

Polymerization of 4-(4'-N-1,8-Naphthalimidophenyl)-1,2,4-triazolidine-3,5-dione with Diisocyanates

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ABSTRACT: 4-(4'-Aminophenyl)-1,2,4-triazolidine-3,5-dione (1) was reacted with 1,8-naphthalic anhydride (2) in a mixture of acetic acid and pyridine (3 : 2) under refluxing temperature and gave 4-(4'-N-1,8-naphthalimidophenyl)-1,2,4-triazolidine-3,5-dione (NIPTD) (3) in high yield and purity. The compound NIPTD was reacted with excess *n*-propylisocyanate in *N,N*-dimethylacetamide solution and gave 1-(*n*-propylamidocarbonyl)-4-[4'-(1,8-naphthalimidophenyl)]-1,2,4-triazolidine-3,5-dione (4) and 1,2-bis(*n*-propylamidocarbonyl)-4-[4'-(1,8-naphthalimidophenyl)]-1,2,4-triazolidine-3,5-dione (5) as model compounds. Solution polycondensation reactions of monomer 3 with hexamethylene diisocyanate (HMDI), isophorone diisocyanate (IPDI), and tolylene-2,4-diisocyanate (TDI) were performed under microwave irradiation and conventional solution po-

lymerization techniques in different solvents and in the presence of different catalysts, which led to the formation of novel aliphatic-aromatic polyureas. The polycondensation proceeded rapidly, compared with conventional solution polycondensation, and was almost completed within 8 min. These novel polyureas have inherent viscosities in a range of 0.06–0.20 dL g⁻¹ in conc. H₂SO₄ or DMF at 25°C. Some structural characterization and physical properties of these novel polymers are reported. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2861–2869, 2003

Key words: step-growth polymerization; viscosity; 4-(4'-N-1,8-naphthalimidophenyl)-1,2,4-triazolidine-3,5-dione (NIPTD); thermogravimetric analysis (TGA); irradiation

INTRODUCTION

Urazole derivatives are very interesting five-membered heterocyclic compounds, which at position 4 can provide a wide variety of aliphatic as well as aromatic substituents. These heterocyclic compounds have two N—H protons, which 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 a pK_a value of 4.71, which is almost the same as that of acetic acid.¹ The urazole compounds 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.² A simplified procedure for the N-acylation of oxazolidin-2-one chiral auxiliaries has also been reported.³

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

by N-alkylation and N-acylation reactions.^{4,5} Polymerization of 4-phenylurazole (PHU) with phosgene, terephthaloyl chloride, and epichlorohydrin has been reported to give insoluble polymers.⁶ Polymerization of compound PHU with aliphatic diacid chlorides gave soluble polyamides with inherent viscosity of 0.39 dL g⁻¹.⁷ Copolymerization of 4-cyclohexylurazole (CHU) with aliphatic diacid chlorides gave soluble polyamides.⁸ We have also reported the reaction of PHU and other urazole derivatives with diisocyanates.^{9–14} The resulting novel polyureas have inherent viscosities in a range of 0.04–0.23 dL g⁻¹ and some of them are photoactive materials as well as polymeric dyes.

Polyureas are polyamides of carbonic acid and are tough, high melting, and suitable for fiber applications.¹⁵ 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, inks, dyes, and the modification of wool fibers by interfacial grafting techniques.¹⁶

The purpose of this investigation was to examine the step-growth polymerization reactions of NIPTD as a monomer with diisocyanates. In the present study

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we report on the successful polycondensation reaction where NIPTD as a novel monomer is used for the synthesis of aliphatic and aromatic polyureas.

EXPERIMENTAL

Materials and equipment

Reagents were purchased from Fluka Chemie (Buchs, Switzerland), Aldrich Chemical (Milwaukee, WI), and Riedel-de Haën AG (Seelze, Germany). 4-(4'-Aminophenyl)-1,2,4-triazolidine-3,5-dione (**1**) was prepared in six steps according to our previous work.¹⁷ DMAc (*N,N*-dimethylacetamide) was dried over BaO and then distilled under reduced pressure. Proton nuclear magnetic resonance ¹H-NMR (90 and 500 MHz) spectra were recorded on a Varian EM-390 (Varian Associates, Palo Alto, CA) and a Bruker (Germany) Advance 500 instrument, respectively. Tetramethylsilane (TMS) was used as an internal reference. IR spectra were recorded on a Shimadzu (Kyoto, Japan) 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 (Greifensee, Switzerland). Elemental analyses were performed by Malek Ashter University, Tehran, Iran. The apparatus used for the polycondensation was a Samsung domestic microwave oven (2450 MHz, 900 W) without any modification, although all of the polymerization reactions were carried out in a hood with strong ventilation.

Preparation of 4-(4'-*N*-1,8-naphthalimidophenyl)-1,2,4-triazolidine-3,5-dione (NIPTD) (**3**)

Into a 100-mL round-bottom flask, 4-(4'-aminophenyl)-1,2,4-triazolidine-3,5-dione (**1**) (3.00 g, 1.56×10^{-2} mol) and 1,8-naphthalic anhydride (**2**) (3.094 g, 1.56×10^{-2} mol) were dissolved in a mixture of 16 mL of pyridine and 24 mL of acetic acid. The solution was refluxed for 5 h. The reaction mixture was concentrated to 5 mL and the resulting white solid was poured into 50 mL of water. The white solid was filtered off and washed with 50 mL of water to give 2.93 g (98%) of white solid. Recrystallization from acetic acid gave white crystals; m.p. 322°C (dec.).

IR (KBr): 3600 (m), 3470 (m), 3210 (m), 3070 (m), 3020 (m), 2910 (w), 2820 (w), 1773 (m), 1708 (s), 1657 (s), 1627 (m), 1587 (s), 1515 (s), 1462 (w), 1435 (s), 1378 (s), 1360 (s), 1315 (w), 1293 (w), 1265 (w), 1239 (s), 1190 (s), 1142 (w), 1122 (m), 1098 (m), 1080 (w), 1025 (m), 957 (m), 902 (s), 855 (m), 830 (m), 780 (s), 740 (m), 712 (w), 700 (w), 680 (w), 660 (w), 620 (m), 590 (m), 550 (w), 535 (m) cm⁻¹. ¹H-NMR (90 MHz, DMSO-*d*₆, TMS): δ 7.4–8.0 (m, 6H, Ar—H), 8.4–8.6 (m, 4H, Ar—H),

10.4 (s, br, 2H, N—H). ANAL. calcd for C₂₀H₁₂N₄O₄: C, 64.52%; H, 3.25%; N, 15.05%. Found: C, 64.14%; H, 3.62%; N, 15.18%.

Preparation of 1-(*n*-propylamidocarbonyl)-4-[4'-(1,8-naphthalimidophenyl)]-1,2,4-triazolidine-3,5-dione (model compound **4**)

In a 25-mL round-bottom flask, *n*-propylisocyanate (0.5 mL, 5.37×10^{-3} mol) was added to a solution of NIPTD (**3**) (0.200 g, 5.76×10^{-4} mol) in 1.5 mL of dry DMAc. The solution was stirred for 24 h at room temperature, then 13 h at 75°C. The excess *n*-propylisocyanate was removed by aspirator and the residue was precipitated in 50 mL of water. The resulting solid was filtered off and dried to give 0.168 g (84%) of white solid **4**. This solid was recrystallized from acetic acid; m.p. 310°C (dec.).

IR (KBr): 3350 (m), 3100 (w), 2970 (m), 2950 (m), 2900 (w), 1790 (w), 1738 (s), 1708 (s), 1668 (s), 1630 (w), 1592 (s), 1545 (m, sh), 1520 (s), 1465 (w), 1423 (s), 1378 (s), 1358 (s), 1268 (w), 1238 (s), 1192 (m), 1155 (m), 1120 (w), 1078 (w), 1050 (w), 1027 (m), 953 (w), 905 (m), 850 (m), 832 (m), 782 (s), 750 (m), 712 (w), 590 (w), 537 (m) cm⁻¹. ¹H-NMR (500 MHz, DMSO-*d*₆): δ 0.89–0.91 (t, 3H, *J* = 7.2 Hz, CH₃), 1.54–1.55 (m, 2H, CH₂), 3.23–3.26 (m, 2H, CH₂), 7.55–7.56 (d, 2H, *J* = 8.10 Hz, Ar—H), 7.64–7.66 (d, 2H, *J* = 8.10 Hz, Ar—H), 7.84 (distorted t, 1H, N—H), 7.90–7.93 (distorted dd, 2H, *J* = 7.50 Hz, Ar—H), 8.52–8.54 (d, 4H, *J* = 7.60 Hz, Ar—H), 10.58 (s, 1H, N—H). ANAL. calcd for C₂₄H₁₉N₅O₅: C, 63.02%; H, 4.19%; N, 15.31%. Found: C, 61.55%; H, 3.95%; N, 15.09%.

Preparation of 1,2-bis(*n*-propylamidocarbonyl)-4-[4'-(1,8-naphthalimidophenyl)]-1,2,4-triazolidine-3,5-dione (model compound **5**)

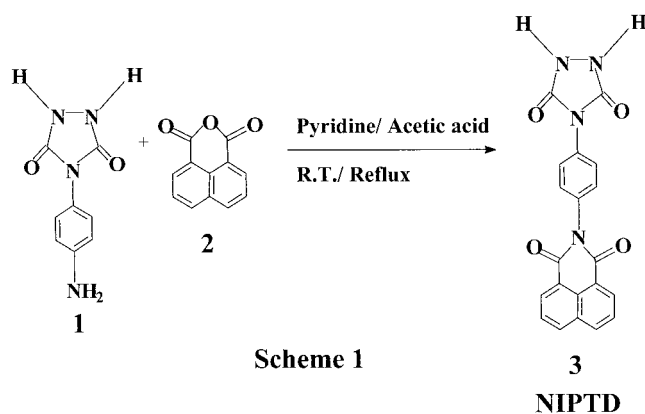
In a 25-mL round-bottom flask, *n*-propylisocyanate (0.5 mL, 5.37×10^{-3} mol) was added to a solution of NIPTD (**3**) (0.200 g, 5.76×10^{-4} mol) in 1.5 mL of dry DMAc. The solution was stirred for 24 h at room temperature, then 32 h at 75°C. The excess *n*-propylisocyanate was removed by aspirator and the residue was precipitated in 50 mL of water. The resulting solid was filtered off and dried to give 0.173 g (86.5%) of white solid **5**. This solid was recrystallized from acetic acid; m.p. 325°C (dec.).

IR (KBr): 3350 (m), 3070 (m), 2970 (m), 2930 (w), 2860 (w), 1775 (m), 1738 (s), 1700 (s), 1665 (s), 1626 (w), 1588 (s), 1540 (s), 1516 (s), 1476 (w), 1435 (s), 1375 (s), 1355 (s), 1310 (w), 1270 (m), 1235 (s), 1190 (m), 1150 (w), 1070 (w), 1046 (w), 1022 (m), 980 (w), 938 (w), 900 (m), 836 (m), 778 (s), 732 (m), 710 (w), 690 (w), 583 (w), 546 (w), 530 (w) cm⁻¹. ANAL. calcd for C₂₈H₂₆N₆O₆: C, 61.99%; H, 4.83%; N, 15.49%. Found: C, 60.50%; H, 3.92%; N, 14.85%.

Polymerization of NIPTD with HMDI

Method I

In a 25-mL round-bottom flask NIPTD (0.1252 g, 3.36×10^{-4} mol) was added to a solution of HMDI (**6**)



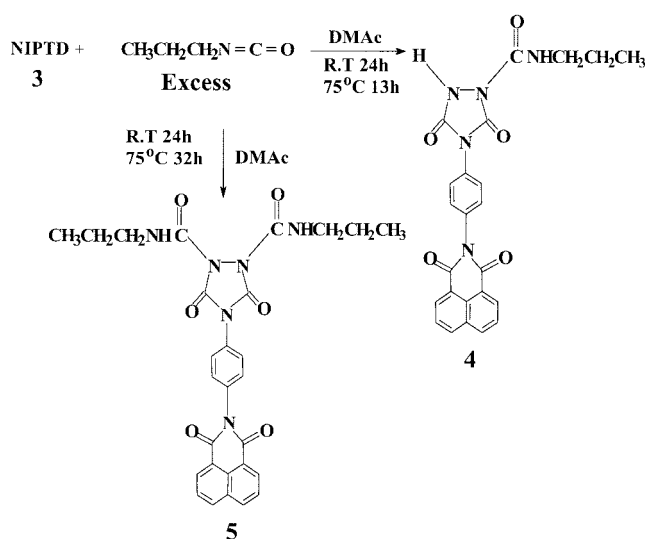
(0.0565 g, 3.36×10^{-4} mol) and pyridine (0.054 mL, 6.45×10^{-4} mol) in 1.30 mL of DMAc. The solution was stirred for 4 h at room temperature, then for 24 h at 60°C, and finally for 62 h at 90°C. The viscous solution was precipitated in 50 mL of distilled water. The solid was filtered off and dried to give 0.118 g (65%) of pale-brown polyurea **PU1A**; m.p. 239°C (dec.).

Method II

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

Method III

The above polymerization was repeated, but the reaction mixture was irradiated in a microwave oven at 100% of its power for 6 min in NMP, using triethylamine as a catalyst.



Scheme 2

IR (KBr): 3330 (m), 3100 (w), 2930 (m), 2870 (w), 2800 (w), 1790 (sh, w), 1733 (s), 1710 (s), 1668 (s), 1630 (sh, m), 1588 (s), 1546 (m), 1513 (s), 1462 (w), 1420 (s), 1374 (s), 1354 (s), 1262 (sh, m), 1238 (s), 1188 (w), 1155 (w), 1138 (w), 1117 (w), 1070 (w), 1020 (w), 950 (w), 888 (m), 830 (s), 780 (s), 735 (w) cm^{-1} . $^1\text{H-NMR}$ (500 MHz, $\text{DMSO-}d_6$): δ 0.77–1.35 (m, br), 3.17–3.37 (m, br), 5.76 (s, NH_2), 7.53 (distorted d, Ar—H), 7.62–7.64 (distorted d, Ar—H), 7.90–7.92 (m, N—H, Ar—H), 8.52 (s, br, Ar—H), 10.59 (s, br, N—H). ANAL. calcd for $\text{C}_{28}\text{H}_{24}\text{N}_6\text{O}_6$: C, 62.22%; H, 4.47%; N, 15.55%. Found: C, 61.70%; H, 4.75%; N, 14.75%.

Polymerization of NIPTD with IPDI

Method I

In a 25-mL round-bottom flask **NIPTD** (0.1399 g, 3.76×10^{-4} mol) was added to a solution of **IPDI** (7) (0.0835 g, 3.76×10^{-4} mol) and pyridine (0.06 mL, 7.52×10^{-4} mol) in 1.30 mL of DMAc. The solution was stirred for 4 h at room temperature, then for 10 h at 60°C, and finally for 36 h at 90°C. During this time 1.20 mL of DMAc was added. The viscous solution was precipitated in 30 mL of distilled water. The solid was filtered off and dried to give 0.166 g (74.5%) of off-white polyurea **PU2A**; m.p. 241°C (dec.).

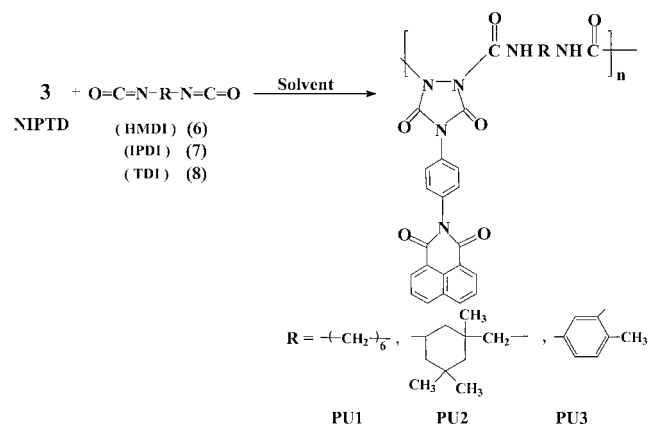
Method II

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

Method III

The above polymerization was repeated, but the reaction mixture was irradiated in a microwave oven at 100% of its power for 8 min in NMP, using triethylamine as a catalyst.

IR (KBr): 3330 (m), 2900 (m), 2260 (w), 1786 (m), 1738 (s), 1708 (s), 1670 (s), 1630 (w), 1590 (s), 1540 (s), 1515 (s), 1460 (w), 1420 (s), 1375 (s), 1355 (s), 1310 (w), 1236 (s), 1190 (m),



Scheme 3

TABLE I
Reaction Conditions for the Polymerization of Monomer NIPTD (3) with HMDI by Different Methods and Some Physical Properties for PU1A–PU1H

Polymer	Method ^a	Solvent	Catalyst ^b	Reaction time	Non-solvent	Yield (%)	Inherent viscosity (dL/g)	m.p. dec. (°C)
PU1A	I	DMAc	Py	4 h, RT; 24 h, 60°C; 62 h, 90°C	Water	65.0	0.08 ^c	239
PU1B	I	DMAc	DBTDL	4 h, RT; 24 h, 60°C; 62 h, 90°C	Water	72.0	0.06 ^c	244–256
PU1C	I	DMAc	TEA	8 h, RT; 20 h, 60°C; 62 h, 90°C	Water	71.0	0.08 ^c	234
PU1D	II	NMP	Py	1 min	Water	73.0	0.10 ^d	192–212
PU1E	II	NMP	Py	10 min	MeOH	89.0	0.16 ^d	207
PU1F	II	NMP	DBTDL	30 min	MeOH	88.5	0.13 ^d	219
PU1G	II	NMP	TEA	30 min	MeOH	72.0	0.20 ^d	212
PU1H	III	NMP	TEA	6 min	MeOH	91.0	0.13 ^d	198–204

^a Method I: graduated heating at different temperature; Method II: refluxing at different times; Method III: irradiating by a domestic microwave oven at 100% its power.

^b Py, pyridine; DBTDL, dibutyltin; TEA, triethylamine.

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

^d Measured at a concentration of 0.5 g/dL in H₂SO₄ at 25°C.

1152 (w), 1115 (w), 1090 (w), 1070 (w), 1050 (w), 1020 (m), 950 (w), 900 (m), 850 (m), 830 (m), 780 (s), 755 (m), 740 (m), 710 (w), 690 (w), 540 (w, sh), 530 (m) cm⁻¹. ¹H-NMR (500 MHz, DMSO-*d*₆): δ 0.77–1.23 (m, br), 1.48–1.53 (m, br), 2.70–3.12 (m, br), 3.71 (s), 5.58–5.87 (m, br), 7.52–7.54 (d, Ar—H, *J* = 8.45 Hz), 7.62–7.63 (d, Ar—H, *J* = 8.45 Hz), 7.65 (distorted t, N—H), 7.90–7.93 (distorted dd, Ar—H), 8.52–8.53 (d, Ar—H, *J* = 8.30 Hz), 10.57 (s, br, N—H). ANAL. calcd for C₃₂H₃₀N₆O₆: C, 64.64%; H, 5.08%; N, 14.13%. Found: C, 63.86%; H, 6.51%; N, 14.52%.

Polymerization of NIPTD with TDI

Method I

In a 25-mL round-bottom flask NIPTD (0.1467 g, 3.94 × 10⁻⁴ mol) was added to a solution of TDI (8) (0.0686 g, 3.94 × 10⁻⁴ mol) and pyridine (0.063 mL, 7.88 × 10⁻⁴ mol) in 1.20 mL of DMAc. The solution was stirred for 4 h at room temperature, then for 10 h at 60°C, and finally for 36 h at 90°C. During this time 0.8 mL of DMAc was added. The viscous solution was precipitated in 30 mL of distilled water. The solid was

filtered off and dried to give 0.149 g (69%) of pale-brown polyurea PU3A; m.p. 242°C (dec.).

Method II

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

Method III

The above polymerization was repeated, but the reaction mixture was irradiated in a microwave oven at 100% of its power for 8 min in NMP, using triethylamine as a catalyst.

IR (KBr): 3450 (w), 3270 (m, br), 3050 (w), 1780 (m, sh), 1710 (s), 1662 (s), 1625 (m), 1585 (s), 1535 (s), 1510 (s), 1430 (w), 1410 (m), 1375 (s), 1353 (s), 1307 (w), 1235 (s), 1188 (m), 1150 (w), 1132 (w), 1112 (w), 1070 (w), 1020 (w), 940 (w), 893 (m), 823 (m), 775 (s), 730 (m) cm⁻¹. ¹H-NMR (500 MHz, DMSO-*d*₆): δ 2.22 (s, br, CH₃), 7.06–7.70 (m, N—H, Ar—H), 7.91 (s, Ar—H), 8.52 (m, Ar—H), 10.08 (s, br, N—H). ANAL. calcd for

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

Polymer	Method ^a	Solvent	Catalyst ^a	Reaction time	Non-solvent	Yield (%)	Inherent viscosity (dL/g)	m.p. dec. (°C)
PU2A	I	DMAc	Py	4 h, RT; 10 h, 60°C; 36 h, 90°C	Water	74.5	0.06 ^b	241
PU2B	II	NMP	Py	60 min	MeOH	68.0	0.11 ^b	257
PU2C	II	NMP	DBTDL	60 min	MeOH	79.0	0.09 ^c	264
PU2D	II	NMP	TEA	60 min	MeOH	69.5	0.13 ^b	252
PU2E	III	NMP	TEA	8 min	MeOH/water	89.0	0.11 ^b	268

^a Methods and catalysts are described in Table I.

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

^c Measured at a concentration of 0.5 g/dL in H₂SO₄ at 25°C.

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

Polymer	Method ^a	Solvent	Catalyst ^a	Reaction time	Non-solvent	Yield (%)	Inherent viscosity (dL/g)	m.p. dec. (°C)
PU3A	I	DMAc	Py	4 h, RT; 10 h, 60°C; 36 h, 90°C	Water	69.0	0.08 ^b	242
PU3B	II	NMP	Py	60 min	MeOH	71.5	0.12 ^c	247
PU3C	II	NMP	DBTDL	60 min	MeOH	72.5	0.13 ^b	269
PU3D	II	NMP	TEA	60 min	MeOH	66.5	0.16 ^c	252
PU3E	III	NMP	TEA	8 min	MeOH/Water	90.0	0.12 ^d	238

^a Methods and catalysts are described in Table I.

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

^c Measured at a concentration of 0.5 g/dL in H₂SO₄ at 25°C.

C₂₅H₁₈N₆O₆: C, 63.74%; H, 3.32%; N, 15.38%. Found: C, 63.71%; H, 4.87%; N, 15.60%.

RESULTS AND DISCUSSION

Monomer synthesis

The monomer 4-(4'-*N*-1,8-naphthalimidophenyl)-1,2,4-triazolidine-3,5-dione (NIPTD) (3) was prepared from the reaction of 4-(4'-aminophenyl)-1,2,4-triazolidine-3,5-dione (1) with 1,8-naphthalic anhydride (2) in a mixture of acetic acid and pyridine (3 : 2) under refluxing temperature (Scheme 1). The purity of monomer 3 was checked by TLC, which shows one spot in a chloroform/methanol mixture (60 : 40) with $R_f = 0.54$. The structure of this monomer was confirmed by IR, ¹H-NMR, UV-vis spectra, and elemental analysis.

Model compounds studies

NIPTD (3) was allowed to react with excess *n*-propylisocyanate in DMAc solution at room temperature for 24 h then at 75°C for 13 h and gave 1-(*n*-propylamidocarbonyl)-4-[4'-(1,8-naphthalimidophenyl)]-1,2,4-triazolidine-3,5-dione (4) in high yield (Scheme 2). Compound 4 was characterized by IR, ¹H-NMR, UV-vis spectra, and elemental analysis. The IR spectrum of 4 showed a medium peak at 3350 cm⁻¹ for the N—H bond, two medium peaks at 2970 and 2950 cm⁻¹ for the methylene and methyl C—H bond, and four peaks at 1790, 1738, 1708, and 1680 cm⁻¹ for the carbonyl groups. The first two peaks show the characteristic pattern for the urazole moiety. The ¹H-NMR spectrum of 4 showed all peaks that are in agreement with the structure of compound 4. This compound was recrystallized from acetic acid. Although we tried to dry it under vacuum, the ¹H-NMR spectrum still showed the presence of a small amount of acetic acid in this compound; thus its elemental analysis result is slightly off. The purity of this model compound 4 was

checked by TLC, which shows one spot in the cyclohexane/ethylacetate mixture (20 : 80) with $R_f = 0.42$.

The above experiment was repeated, but the reaction mixture was allowed to stand at room temperature for 24 h then at 75°C for 32 h and gave 1,2-bis(*n*-propylamidocarbonyl)-4-[4'-(1,8-naphthalimidophenyl)]-1,2,4-triazolidine-3,5-dione (5) in high yield (Scheme 2). Compound 5 was characterized by IR, UV-vis spectra, and elemental analysis. The IR spectrum of 5 showed all peaks that are in agreement with the structure of compound 5. This compound was also recrystallized from acetic acid. Although we tried to dry it under vacuum it still contained some of the acetic acid in its lattice structure, and thus its elemental analysis result is slightly off. The insolubility of this compound precluded any NMR measurement. The purity of this model compound 5 was checked by

TABLE IV
UV-Vis Spectra of Monomer 3, Model Compounds
4 and 5, and Polymers PU1D–PU3D in DMF

Code	Color	λ_{\max} (Å, ϵ M ⁻¹ cm ⁻¹)
Compound 3	White	265 (0.193, 3596)
		336 (0.428, 7963)
		348 (0.383, 7128)
Compound 4	White	269 (0.587, 24,227)
		336 (0.853, 35,173)
		350 (0.737, 30,412)
Compound 5	White	267 (0.547, 48,442)
		336 (0.742, 65,672)
		355 (0.622, 55,062)
PU1D	Yellow	225 (0.700, 43,077)
PU2D	Gray	388 (0.451, 27,668)
		411 (0.431, 26,511)
		268 (0.198, 13,062)
PU3D	Yellow	313 (0.209, 13,840)
		334 (0.272, 17,944)
		349 (0.231, 15,281)
		270 (1.167, 28,979)
		320 (0.473, 11,744)
		334 (0.574, 14,268)
		348 (0.518, 12,864)

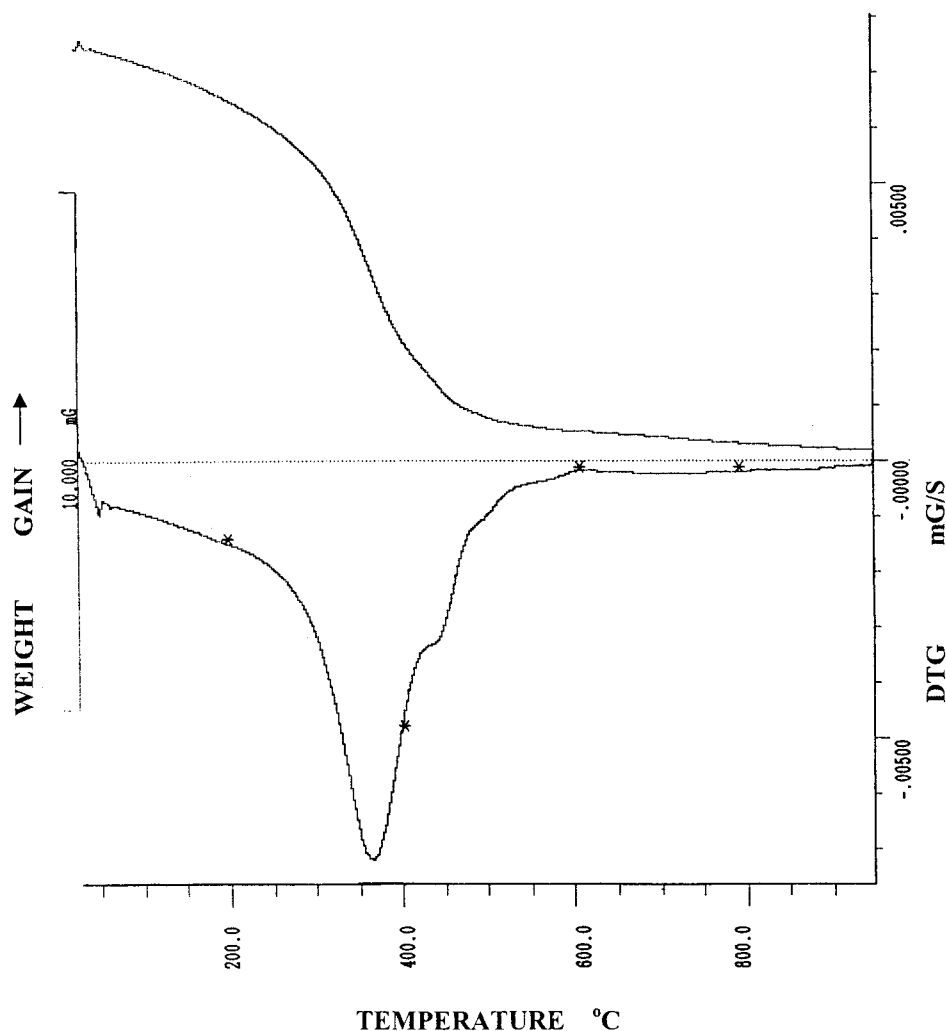


Figure 1 TGA and DTG thermograms of polymer PU1G under nitrogen atmosphere.

TLC, which shows one spot in the chloroform/methanol mixture (60 : 40) with $R_f = 0.51$. Compounds **4** and **5** were used as model compounds for the polymerization reactions.

Polymerization reactions

Because model compounds **4** and **5** were synthesized in high yield and purity we became interested to perform this type of reaction for the formation of novel naphthalene-containing polyureas. Thus HMDI (**6**), IPDI (**7**), and TDI (**8**) were selected as diisocyanates. The polymerization reaction of monomer **3** with these diisocyanates was performed under microwave irradiation as well as conventional solution polymerization techniques in the presence of different catalysts PU1–PU3 (Scheme 3).

The polymerization reaction of monomer **3** with HMDI was performed with three different methods. In method I the reaction mixture was heated gradually from room temperature to 90°C in the pres-

ence of pyridine, dibutyltin dilaurate, and triethylamine, respectively. The resulting polyureas PU1A–PU1C had good yield but low inherent viscosity. In method II the reaction mixture was refluxed up to 30 min in NMP. The resulting polyureas PU1D–PU1G had high yield and high inherent viscosity. In method III the polymerization reaction was performed in NMP under microwave irradiation in the presence of triethylamine as a catalyst. The resulting polyurea PU1H had high yield and good inherent viscosity. Reaction conditions and some physical properties for PU1A–PU1H are summarized in Table I. The resulting polymers were characterized by IR, $^1\text{H-NMR}$, elemental analysis, UV–vis, and TGA. The IR spectrum of polymer PU1 showed two peaks at 1790 and 1733 cm^{-1} for the carbonyl groups, which are characteristic patterns for the urazole moiety. The $^1\text{H-NMR}$ spectrum of polymer PU1 showed all peaks for aliphatic and aromatic as well as N–H protons. Elemental analysis results are also in good agreement with calculated percentages for

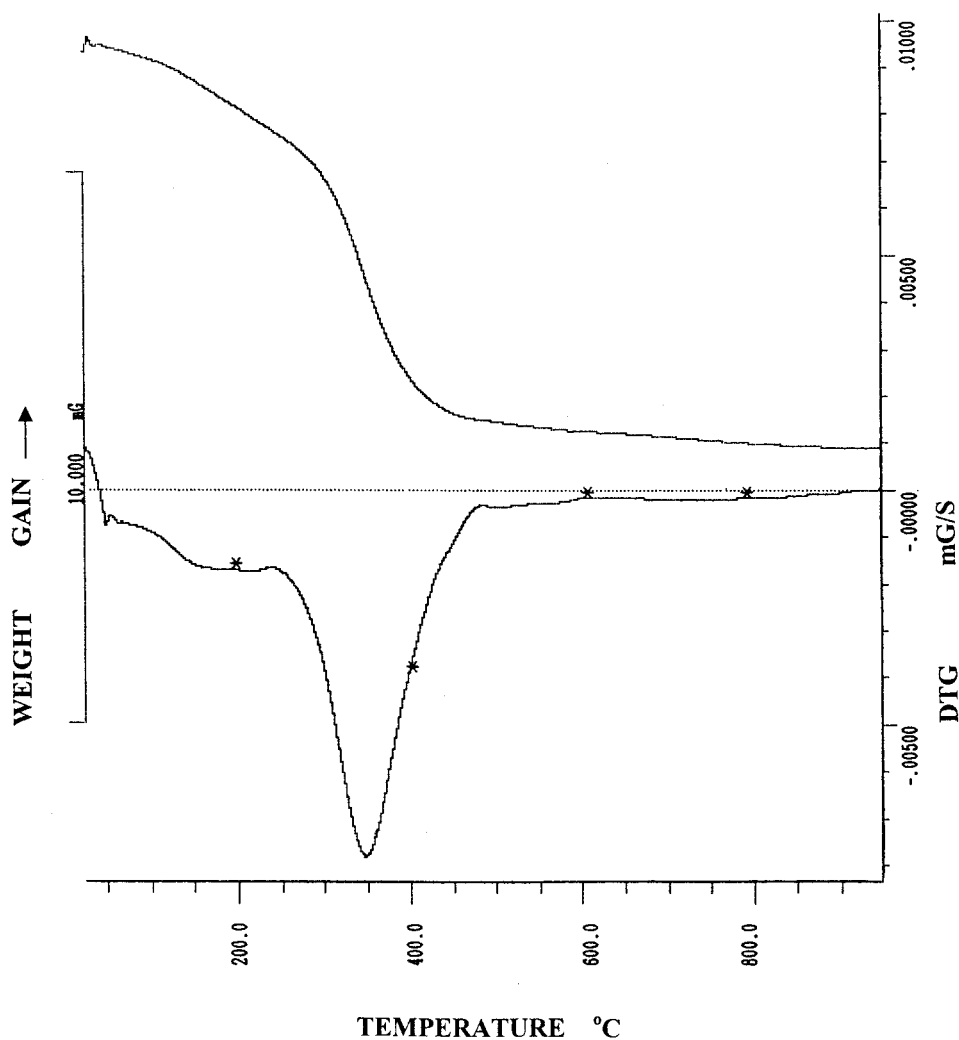


Figure 2 TGA and DTG thermogram of polymer PU2D under nitrogen atmosphere.

carbon, hydrogen, and nitrogen contents in the polymer repeating unit.

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 under microwave irradiation a shorter reaction time, higher yield, and higher viscosity were obtained. The IR spectrum of polymer PU2 showed two strong peaks at 1786 and 1733 cm^{-1} for the carbonyl groups, which are related to the urazole moiety. The $^1\text{H-NMR}$ spectrum of polymer PU2 showed peaks that confirm its chemical structure. Elemental analysis results are also in good agreement with calculated percentages for 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 also is method III in which under microwave irradiation a shorter reaction time, higher yield, and good viscosity were

obtained. The IR spectrum of polymer PU3 showed two strong peaks at 1780 and 1710 cm^{-1} for the carbonyl groups, which are related to the urazole moiety. The $^1\text{H-NMR}$ spectrum of polymer PU2 showed peaks that confirm its chemical structure. Elemental analysis results are also in good agreement with calculated percentages for carbon, hydrogen, and nitrogen contents in the polymer repeating unit of PU3.

The UV-vis spectra of monomer **3**, model compounds **4** and **5**, and polyureas PU1, PU2, and PU3 were recorded in DMF and the data are shown in Table IV. It is apparent that the wavelength of maximum absorptions are related to the naphthalene moieties in the compounds. The UV-vis spectra of all of these compounds show an almost identical pattern.

The polymers PU1, PU2, and PU3 are soluble in organic solvents such as DMF, DMSO, DMAc, and H_2SO_4 , and are insoluble in solvents such as water, methanol, acetone, cyclohexane, and chloroform.

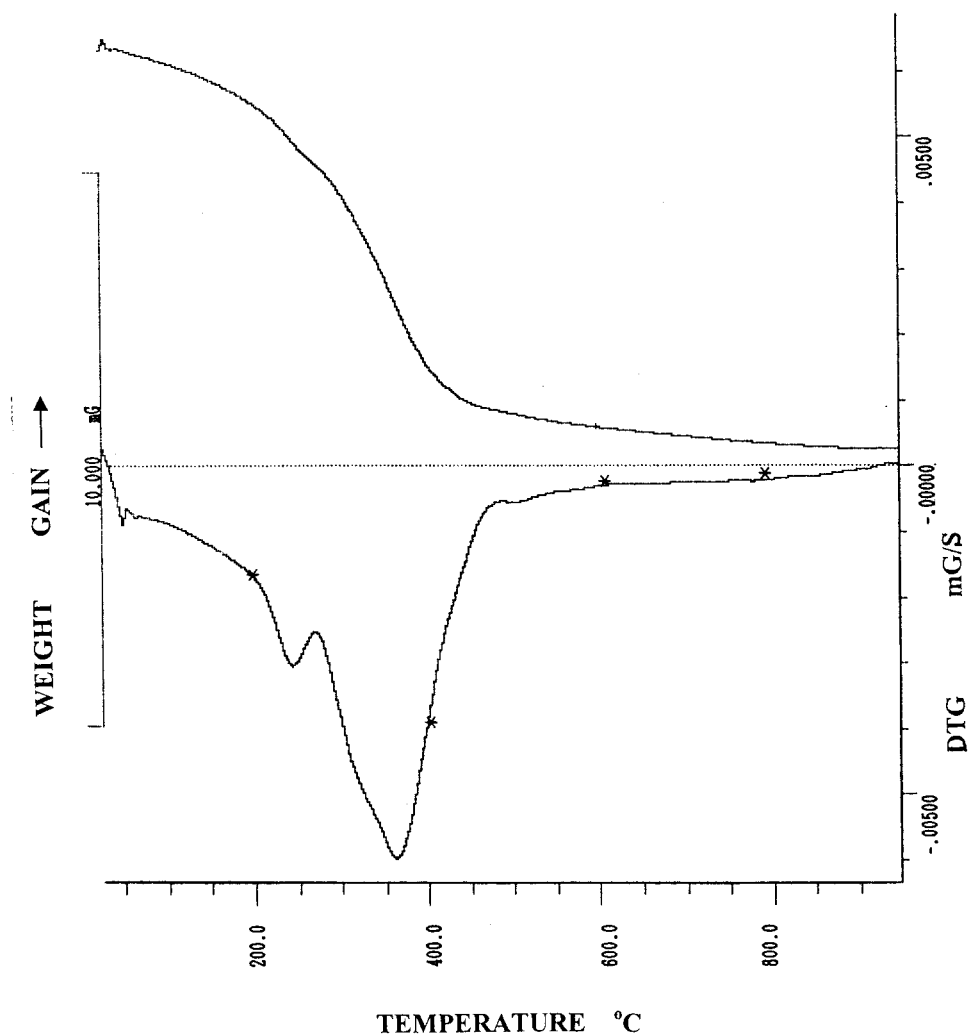


Figure 3 TGA and DTG thermogram of polymer PU3D under nitrogen atmosphere.

Thermal properties

The thermal behavior of polyureas PU1G, PU2D, and PU3D was measured by TGA at a rate of 10°C/min in nitrogen atmosphere (Figs. 1–3). An examination of the data reveals that all of the above polyureas are thermally stable up to 200°C. Some weight loss below 150°C is attributed to water or solvent loss. The maximum decomposition temperatures for PU1G, PU2D, and PU3D are 366, 347, and 361°C, respectively. These polymers have char yields at 600°C of 6.3, 9.6, and 13.6%, respectively.

CONCLUSIONS

This investigation has shown that NIPTD (3) 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. Thus compound 3 can act as a bifunctional monomer and its polymerization reaction with aliphatic and aromatic di-

isocyanates gave novel polyureas with naphthalene-containing urazole linkages having inherent viscosities of 0.06–0.20 dL/g, which roughly correspond to molecular weights of 4000 to 10,000 g/mol. In this work the polycondensation reaction under microwave irradiation is the best method for the synthesis of polyureas PU1–PU3. Furthermore, the above results demonstrate that microwave heating is an efficient method (shorter reaction time and high efficiency of energy) for the polycondensation reactions. We are currently using this method for the synthesis of novel polymers and modification of polymers. Because these polyureas have naphthalene moieties, they have the potential to be used as photoactive materials.

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