4-triazolidine-3,5-dione [4-(4'-aminophenyl)urazole] (**1**) was prepared in six steps according to our previous work.<sup>17</sup> *N,N*-Dimethylacetamide (DMAc) was dried over BaO and then distilled under reduced pressure. The <sup>1</sup>H-NMR spectra at 90 and 500 MHz were recorded on a Varian EM-390 (Varian Associates, Palo Alto, CA) and a Bruker Avance 500 instrument, respectively. Tetramethylsilane (TMS) was used as an internal reference. The IR spectra were recorded on a Shimadzu 435 IR spectrophotometer, and the spectra of the solids were determined using KBr pellets.

The apparatus used for the polycondensation was a Samsung domestic microwave oven (2450 MHz, 900 W) without any modification. However, all of the polymerization reactions were carried out in a hood with strong ventilation.

All melting points were taken with a Gallenham melting point apparatus. The inherent viscosities were measured by a standard procedure using a Cannon Fensk Routine viscometer. The thermogravimetric analysis (TGA) data for the polymers were gathered on a Mettler TGA-50. Elemental analyses were performed at Malek Ashter University (Tehran).

### Preparation of APTD (**3**)

Compound **1** (3.00 g,  $1.56 \times 10^{-3}$  mol) was dissolved in 3 mL of dry DMAc in a 25-mL round-bottom flask. The solution was cooled to  $-15^{\circ}\text{C}$  in an ice-salt bath. A solution of 1.22 g ( $1.56 \times 10^{-3}$  mol, 1.11 mL) of acetyl chloride (**2**) in 0.5 mL of dry DMAc was added dropwise, and the mixture was kept at this temperature for 8 h. Then it was stirred at room temperature overnight. The reaction mixture was poured into 50 mL of water. The white solid was filtered off and dried to give a yield of 3.33 g (91%). Recrystallization from hot water produced white crystals (m.p.  $292\text{--}293^{\circ}\text{C}$ ).

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)  $\text{cm}^{-1}$ . <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ ): 2.09 (s, 3H, CH<sub>3</sub>), 7.34–7.36 (d, 2H, Ar—H, *J* = 8.75 Hz), 7.65–7.67 (d, 2H, Ar—H, *J* = 8.75 Hz), 10.09 (s, 1H, N—H), 10.41 (s, br, 2H, N—H). ANAL. Calcd for C<sub>10</sub>H<sub>10</sub>N<sub>4</sub>O<sub>3</sub>: C, 51.28%; H, 4.30%; N, 23.92%. Found: C, 51.60%; H, 4.61%; N, 24.65%.

### Reaction of APTD with *n*-propylisocyanate (model compound **4**)

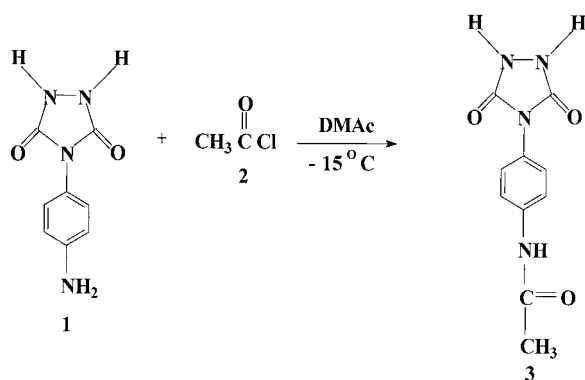
Compound **3** (0.30 g,  $7.42 \times 10^{-4}$  mol) was dissolved in 1 mL of dry DMAc in a 25-mL round-bottom flask; excess *n*-propylisocyanate (0.695 mL,  $7.42 \times 10^{-3}$  mol) was added to it, and the solution was stirred for 16 h at room temperature. The excess *n*-propylisocyanate was removed under a vacuum. The reaction mixture was precipitated in 50 mL of distilled water. The resulting solid was filtered off and dried to give 0.453 g (87.5%) of a white solid. This solid was recrystallized from acetone-water and yielded white crystals of 1,2-bis-(*n*-propylamidocarbonyl)-4-[4'-(acetamidophenyl)]-1,2,4-triazolidine-3,5-dione (**4**; m.p.  $262^{\circ}\text{C}$ , dec).

IR (KBr): 3350 (m, sh), 3310 (m), 3100 (w), 2960 (m), 2940 (m), 2870 (w), 1792 (m), 1730 (s), 1667 (s), 1600 (m), 1520 (s), 1457 (w), 1410 (s), 1380 (w, sh), 1370 (w), 1320 (m), 1260 (m), 1250 (m), 1207 (m), 1180 (w), 1157 (w), 1110 (w), 1070 (w), 1045 (w), 1015 (w), 970 (w), 847 (w, sh), 820 (m), 750 (m), 690 (w), 670 (w), 593 (w), 518 (m)  $\text{cm}^{-1}$ . <sup>1</sup>H-NMR (90 MHz, DMSO-*d*<sub>6</sub>, TMS,  $\delta$ ): 0.80–1.05 (t, 6H, *J* = 4.50 Hz), 1.40–1.70 (m, 4H), 2.05–2.20 (s, 3H), 3.00–3.45 (m, 4H), 7.40–7.60 (d, 2H, *J* = 4.50 Hz), 7.75–8.05 (m, 4H), 10.15–10.25 (s, 1H). ANAL. Calcd for C<sub>18</sub>H<sub>24</sub>N<sub>6</sub>O<sub>5</sub>: C, 53.46%; H, 5.98%; N, 20.78%. Found: C, 52.82%; H, 6.18%; N, 20.74%.

### Polymerization of APTD with hexamethylene diisocyanate (HMDI)

#### Method I

The APTD (0.1614 g,  $6.89 \times 10^{-4}$  mol) was added to a solution of HMDI (**5**; 0.1159 g,  $6.89 \times 10^{-4}$  mol) and pyridine (0.112 mL,  $1.38 \times 10^{-3}$  mol) in 0.5 mL of dry DMAc in a 25-mL round-bottom flask. The solution was stirred for 24 h at room temperature, 24 h at  $60^{\circ}\text{C}$ , and 92 h at  $75^{\circ}\text{C}$ . During this period we added 0.3 mL of DMAc. The viscous solution was precipitated in 30 mL of methanol/distilled water (50:50). The solid was filtered off and dried to give 0.220 g (79.5%) of off-white polyurea (PU1A; m.p.  $184^{\circ}\text{C}$ , dec). This polymerization was also repeated using dibutyltin dilaurate (DBTDL) and triethylamine (TEA) as catalysts.



Scheme 1 The synthesis of monomer 3.

#### Method II

The above polymerization was repeated, but the reaction mixture was refluxed in DMAC in the presence of DBTDL as a catalyst.

#### Method II

The same polymerization was used, but the reaction mixture was irradiated in a microwave oven at 100% power for 8 min in DMAC using pyridine as a catalyst.

IR (KBr): 3300 (m), 2920 (m), 2850 (m), 1780 (m), 1730 (s), 1690 (m), 1670 (m), 1610 (m), 1570 (m), 1542

(m), 1510 (s), 1472 (w), 1425 (w, sh), 1410 (m), 1370 (w), 1312 (m), 1250 (m), 1180 (w), 1140 (w), 1110 (w), 1070 (w), 1010 (w), 970 (w), 837 (m), 520 (w)  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (500 MHz,  $\text{DMSO-}d_6$ ,  $\delta$ ): 1.24–1.49 (m, br, 8H,  $\text{CH}_2$ ), 2.07 (s, 3H,  $\text{CH}_3$ ), 3.23 (m, br, 4H,  $\text{CH}_2$ ), 5.74 (s, br, N—H), 7.38 (s, br, 2H, Ar—H), 7.67 (s, br, 2H, Ar—H), 7.80 (s, br, N—H), 10.12 (s, 1H, N—H), 11.75 (s, br, N—H). ANAL. Calcd for  $\text{C}_{18}\text{H}_{22}\text{N}_6\text{O}_5$ : C, 53.73%; H, 5.51%; N, 20.88%. Found: C, 54.39%; H, 7.12%; N, 20.52%.

#### Polymerization of APTD with isophorone diisocyanate (IPDI)

##### Method I

In a 25-mL round-bottom flask the APTD (0.1385 g,  $5.91 \times 10^{-4}$  mol) was added to a solution of IPDI (6; 0.1314 g,  $5.91 \times 10^{-4}$  mol) and pyridine (0.095 mL,  $1.18 \times 10^{-3}$  mol) in 0.6 mL of dry DMAC. The solution was stirred for 24 h at room temperature, 24 h at  $70^{\circ}\text{C}$ , and 44 h at  $85^{\circ}\text{C}$ . DMAC (0.3 mL) was added during this period. The viscous solution was precipitated in 30 mL of methanol/distilled water (80:20), and the solid was filtered off and dried to give 0.240 g (83%) of off-white polyurea (PU2A; m.p.  $229^{\circ}\text{C}$ , dec). This polymerization was also repeated using DBTDL and TEA as catalysts.

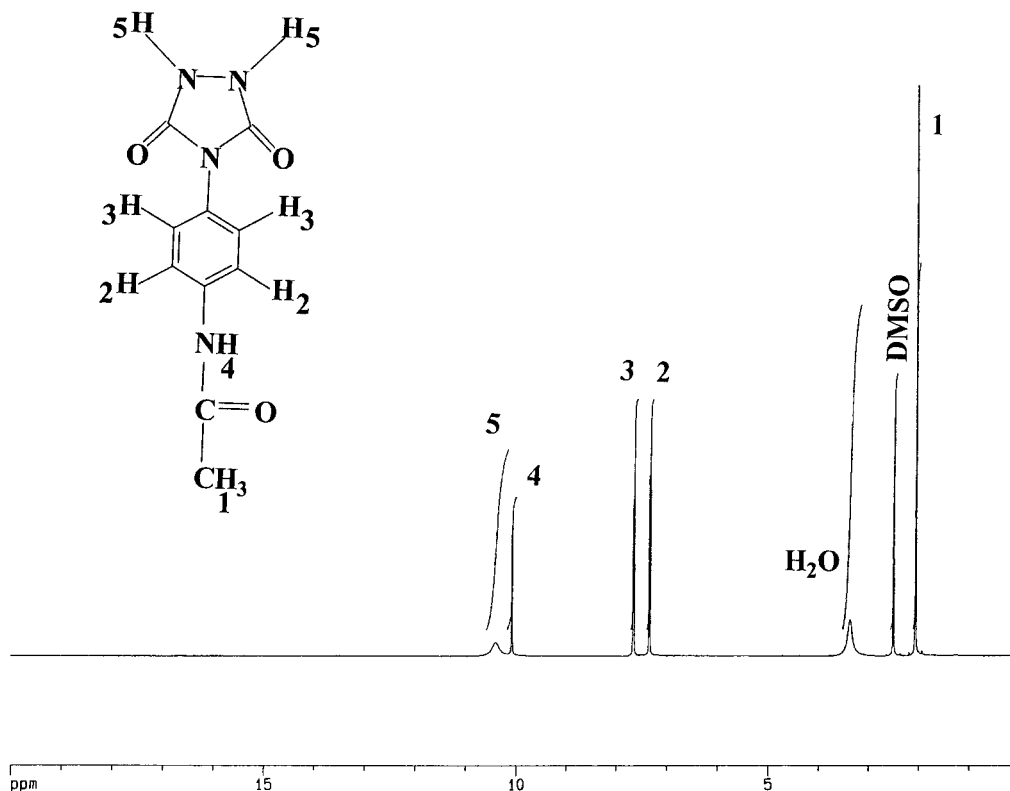
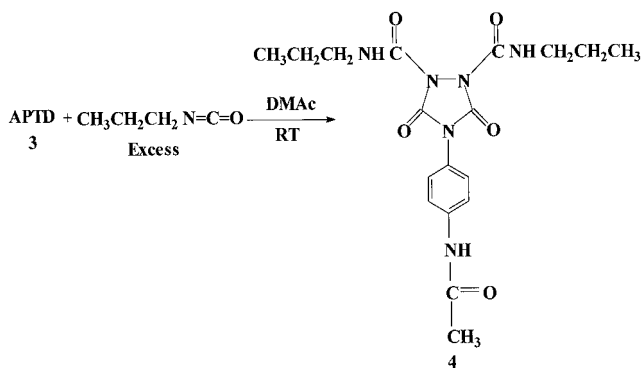


Figure 1 The  $^1\text{H-NMR}$  (500 MHz) spectrum of monomer 3 in  $\text{DMSO-}d_6$  at room temperature.



**Scheme 2** The preparation of model compound **4**.

#### Method II

This polymerization was repeated, but the reaction mixture was refluxed in DMAc in the presence of DBTDL as a catalyst.

#### Method III

The same polymerization was utilized, but the reaction mixture was irradiated in a microwave oven at

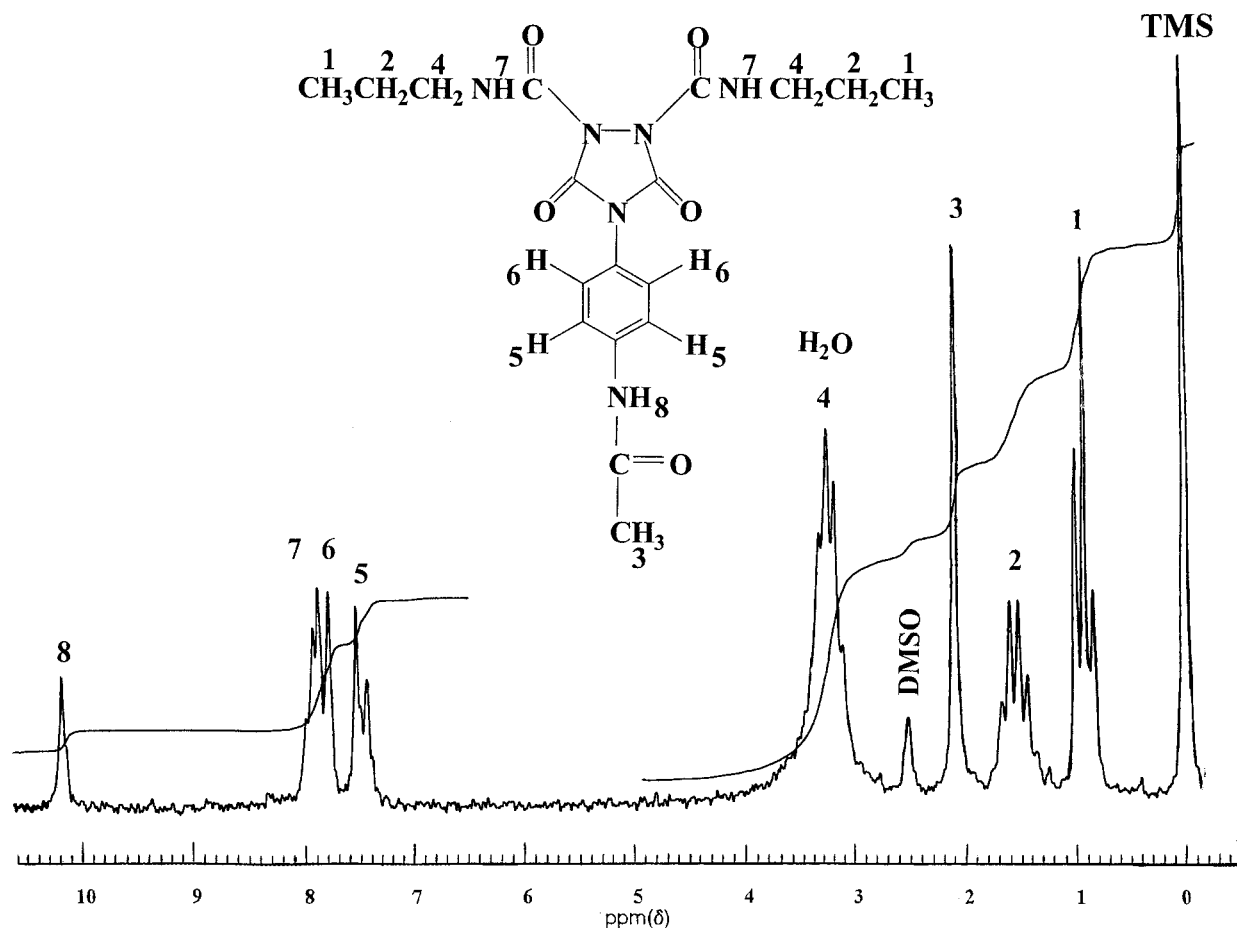
100% power for 8 min in DMAc with pyridine as a catalyst.

IR (KBr): 3330 (m), 2900 (m), 1770 (m), 1740–1690 (s, br), 1605 (m), 1560 (m), 1505 (s), 1460 (m), 1420 (s, sh), 1410 (s), 1385 (m), 1370 (m), 1310 (m), 1250 (m, br), 1140 (m), 1050 (w), 1012 (w), 960 (w), 940 (w), 832 (m), 752 (m), 733 (m), 710 (w), 520 (w)  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (500 MHz,  $\text{DMSO-}d_6$ ,  $\delta$ ): 0.88–1.05 (m, br, 11H,  $\text{CH}_3$ ,  $\text{CH}_2$ ), 1.30–1.77 (m, br, 4H,  $\text{CH}_2$ ), 2.07 (s, 3H,  $\text{CH}_3$ ), 2.73–2.79 (m, 2H,  $\text{CH}_2$ ), 3.67 (m, br, 1H, CH), 5.52–5.90 (m, br), 7.36–7.69 (m, 6H, Ar—H, N—H), 10.14 (s, 1H, N—H), 11.91 (s, br, N—H). ANAL. Calcd for  $\text{C}_{22}\text{H}_{28}\text{N}_6\text{O}_5$ : C, 57.88%; H, 6.18%; N, 18.41%. Found: C, 60.14%; H, 6.04%; N, 16.92%.

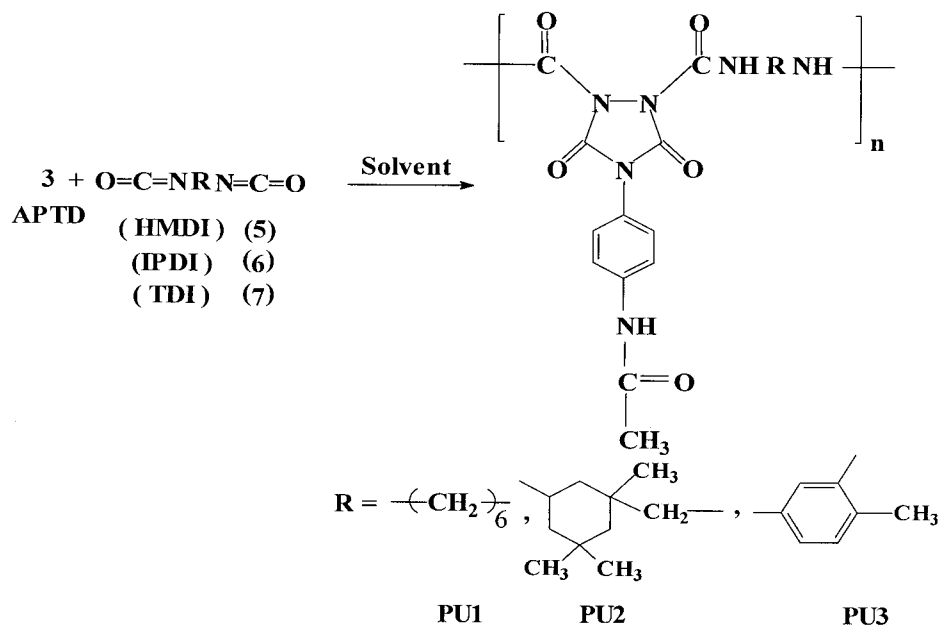
#### Polymerization of APTD with tolylene-2,4-diisocyanate (TDI)

##### Method I

APT D (0.1252 g,  $5.34 \times 10^{-4}$  mol) was added to a solution of TDI (7; 0.0931 g,  $5.34 \times 10^{-4}$  mol) and TEA (0.149 mL,  $1.07 \times 10^{-3}$  mol) in 0.5 mL of dry DMAc in a 25-mL round-bottom flask. The solution was stirred for 24 h at room temperature, 24 h at  $70^\circ\text{C}$ , and 46 h at



**Figure 2** The  $^1\text{H-NMR}$  (90 MHz) spectrum of model compound **4** in  $\text{DMSO-}d_6$  at room temperature.



**Scheme 3** The polycondensation reactions of monomer 3 with diisocyanates.

85°C. Over this period we added 1.0 mL of DMAc. A viscous solution was precipitated in 30 mL of methanol/distilled water (20:80). The solid was filtered off and dried to yield 0.1801 g (82.5%) of pale-brown polyurea (PU3C; m.p. 265°C, dec). This polymerization was also repeated using DBTDL and pyridine as catalysts.

#### Method II

We repeated the above polymerization, but the reaction mixture was refluxed in DMAc in the presence of DBTDL as the catalyst.

#### Method III

The same polymerization was used, but the reaction mixture was irradiated in a microwave oven at 100% power for 8 min in DMAc with pyridine as the catalyst.

IR (KBr): 3450–3200 (s, br), 2950 (m), 1780 (w), 1650 (s), 1610 (s), 1520 (s, br), 1470 (w), 1408 (m), 1310 (m), 1220 (m), 1120 (w), 1040 (w), 1010 (w), 960 (w), 940 (w), 870 (w), 810 (w), 667 (w), 600 (w, br), 540 (w)  $\text{cm}^{-1}$ .  
 $^1\text{H-NMR}$  (500 MHz,  $\text{DMSO-}d_6$ ,  $\delta$ ): 2.09–2.22 (s, br, 6H,  $\text{CH}_3$ ), 7.06–8.49 (m, 7H, Ar–H, N–H), 8.95–9.09 (m, br, Ar–H), 10.10 (s, 1H, N–H), 10.43 (s, br, N–H).

**TABLE I**  
 Reaction Conditions for Polymerization of Monomer APTD (3) with HMDI by Different Methods and Physical Properties for PU1A–PU1E

Polymer	Method <sup>a</sup>	Solvent	Catalyst	Reaction time	Nonsolvent	Yield (%)	Inherent viscosity (dL/g)	m.p. dec (°C)
PU1A	I	DMAc	Pyr	24 h, RT; 24 h, 60°C; 92 h, 75°C	MeOH/water	79.5	0.12 <sup>b</sup>	184
PU1B	I	DMAc	DBTDL	24 h, RT; 24 h, 60°C; 92 h, 75°C	MeOH/water	73.0	0.17 <sup>c</sup>	204–207
PU1C	I	DMAc	TEA	24 h, RT; 24 h, 60°C; 92 h, 75°C	MeOH/water	74.5	0.13 <sup>c</sup>	195
PU1D	II	DMAc	DBTDL	2 h	MeOH/water	62.0	0.09 <sup>c</sup>	186
PU1E	III	DMAc	Pyr	8 min	MeOH/water	82.5	0.15 <sup>c</sup>	198

Pyr, pyridine; DBTDL, dibutyltin dilaurate; TEA, triethylamine.

<sup>a</sup> Method I: gradual heating at different temperatures; method II: refluxing; method III: irradiating with a domestic microwave oven at 100% of its power.

<sup>b</sup> Measured at a concentration of 0.5 g/dL in DMF at 25°C.

<sup>c</sup> Measured at a concentration of 0.5 g/dL in  $\text{H}_2\text{SO}_4$  at 25°C.

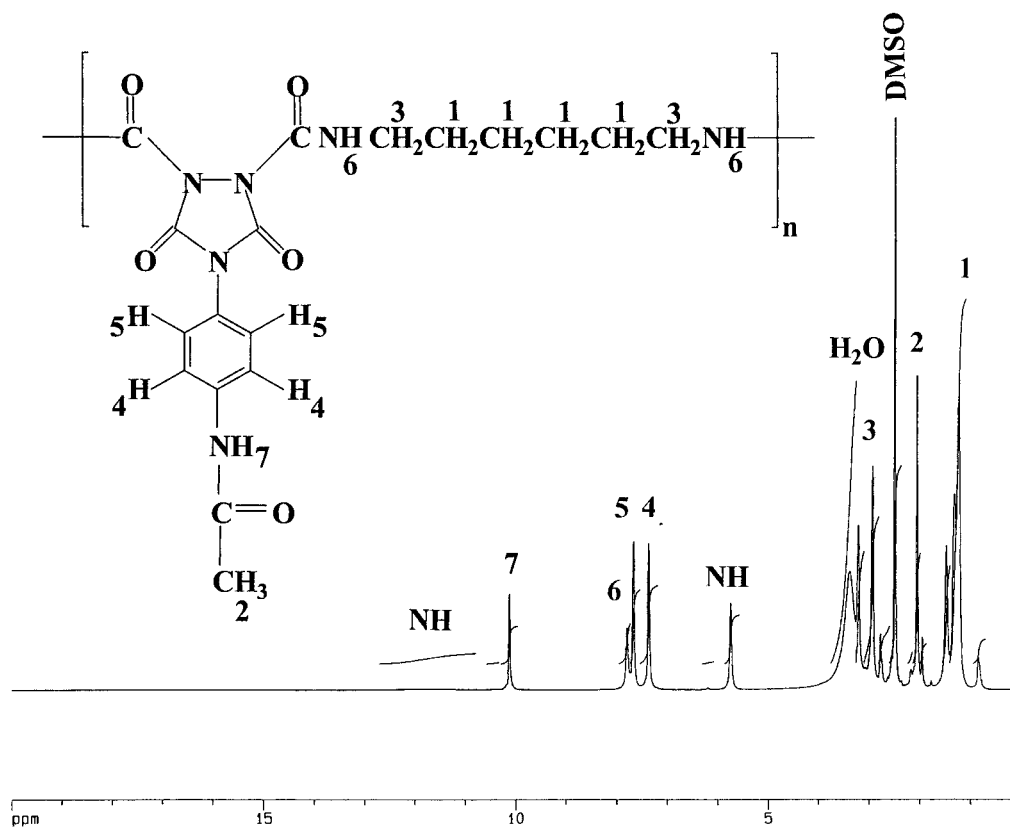


Figure 3 The  $^1\text{H-NMR}$  (500 MHz) spectrum of polymer PU1 in  $\text{DMSO-}d_6$  at room temperature.

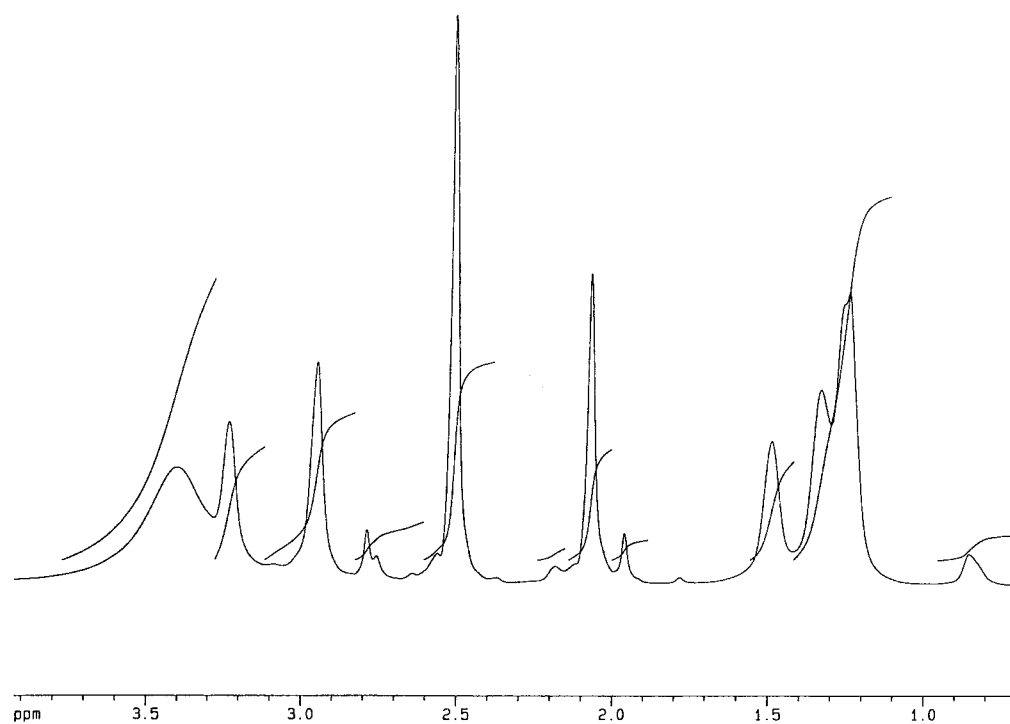
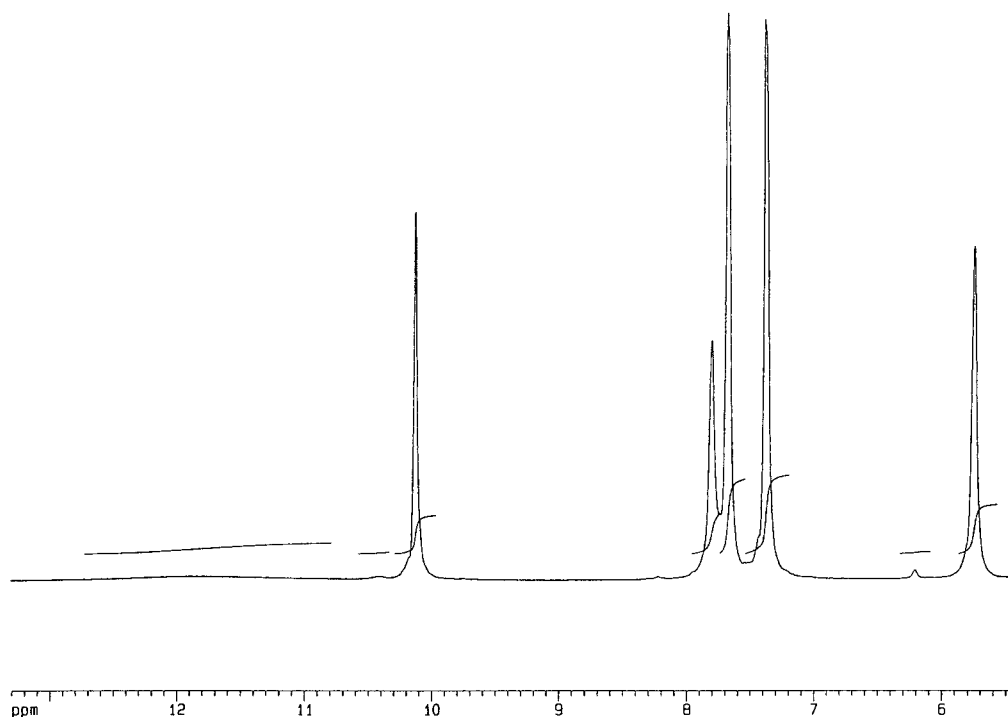


Figure 4 The  $^1\text{H-NMR}$  (500 MHz) spectrum of polymer PU1 in  $\text{DMSO-}d_6$  at room temperature. The expanded region is for aliphatic protons.



**Figure 5**  $^1\text{H-NMR}$  (500 MHz) spectrum of polymer PU1 in  $\text{DMSO-}d_6$  at room temperature. The expanded region is for aromatic protons.

ANAL. Calcd for  $\text{C}_{19}\text{H}_{16}\text{N}_6\text{O}_5$ : C, 55.88%; H, 3.95%; N, 20.58%. Found: C, 56.58%; H, 4.79%; N, 21.03%.

## RESULTS AND DISCUSSION

### Monomer synthesis

Compound **1** was prepared in six steps starting from 4-nitrobenzoic acid.<sup>13</sup> This compound has three N—H

sites with different reactivities. Therefore, it was reacted with 1 mol of acetyl chloride at  $-15\text{ }^\circ\text{C}$  (Scheme 1). Only the  $\text{NH}_2$  attached to the phenyl group was reacted, and two N—H groups of urazole were unaffected. The structure of compound **3** was confirmed by IR and  $^1\text{H-NMR}$  spectra and elemental analysis. The IR spectrum of **3** showed a strong peak at  $3340\text{ cm}^{-1}$  for the N—H bond and three peaks at 1780, 1710, and

**TABLE II**  
Reaction Conditions for Polymerization of Monomer APTD (**3**) with IPDI by Different Methods and Physical Properties for PU2A–PU2E

Polymer	Method <sup>a</sup>	Solvent	Catalyst	Reaction time	Nonsolvent	Yield (%)	Inherent viscosity (dL/g)	m.p. dec (°C)
PU2A	I	DMAc	Pyr	24 h, RT; 24 h, 70°C; 44 h, 85°C	MeOH/water	83.0	0.11 <sup>b</sup>	229
PU2B	I	DMAc	DBTDL	24 h, RT; 24 h, 70°C; 44 h, 85°C	MeOH/water	81.0	0.14 <sup>c</sup>	238
PU2C	I	DMAc	TEA	24 h, RT; 24 h, 70°C; 44 h, 85°C	MeOH/water	77.5	0.13 <sup>c</sup>	219
PU2D	II	DMAc	DBTDL	2 h	MeOH/water	64.0	0.14 <sup>c</sup>	228
PU2E	III	DMAc	Pyr	8 min	MeOH/water	77.5	0.14 <sup>c</sup>	232

Pyr, pyridine; DBTDL, dibutyltin dilaurate; TEA, triethylamine.

<sup>a</sup> Method I: gradual heating at different temperatures; method II: refluxing; method III: irradiating with a domestic microwave oven at 100% of its power.

<sup>b</sup> Measured at a concentration of 0.5 g/dL in DMF at 25°C.

<sup>c</sup> Measured at a concentration of 0.5 g/dL in  $\text{H}_2\text{SO}_4$  at 25°C.

**TABLE III**  
**Reaction Conditions for Polymerization of Monomer APTD (3) with TDI by Different Methods**  
**and Physical Properties for PU3A–PU3E**

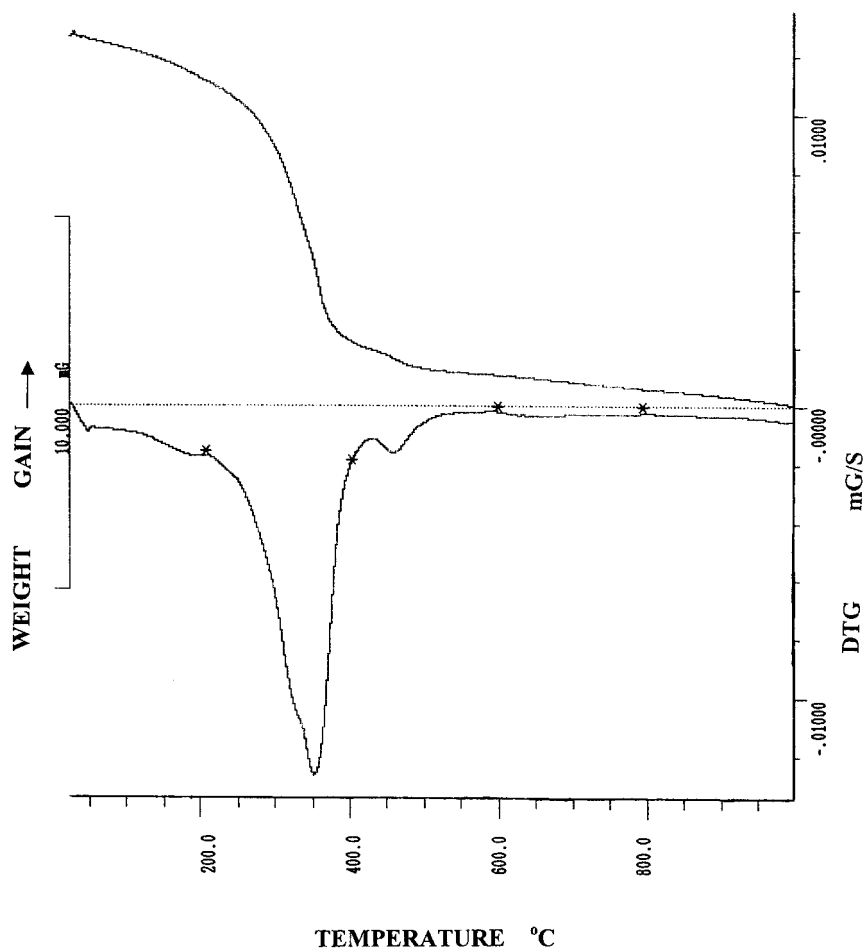
Polymer	Method <sup>a</sup>	Solvent	Catalyst	Reaction time	Nonsolvent	Yield (%)	Inherent viscosity (dL/g)	m.p. dec (°C)
PU3A	I	DMAc	Pyr	24 h, RT; 24 h, 70°C; 46 h, 85°C	MeOH/water	81.0	0.09 <sup>b</sup>	235
PU3B	I	DMAc	DBTDL	24 h, RT; 46 h, 85°C	MeOH/water	73.5	0.14 <sup>b</sup>	208
PU3C	I	DMAc	TEA	24 h, RT; 24 h, 70°C; 46 h, 85°C	MeOH/water	82.5	0.13 <sup>c</sup>	265
PU3D	II	DMAc	DBTDL	2 h	MeOH/water	68.5	0.14 <sup>b</sup>	248
PU3E	III	DMAc	Pyr	8 min	MeOH/water	81.0	0.13 <sup>b</sup>	230

Pyr, pyridine; DBTDL, dibutyltin dilaurate; TEA, triethylamine.

<sup>a</sup> Method I: gradual heating at different temperatures; method II: refluxing; method III: irradiating with a domestic microwave oven at 100% of its power.

<sup>b</sup> Measured at a concentration of 0.5 g/dL in H<sub>2</sub>SO<sub>4</sub> at 25°C.

<sup>c</sup> Measured at a concentration of 0.5 g/dL in DMF at 25°C.



**Figure 6** TGA and derivative TG (DTG) thermograms of polymer PU1 under a nitrogen atmosphere.



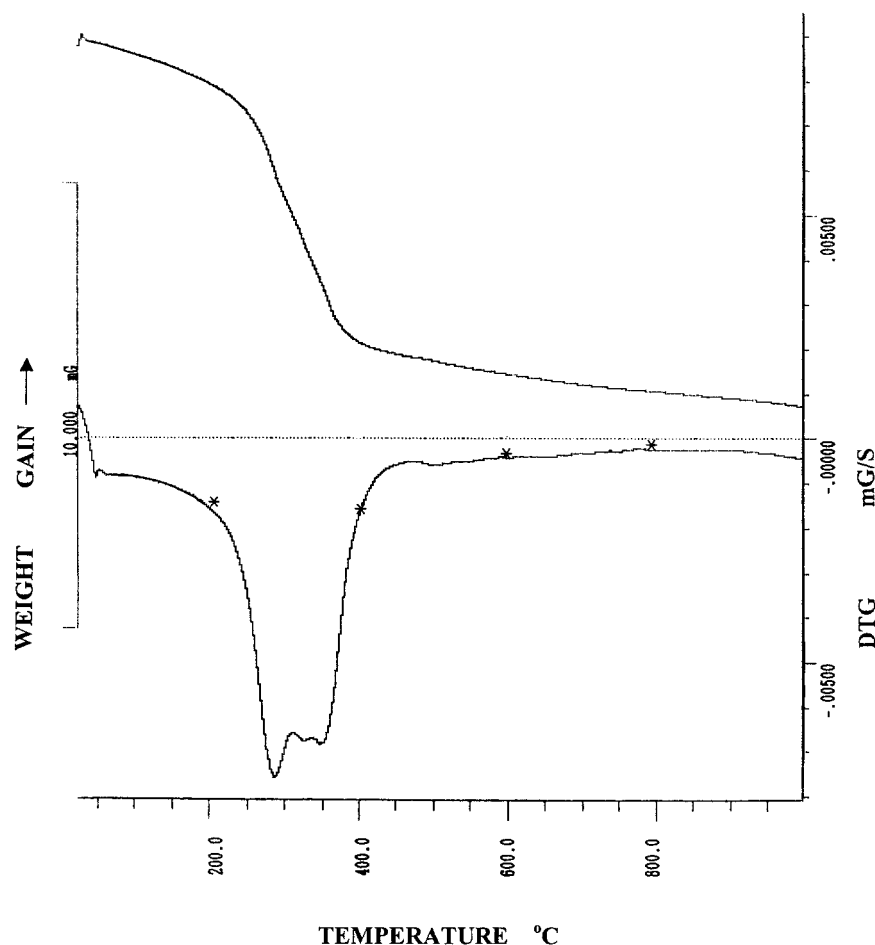


Figure 7 TGA and derivative TG (DTG) thermograms of polymer PU2 under a nitrogen atmosphere.

1673  $\text{cm}^{-1}$  for the carbonyl groups. The first two peaks are characteristic patterns for the urazole moiety. The  $^1\text{H-NMR}$  spectrum (Fig. 1) of **3** showed all peaks that are in agreement with the structure of compound **3**. The elemental analysis results are in good agreement with the structure of model compound **3**. The purity of **3** was checked by thin-layer chromatography, which shows one spot in the chloroform/methanol (50:50) mixture with a distance moved by substance ( $R_f$ ) value of 0.54. Compound **3** was used as a monomer for the polycondensation reactions.

#### Model compound studies

Because the APTD monomer has two N—H sites that can react with isocyanates, it would be interesting to examine the reactivity of these toward isocyanates. Thus, APTD was allowed to react with excess *n*-propylisocyanate in dry DMAc solution, which produced compound **4** in high yield (Scheme 2). Model compound **4** was characterized by IR,  $^1\text{H-NMR}$ , and elemental analysis. The IR spectrum of **4** showed a peak at 3350  $\text{cm}^{-1}$  for the N—H bond and three peaks at

1792, 1730, and 1667  $\text{cm}^{-1}$  for the carbonyl groups. The first two peaks are the characteristic pattern for the urazole moiety. The  $^1\text{H-NMR}$  spectrum (Fig. 2) of **4** showed all peaks that are in agreement with its structure. The elemental analysis results are in good agreement with the structure of model compound **4**. The purity of **4** was checked by thin-layer chromatography, which shows one spot in the ethyl acetate/cyclohexane (80:20) mixture with an  $R_f$  value of 0.47.

#### Polymerization reactions and characterization

Because model compound **4** was synthesized in good yield and purity, we became interested in performing this type of reaction for the formation of novel polyureas. Thus, HMDI (**5**), IPDI (**6**), and TDI (**7**) were selected as diisocyanates. The polymerization reactions of monomer **3** with these diisocyanates were performed under microwave irradiation as well as conventional solution polymerization techniques in the presence of catalysts PU1–PU3 (Scheme 3). The polymerization reaction of monomer **3** with HMDI was performed with three different methods. In

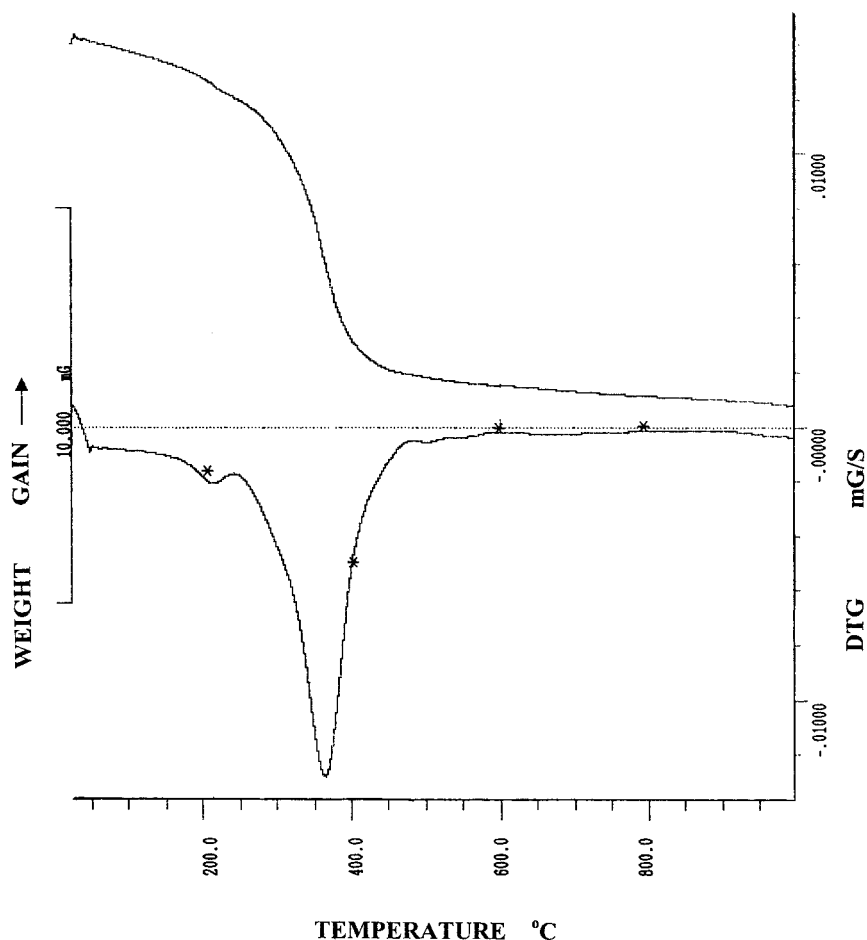


Figure 8 TGA and derivative TG (DTG) thermograms of polymer PU3 under a nitrogen atmosphere.

method I the reaction mixture was heated gradually from room temperature to 75°C in the presence of pyridine, DBTDL, and TEA. The resulting polyureas (PU1A–PU1C) have good yields and good inherent viscosities. In method II the reaction mixture was refluxed up to 120 min in DMAc. The resulting polyurea (PU1D) had a low yield and low inherent viscosity. In method III the polymerization reaction was performed in DMAc under microwave irradiation in the presence of pyridine as the catalyst. The resulting polyurea (PU1E) had a high yield and good inherent viscosity. The reaction conditions and physical properties for PU1A–PU1E are summarized in Table I. The resulting polymers were characterized by IR,  $^1\text{H-NMR}$ , elemental analysis, and TGA.

The IR spectrum of polymer PU1 showed a medium peak at  $3300\text{ cm}^{-1}$  for the N—H bond and two peaks at  $1780$  and  $1730\text{ cm}^{-1}$  for the carbonyl groups, which are characteristic patterns for the urazole moiety. The  $^1\text{H-NMR}$  (500 MHz) spectrum (Fig. 3) of polymer PU1 showed all peaks for aliphatic, aromatic, and N—H protons. The elemental analysis results are also in good agreement with the calculated percentages for the carbon, hydrogen, and nitrogen contents in the

polymer repeating unit. Figures 4 and 5 show the expanded region for aliphatic and aromatic protons.

The polymerization reaction of monomer 3 with IPDI was also carried out with three different methods (Table II). The best method is method III in which microwave irradiation was used and a shorter reaction time, high yield, and high viscosity were obtained. The IR spectrum of polymer PU2 showed two strong peaks at  $1770$  and  $1740\text{ cm}^{-1}$  for the carbonyl groups that are related to the urazole moiety. The  $^1\text{H-NMR}$  spectrum of polymer PU2 showed peaks that confirm its chemical structure. The elemental analysis results are also in good agreement with the calculated percentages for the carbon, hydrogen, and nitrogen contents in the polymer repeating unit of PU2.

The polymerization reaction of monomer 3 with TDI was also performed with three different methods (Table III). The best method in this case was also method III; a shorter reaction time, high yield, and good viscosity were obtained under microwave irradiation. The IR spectrum of polymer PU3 showed peaks and the  $^1\text{H-NMR}$  spectrum of polymer PU2 showed peaks that confirm their chemical structures. The elemental analysis results are also in good agree-

ment with the calculated percentages for the carbon, hydrogen, and nitrogen contents in the polymer repeating unit of PU3.

Polymers PU1, PU2, and PU3 are soluble in organic solvents such as DMF, DMSO, DMAc, and H<sub>2</sub>SO<sub>4</sub>. They are insoluble in solvents such as water, methanol, acetone, cyclohexane, and chloroform.

### Thermal properties

The thermal behavior of polyureas PU1, PU2, and PU3 were measured by TGA and derivative TGA at a rate of 10°C/min in a nitrogen atmosphere (Figs. 6–8). An examination of the data reveals that all of the above polyureas are thermally stable up to 200°C in the nitrogen atmosphere. All of these polymers show some weight loss below 100°C, which could be due to water or solvent loss. Polymers PU1, PU2, and PU3 show a 10% weight loss at 185, 213, and 206°C, respectively.

### CONCLUSIONS

This investigation has shown that APTD is an interesting monomer for polycondensation reactions. The compound has two acidic N—H groups, and it can be readily reacted with *n*-propylisocyanate to give a 1:2 adduct with high yield and high purity. Thus, compound **3** can act as a bifunctional monomer and its polymerization reaction with aliphatic and aromatic diisocyanates gave novel polyureas that contain urazole linkages in two dimension. The polycondensation reaction under microwave irradiation is the best method in this work for the synthesis of polyureas PU1–PU3. Furthermore, our results demonstrate that microwave heating is an efficient method (shorter reaction time and high energy efficiency) for polycon-

densation reactions. We are currently using this method for the synthesis of novel polymers and modification of polymers.

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