

Microwave-induced and High Temperature Solution Polymerization of 4-(4'-*t*-Butylphenyl)-1,2,4-triazolidine-3,5-dione with Diisocyanates

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ABSTRACT

4-(4'-*tert*-Butylphenyl)-1,2,4-triazolidine-3,5-dione, 4-(4'-*tert*-butylphenyl)urazole (TBPTD) was prepared from 4-*tert*-butylbenzoic acid in 5 steps. TBPTD was reacted with *n*-propylisocyanate in dry *N,N'*-dimethylformamide and the resulting bis-urea derivative was obtained in high yield and it was finally used as a model for polymerization reaction. The step-growth polymerization reactions of monomer TBPTD with hexamethylene diisocyanate, isophorone diisocyanate and toluene-2,4-diisocyanate were performed in *N,N'*-dimethylacetamide solution in the presence of pyridine, triethylamine or dibutyltin dilaurate as a catalyst. The step-growth reactions were performed under microwave irradiation as well as high temperature solution polymerization. The polycondensation proceeded rapidly, compared with the conventional solution polycondensation and it was almost completed within 10-18 min. The resulting novel polyureas have an inherent viscosity (inh.) in a range of 0.025-0.306 dL/g in DMF or sulphuric acid at 25°C. These new polyureas were characterized by IR, ¹H NMR, elemental analysis and TGA. Some physical properties and structural characterization of these novel polyureas are reported.

Key Words:

4-(4-*tert*-butylphenyl)urazole;
polyureas; inherent viscosity;
step-growth polymerization;
thermal properties;
thermogravimetric analysis (TGA);
microwave.

INTRODUCTION

Among non-vinyl polymers, synthesis, characterization and applications of polyesters, polyamides, polyurethane and polyimide have been widely used, but little works have been reported on the synthesis of polyureas. These could be due to

their low solubility and high melting points. Because of the presence of -NH-CO-NH- functional group in these polymers can make H-bonding from different sides. Polyureas are polyamides of carbonic acid and are tough, high melting, and suitable for

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fibre applications [1]. A number of methods have been used to prepare polyureas, but the best method is reaction of diamines 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 the modification of wool fibres by interfacial grafting techniques [2].

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, which seems to be very acidic. The acidity of this proton has been measured and it is quite acidic with pK_a of 4.71 which is almost the same as that of acetic acid [3]. The urazole compounds have potential to undergo *N*-acylation. 4-Substituted urazoles 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-phenylurazolyl) pyrrole and synthesis novel 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 paper we 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. Since the monomer TBPTD has *tert*-butyl side group, it could be expected that the resulting polymers from this monomer show better solubility in common organic solvents. Thus, here we report the successful microwave assisted step-growth polymerization reactions where TBPTD as a novel monomer is used for the

synthesis of soluble polyureas.

EXPERIMENTAL

Materials and Equipment

Reagents were purchased from Fluka Chemical (Buchs, Switzerland), Aldrich Chemical (Milwaukee, WI) and Riedel-deHaen AG (Seelze, Germany). 4-(4'-*tert*-butylphenyl)-1,2,4-triazolidine-3,5-dione [4-(4'-*tert*-butylphenyl)urazole] (6) was prepared from *tert*-butylbenzoic acid in 5 steps. DMAc (*N,N'*-dimethylacetamide) was dried over BaO and then it was distilled under reduced pressure. Proton nuclear magnetic resonance ^1H NMR (90 MHz) and (500 MHz) spectra were recorded on a Varian EM-390 (Varian Associates, Palo Alto, CA) and Bruker (Germany), Advance 500 instrument, respectively. 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.

The apparatus used for the polycondensation was a Samsung domestic microwave oven (2450 MHz, 900W) without any modification, but 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. 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 analyses were performed

Preparation of 4-*tert*-Butylbenzoyl Azide (3)

Into a 25 mL one-necked round-bottomed flask was placed a solution of 1.10 g (5.61×10^{-3} mol) of 4-*tert*-butylbenzoyl chloride in 2 mL of acetone. The mixture was cooled in an ice bath, while the solution was gently stirred by a magnetic stirrer, a solution of 0.383 g (5.89×10^{-3} mol) of sodium azide in 1.5 mL of water was added dropwise in a period of 10 min. The mixture was then stirred for a further 60 min. Then stirring was continued for additional 60 min at room temperature. The white solid was filtered off, and dried in air to give 1.09 g (96%) of white solid, mp 63-64°C (lit. [13] 63-65°C).

Preparation of 1-Ethoxycarbonyl-4-(4'-*tert*-butylphenyl) Semicarbazide (5)

Into a 100 mL one-necked round-bottomed flask, which was equipped with a magnetic stirrer, 1.0 g (4.90×10^{-3} mol) of 4-*tert*-butylbenzoyl azide and 10 mL of dry toluene were added. The stirrer was started and the reaction mixture was refluxed under nitrogen atmosphere for 11 h. At the end of refluxing the reaction mixture was cooled, then filtered off immediately. The clear solution was transferred into a 100-mL two-necked round-bottom flask, equipped with a condenser. The solution was cooled in an ice bath up to 5°C and a solution of 0.512 g (4.92×10^{-3} mol) of ethyl carbazide in 20 mL of dry toluene was added dropwise in a period of 15 min. The suspension was stirred for 30 min in an ice bath, then for 3 h at room temperature. Finally the reaction mixture was refluxed for 2 h, then cooled, filtered off and dried to give 1.32 g (96%) of white solid, mp 173-175°C; IR (KBr): 3340 (s), 3200 (s), 3100 (s), 2950 (s), 1745 (s), 1690 (s), 1593 (s), 1525 (s), 1477 (s), 1412 (s), 1363 (m), 1295 (m), 1250 (s), 1210 (s), 1112 (w), 1057 (s), 992 (w), 870 (m), 835 (s), 768 (m), 665 (m), 601 (m), 543 (m), 480 (m, br) cm^{-1} ; ^1H NMR (90 MHz, DMSO- d_6 , TMS): δ 1.10-1.40 (m, 12H); 4.00-4.30 (q, 2H, $J = 6.0$ Hz); 7.30-7.75 (d, 4H, $J = 7.5$ Hz); 8.00-8.15 (s, ^1H); 8.70-8.85 (s, ^1H); 8.90-9.10 (s, ^1H).

Preparation of 4-(4'-*tert*-butylphenyl)-1,2,4-triazolidine-3,5-dione TBPTD (6)

Into a 100 mL one necked round bottom flask 1.567 g (5.61×10^{-3} mol) of 1-ethoxycarbonyl-4-(4'-*tert*-butylphenyl) semicarbazide (5) and a water solution of potassium hydroxide (9.0 mL of 4 M) were added. The solution was heated at 80°C in a water bath for a period of 2.5 h and then it was cooled and conc. HCl was added until the pH of the solution was around 2. The white solid (1.31 g, 98 %) was recrystallized from acetone/water gave white needle like crystal. mp 278-280°C; IR (KBr): 3200-2900 (s, br), 1770 (w), 1680 (s), 1518 (m), 1440 (s), 1360 (w), 1220 (m), 1180 (sh, w), 1116 (m), 835 (m), 797 (s), 773 (sh, m), 665 (m) cm^{-1} ; ^1H NMR (DMSO- d_6 , TMS): δ 1.10-1.50 (s, 9H); 7.40-7.75 (s, br, 4H); 9.80-10.70 (s, br, 2H). Anal. calcd for $\text{C}_{12}\text{H}_{15}\text{N}_3\text{O}_2$: C, 61.79%; H, 6.48%; N, 18.01%. Found: C, 61.69%; H, 6.97%; N 19.77%.

Reaction of TBPTD with n-propylisocyanate (model compound 7)

Into a 25 mL round bottom flask, TBPTD (6) (0.20 g, 8.57×10^{-4} mol) was dissolved in 0.5 mL of dry DMF then excess n-propylisocyanate (0.65 mL, 8.57×10^{-3} mol) and two drops of pyridine were added to it and the solution was stirred for 2 h at room temperature, then it was heated at 60°C for 10 h. The excess n-propylisocyanate was removed under vacuum. The reaction mixture was precipitated in 50 mL of distilled water. The resulting solid was filtered off, dried to give 0.294 g (85%) of white solid. This solid was recrystallized from acetone-water to give white crystals, mp 150-152°C of 1,2-bis-(n-propylamidocarbonyl)-4-[4'-(*tert*-butylphenyl)]-1,2,4-triazolidine-3,5-dione 7; IR(KBr): 3375 (s), 2950 (s), 2900 (m), 2850 (m), 1785 (m), 1738 (s), 1717 (s, sh), 1518 (s), 1460 (m), 1421 (s), 1380 (m), 1360 (w), 1260 (s), 1212 (s), 1150 (m), 1105 (m), 1018 (m), 750 (s), 590 (m, br), 550 (m) cm^{-1} ; ^1H NMR (90 MHz, DMSO- d_6 , TMS): 0.70-1.00 (t, 4H, $J = 6$ Hz), 1.20-1.70 (m, 15H), 3.05-3.40 (m, 4H), 7.35-7.70 (m, 4H), 7.75-8.00 (m, 2H). Anal. calcd for $\text{C}_{20}\text{H}_{29}\text{N}_5\text{O}_4$: C, 59.53%; H, 7.24%; N, 17.35%. Found: C, 60.41%; H, 7.16%; N, 17.28%.

Polymerization of TBPTD with HMDI

Method I

In a 5 mL round bottom flask TBPTD (0.1386 g, 5.945×10^{-4} mol) was added to a solution of HMDI (8) (0.100 g, 5.945×10^{-4} mol) and pyridine (0.047 g, 1.19×10^{-3} mol) in 1.0 mL of dry DMAc. The solution was stirred for 0.5 h at room temperature, then it was refluxed under nitrogen atmosphere for 2 h. The viscous solution was diluted with 0.3 mL of DMF and it was precipitated in 50 mL of distilled water. The solid was filtered off, dried to give 0.143 g (60%) of white polyurea PU1B mp 250°C. This polymerization was also repeated using triethylamine and dibutyltin dilaurate as catalysts.

Method II

The above polymerization was repeated, but the reaction mixture was heated gradually in a range of temperature for different periods of time in DMAc, using pyridine or dibutyltin dilaurate or triethylamine as a catalyst.

Method III

The above polymerization was repeated, but the reaction mixture was irradiated in a microwave oven at 100% of its power for different periods of time in DMAc, using pyridine or dibutyltin dilaurate or triethylamine as a catalyst.

IR(KBr): 3310 (s), 2900 (s), 2850 (w), 1790 (s), 1730 (s), 1700 (m, br), 1635 (m), 1605 (m, sh), 1517 (s), 1410 (m), 1360 (s), 1297 (m), 1250 (s, br), 1105 (m), 1060 (w), 1112 (m), 825 (s), 767 (s), 650 (m), 550 (s) cm^{-1} . $^1\text{H NMR}$ (500 MHz, DMSO- d_6): δ 1.31 (s, 9H, CH_3), 1.41 (s, br, 4H, CH_2), 1.49 (s, br, 4H, CH_2), 3.07-3.34 (m, CH_2), 7.38 (s, br, 2H, Ar-H), 7.51 (s, br, 2H, Ar-H), 7.77 (s, br, ^1H , N-H), 7.89 (s, br, N-H), 8.20 (s, br, N-H). Anal. calcd for $\text{C}_{18}\text{H}_{27}\text{N}_5\text{O}_4$: C, 59.83%; H, 6.77%; N, 17.44%. Found: C, 60.22%; H, 7.17%; N, 17.47%.

Polymerization of TBPTD with IPDI

Method I

In a 5 mL round bottom flask TBPTD (0.1092 g, 4.68×10^{-4} mol) was added to a solution of IPDI (9) (0.1041 g, 4.68×10^{-4} mol) and dibutyltin dilaurate (0.030 g, 4.75×10^{-5} mol) in 1.3 mL of dry DMAc. The solution was refluxed for 4 h. The viscous solution was diluted with 0.5 mL of DMF and was precipitated in 50 mL of distilled water. The solid was filtered off, dried to give 0.141 g (66%) of yellow polyurea PU2A, mp 180°C. This polymerization was also repeated using pyridine and triethylamine as catalysts.

Method II

The above polymerization was repeated, but the reaction mixture was heated gradually in a range of temperature for different periods of time in DMAc, using pyridine or triethylamine or dibutyltin dilaurate as a catalyst.

Method III

The above polymerization was repeated, but the reaction mixture was irradiated in a microwave oven at 100% of its power for different periods of time in DMAc, using pyridine or dibutyltin dilaurate or triethylamine as a catalyst.

IR(KBr): 3340 (m, br), 2900 (s), 1770 (w), 1738 (s), 1707 (s), 1650 (br, m), 1540 (s), 1518 (s), 1457 (w), 1420 (s), 1240 (m, br), 835 (m), 760 (m) cm^{-1} . $^1\text{H NMR}$ (500 MHz, DMSO- d_6): δ 0.88-1.04 (m, br, 9H, CH_3), 1.30-1.40 (m, br, 9H, CH_3), 3.20-3.50 (s, br, 8H, CH_2), 3.60-

4.00 (m, br, ^1H , CH), 4.95-6.00 (m, br, N-H) 7.38 (s, 2H, Ar-H), 7.51 (s, 2H, Ar-H), 7.80 (m, br, N-H). Anal. calcd for $\text{C}_{24}\text{H}_{33}\text{N}_5\text{O}_4$: C, 63.27%; H, 7.30%; N, 15.37%. Found: C, 63.30%; H, 7.92%; N, 15.68%.

Polymerization of TBPTD with TDI

Method I

In a 5 mL round bottom flask TBPTD (0.1661 g, 7.19×10^{-4} mol) was added to a solution of TDI (10) (0.1240 g, 7.19×10^{-4} mol) and dibutyltin dilaurate (0.041 g, 6.49×10^{-5} mol) in 1.5 mL of dry DMAc. The solution was refluxed for 4 h. The viscous solution was diluted with 0.5 mL of DMF and it was precipitated in 50 mL of distilled water. The solid was filtered off, dried to give 0.203 g (70%) of polyurea PU3A, mp 200°C. This polymerization was also repeated using pyridine and triethylamine as catalysts.

Method II

The above polymerization was repeated, but the reaction mixture was heated gradually in a range of temperature for different periods of time in DMAc, using pyridine or triethylamine or dibutyltin dilaurate as a catalyst.

Method III

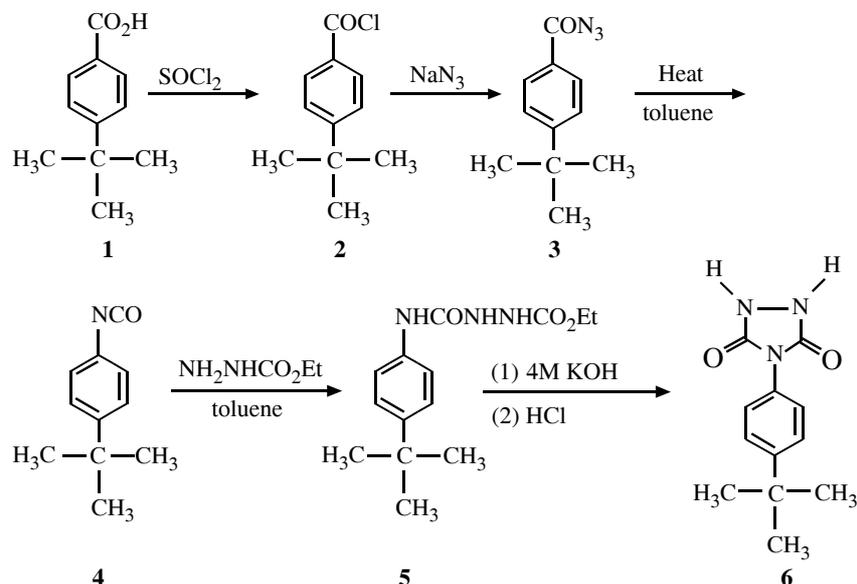
The above polymerization was repeated, but the reaction mixture was irradiated in a microwave oven at 100% of its power for different periods of time in DMAc, using pyridine or triethylamine or dibutyltin dilaurate as a catalyst.

IR(KBr): 3320 (s, br), 3100 (m, br), 2950 (s), 1797 (m), 1710-1680 (s, br), 1600 (m), 1540-1510 (s, br), 1440 (w), 1210 (s), 830 (m), 760 (m), 650 (m), 550 (m) cm^{-1} . $^1\text{H NMR}$ (500 MHz, DMSO- d_6): 1.20-1.40 (s, br, 6H, CH_3), 2.09-2.45 (m, 3H, CH_3), 3.35 (s, br, CH_3), 7.06-7.79 (m, br, 7H, Ar-H), 7.80-9.30 (m, br, N-H). Anal. calcd for $\text{C}_{21}\text{H}_{21}\text{N}_5\text{O}_4$: C, 61.90%; H, 5.19%; N, 17.89%. Found: C, 62.97%; H, 6.17%; N, 17.69%.

RESULTS AND DISCUSSION

Monomer Synthesis

4-(4'-*tert*-Butylphenyl)-1,2,4-triazolidine-3,5-dione TBPTD [4-(4'-*tert*-butylphenyl)urazole] (**6**) was prepared in 5 steps starting from 4-*tert*-butylbenzoic acid (Scheme I). The structures of compound TBPTD (**6**)



Scheme I. Synthesis of monomer **6**.

was confirmed by IR and ^1H NMR (Figure 1) spectra and elemental analyses. The IR and ^1H NMR spectra of **6** showed all the peaks which are in agreement with the structure of compound **6**. The elemental analysis results are in good agreement with the structure of compound **6**. The purity of monomer **6** was checked by TLC which shows one spot in ethylacetate/cyclohexane mixture (50:50) with $R_f = 0.32$. The compound TBPTD **6** was used as a monomer for the polycondensation reactions.

Model Compound Studies

Monomer TBPTD has *tert*-butyl group which could

make it more soluble in common organic solvents. It also has two sites of N-H which can react with isocyanates, it would be interesting to examine the reactivity of these NHs towards isocyanates. Thus, TBPTD (**6**) was allowed to react with excess *n*-propylisocyanate in dry DMF solution, and gave 1,2-bis-(*n*-propylamidocarbonyl)-4-[4'-(*tert*-butylphenyl)]-1,2,4-triazolidine-3,5-dione **7** in high yield (Scheme II). The model compound **7** was characterized by IR, ^1H NMR, and elemental analysis. The IR spectrum of **7** showed a peak at 3350 cm^{-1} for the N-H bond, three peaks at

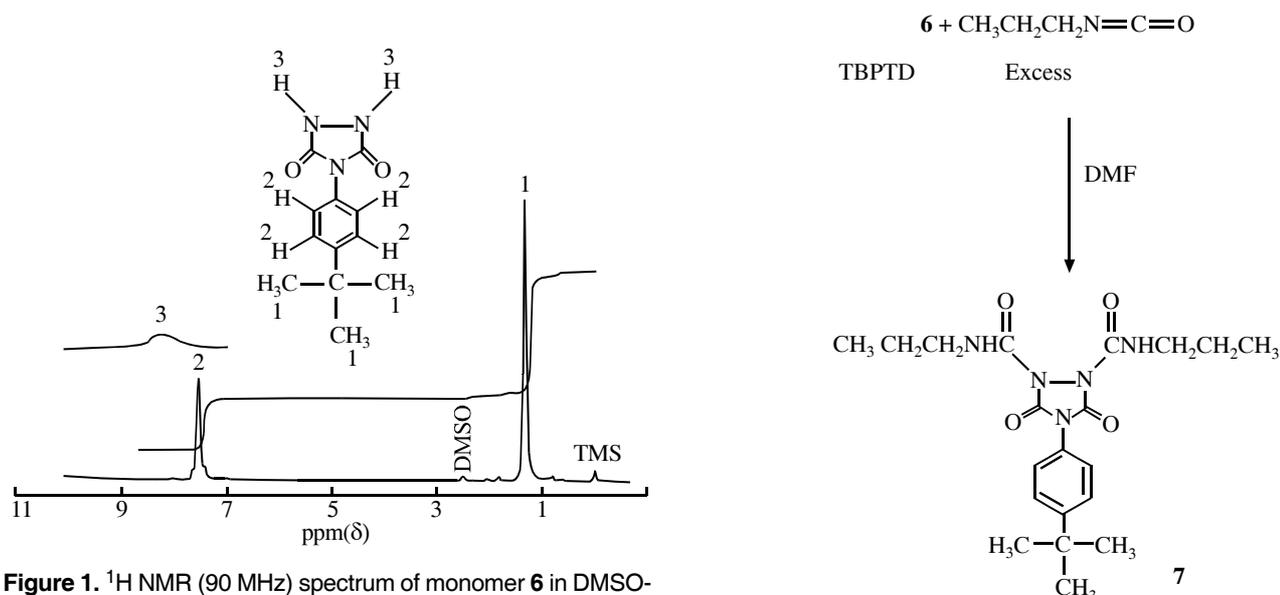
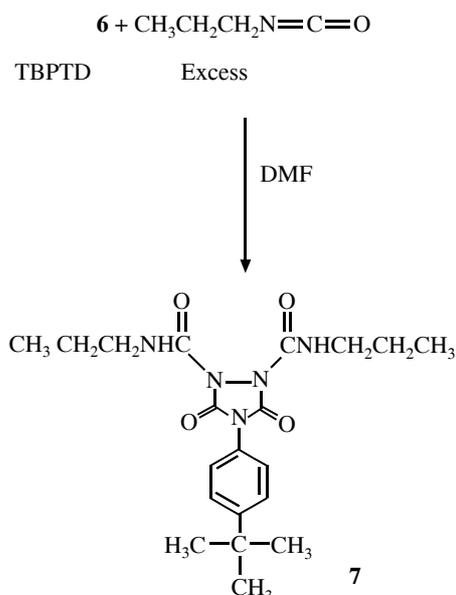


Figure 1. ^1H NMR (90 MHz) spectrum of monomer **6** in $\text{DMSO}-d_6$ at room temperature. Peak number 3 is off-set by 2 ppm.

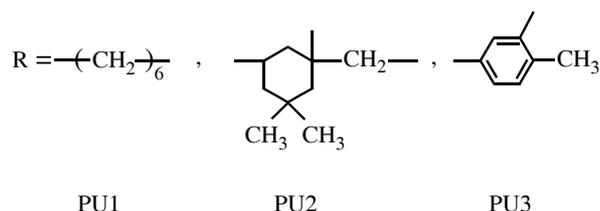
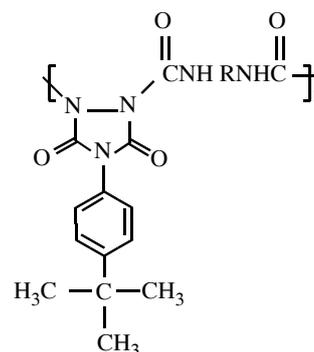
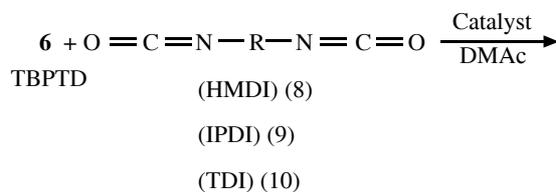


Scheme II. Preparation of model compound **7**.

1785, 1738 and 1717 cm^{-1} for the carbonyl groups. The first two peaks are characteristic pattern for the urazole moiety. The ^1H NMR spectrum (Figure 2) of **7** showed all the peaks which 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 ethylacetate/cyclohexane mixture (50:50) with $R_f = 0.23$.

Polymerization Reactions and Characterization

Because 1,2-bis-(*n*-propylamidocarbonyl)-4-[4'-(*tert*-butylphenyl)]-1,2,4-triazolidine-3,5-dione **7** as model compound was synthesized in good yield and purity, we became interested to perform this type of the reaction for the formation of the novel polyureas. Thus HMDI (**5**), IPDI (**6**) and TDI (**7**) were selected as diisocyanates. The polymerization reaction of monomer **6** with these diisocyanates were performed under microwave irradiation as well as conventional solution polymerization techniques in the presence of different catalysts PU1-PU3 (Scheme III). The polymerization reaction of monomer **6** with HMDI was performed with three different methods. In method I, the reaction mixture was refluxed in DMAc in the absence of catalysts as well as in the presence of pyridine, triethylamine and dibutyltin dilaurate, respectively. The polyurea (PU1A), produced without catalyst has low viscosity. The resulting polyureas PU1B-PU1D have good yield and good



Scheme III. Polycondensation reactions of monomer **6** with diisocyanates.

inherent viscosities (Table 1). In this case dibutyltin dilaurate catalyst gave highest viscosity. In method II the reaction mixture was heated gradually from room temperature up to 135°C in the presence of pyridine, triethylamine and dibutyltin dilaurate, respectively. In this method the resulting polyureas (PU1E-PU1H) have rather low yields and low inherent viscosities, therefore this method is not suitable for the synthesis of PU1. In method III the polymerization reaction was performed in DMAc under microwave irradiation in the presence of pyridine, triethylamine and dibutyltin dilaurate, respectively. The resulting polyureas, PU1I-PU1L have high yield and good inherent viscosities. Reaction conditions and some physical properties for PU1A-PU1L are summarized in Table 1. The resulting polymers were characterized by IR, ^1H NMR, elemental analysis and TGA.

The IR spectrum of polymer PU1 showed a medium peak at 3310 cm^{-1} for the N-H bond, two peaks at 1790 and 1730 cm^{-1} for the carbonyl groups, which are characteristic patterns for the urazole moiety. The ^1H NMR

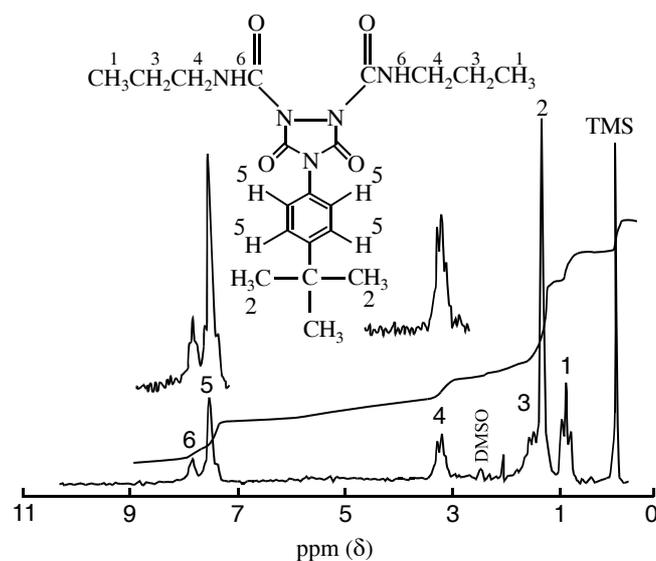


Figure 2. ^1H NMR (90 MHz) spectrum of model compound **7** in DMSO-d_6 at room temperature.

Table 1. Reaction conditions for the polymerization of monomer TBPTD (**6**) with HMDI in DMAc by different methods and some physical properties for PU1A-PU1L.

Polymer	Method ^a	Catalyst	Reaction time	Colour	Yield (%)	Inherent viscosity (dL/g)	mp dec. (°C)
PU1A	I	-	0.5 h, RT; 2 h	W	92	0.025 ^e	250
PU1B	I	Py ^b	0.5 h, RT; 2 h	G	60	0.070 ^e	250
PU1C	I	TEA ^d	0.5 h, RT; 2 h	W	57	0.116 ^f	95
PU1D	I	DBTDL ^c	0.5 h, RT; 2 h	W	63	0.306 ^f	245
PU1E	II	-	72 h, 110-120°C	W	70	0.001 ^f	200
PU1F	II	Py	2 h, RT; 10 h, 60°C; 14 h, 110-120°C	Y	65	0.068 ^e	130
PU1G	II	TEA	2 h, RT; 4 h, 125-135°C	G	32	-	120
PU1H	II	DBTDL	2 h, RT; 12 h, 60°C; 8 h, 125-135°C	Y	84	0.037 ^e	115
PU1I	III	-	10 min	W	55	0.114 ^e	190
PU1J	III	Py	15 min	W	87	0.098 ^e	140
PU1K	III	TEA	15 min	W	100	0.204 ^e	110
PU1L	III	DBTDL	10 min	OW	70	0.140 ^e	180

(a)Method I: Refluxing. Method II: Gradual heating at different temperatures. Method III: Irradiating by a domestic microwave oven at 100% of its power. (b)Pyridine, (c)dibutyltin dilaurate, (d)triethylamine. (e)Measured at a concentration of 0.5 g/dL in DMF at 25°C. (f)Measured at a concentration of 0.5 g/dL in H₂SO₄ at 25°C. G = grey, OW = off-white W= white, Y = yellow.

(500 MHz) spectrum (Figure 3) of polymer PU1 showed all the peaks for aliphatic and aromatic as well as N-H protons. The elemental analysis result is also in good agreement with calculated percentages for carbon, hydrogen and nitrogen contents in polymer repeating unit.

The polymerization reaction of monomer **6** with IPDI was also carried out with three different methods (Table 2). The best method is method II in which under graduate heating higher yields and viscosities were obtained. The IR spectrum of polymer PU2 showed two strong peaks at 1770 and 1738 cm⁻¹ for the carbonyl groups which are related to the urazole moiety. The ¹H NMR spectrum of polymer 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 polymerization reaction of monomer **6** with TDI was also performed with three different methods (Table 3). The best method in this case is method III in which under microwave irradiation shorter reaction time, high yield and good viscosity were obtained. The

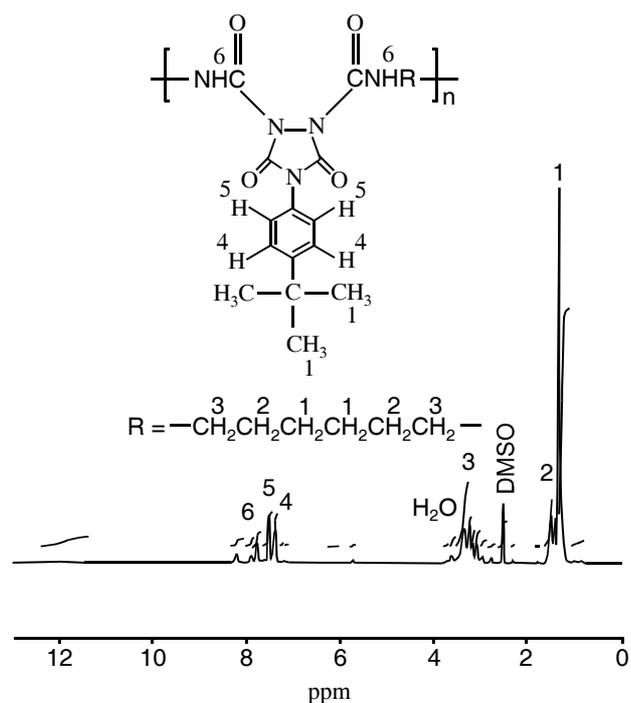


Figure 3. ¹H NMR (500 MHz) spectrum of polymer PU1 in DMSO-d₆ at room temperature Peak at 11.85 ppm is due to N-H of urazole end group.

Table 2. Reaction conditions for the polymerization of monomer TBPTD (**6**) with IPDI in DMAc by different methods and some physical properties for PU2A-PU2H.

Polymer	Method	Catalyst	Reaction time	Colour	Yield (%)	Inherent viscosity (dL/g)	mp dec. (°C)
PU2A	I	DBTDL ^c	4 h	LB	66	0.110 ^e	180
PU2B	II	Py ^b	2 h, RT; 95 h, 110-120°C	Y	90	0.120 ^e	180
PU2C	II	TEA ^d	2 h, RT; 60 h, 110-120°C	G	50	0.134	190
PU2D	II	DBTDL	2 h, RT; 95 h, 130-140°C	LB	83	0.095 ^e	180
PU2E	III	Py	10 min	W	83	0.091 ^e	220
PU2F	III	TEA	10 min	W	60	0.025 ^e	140
PU2H	III	DBTDL	18 min	Y	100	0.030 ^e	145

(a) Method I: Refluxing; Method II: Gradual heating at different temperatures. Method III: Irradiating by a domestic microwave oven at 100% of its power.

(b) Pyridine, (c) dibutyltin dilaurate, (d) triethylamine. (e) Measured at a concentration of 0.5 g/dL in DMF at 25°C. Measured at a concentration of 0.5 g/dL in H₂SO₄ at 25°C. G = grey, LB = light-brown, OW = off-white, W = white, Y = yellow.

Table 3. Reaction conditions for the polymerization of monomer TBPTD (**6**) with TDI in DMAc by different methods and some physical properties for PU3A-PU3H.

Polymer	Method ^a	Catalyst	Reaction time	Colour	Yield (%)	Inherent viscosity (dL/g)	mp dec. (°C)
PU3A	I	DBTDL ^c	4 h	Y	70	0.175 ^e	200
PU3B	II	Py ^b	2 h, RT; 24 h, 120°C	W	90	0.066 ^e	200
PU3C	II	TEA ^d	2 h, RT; 28 h, 120°C	LB	50	0.072	170
PU3D	II	DBTDL	2 h, RT; 12 h, 130-140°C	Y	60	0.105 ^f	160
PU3E	III	Py	10 min	W	74	0.138 ^e	210
PU3F	III	TEA	10 min	Y	63	0.145 ^e	255
PU3G	III	DBTD	10 min	Y	40	0.106 ^e	150

(a) Method I: Refluxing; Method II: Gradual heating at different temperatures. Method III: Irradiating by a domestic microwave oven at 100% of its power.

(b) Pyridine, (c) dibutyltin dilaurate, (d) triethylamine. (e) Measured at a concentration of 0.5 g/dL in DMF at 25°C. Measured at a concentration of 0.5 g/dL in H₂SO₄ at 25°C. G = grey, LB = light-brown, OW = off-white, W = white, Y = yellow.

IR spectrum of polymer PU3 showed peaks which confirm its chemical structure. The ¹H NMR spectrum of polymer 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 PU3.

The polymers PU1 PU2 are soluble in organic solvents such as DMF, DMSO, DMAc acetic acid, THF, chloroform and H₂SO₄ and PU3 is soluble in organic solvents such as DMF, DMSO, DMAc and H₂SO₄. All of these polymers are insoluble in solvents such as

water, methanol, and cyclohexane.

Thermal Properties

The thermal behaviour of polyureas PU1, PU2 and PU3 were measured by thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) at a rate of 10°C/min in nitrogen atmosphere (Figures 4,5).

An examination of the data reveals that all of the above polyureas are thermally stable up to 200°C in nitrogen atmosphere. The polymers PU1, PU2 and PU3 show 10% weight loss at 257, 259 and 250°C, respectively.

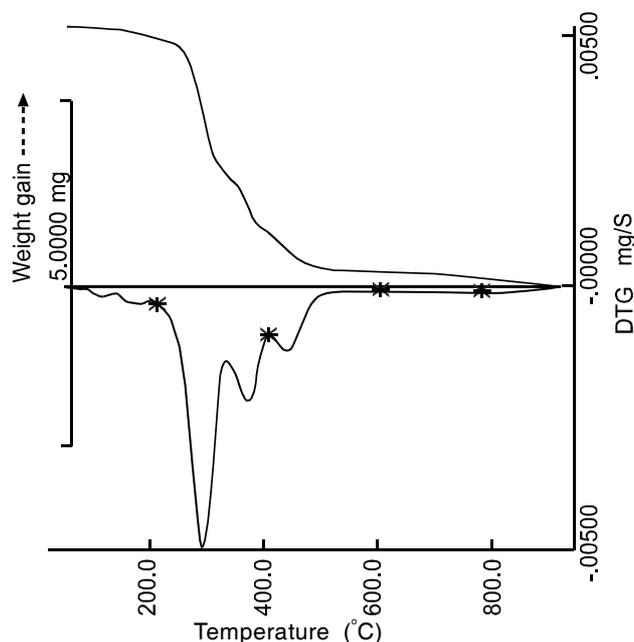


Figure 4. TGA and DTG thermogram of polymer PU1 under nitrogen atmosphere.

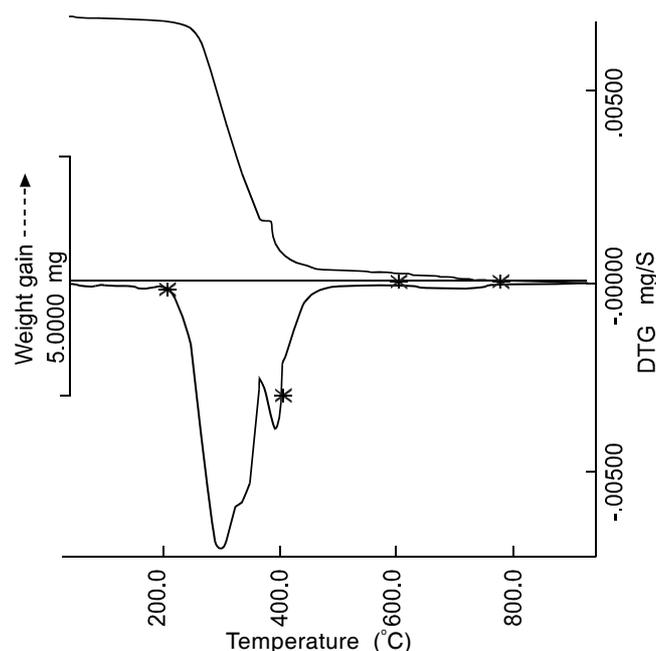


Figure 5. TGA and DTG thermogram of polymer PU2 under nitrogen atmosphere.

CONCLUSION

This investigation has shown that TBPTD (**6**) is an interesting monomer for the polycondensation reac-

tions. This compound has two acidic N-H groups and it can be readily reacted with n-propylisocyanate to give 1:2 adduct in high 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, which contained urazole linkages in two dimensions. The resulting polymers are soluble in many organic solvents. This good solubility is due to presence of *tert*-butyl group. In this work polycondensation reaction under microwave irradiation is a comparable 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.

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