

# Synthesis of New Polyureas Derived from 4-Cyclohexylurazole

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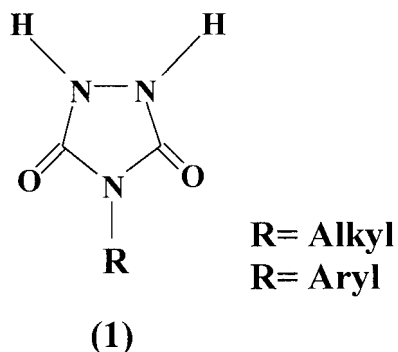
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**ABSTRACT:** 4-Cyclohexylurazole (**1**) R = cyclohexyl (**CHU**) was prepared from cyclohexyl isocyanate in two steps. Polycondensation reactions of compound **CHU** with hexamethylene diisocyanate (**HMDI**), isophorone diisocyanate (**IPDI**), and toluene-2,4-diisocyanate (**TDI**) were performed in DMAc/chloroform and DMAc in the presence of pyridine as a catalyst. The resulting novel polyureas have an inherent viscosity in the range of 0.044–0.206 g/dL in DMF at 25°C. These polyureas were characterized by IR, <sup>1</sup>H-NMR, elemental analysis, and TGA. The resulting polymers are soluble in most organic solvents. Some physical properties and structural characterization of these novel polyureas are reported. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1335–1341, 2001

**Key words:** 4-cyclohexylurazole; polyureas; solution polymerization; inherent viscosity; step-growth polymerization

## INTRODUCTION

4-substituted-Urazoles (**1**) are five-membered heterocyclic compounds and are important precursors for the synthesis of 4-substituted-1,2,4-triazoline-3,5-dione. These compounds



have two N–H protons, which are acidic. The urazole derived from the ene reaction of triazolinediones with alkenes and polydienes has one N–H proton, which seems to be very acidic. The acidity of this proton has been measured and is quite acidic with pK<sub>a</sub> of 4.71, which is almost the same as that of acetic acid.<sup>1</sup> The compounds (**1**) have the potential to undergo N-acylation. 4-substituted-Urazoles were converted to 1-acyl derivatives by acylation reaction with a series of carboxylic acid anhydrides.<sup>2</sup> A simplified procedure for the N-acylation of oxazolidin-2-one chiral auxiliaries has also been reported.<sup>3</sup>

Recently we were able to take advantage of these acidic N–H in a compound, 1-methyl-2,5-bis(4-phenylurazoly) pyrrole, and synthesize novel polymers via N-alkylation and N-acylation reactions.<sup>4,5</sup> Polymerization of compound 4-phenylurazole (**PHU**) with phosgene, terephthaloyl chloride, and epichlorohydrin was previously reported to give insoluble polymers.<sup>6</sup> Polymerization of compound **PHU** with aliphatic diacid chlorides gave soluble polyamides with inherent viscosity of 0.39 dL/g.<sup>7</sup> Copolymerization of 4-cyclohexylura-

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zole (**CHU**) with aliphatic diacid chlorides gave soluble polyamides.<sup>8</sup>

The aim of this investigation is to examine the step-growth polymerization reactions of **CHU** as a monomer with diisocyanates. In the present study we report on the successful polycondensation reaction, in which a **CHU** novel monomer is used for the synthesis of soluble polyureas.

## EXPERIMENTAL

### Materials and Equipment

Reagents were purchased from Fluka Chemical (Milwaukee, WI), Aldrich Chemical (Milwaukee, WI), and Riedel-de Haën AG (Seelze, Germany). DMAc (*N,N*-dimethylacetamide) was dried over BaO and then was distilled under reduced pressure. Chloroform was purified by washing with water, drying with CaCl<sub>2</sub>, and subsequent distillation under normal pressure. Proton nuclear magnetic resonance (<sup>1</sup>H-NMR, 90 MHz) spectra were recorded on a Varian EM-390 instrument (Varian Associates, Palo Alto, CA). Multiplicities of proton resonances are designated as singlet (s), doublet (d), triplet (t), multiplet (m), and broad (br). Tetramethylsilane (TMS) was used as an internal reference. IR spectra were recorded on a Shimadzu 435 IR spectrophotometer (Japan). Spectra of solids were carried out using KBr pellets. Vibrational transition frequencies are reported in wavenumber (cm<sup>-1</sup>). 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 and are uncorrected. Inherent viscosities were measured by standard procedure using a Cannon Fensk routine viscometer (Germany). Thermal gravimetric analysis (TGA) data for polymers were taken on a Mettler TGA-50. Elemental analyses were performed by Research Institute of Petroleum Industry, Tehran, I.R. Iran.

### Preparation of 1-Ethoxycarbonyl-4-cyclohexyl semicarbazide

Into a 500-mL three-necked round-bottom flask, equipped with a mechanical stirrer, water cooled condenser, and additional funnel, a solution of cyclohexyl isocyanate (10 g, 7.99 × 10<sup>-2</sup> mol) in 50 mL of toluene was added to a cooled (<10°C) solution of ethylcarbazate (8.32 g, 7.99 × 10<sup>-2</sup> mol) in 100 mL of toluene. The solution was

stirred at room temperature for 14 h and then was refluxed for 2 h. After cooling in a water bath the white crystals (18.06 g, 98.58%) were collected, mp = 124–125°C.

<sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, TMS): δ 1.0–2.0 (m, 13H); 3.3–3.7 (m, 1H); 4.15 (q, 2H); 6.1 (d, 1H); 7.60 (s, 1H); 8.70 (s, 1H).

### Preparation of 4-Cyclohexylurazole (**CHU**)

Into a 100-mL one-necked round-bottom flask 5.0 g (2.181 × 10<sup>-2</sup> mol) of 1-ethoxycarbonyl-4-cyclohexyl semicarbazide was added to a solution of sodium ethoxide (0.55 g, 0.0239 mol Na/30 mL of EtOH). A reddish-orange color solution was formed and the solution was refluxed for 24 h, during which time a white precipitate was formed. The flask was cooled in an ice bath and rapidly acidified with 2*N* hydrochloric acid (pH = 2) and filtered immediately. The white solid (3.97 g, 99.3%) was recrystallized from hot water, mp = 233–235°C.

IR (KBr): 3020 (s), 2900 (s), 2840 (s), 1760 (m), 1660 (s), 1465 (s), 1385 (m), 1325 (w), 1260 (m), 1235 (m), 1210 (m), 1080 (m), 1050 (w), 1030 (w), 995 (m), 890 (m), 855 (w), 800 (s), 775 (s), 665 (s) cm<sup>-1</sup>; <sup>1</sup>H-NMR (MDSO-*d*<sub>6</sub>, TMS): δ 1.0–2.5 (m, 10H); 3.64 (m, 1H); 10 (s, 2H).

### Polycondensation of CHU with HMDI

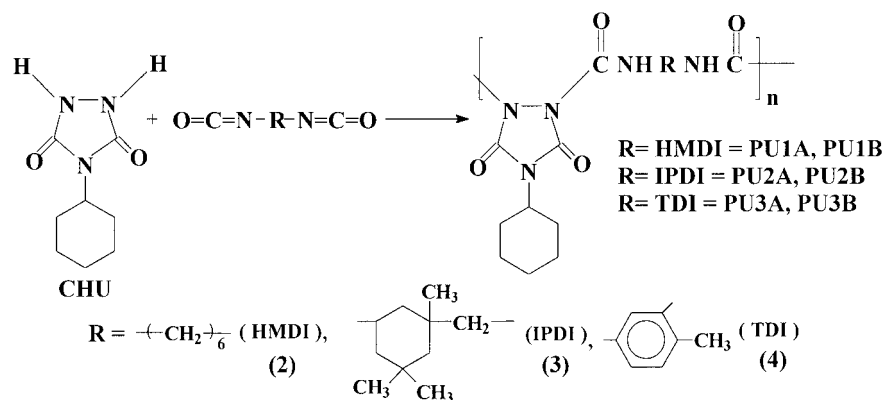
#### Method A

Into a 25-mL round-bottom flask was placed a solution of **CHU** (0.20 g, 1.092 × 10<sup>-3</sup> mol) in 0.6 mL of DMAc, to which was then added 0.25 ml of pyridine. To this solution, **HMDI** (0.175 mL, 0.183 g, 1.092 × 10<sup>-3</sup> mol) in 0.6 ml of dry chloroform was added. The mixture was stirred for 72 h at room temperature. The clear and viscous reaction mixture was precipitated in 50 mL of diethyl ether. The white solid **PU1A** was filtered and dried to give 0.310 g (81%), mp = 95–107°C; inherent viscosity (0.5 g/dL DMF, 25°C) = 0.075 dL/g.

IR (KBr): 3350 (m), 2900 (s), 2850 (s), 2250 (m), 1720 (s, br), 1510 (s, br), 1410 (s), 1380 (s), 1340 (m, sh), 1250 (s), 1200 (s), 1170 (s), 1120 (s), 1000 (s), 920 (m), 880 (m), 800 (w), 750 (s), 660 (w), 520 (m, br) cm<sup>-1</sup>.

#### Method B

The preceding experiment was repeated and only DMAc used as the reaction solvent. The reaction mixture was heated at 60°C for 144 h, then was



precipitated in 50 ml of water. The white solid **PU1B** was filtered off and dried to give 0.384 g (91.15%), mp = 95–99°C; inherent viscosity (0.5 g/dL DMF, 25°C) = 0.207 dL/g.

IR (KBr): 3350 (m), 2900 (s), 2850 (m), 1765 (m, sh), 1725 (s), 1695 (s), 1620 (m, br), 1540 (s, br), 1430 (s), 1380 (m), 1260 (m, br), 760 (m), 640 (m, br) cm<sup>-1</sup>. ANAL. calcd for C<sub>16</sub>H<sub>25</sub>N<sub>5</sub>O<sub>4</sub>: 54.68% C; 7.17% H; 19.93% N. Found: 54.70% C; 7.50% H; 20.20% N.

#### Polycondensation of CHU with IPDI

This polycondensation was performed by two methods similar to the procedures just described. In method A the resulting polymer was precipitated in ether. The white solid **PU2A** was filtered off and dried to give 0.260 g (59.00%), mp = 125–134°C; inherent viscosity (0.5 g/dL DMF, 25°C) = 0.029 dL/g.

IR (KBr): 3300 (w), 2900 (m), 2850 (m, sh), 2250 (m), 1720 (s, br), 1540 (m, sh), 1520 (s, br), 1410 (s), 1380 (m), 1340 (m, sh), 1200 (m, br), 1110 (w), 1000 (w), 740 (m, br) cm<sup>-1</sup>.

In method B the resulting polymer was precipitated in water. The white solid **PU2B** was filtered off and dried to give 0.440 g (99.09%), mp = 157–160°C; inherent viscosity (0.5 g/dL DMF, 25°C) = 0.044 dL/g.

IR (KBr): 3350 (m, br), 2900 (s), 2850 (m, sh), 2250 (w), 1780 (m, sh), 1730 (s), 1700 (s, sh), 1540 (s, br), 1420 (s), 1380 (m), 1310 (w), 1240 (m, br), 1120 (w), 1000 (w), 980 (w), 760 (m, br), 640 (m, br) cm<sup>-1</sup>. <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, TMS): δ 0.65–3.15 (m, br); 3.65–4.15 (m); 5.60 (s, br); 7.75 (s, br). ANAL. calcd for C<sub>20</sub>H<sub>30</sub>N<sub>5</sub>O<sub>4</sub>: 59.38% C; 7.48% H; 17.32% N. Found: 58.80% C; 7.80% H; 17.00% N.

#### Polycondensation of CHU with TDI

This polycondensation was performed by two methods similar to the procedures described earlier. In method A the resulting polymer was precipitated in ether. The white solid **PU3A** was filtered off and dried to give 0.320 g (82.00%), mp = 123–132°C; inherent viscosity (0.5 g/dL DMF, 25°C) = 0.029 dL/g. In method B the resulting polymer was precipitated in water. The white

**Table I** Reaction Conditions for the Polymerization of Monomer CHU with Diisocyanates in DMAC/CHCl<sub>3</sub> at Room Temperature in the Presence of Pyridine and Some Physical Properties for Polyureas PU1A, PU2A, and PU3A

Polyurea	Diisocyanates	Reaction Time (h)	Nonsolvent	Yield (%)	$\eta_{inh}^a$	Melting Point <sup>b</sup>
PU1A	HMDI	72	Ether	81.0	0.075	95–107
PU2A	IPDI	122	Ether	59.0	0.029	125–134
PU3A	TDI	31	Ether	82.0	0.029	123–132

<sup>a</sup> Inherent viscosity dL/g, measured at a concentration of 0.5 g/dL in DMF at 25°C.

<sup>b</sup> Measured by melting-point apparatus.

**Table II** Reaction Conditions for the Polymerization of Monomer **CHU** with Diisocyanates in **DMAc** at 60°C in the Presence of Pyridine and Some Physical Properties for Polyureas **PU1B**, **PU2B**, and **PU3B**

Polyurea	Diisocyanates	Reaction Time (h)	Nonsolvent	Yield (%)	$\eta_{inh}^a$	Melting Point <sup>b</sup>
PU1B	HMDI	144	Water	91.50	0.206	96–99
PU2B	IPDI	144	Water	99.09	0.044	157–160
PU3B	TDI	144	Water	74.36	0.078	233 (dec.)

<sup>a</sup> Inherent viscosity dL/g, measured at a concentration of 0.5 g/dL in DMF at 25°C.

<sup>b</sup> Measured by melting-point apparatus.

solid **PU3B** was filtered off and dried to give 0.290 g (74.36%), mp = 223°C (dec.); inherent viscosity (0.5 g/dL DMF, 25°C) = 0.078 dL/g.

IR (KBr): 3300 (s, br), 2900 (s), 2850 (m, sh), 2250 (w), 1790 (s, sh), 1730 (s), 1700 (s), 1640 (m), 1600 (s), 1540 (s, br), 1480 (m), 1420 (s), 1380 (m), 1310 (w), 1200 (m, br), 1000 (w), 980 (w), 760 (m, br), 680 (m, br) cm<sup>-1</sup>. <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, TMS):  $\delta$  0.85–3.50 (m, br); 3.65–4.30 (m); 7.15–9.55 (m, br); 10.15 (s). ANAL. CALCD FOR C<sub>17</sub>H<sub>19</sub>N<sub>5</sub>O<sub>4</sub>: 57.13% C; 7.05% H; 19.60% N. FOUND: 57.00% C; 7.50% H; 19.30% N.

## RESULTS AND DISCUSSION

### Polymerization Reactions

In a previous study we reported the reaction of **PHU** with diisocyanates.<sup>9</sup> The resulting novel polyureas have an inherent viscosity in the range

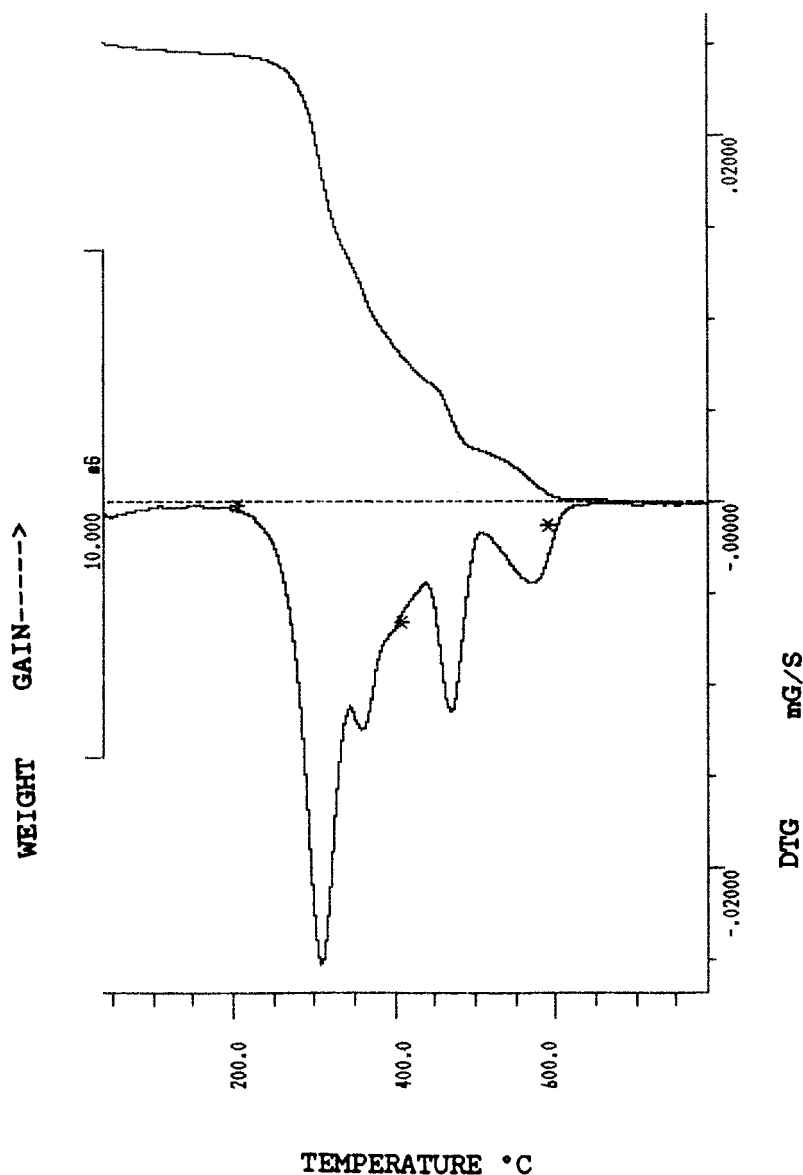
**Table III** Solubility of Polymers **PU1B**, **PU2B**, and **PU3B** in Different Solvents

Solvent	PU1B	PU2B	PU3B
DMSO	+++	+++	+++
DMF	+++	+++	+++
THF	+	+	+
CHCl <sub>3</sub>	+	++	++
Ethyl acetate	+	++	++
CH <sub>3</sub> COOH	+	++	++
CH <sub>2</sub> Cl <sub>2</sub>	+	+	+
Acetone	+	++	+
Toluene	++	++	+
<i>n</i> -Hexane	–	–	–
Ether	–	–	–
Water	–	–	–

Concentration: 5 mg/ml; +++, soluble within 1 h at room temperature; ++, soluble at boiling point of water; +, slightly soluble at boiling point of water; –, insoluble even heated up to 100°C.

of 0.04–0.23 g/dL. Thus we became interested in performing this type of reaction using other monomers such as **CHU** for the formation of the new polyureas. For the other monomers **HMDI** (**2**), **IPDI** (**3**), and **TDI** (**4**) were selected as diisocyanates. The reaction of monomer **CHU** with **HMDI** was performed by two methods via a solution polycondensation reaction. In method A, the reaction was carried out in **DMAc**/CHCl<sub>3</sub> solution with pyridine as a catalyst; the resultant polymer was precipitated in ether, obtaining a high yield (**PU1A**) (Scheme I). The IR spectrum of this polymer showed a peak at 3350 cm<sup>-1</sup> for N–H; a sharp peak at 2250 cm<sup>-1</sup>, attributed to the isocyanate group; and a strong and very broad peak at 1720 cm<sup>-1</sup>, attributed to the carbonyl groups. The <sup>1</sup>H-NMR spectrum of this polymer showed peak 8.00 ppm for N–H, 7.60 ppm for phenyl protons, and 1.40, 3.30 ppm for hexamethylene protons. In method B the step-growth solution polymerization was carried out in **DMAc** in the presence of pyridine, which resulted in a higher yield and a higher inherent viscosity. Because the polyurea **PU1B** was obtained by precipitating in water, its IR spectra does not show the characteristic absorption for the isocyanate functional group.

The reaction of **CHU** with **IPDI** was also performed by two methods via a solution polycondensation reaction. In method A the reaction was carried out in a **DMAc**/CHCl<sub>3</sub> solution with pyridine as a catalyst and the resulting polymer was obtained in low yield (**PU2A**) (Scheme I). In method B the step-growth solution polymerization was carried out in **DMAc** in the presence of pyridine at 60°C, which gave quantitative yield of polyurea **PU2B** with higher inherent viscosity. These polymers were also characterized by IR, <sup>1</sup>H-NMR spectra, and elemental analysis, which are in agreement with the structures **PU2A** and **PU2B**.



**Figure 1** TGA and DTG thermograms of polymer (**PU1B**) under nitrogen atmosphere.

The reaction of **CHU** with **TDI** was carried out in a  $\text{DMAc}/\text{CHCl}_3$  solution and the resulting polymer **PU3A** was obtained in good yield. In method B the step-growth solution polymerization was carried out in  $\text{DMAc}$  in the presence of pyridine at  $60^\circ\text{C}$ , which gave good yield of polyurea **PU3B** with higher inherent viscosity. These polymers were also characterized by IR,  $^1\text{H-NMR}$  spectra, and elemental analysis, which are in agreement with structures **PU3A** and **PU3B**. It is interesting to mention that all polyureas **PU1B**, **PU2B**, and **PU3B** in their IR spectra showed two strong peaks around  $1780$  and  $1730\text{ cm}^{-1}$  for the carbonyl groups. These are characteristic patterns for the urazole moiety.

Polymers **PU1A**, **PU1B**, **PU2A**, **PU2B**, **PU3A**, and **PU3B** are soluble in most organic solvents such as  $\text{DMSO}$ ,  $\text{DMF}$ , and  $\text{CHCl}_3$  and are insoluble in solvents such as water, methanol, and acetone as well as in nonpolar solvents such as cyclohexane and *n*-hexane. The reaction conditions and some physical properties for these novel polyureas are summarized in Tables I, II, and III.

#### Thermal Properties

The thermal behavior of polyureas **PU1B**, **PU2B**, and **PU3B** was measured by thermogravimetric analysis (TGA) at a rate of  $10^\circ\text{C}/\text{min}$  in nitrogen atmosphere (Figs. 1–3). An examination of the

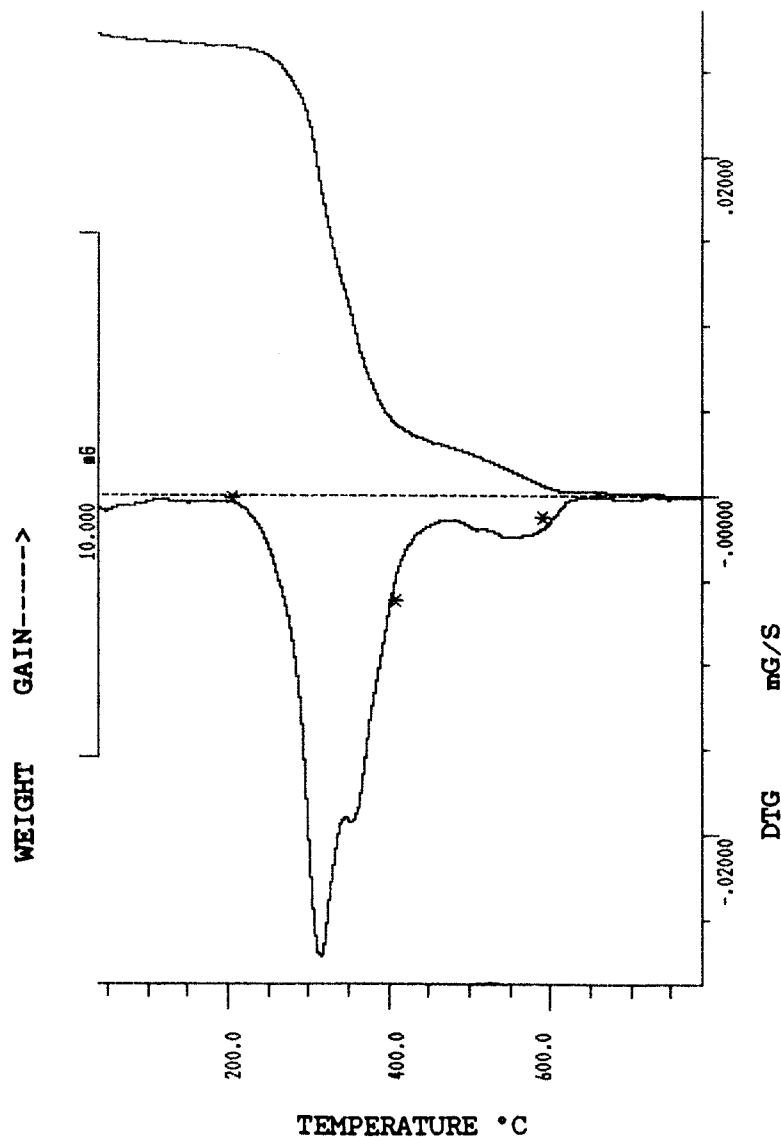


Figure 2 TGA and DTG thermogram of polymer (PU2B) under nitrogen atmosphere.

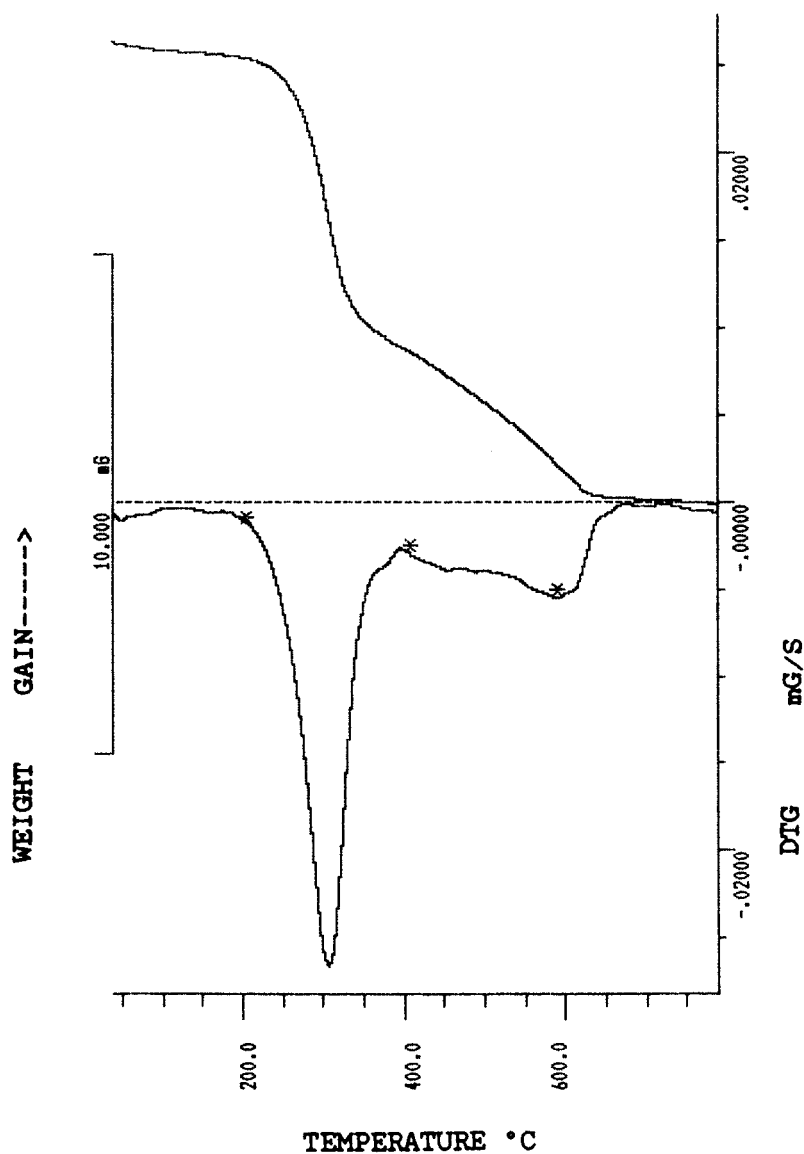
data reveals that all of the above-noted polyureas are thermally stable up to 200°C in nitrogen atmosphere. Polymers **PU1B**, **PU2B**, and **PU3B** show 5% weight loss at 260, 226, and 240°C, respectively.

## CONCLUSIONS

The present work has shown that 4-cyclohexylurazole (**CHU**) is an interesting monomer for polycondensation reactions. The compound (**CHU**) has two acidic N-H groups and can be readily polymerized with isocyanates. Thus compound (**CHU**) can act as a bifunctional monomer and its polycondensation reactions with diisocyanates

gave novel polyureas with urazole linkages. The best condition for obtaining a polymer with high yield and viscosity is solution polymerization in a DMAc system. The resulting polyureas are soluble in most organic solvents and can be used as thermoplastic materials. Because the 4-position of the urazole group can readily be substituted with a wide variety of the functional groups, one can readily achieve properties such as supermolecular aggregation by hydrogen bonding, yielding optically active and liquid crystal polymers.

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**Figure 3** TGA and DTG thermogram of polymer (PU3B) under nitrogen atmosphere.

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