

Synthesis and Characterization of New Polyureas Derived from 4-(4'-Methoxyphenyl)urazole

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Received 9 June 2001; accepted 6 September 2001

ABSTRACT: 4-(4'-Methoxyphenyl)urazole (**MPU**) was prepared from 4-methoxybenzoic acid in five steps. The reaction of monomer **MPU** with *n*-isopropylisocyanate was performed at room temperature in *N,N*-dimethylformamide solution, and the resulting bis-urea derivative was obtained in high yield and was finally used as a model for polymerization reaction. The step-growth polymerization reactions of monomer **MPU** with hexamethylene diisocyanate, isophorone diisocyanate, and toluene-2,4-diisocyanate were performed in *N,N*-dimethylacetamide solution in the presence of pyridine as a catalyst. The resulting novel polyureas have an inherent viscosity (η_{inh}) in a range of 0.07–0.21 dL/g in DMF and sulfuric acid at 25°C. These polyureas were characterized by IR, ¹H-NMR, elemental analysis, and TGA. Some physical properties and structural characterization of these novel polyureas are reported. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1141–1146, 2002

Key words: step-growth polymerization; thermal properties; thermogravimetric analysis (TGA)

INTRODUCTION

Polyureas are a class of polymers which has a —NH—CO—NH— functional group. They are polyamide of carbonic acid and are tough, high melting, and suitable for fiber applications.¹ 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 pharmaceutical, ink,

dyes, and so on, and the modification of wool fibers by interfacial grafting techniques.²

4-Substituted urazoles are five-membered 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, which seems to be very acidic. The acidity of this proton has been measured and is quite acidic with pKa of 4.71, which is almost the same as that of acetic acid.³ The compounds **1** have potential to undergo N-acylation. 4-Substituted-urazole were converted to 1-acyl derivatives by acylation reaction with a series of carboxylic acid anhydrides.⁴ A simplified procedure for the N-acylation of oxazolidin-2-one chiral auxiliaries has also been reported.⁵

Recently we have been able to take advantage of these acidic N—H in a compound, 1-methyl-2,5-bis(4-phenylurazoly) pyrrole and synthesis novel

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Contract grant sponsor: Research Affairs Division, Isfahan University of Technology (IUT), Isfahan, I.R. Iran.

Journal of Applied Polymer Science, Vol. 85, 1141–1146 (2002)
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polymers via N-alkylation and N-acylation reactions.^{6,7} Polymerization of compound 4-phenylurazole (**PHU**) with phosgene, terephthaloyl chloride, and epichlorohydrin has been reported to give insoluble polymers.⁸ Polymerization of compound **PHU** with aliphatic diacid chlorides gave soluble polyamides with inherent viscosity of 0.39 dL/g.⁹ Copolymerization of 4-cyclohexylurazole (**CHU**) with aliphatic diacid chlorides gave soluble polyamides.¹⁰

In a previous article we have reported the reaction of **PHU** and **CHU** with diisocyanates.^{11,12} The resulting novel polyureas have an inherent viscosity in a range of 0.04–0.23 dL/g and 0.044–0.206 dL/g, respectively. Thus, we became interested in performing this type of reaction using other monomers such as **MPU** (**6**) for the formation of the new polyureas. In the present article we report on the successful step-growth polymerization reactions where **MPU** as a novel monomer is used for the synthesis of soluble polyureas.

EXPERIMENTAL

Materials and Equipments

Reagents were purchased from Fluka Chemical (Buchs, Switzerland), Alderich Chemical (Milwaukee, WI) and Riedel-deHaen AG (Seelze, Germany). 4-Methoxybenzoyl chloride (**2**) was prepared by the reaction of 4-methoxybenzoic acid (**1**) with thionyl chloride according to procedure described previously.¹³ 4-Methoxybenzoyl azide (**3**) was prepared from the reaction of acid chloride **2** with sodium azide.¹⁴ DMAc (*N,N*-dimethylacetamide) was dried over BaO and then was distilled under reduced pressure. Chloroform was purified by washing with water, drying with CaCl₂, and subsequent distillation under normal pressure. Proton nuclear magnetic resonance (¹H-NMR, 90 MHz) spectra were recorded on a Varian EM-390 instrument. Tetramethylsilane (TMS) was used as an internal reference. IR spectra were recorded on a Shimadzu 435 IR spectrophotometer. 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 anal-

yses were performed by Tarbiet Moderres University, Tehran, I.R. Iran.

Preparation of 1-Ethoxycarbonyl-4-(4'-methoxyphenyl) Semicarbazid (**5**)

Into a 250-mL one-necked round-bottom flask equipped with a magnetic stirrer and water cooled condenser a solution of 4-methoxybenzoyl azide (**3**) (3.13 g, 1.76×10^{-2} mol) in 40 mL of absolute toluene was added. The solution was refluxed under nitrogen atmosphere for 10 h and the progress of the reaction was monitored by TLC, then it was cooled and filtered to remove small amount of undissolved solid and transferred to a two-necked round-bottom flask equipped with a magnetic stirrer and water-cooled condenser. The isocyanate **4** was not isolated, and was used directly for the next step of reaction. This clear pale-yellow was cooled in an ice bath and a solution of ethylcarbazine (1.83 g, 1.76×10^{-2} mol) in 30 mL of absolute toluene was added dropwise in a period of 15 min. The reaction mixture was stirred at room temperature for 1 h and then was refluxed for 2.5 h. After cooling in water bath the white crystals (4.38 g, 98%) was collected, m.p. = 165–166°C (lit. 170.5–171.5°C)¹⁵; ¹H-NMR (DMSO-d₆, TMS): δ 1.1–1.4 (t, 3H, $J = 7.5$ Hz); 3.75 (s, 3H); 3.95–4.25 (q, 2H, $J = 7.5$ Hz); 6.80–7.00 (d, 2H, $J = 9.0$ Hz); 7.35–7.60 (d, 2H, $J = 9.0$ Hz); 7.85 (s, 1H); 8.55 (s, 1H), 8.85 (s, 1H).

Preparation of 4-(4'-Methoxyphenylurazole) (MPU) (**6**)

Into a 100-mL one-necked round-bottom flask 4.38 g (1.73×10^{-2} mol) of 1-ethoxycarbonyl-4-(4'-methoxyphenyl) semicarbazide (**5**), a water solution of potassium hydroxide (18.5 mL of 4 M) were added. The solution was heated at 80°C in a water bath for a period of 1.5 h then it was cooled and 7.5 mL of conc. HCl was added. The white solid (3.22 g, 90 %) was recrystallized from hot water m.p. = 211–213°C (lit. 219.0–220.5)¹¹; IR (KBr): 3420 (m), 3240 (s,br), 1770 (m, sh), 1679 (s), 1610 (m), 1510 (s), 1440 (m), 1305 (m), 1250 (s), 1255(s), 1220 (m), 1180 (m), 1120 (m), 1045 (w), 1020 (w), 840 (m), 800 (s), 770 (w), 570 (w), 530 (w) cm⁻¹; ¹H-NMR (MDSO-d₆, TMS): δ 3.85 (s, 3H); 7.00–7.30 (d, 2H, $J = 9.0$ Hz); 7.40–7.60 (d, 2H, $J = 9.0$ Hz); 10.20 (s, br, 2H).

Preparation of 1,2-bis(*n*-Propylamidocarbonyl)-4-(4'-methoxy-phenyl)-1,2,4-triazolidine-3,5-dione (Model Compound 7)

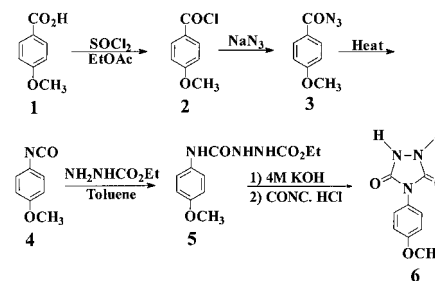
Into a 25-mL round-bottom flask, *n*-propylisocyanate (0.90 mL, 9.5×10^{-3} mol) and MPU (6) (0.200 g, 9.65×10^{-4} mol) were dissolved in 1 mL of DMF. The solution was stirred for 24 h at room temperature. The excess *n*-propylisocyanate was removed under reduced pressure and the residue was precipitated in 20 mL of distilled water. The resulting solid was filtered off, dried to give 0.29 g (80%) of white solid 2. This solid was recrystallized from water–acetone mixture, m.p. 123.5–125°C; IR(KBr): 3380 (s), 2960 (s), 2940 (s), 2880 (w), 1780 (s, sh), 1730 (s,br), 1680 (m, sh), 1610 (m), 1590 (w), 1505 (s), 1420 (s), 1305 (w), 1250 (s), 1200 (s), 1170 (s), 1075 (m), 1055 (w), 1025 (m), 820 (m), 755 (m), 730 (m, sh), 635 (w), 575 (m) cm^{-1} ; ^1H NMR (DMSO- d_6 , TMS): δ 0.70–1.05 (t, 6H, $J = 6.25$ Hz), 1.20–1.80 (m, 4H), 3.00–3.45 (m, 4H), 3.85 (s, 3H), 6.95–7.25 (d, 2H, $J = 9.0$ Hz), 7.30–7.60 (d, 2H, $J = 9.0$ Hz), 7.70–8.10 (t, 2H, $J = 6.00$ Hz). Anal. calcd for $\text{C}_{17}\text{H}_{23}\text{N}_5\text{O}_5$: 54.10% C; 6.14% H; 18.55% N. Found: 53.91% C; 5.95% H; 18.42% N.

Polycondensation of MPU with HMDI

Into a 25-mL round-bottom flask was placed a solution of MPU (0.1175 g, 5.60×10^{-4} mol) in 0.4 mL of DMAc. Then 0.137 mL of pyridine was added. To this solution, HMDI (0.0954 g, 5.60×10^{-4} mol) was added. The mixture was stirred for 24 h at room temperature and then 108 h at 70°C; during this period 0.35 mL of DMAc was added. The viscous reaction mixture was precipitated in 25 mL of distilled water. The white solid PU1 was filtered, dried to give 0.1475 g (70%), m.p. = 190°C; Inherent viscosity (0.5 g/dL DMF, 25°C) = 0.21 dL/g; IR(KBr): 3320 (s), 3100 (w), 2920 (s), 2850 (m), 1770 (m, sh) 1730 (s, br), 1700 (s, sh) 1620 (m), 1540 (s, sh), 1510 (s), 1430 (s, br), 1300 (m), 1250 (s), 1200 (s), 1170 (m), 1140 (m), 1020 (m), 830 (m), 800 (w), 760 (w), 730 (w), 600 (m), 520 (w) cm^{-1} . ^1H -NMR (DMSO- d_6 , TMS): δ 1.00–1.75 (m, br); 2.70–3.45 (m, br); 5.60 (s, br); 6.90–7.25 (d, br), 7.30–7.60 (d, br), 7.82 (s, br). Anal. calcd for $\text{C}_{17}\text{H}_{21}\text{N}_5\text{O}_5$: 54.39% C; 5.64% H; 18.65% N. Found: 54.69% C; 6.30%, H; 18.71% N.

Polycondensation of MPU with IPDI

This polycondensation was performed by the method similar to the above procedure. The mix-



Scheme 1 Synthesis of monomer 6.

ture was stirred for 24 h at room temperature and then 132 h at 70°C; during this period 0.6 mL of DMAc was added. The viscous reaction mixture was precipitated in 25 mL of distilled water. The white solid PU2 was filtered off and dried to give 0.55 g (90%), m.p. = 160°C; Inherent viscosity (0.5 g/dL DMF, 25°C) = 0.07 dL/g; IR (KBr): 3350 (m, br), 2940 (m), 2850 (m, sh), 1780 (m, sh), 1730 (s), 1710 (s, sh), 1650 (m), 1610 (w), 1540 (s, br), 1510 (s), 1420 (s), 1380 (w), 1360 (w), 1300 (m), 1250 (s), 1170 (w), 1140 (w), 1025 (m), 830 (m), 800 (w), 760 (m), 690 (w), 600 (m) cm^{-1} . ^1H -NMR (DMSO- d_6 , TMS): δ 0.35–1.30 (m, br); 1.40–1.90 (m, br); 2.70–3.20 (m, br), 3.85 (s), 5.75 (s, br); 7.00–7.30 (d, $J = 9.0$ Hz), 7.35–7.75 (d, $J = 9.0$ Hz), 7.90 (s, br). Anal. calcd for $\text{C}_{21}\text{H}_{27}\text{N}_5\text{O}_5$: 58.72% C; 6.34% H; 16.31% N. Found: 58.72% C; 6.80%, H; 16.26% N.

Polycondensation of MPU with TDI

This polycondensation was performed by the method similar to the above procedure. The reaction mixture was stirred for 24 h at room temperature and then 132 h at 70°C, during this period 3.0 mL of DMAc was added. The viscous reaction mixture was precipitated in 25 mL of distilled water. The white solid PU3 was filtered off and dried to give 0.341 g (90%), m.p. = 284°C; Inherent viscosity (0.5 g/dL H_2SO_4 , 25°C) = 0.11 dL/g; IR (KBr): 3350 (s, br), 2950 (m, sh), 1660 (s, br), 1600 (s, br), 1540 (s, br), 1470 (w), 1450 (w), 1410 (w), 1300 (w), 1220 (s), 1030 (w), 880 (w), 820 (w), 760 (w), cm^{-1} . Anal. calcd for $\text{C}_{18}\text{H}_{15}\text{N}_5\text{O}_5$: 56.69% C; 3.96% H; 18.36% N. Found: 59.87% C; 5.31%, H; 17.79% N.

RESULTS AND DISCUSSION

Monomer Synthesis

4-(4'-Methoxyphenyl)urazole MPU (6) was prepared in five steps starting from 4-methoxyben-

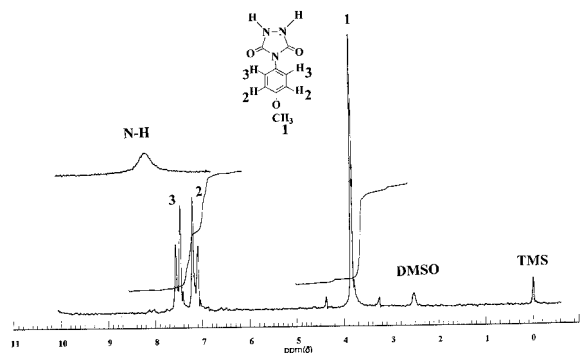
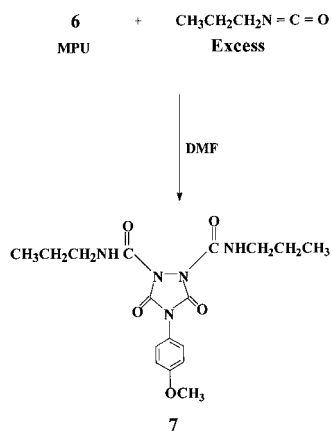


Figure 1 $^1\text{H-NMR}$ (90 MHz) spectrum of monomer **6** in DMSO-d_6 at rt. N—H peak appeared at 10.20 ppm.

zoic acid (Scheme 1). The structures of all compounds were confirmed by IR and $^1\text{H-NMR}$ spectra. The purity of monomer **6** was checked by TLC, which shows one spot in cyclohexane/ethylacetate mixture (30:70) with $R_f = 0.24$. The structure of monomer **6** was characterized by IR and $^1\text{H-NMR}$ (Fig. 1) spectra, which are in agreement with structure of monomer **6**.

Model Compound Studies

MPU (**1**) was allowed to react with excess *n*-propylisocyanate in DMF solution, and gave 1,2-bis(*n*-propylamidocarbonyl)-4-(4'-methoxyphenyl)-1,2,4-triazolidine-3,5-dione (**7**) in high yield (Scheme 2). The model compound **7** was characterized by IR, $^1\text{H-NMR}$, elemental analysis. The IR spectrum of **7** showed a strong peak at 3380 cm^{-1} for the N—H bond, two medium peaks at 2960 and 2940 cm^{-1} for the methylene and methyl C—H bond, also three peaks at 1780 , 1730 , and 1680 cm^{-1} for the carbonyl groups. The



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

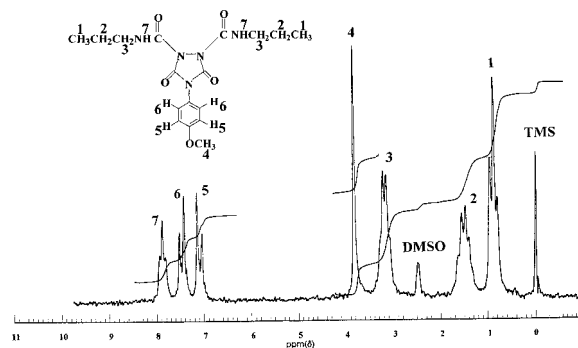
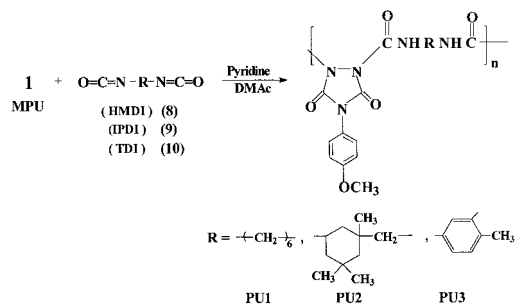


Figure 2 $^1\text{H-NMR}$ (90 MHz) spectrum of model compound **7** in DMSO-d_6 at rt.

first two peaks are characteristic pattern for the urazole moiety. The $^1\text{H NMR}$ spectrum (Fig. 2) of **7** showed all peaks that are in agreement with the structure of compound **7**. The elemental analysis results are in good agreement with the structure of model compound **7**. The purity of model compound **7** was checked by TLC, which shows one spot in cyclohexane/ethylacetate mixture (30 : 70) with $R_f = 0.71$.

Polymerization Reactions and Characterization

Because 1,2-bis(*n*-propylamidocarbonyl)-4-(4'-methoxyphenyl)-1,2,4-triazolidine-3,5-dione (**7**) as a model compound was synthesized in good yield and purity, we became interested to perform this type the reaction for the formation of the novel polyureas. Thus, **HMDI** (**8**), **IPDI** (**9**), and **TDI** (**10**) were selected as diisocyanates. The reaction of monomer **1** with these diisocyanates was performed via solution polymerization. The reactions were carried out in DMAc solution in the presence of pyridine as a catalyst, and the resulting polyureas **PU1-PU3** were obtained as white solids in good yield (**Scheme 3**). The mechanism of the



Scheme 3 Ploycondensation reactions of monomer **6** with diisocyanates.

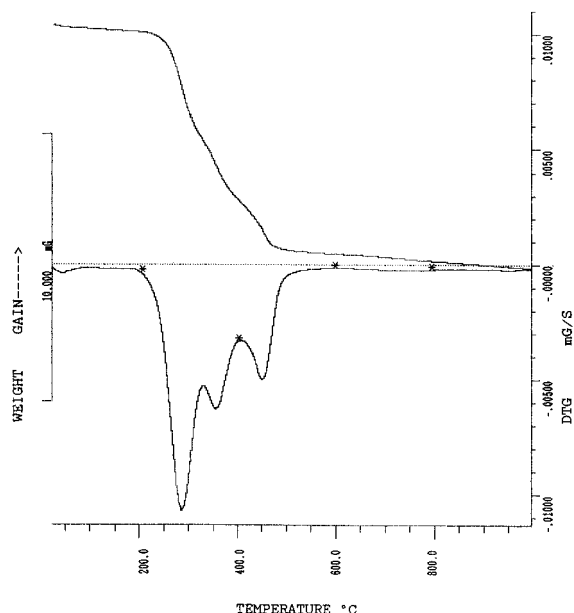


Figure 3 TGA and DTG thermograms of polymer (**PU1**) under nitrogen atmosphere.

reaction of monomer **6** with above diisocyanates is a step-growth addition of N—H of the urazole group across the carbon–nitrogen double bond, and there is no by-product, which simplifies the polymerization process.

The resulting polymers were characterized by IR, $^1\text{H-NMR}$, elemental analysis, and TGA. The IR spectrum of polymer **PU1** showed a strong peak at 3320 cm^{-1} for the N—H bond, strong peaks at 2920 and 2850 cm^{-1} for the aliphatic C—H bonds, also three strong peaks at 1770 , 1730 , and 1700 cm^{-1} for the carbonyl groups. These peaks are characteristic patterns for the urazole moiety. The $^1\text{H NMR}$ spectrum of **PU1** showed a multiplet at 1.35 ppm for the four central methylene groups and a multiplet at 3.00 ppm for the other two methylene groups attached to the amide groups. A singlet at 3.85 ppm for the methyl of the methoxy group, a broad peak at 5.70 ppm for the N—H of the amines end groups, a doublet at 7.10 ppm for the two aromatic protons, which are in *ortho* position to the methoxy group, and another doublet at 7.50 ppm for other two aromatic protons, a broad peak at 7.85 for the N—H of amide group. The elemental analysis results are also in good agreement with the structure of **PU1**.

The IR spectrum of polymer **PU2** showed a medium broad peak at 3350 cm^{-1} for the N—H bond, It also show peaks for the methylene and

methyl C—H bond and peaks for the carbonyl groups. The $^1\text{H-NMR}$ spectrum of **PU2** showed peaks that confirm its chemical structure. The elemental analysis results are also in good agreement with calculated percentages for carbon, hydrogen, and nitrogen contents in polymer repeating unit of **PU2**.

The IR spectrum of polymer **PU3** showed a strong broad peak at 3270 cm^{-1} , which covers the area for the N—H, aromatic C—H, and aliphatic C—H bonds. The insolubility of the **PU3** precluded any NMR measurement. Although in elemental analysis data the nitrogen content is a good agreement with the calculated data, due to some impurity we were not able to have satisfactory data on this polymer.

The polymers **PU1** and **PU2** are soluble in organic solvents such as DMF, dioxane, DMSO, DMAc, and DMF, and are insoluble in solvents such as water, methanol, cyclohexane, and chloroform. The **PU3** has low solubility in DMF, dioxane, DMSO, DMAc, and DMF, but it is readily soluble in concentrated H_2SO_4 .

Thermal Properties

The thermal behavior of polyureas **PU1**, **PU2**, and **PU3** were measured by thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) analysis at a rate of $10^\circ\text{C}/\text{min}$ in nitrogen

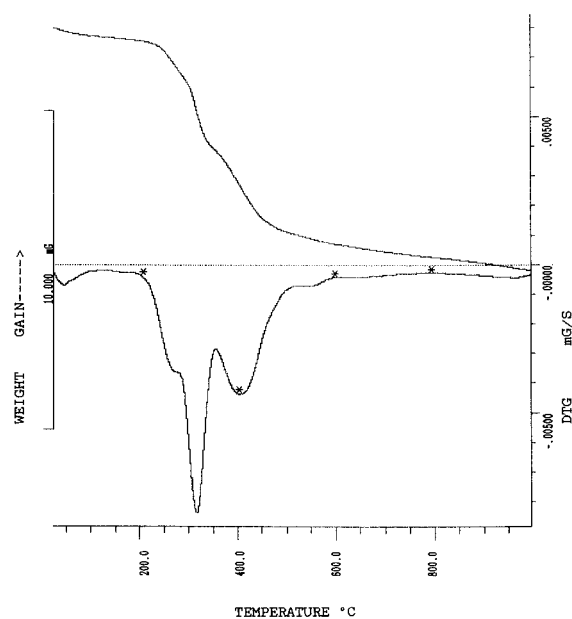


Figure 4 TGA and DTG thermogram of polymer (**PU3**) under nitrogen atmosphere.

Table I Thermal Properties of PU1, PU2, and PU3

Polymer	Decomposition Temperature (°C)		Char Yield (%) ^c
	T_5^a	T_{10}^b	
PU1	255	270	8.0
PU2	250	271	2.4
PU3	265	290	27.0

^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 maximum temperature 600°C in N₂.

atmosphere (Figs. 3 and 4). An examination of the data reveals that all of the above polyureas are thermally stable up to 250°C in nitrogen atmosphere (Table I). The polymers **PU1**, **PU2**, and **PU3** show 5% weight loss at 255, 250, and 265°C, respectively, and they also show 10% weight loss at 270, 271, and 290°C, respectively. It is interesting to note that **PU3**, which is aromatic polyurea, show better thermal stability.

CONCLUSIONS

This investigation has shown that **MPU (6)** is an interesting monomer for the polycondensation reactions. This compound has two acidic N—H groups, and it can be readily reacted with *n*-propylisocyanate to give 1,2-bis(*n*-propylamido-carbonyl)-4-(4'-methoxyphenyl)-1,2,4-triazolidine-3,5-dione (**7**) in good yield and high purity. Thus, compound (**6**) can act as a bifunctional monomer, and its polymerization reaction with

aliphatic and aromatic diisocyanates gave novel polyureas with methoxyphenyl containing urazole linkages.

Partial financial support from the Research Affairs Division, Isfahan University of Technology (IUT), Isfahan, I.R. Iran, is gratefully acknowledged.

REFERENCES

- Morgan, P. W. *Condensation Polymers: By Interfacial and Solution Methods*; Wiley-Interscience: New York, 1965, Chap. 5.
- Steuben, K. C.; Barnabeo, A. E. In *Interfacial Synthesis*; Millich, F.; Carraher, C. E., Eds.; Dekker: New York, 1977, Chap. 18, vol. 2.
- Ohashi, S.; Leong, K. W.; Matyjaszewski, K.; Butler, G. B. *J Org Chem* 1980, 45, 3467.
- Simlot, R.; Izydore, R. A.; Wong, O. T.; Hall, I. H. *J Pharm Sci* 1993, 82, 408.
- Ager, D. J.; Allen, D. R.; Schaad, D. R. *Synthesis* 1996, 1283.
- Mallakpour, S. E.; Karami-Dezcho, B.; Sheikholeslami, B. *Polym Int* 1998, 45, 98.
- Mallakpour, S. E.; Sheikholeslami, B. *Iranian Polym J* 1998, 7, 121.
- Bausch, M. J.; David, B.; Selmarten, D.; Wang, L. H. *Compos Technol Annu Conf Mater Technol* 1991, 7, 41.
- Mallakpour, S. E.; Sheikholeslami, B. *Polym Int* 1999, 48, 41.
- Mallakpour, S. E.; Nasr-Isfahani, N. *Polym Sci Ser B*, 2001, 43, 105.
- Mallakpour, S. E.; Sheikholeslami, B. *Iranian Polym. J* 1999, 8, 61.
- Mallakpour, S. E.; Rostamizadeh, H. *J Appl Polym Sci* 2001, 80, 1335.
- Vanderhaeghe, H.; Kolosky, P.; Claesen, M. *J Pharm Pharmacol* 1954, 6, 119.
- Yukawa, Y.; Tsuno, Y. *J Am Chem Soc* 1957, 79, 5530.
- Stickler, J. C.; Pirkle, W. H. *J Org Chem* 1966, 31, 3444.