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Efficient combination of ionic liquids and microwave irradiation as a green protocol for polycondensation of 4-(3-hydroxynaphthalene)-1,2,4-triazolidine-3,5-dione with diisocyanates

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Abstract

In this investigation, a novel urazole containing 3-hydroxynaphthalene group, 4-(3-hydroxynaphthalene)-1,2,4-triazolidine-3,5-dione (**3HNTD**) was synthesized in six steps starting from 3-hydroxy-2-naphthalene carboxylic acid. The reaction of **3HNTD** with *n*-propylisocyanate was performed in *N*,*N*-dimethylacetamide solution at different molar ratios, and the resulting monosubstituted as well as disubstituted urea derivatives were obtained in high yields and were used as model compounds for polymerization studies. An efficient, fast and easy method for the preparation of new soluble poly(urea-urethane)s (**PUU**)s containing heterocyclic and chromophoric moieties from **3HNTD** and various diisocyanates are employed using room temperature ionic liquids and molten tetrabutylammonium bromide under microwave irradiation as well as conventional heating. The polymerization reactions occurred rapidly under microwave and produced a series of **PUU**s with good yields and moderate inherent viscosities of 0.21−0.46 dL/g. All of the new **PUU**s showed good solubility and were readily dissolved in organic solvents.

Keywords: 4-(3-Hydroxynaphthalene)-1,2,4-triazolidine-3,5-dione; Microwave irradiation; Room temperature ionic liquids

1. Introduction

Ionic liquids **IL**s, as a class of molten salts, are a new category of solvent, with attractive properties. **IL**s are non-volatile and non-flammable, and are considered to be environmentally friendly alternatives to volatile organic compounds (VOC) and proper solvents for green physical and chemical processes. **IL**s contain a number of interesting properties, such as their large liquid range and generally can be easily separated from reaction products. Many characterization of **IL**s can be adjusted over broad ranges, by varying the types of anion and cation. Owing to these special properties, **IL**s have found variety of applications in many areas predominantly as a new series of materials and solvents for green chemistry. The toxicological studies available show that **IL**s are relatively non-toxic substances (LD_{50} is 1400 mg/kg). A number of outstanding publications are already presented in which the properties and various uses of these environmentally benign media have been investigated [1−5]. They have also been applied as reaction media in different polymerization systems, such as olefin [6], oxidative [7], condensation [8,9], enzymatic [10], conventional free-radical [11], and atom transfer radical polymerization [12].

Microwave irradiation is an alternative to thermal heating for converting electromagnetic energy into heat. Microwave irradiation as a non-conventional energy source has become a very well-known and useful technology in organic chemistry as well as macromolecular chemistry [13−17]. **IL**s are also appropriate for microwave chemistry. To merge the benefits of microwave technique and **IL**s, recently, several organic reactions as well as polymerization reactions have been studied in **IL** under microwave irradiation [18−21]. Since **IL**s contain

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organic cations and suitable anions, from the perspective of microwave chemistry the most important properties of **IL**s that can be utilized are their polarity (about that of methanol) and their stability at high temperatures. The combination of **IL** and microwave irradiation leads to large reductions in reaction times, very high heating rate with many benefits of the eco-friendly approach, named green chemistry. **IL**s absorb microwave emission in a very efficient way because of their high polarity and furthermore, they display a very low vapor pressure, thereby enhancing their fitness even further for microwave heating [20,21].

Urazoles (1,2,4-triazolidine-3,5-diones) are very significant chemical reagents in the laboratory as well as in industry. Technologically urazoles are used as a blowing agent in plastics, in the production of automobile air bags, in the manufacture of herbicides [22], antifungal compounds and in polymeric material [23,24]. They are also utilized in the production of anti-tumor drugs [25] and as a stabilizer in milk. Urazoles have been used as a laboratory reagent for preparation of novel heterocyclic [26], and organometallic compounds. Some urazole derivatives were found to be potent cytotoxic gents in murrain and human cancer cell lines and also reduce DNA synthesis considerably with moderate reduction in RNA synthesis. Other pharmaceutical properties of urazole derivatives are hypolipidemic activity via lowering serum cholesterol and triglyceride levels [27], pesticides [28] and insecticides [29]. Preparations of thermoplastics, production of heat resistant coatings [30], tire rubbers with high gripability [31] and melamine resins [32] are among the applications in the field of polymerization of urazole derivatives. Urazoles could also be oxidized to the corresponding triazolinedione derivatives [33] which are very active species toward cycloaddition and ene reactions [34]. The synthesis and characterization of the macromolecules restrain heterocyclic rings in the main chains has been the topic of considerable interest because of their relatively good thermal stability and some attractive novel properties [35].

Chromophoric macromolecules have been widely investigated in the last decade because of their potential technological use in electronic and opto-electronic tools [36]. Naphthalene structure as a chromophore gave special characteristics such as rigid, bulky, moisture resistance and low coefficient of thermal expansion to polymer. The insertion of naphthalene as a pendant group in a polymer chain has resulted in decreased crystallinity, enhanced solubility and thermal stability [37].

In view of the emerging importance of the **IL**s as reaction media and our general interest in microwave-assisted chemical processes, we decided to investigate a simple, rapid, green and efficient methodology for the synthesis of new heterocyclic chromophoric poly(urea-urethane)s (**PUU**)s in **IL**s under microwave irradiation.

2. Experimental

2.1. Materials and equipments

Reagents were purchased from Fluka Chemical (Buchs, Switzerland), Aldrich Chemical (Milwaukee, WI) and Riedel-deHaen AG (Seelze, Germany). Tetrabutylammonium bromide (**TBAB**) was purchased from Merck Co. (Darmstadt, Germany) and was used without further purification. All room temperature ionic liquids **RTIL**s were prepared by reported procedure [8,9]. The microwave apparatus used for the polycondensation was a Samsung (Seoul, South Korea) microwave oven (2450 MHz and 900 W). ^{1}H NMR (500 MHz) spectra were recorded on a Bruker (Germany), Avance 500 instrument. Multiplicities of proton resonance were designated as singlet (s), triplet (t), quartet (q) and multiplet (m). FTIR and IR spectra were recorded on a Nicolet Impact 400_D IR spectrophotometer and on Shimadzu (Kyoto, Japan) 435 IR spectrophotometer, respectively. Spectra of solids were carried out using KBr pellets. Vibrational transition frequencies are reported in wave number (cm^{-1}). 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. Inherent viscosities were measured by standard procedure using a Cannon Fenske Routine viscometer. Quantitative solubility was determined using 0.05 g of the polymer in 1 mL of solvent. Elemental analyses were performed by Research Institute of Polymer and Petrochemical of Iran (IPPI). Fluorescence and UV–vis spectra were recorded on a spectrofluorometer, JASCO, FP-750 and UV/Vis/NIR spectrophotometer, JASCO, V-570, respectively. Mass spectrum was recorded on a spectroscopy Fisons (Trio 1000). Thermal Gravimetric Analysis (TGA) data for polymers were taken on a TGA-Perkin Elmer (Pyris 1) at a heating rate of 10 °C/ min under N_2 atmosphere by the Research Institute of Polymer and Petrochemical of Iran (IPPI). DSC data were recorded on a DSC-PL-1200 instrument under N_2 atmosphere by IPPI. Glass transition temperatures (T_g) were read at the middle of the transition in the heat capacity taken from the heating DSC traces.

2.2. Synthesis of monomer

*2.2.1. Preparation of 3-acetoxynaphthalene-2-carboxylic acid (**2**)*

Into a 100-mL round bottom flask, 3-hydroxynaphthalene-2-carboxylic acid (**1**) (3.00 g, 1.59×10^{-2} mol), 7 mL of acetic anhydride and two drops of sulfuric acid were added. The suspension was stirred for 1 h between 50 and 60 °C and then poured into 100 mL of water. The solid was collected by filtration, and dried to give 3.49 g (95%) of white solid **2**. Melting point: 172–174 °C, lit: melting point: 173.5 °C [38]. IR (KBr, cm^{-1}): 3000 (s, br), 2650 (m), 1760 (s), 1690 (s), 1630 (m), 1593 (m), 1500 (m), 1460 (s), 1444 (m), 1405 (m), 1360 (m), 1330 (m), 1290 (s), 1200 (s), 1158 (m), 1140 (m), 1060 (m), 1000 (m), 960 (w), 925 (m, sh), 900 (s), 820 (w) 685 (w), 642 (m).

*2.2.2. Preparation of 3-acetoxynaphthalene-2-carbonyl chloride (**3**)*

Into a 25-mL round bottom flask was placed, acid **2** (2.00 g, 8.69×10^{-3} mol) and 6 mL of thionyl chloride (excess amount). The suspension was stirred for 1 h at 70 °C which gave clear pale-yellow solution. Unreacted thionyl chloride was removed under reduced pressure, and the residue was washed with *n*-hexane. The product was dried to leave 2.70 g (96%) of acid chloride **3**. Melting point: 94 °C. IR (KBr, cm^{-1}): 3000 (w), 1760 (s), 1700 (s), 1620 (s), 1590 (m), 1490 (m), 1450 (m), 1400 (m), 1370 (s), 1330 (m), 1290 (m), 1270 (m), 1190 (s), 1170 (m), 1140 (m), 1100 (m), 1060 (m), 1040 (m), 1010 (m), 930 (m), 900 (m), 825 (m), 790 (m), 750 (m).

2.2.3. Preparation of 3-acetoxy-2-naphthaloyl azide (4)

Into a 25 mL one-necked round bottomed flask was placed a solution (2.00 g, 8.04×10^{-3} mol) of acid chloride **3** in 7 mL of acetone. The mixture was cooled in an ice bath. While the solution was gently stirred by a magnetic stirrer, a solution of 0.52 g (8.04×10^{-3} mol) of sodium azide in 5 mL of water was added dropwise in a period of 10 min. The mixture was stirred for a further 1 h. Then 10 mL of water was added and stirring was continued for additional 1 h at room temperature. The solid was filtered off, and dried in air to give 1.95 g (95%) of white solid **4**. Melting point: 104 °C. IR (KBr, cm^{-1}): 3000 (w), 2250 (s), 2150 (s), 1770 (s), 1680 (s), 1622 (s), 1595 (s), 1550 (s), 1500 (s), 1460 (s), 1420 (m), 1360 (s), 1340 (m), 1270 (s), 1230 (s), 1200 (s), 1170 (s), 1122 (s), 1098 (s), 1040 (s), 1000 (m), 907 (m), 809 (s), 760 (s), 740 (m).

2.2.4. Preparation of 1-ethoxycarbonyl-4-(3-acetoxy-2-naphthyl) semicarbazide (6)

Into a 100-mL round bottom flask, acyl azide **4** (2.00 g, 7.48×10^{-3} mol) and 25 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. The solution was cooled in an ice bath and a solution of 0.82 g (7.48×10^{-3} mol) of ethyl carbazate in 10 mL of dry toluene was added dropwise in a period of 10 min. The suspension was stirred for 1 h in ice bath, then for 10 h at room temperature. The solid was filtered off, and dried to give 2.22 g (98%) of white solid **6**. Melting point: 177–178 °C. IR (KBr, cm^{-1}): 3350 (s), 3250 (s), 3000 (m), 2900 (m), 1770 (s), 1735 (s), 1650 (s), 1580 (s), 1558 (s), 1492 (s), 1440 (s), 1370 (s), 1315 (m), 1270 (s), 1215 (s), 1145 (s), 1100 (m), 1048 (s), 1023 (s), 980 (m), 950 (m), 920 (m), 800 (w), 770 (s), 680 (m), 630 (m), 505 (m).

2.2.5. Preparation of 4-(3-hydroxy-2-naphthalene)-1,2,4-triazolidine-3,5-dione, **3HNTD** (7)

Into a 100 mL one-necked round bottom flask 1.00 g (3.46×10^{-3} mol) of semicarbazide **6** and a water solution of potassium hydroxide (5 mL of 4 M) were added. The solution was heated between 50 and 54 °C for a period of 2 h and then it was cooled and conc. HCl was added until the pH of the solution was around 1. The mixture was stirred for 0.5 h in ice bath and then was filtered off. The white solid 0.79 g (92.5%) was recrystallized from water. Melting point: 230–232 °C. IR (KBr, cm^{-1}): 3150 (s), 3050 (s), 1760 (m), 1690 (s), 1630 (s), 1600 (m), 1530 (m), 1480 (m), 1450 (s), 1395 (m), 1360 (m), 1220 (m), 1200 (m), 1150 (m), 1050 (m), 990 (w), 870 (m), 840 (w), 790 (m), 750 (m). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.28–7.85 (m, 6H, Ar-H), 10.42 (s, 2H, N–H), 11.53 (s, 1H, O–H). Mass (EI), *m/z*: 243 ([M$^+$], 23.5%), 241 (94.2%), 185 (90.4%), 184 (25.2%), 115 (45.2%), 114 (37.0%), 102 (37.0%), 57 (100%). UV (DMF): λ_{max} (ε) = 275 (181,326), 329 nm (46,630 L mol^{-1} cm^{-1}).

2.3. Preparation of model compounds 8 and 9

2.3.1. **3HNTD** (7) to isocyanate 1:12, compound 9

Model compounds were prepared in order to obtain information about the reactivity of active sites in the new monomer **7**. All model compounds were prepared by the same procedure with different molar ratios of **3HNTD** (**7**) to isocyanate (1:1, 1:2, 1:3 and 1:12), with 1:12 ratio as an example.

Into a 25-mL round bottom flask, *n*-propylisocyanate (1.0 mL, 9.87×10^{-3} mol) was added to a solution of **3HNTD** (**7**) (0.200 g, 8.22×10^{-4} mol) in 1 mL of dry *N*,*N*-dimethylacetamide (DMAc). The solution was stirred for 24 h at room temperature. The excess *n*-propylisocyanate was removed by aspirator and the residue was precipitated in 30 mL of water. The resulting solid was filtered off, dried to give 0.316 g (93%) of white solid **9**. This solid was recrystallized from methanol. Melting point: 158–160 °C. IR (KBr, cm^{-1}): 3359 (m), 3100 (w), 2950 (w), 2927 (m), 2850 (w), 1773 (m), 1730 (s), 1699 (s), 1612 (s), 1472 (s), 1400 (s), 1330 (s), 1300 (m), 1273 (m), 1231 (m), 1200 (s), 1165 (s), 1142 (s), 1080 (s), 1020 (s), 970 (m), 925 (m), 880 (s), 810 (m), 750 (s), 730 (s), 630 (m), 540 (m). ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.83–0.88 (t, 6H, $J = 7.4$ Hz), 1.46–1.53 (m, 4H), 3.13–3.20 (q, 4H, $J = 6.7$ Hz), 6.54–7.45 (m, 6H, Ar-H), 7.72 (s, 2H, N–H amide), 9.96 (s, 1H, N–H urazole). Elemental analysis calculated for $C_{20}H_{23}N_5O_5$: C, 58.10%; H, 5.61%; N, 16.94%. Found: C, 58.51%; H, 5.81%; N, 16.61%. UV (DMF): λ_{max} (ε) = 277 (109,313), 329 nm (44,000 L mol^{-1} cm^{-1}).

2.3.2. **3HNTD** (7) to isocyanate 1:1, compound 8

Melting point: 226–228 °C. IR (KBr, cm^{-1}): 3300 (s), 3000 (s), 2850 (w), 1780 (s), 1730 (s), 1700 (s), 1610 (s), 1590 (s), 1510 (s), 1380 (w), 1360 (w), 1260 (s), 1200 (s), 1160 (s), 1090 (w), 1070 (w), 1040 (w), 810 (m), 850 (m), 830 (m), 570 (m). ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.78–0.87 (t, 3H, $J = 7.3$ Hz), 1.29–1.35 (m, 2H), 2.88–2.97 (q, 2H, $J = 6.9$ Hz), 6.97–7.58 (m, 6H, Ar-H), 7.76 (s, 1H, N–H amide), 10.15 (s, 1H, N–H urazole), 11.85 (s, 1H, O–H). Elemental analysis calculated for $C_{16}H_{16}N_4O_4$: C, 58.53%; H, 4.91%; N, 17.06%. Found: C, 58.35%; H, 4.72%; N, 17.35%. UV (DMF): λ_{max} (ε) = 276 (212,127), 333 nm (44,894 L mol^{-1} cm^{-1}).

The other model compounds (1:2 and 1:3 ratios of **3HNTD** (**7**) to isocyanate) gave similar results compared with 1:1 ratio.

2.4. Synthesis of polymer

*2.4.1. Method I: polymerization of **3HNTD** with diisocyanates in **RTIL** and **TBAB** under microwave heating*

Before each experiment, the **RTIL**s were dried at 75 °C under reduced pressure. Several **RTIL**s were used in this work, but 1,3-diallylimidazolium bromide, [1,3-(All)$_2$im]Br was selected for all the polymerization reactions under optimum conditions.

General procedure for preparation of **PUU**s in **RTIL** and **TBAB**: as an example for the preparation of **PUU1AI**, mixture of 0.1083 g (4.45×10^{-4} mol) of **3HNTD** and 0.200 g (1.35×10^{-3} mol) of [1,3-All$_2$im]Br or 0.3000 g (9.23×10^{-4} mol) of **TBAB** were placed in a porcelain dish and the mixture was pulverized completely for 5 min., then 0.0749 g (4.45×10^{-4} mol) of **HMDI** (**10**) was added and the mixture was ground for 3 min. The reaction mixture was irradiated in the microwave oven for a period of 60 + 30 + 30 s at 70% of power level. The resulting polymer was isolated by addition of 30 mL of methanol. The white solid was filtered off, dried to give 0.163 g (89%) of **PUU1AI**.

*2.4.2. Method II: polymerization of **3HNTD** with diisocyanates in **RTIL** under conventional heating*

General procedure for preparation of **PUU**s in **RTIL**: as an example for the preparation of **PUU1AII**, 0.0876 g (5.21×10^{-4} mol) of **HMDI** (**10**), 0.1267 g (5.21×10^{-4} mol) of **3HNTD** and 0.300 g (2.02×10^{-3} mol) of [1,3-All$_2$im]Br were stirred at 120 °C for 12 h. The viscous solution was precipitated in 30 mL of methanol. The white solid was filtered off, dried to give 0.201 g (94%) of **PUU1AII**.

*2.4.3. Polymerization of **3HNTD** with diisocyanates in molten **TBAB***

General procedure for preparation of **PUU**s in molten **TBAB**: as an example for the preparation of **PUU1BII**, mixture of 0.1043 g (4.29×10^{-4} mol) of **3HNTD** and 0.3000 g (9.23×10^{-4} mol) of **TBAB** were placed in a reaction vessel and the mixture was ground until a powder was formed. The mixture was transferred into a 25-mL round bottom and 0.0721 g (4.29×10^{-4} mol) of **HMDI** (**10**) was added to the mixture and was stirred until homogeneous solution was formed. The solution was stirred for 12 h at 120 °C. The viscous solution was precipitated in 30 mL of methanol. The white solid was filtered off, dried to give 0.137 g (78%) of **PUU1BII**.

The other polymers **PUU2** and **PUU3** were prepared by the same procedure using isophorone diisocyanate (**IPDI**), (**11**) and toluylene-2,4-diisocyanate (**TDI**), (**12**) as diisocyanate, respectively.

PUU1: FTIR (KBr, cm^{-1}): 3351 (m), 3090 (m), 2933 (m), 2857 (m), 1772 (m), 1721 (s), 1634 (s), 1542 (s), 1476 (s), 1417 (m), 1361 (m), 1323 (m), 1287 (m), 1248 (m), 1168 (m), 1116 (w), 1061 (w), 874 (w), 840 (w), 749 (m), 655 (w), 621 (w), 597 (w). ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.15−1.76 (m, br, 8H, CH$_2$), 3.25−3.85 (m, br, 4H, CH$_2$), 7.52−8.32 (m, br, 6H, Ar-H), 10.31 (s, 1H, N−H). Elemental analysis calculated for $C_{20}H_{21}N_5O_5$ (411.418 g/mol): C, 58.39%; H, 5.14%; N, 17.02%. Found: C, 57.51%; H, 5.58%; N, 16.46%. UV (DMF): λ_{max} (ε) = 275 (171,877), 331 nm (25,842 L mol^{-1} cm^{-1}).

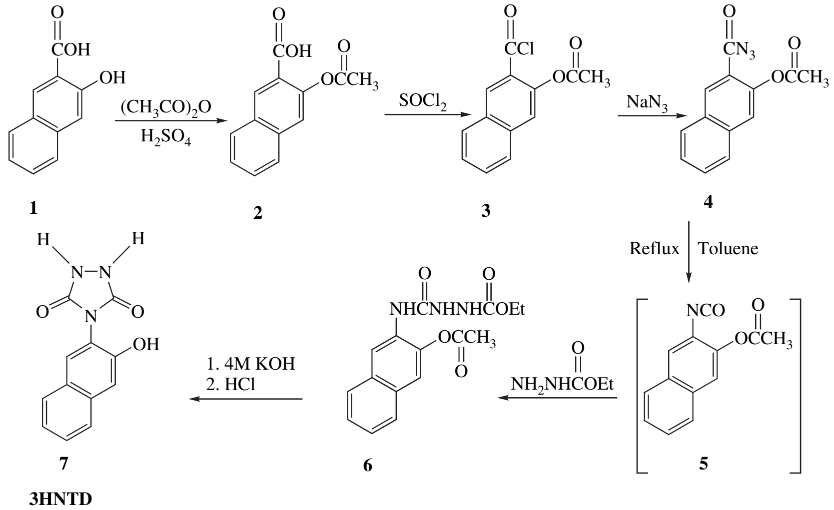
PUU2: FTIR (KBr, cm^{-1}): 3352 (m), 2955 (m), 2873 (m), 1770 (m), 1718 (s), 1650 (s), 1556 (s), 1462 (s), 1385 (s), 1364 (s), 1307 (s), 1238 (s), 1168 (m), 1100 (m), 1062 (m), 954 (w), 925 (w), 871 (m), 747 (m), 661 (m). ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.83−1.30 (m, br, 11H, CH$_3$, CH$_2$), 1.38−1.43 (m, br, 4H, CH$_2$), 2.79 (m, br, 2H, CH$_2$), 3.58 (m, br, 1H, CH), 7.56−8.25 (m, 8H, Ar-H, N−H), 10.63 (s, 1H, N−H). Elemental analysis calculated for $C_{24}H_{27}N_5O_5$ (465.509 g/mol): C, 61.92%; H, 5.85%; N, 15.04%. Found: C, 62.04%; H, 6.08%; N, 14.82%. UV (DMF): λ_{max} (ε) = 276 (108,229), 333 nm (30,688 L mol^{-1} cm^{-1}).

PUU3: FTIR (KBr, cm^{-1}): 3330 (m), 2932 (m), 2856 (m), 1740 (m), 1619 (s), 1576 (s), 1747 (m), 1462 (m), 1380 (m), 1337 (m), 1254 (m), 1215 (m), 1077 (m), 1038 (m), 736 (m), 630 (m). ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.15 (m, br, 3H, CH$_3$), 7.51−8.32 (m, br, Ar-H), 7.62−8.22 (m, br, Ar-H, N−H), 10.23 (s, 1H, N−H). Elemental analysis calculated for $C_{21}H_{15}N_5O_5$ (417.381 g/mol): C, 60.43%; H, 3.62%; N, 16.78%. Found: C, 61.75%; H, 3.90%; N, 16.47%. UV (DMF): λ_{max} (ε) = 276 (159,474), 331 nm (48,947 L mol^{-1} cm^{-1}).

3. Results and discussion

3.1. Monomer synthesis

Urazole ring containing 3-hydroxynaphthalene moiety was synthesized by the route shown in Scheme 1. Thus, the novel monomer **3HNTD** was synthesized by a series of chemical transformation in which 3-hydroxynaphthalene-2-carboxylic acid (**1**) was reacted with acetic anhydride to give compound **2** in high yield. This acid **2** by reacting with thionyl chloride gave the corresponding acid chloride **3**. This acid chloride was reacted with sodium azide, and acyl azide **4** was obtained in excellent yield. The acyl azide was subjected to thermal decomposition in dry toluene to yield isocyanate **5**. Semicarbazide **6** was prepared by condensing ethyl carbazate with isocyanate. Cyclization followed by deprotection in the presence of potassium hydroxide (4 M) between 50 and 60 °C gave **3HNTD** (**7**) as a novel monomer. The purity of monomer **7** was checked by thin layer chromatography (TLC). The ^{1}H NMR spectrum of **7** showed all peaks which were in good agreement with the proposed structure of compound **7** (Fig. 1). The structure of this synthesized compound was also confirmed by IR, UV−vis, fluorimetric and Mass spectra. We also applied one easy and convenient method to quickly verify the formation of urazole. We treated the urazole in dichloromethane with *N*-bromosuccinimide (NBS) reagent, which oxidizes white color urazole to the red color triazolinedione (a colorimetric test). Appearance of red color upon addition of NBS confirmed the formation of urazole **7**.



Scheme 1. Synthesis of monomer **7**.

3.2. Model compounds' studies

Because **3HNTD** (**7**) has two N–H and one O–H sites which can react with isocyanates, before the polymerization, we decided to examine the reactivity of these sites toward *n*-propylisocyanate. Thus, **3HNTD** (**7**) was allowed to react with different molar ratios of **3HNTD** (**7**) to *n*-propylisocyanate (1:1, 1:2, 1:3 and 1:12) in DMAc solution. Compound **7** was reacted with *n*-propylisocyanate (1:1, 1:2 and 1:3) and 1-(*n*-propylamidocarbonyl)-4-(3-hydroxynaphthyl)-1,2,4-triazolidine-3,5-dione (**8**) was obtained in high yield and purity. **3HNTD** (**7**) also was reacted with *n*-propylisocyanate (1:12) which produced compound **9**. The purity of model compounds was checked with TLC. The structure of model compounds were confirmed by IR, ^{1}H NMR, elemental analysis, UV–vis, fluorimetric spectroscopy and chemical tests, which in case of chemical test both model compounds did not react with NBS which indicates one or two N–Hs reacted with isocyanate and compound **8** reacted with $FeCl_3$ which proves the presence of O–H in the ring, but compound **9** did not react with $FeCl_3$ (Schemes 2 and 3). The IR spectrum of compound **8** showed a broad strong peak at 3330 cm^{-1} for the N–H and O–H bonds and three peaks at 1780, 1730 and 1700 cm^{-1} for the carbonyl groups. The first two peaks are characteristic of the urazole moiety. The IR spectrum of compound **9** showed a sharp strong peak at 3359 cm^{-1} for the N–H bond and three peaks at 1773, 1730 and 1699 cm^{-1} for the carbonyl groups. The ^{1}H NMR spectra of compounds **8** and **9** (Figs. 2 and 3) showed all the peaks, which are in agreement with the structure of compounds **8** and **9**. The elemental analysis results were in good agreement with the structure of model compounds **8** and **9**. It is interesting to mention that under even large excess of isocyanate only one N–H and O–H reacted with it. This may be explained in terms of reactivity of two N–H groups. When one N–H is reacted the other one will become less reactive than O–H group, therefore O–H reacts with isocyanate. These data are very useful for the polymerization and this method prevents the formation of crosslinked, insoluble polymers.

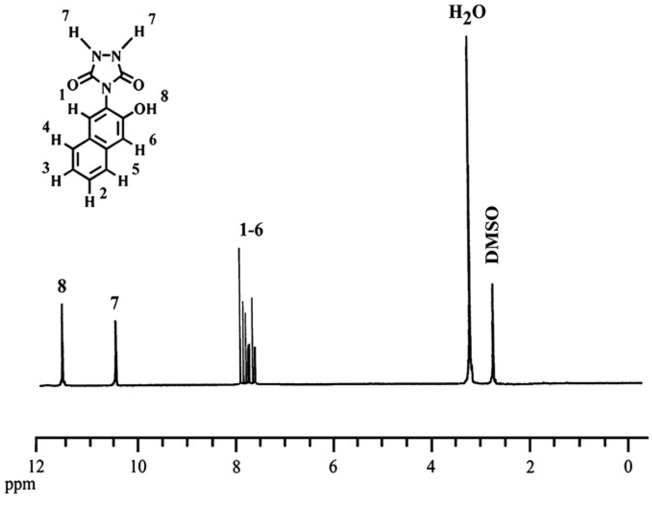
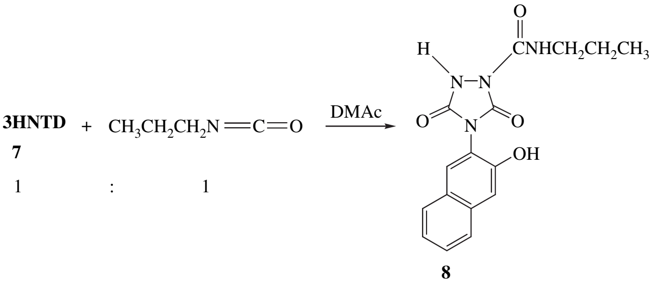


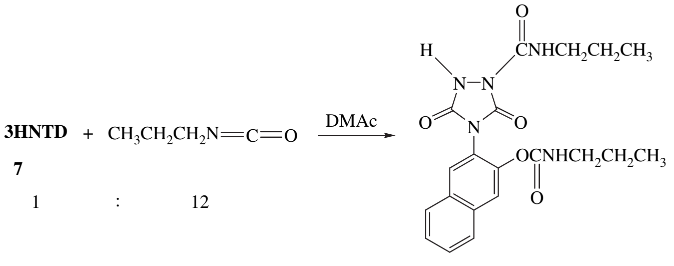
Fig. 1. ^{1}H NMR (500 MHz) spectrum of monomer compound **7** in DMSO-d_6 at room temperature.

3.3. Polymer synthesis

In this study, we reported polycondensation reaction of novel monomer **3HNTD** with diisocyanates both under microwave conditions (*method I*) and conventional heating (*method*



Scheme 2. Synthesis of model compound **8**.



9

Scheme 3. Synthesis of model compound **9**.

II) in **RTIL**s and **TBAB** as reaction media. **RTIL**s, predominantly those based on substituted imidazolium cations, which can be prepared simply from the commercially available starting material, *N*-trimethylsilylimidazole and alkyl halides, were used in this investigation [8,9]. Thus, [1,3-Pr$_2$im]Br, [1,3-Isopr$_2$im]Br, [1,3-Bu$_2$im]Br, [1,3-Pent$_2$im]Br, [1,3-Hex$_2$im]Br, [1,3-Hex$_2$im]Br, [1,3-Hep$_2$im]Br, [1,3-All$_2$im]Br, [1,3-Bz$_2$-im]Br and molten **TBAB** as **IL**s were selected. In the first step, we examined the formation of **PUU**s via polycondensation of **3HNTD** with the **HMDI** in **RTIL**s under microwave irradiation (*method I*). The optimization of the procedure by varying different types of **IL**s, the amount of **IL**, the time of irradiation, power level of microwave instrument, and using of catalyst was carried out to achieve polymers with high yields and moderate inherent viscosities. As it is shown in Tables 1 and 2 all of these parameters has significant effect on the polymer chain growth.

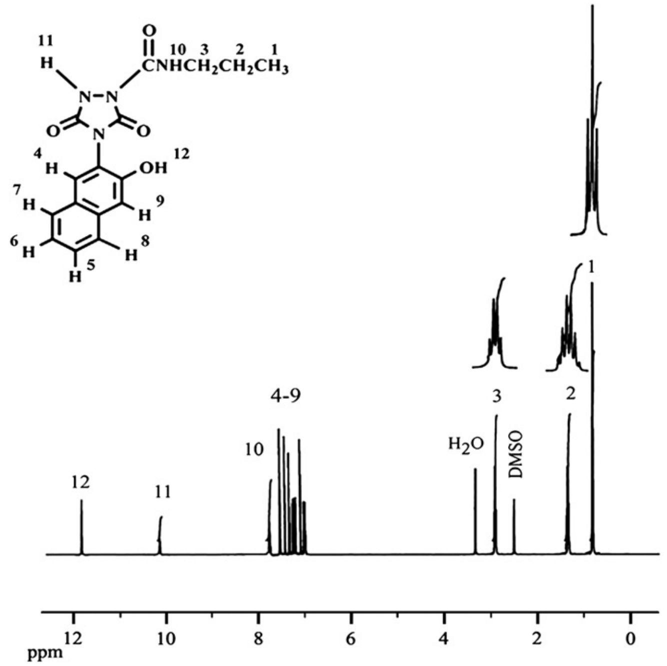


Fig. 2. ^1H NMR (500 MHz) spectrum of model compound **8** in DMSO-d_6 at room temperature.

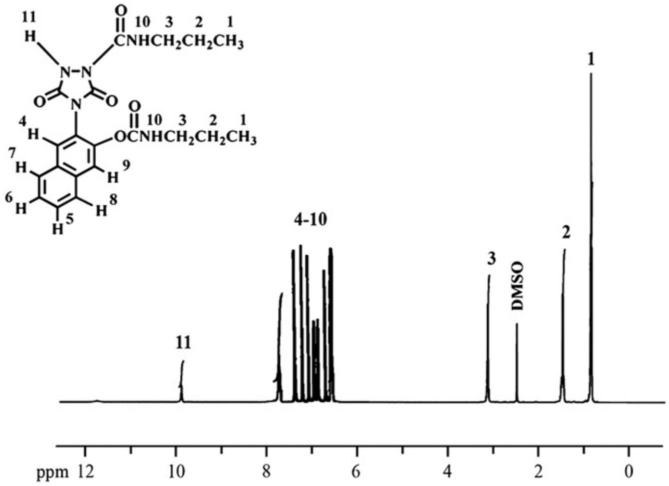


Fig. 3. ^1H NMR (500 MHz) spectrum of model compound **9** in DMSO-d_6 at room temperature.

In order to optimize the reaction conditions, initially, the effect of **IL**s nature was studied. In case of imidazolium type **RTIL**s, [1,3-All$_2$im]Br gave better results (Table 2), therefore it was selected for the synthesis of other **PUU**s (**PUU1**–**PUU3**). As alkyl chain in **IL**s was increased, yields and inherent viscosities decreased. This may be explained by the decrease of polarity and as a result, the lower solubility power of longer alkyl chain of **IL**s. We also studied the effect of microwave power on the reaction of **3HNTD** with **HMDI** using [1,3-All$_2$im]Br as the reaction medium (Table 1). A collection of experiments were performed with different reaction times and power levels under microwave irradiations revealed that the optimal results were obtained after 60 + 30 + 30 s at 70% of power level. When the reaction mixture was irradiated at 100% of power level and times 60–180 s, no polymer was obtained. Overheating of the reaction mixture took place with evolution of vapor, leading to decomposition of the reaction mixture probably due to the localized heating of the **IL**, which ultimately results in lower yields. This problem can be circumvented with exact control of both temperature and radiation intensity by intermittent heating and mixing at a moderate power level to afford better yields and cleaner polymers formation. In the present case, the problem may be explained by the fact that **IL**s are high polar and likely to be strongly microwave gripping. After the first irradiation for 60 s at 70% of power level the homogeneity of the reaction mixture changes due to creation of polymer. The reaction mixture is then taken out, mixed again for 10 s and then heated at the same power level for an additional of 30 s. This step is repeated for another 30 s. At this step, a clear polymeric film was formed. It is important to note that because of highly polar character of **IL**s, polymers have higher solubility in them than organic solvents. To explore the efficiency of amount of **RTIL**s in **PUU**s synthesis under microwave heating, the polycondensation of **3HNTD** with **HMDI** was carried out in different amounts of [1,3-All$_2$im]Br, and the best results are obtained with 0.20 g of **RTIL** under reaction conditions, so this amount was used for the other polymerization reactions (Table 1). Because of the strong microwave absorption capacity of **IL**s, the reaction temperature increases rapidly so

Table 1
Optimization of reaction conditions for the preparation of **PUU1** using microwave irradiation (*method I*) and conventional heating (*method II*)

Entry	Method	Microwave power	Reaction temperature (°C)	Reaction time	Amount of **IL**[b] (g)	Yield (%)	η_{inh}[c] (dL/g)
1[a]	I	100	–	180 s	0.30	–	–
2[a]	I	100	–	120 s	0.30	–	–
3	I	100	–	80 s	0.30	42	–
4	I	100	–	60 s	0.30	48	–
5	I	80	–	120 s	0.30	62	0.13
6	I	80	–	80 s	0.30	61	0.11
7	I	80	–	60 s	0.30	58	0.09
8	I	70	–	60 + 30 + 30 s	0.30	78	0.25
9	I	70	–	60 + 30 + 30 s	0.20	89	0.46
10	I	70	–	60 + 30 + 30 s	0.15	87	0.32
11	I	60	–	60 + 30 + 30 s	0.30	82	0.31
12	I	60	–	60 + 30 + 30 s	0.20	88	0.34
13	I	60	–	60 + 30 + 30 s	0.15	81	0.28
14	II	–	120	12 h	0.30	94	0.42
15	II	–	100	12 h	0.30	79	0.31
16	II	–	80	12 h	0.30	69	0.17
17	II	–	70	12 h	0.30	68	0.19
18	II	–	120	10 h	0.30	82	0.31
19	II	–	120	8 h	0.30	71	0.28
20	II	–	120	7 h	0.30	78	0.22
21	II	–	120	6 h	0.30	79	0.21
22	II	–	120	12 h	0.2	77	0.20
23	II	–	120	12 h	0.15	78	0.17
24	II	–	120	12 h	0.30	94	0.42

[a] Decomposition occurred at higher power or extended irradiation time.

[b] **IL** = [1,3-All$_2$im]Br; **HMDI** = **3HNTD** = 4.45×10^{-4} mol (*Method I*); **HMDI** = **3HNTD** = 5.21×10^{-4} mol (*Method II*).

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

when the amount of **IL** was higher, the reaction mixture changed to dark color and burned. On the other hand, the amount of **IL** that was used for microwave conditions was less than conventional conditions. To compare the microwave-assisted method with conventional heating polycondensation method, we also performed the polymerization reactions under conventional heating in **IL**s (*method II*). The optimization of this process by varying type of **IL**s, amount of **IL**, temperature, time and catalyst loading was done (Tables 1 and 2). When the same experiment was conducted by conventional heating in the presence of [1,3-All$_2$im]Br as a solvent, it took very long time (12 h) for completion of the reaction. Thus, notable rate acceleration was observed under the microwave conditions. This demonstrated the beneficial effect of microwave as the energy source. The yields and inherent viscosities of the products obtained by microwave irradiation versues thermal heating are higher. The optimum conditions which were obtained under microwave and conventional heating conditions have been applied for the preparation of other **PUU**s by the reaction of monomer **7** with **IPDI** and **TDI**, respectively (Scheme 4) and the results are shown in Table 3. The unsymmetric diisocyanates such as **TDI** and **IPDI** gave polymers with lower inherent viscosities, compared to the symmetric **HMDI**. This could pertain to the better possibility of chain arrangement and chain growth, when a step-growth polymerization reaction mechanism is performed during a define reaction time. The inherent viscosities of the resulting polymers under microwave irradiation were in the range of 0.21–0.46 dL/g and the yields were 81–94%. Some physical properties of these novel **PUU**s under optimum conditions are listed in Table 3. The comparative results are summarized in Table 4. Molten **TBAB** also gave high yields and moderate inherent viscosities. The polymerization reactions were also carried out in **RTIL**s and molten **TBAB** in the presence and in the absence of catalyst, dibutyltin dilaurate

Table 2
The influence of **IL** cation upon yield and molecular weight (η_{inh}) of **PUU1**

Entry	**IL**	Yield[i] (%)	η_{inh}[i,k] (dL/g)	Yield[j] (%)	η_{inh}[j,k] (dL/g)
1	[1,3-pr$_2$im]Br[a]	91	0.28	87	0.29
2	[1,3-Isopr$_2$im]Br[b]	92	0.30	85	0.28
3	[1,3-Bu$_2$im]Br[c]	85	0.24	89	0.26
4	[1,3-Pent$_2$im]Br^{-}[d]	72	0.23	85	0.22
5	[1,3-Hex$_2$im]Br[e]	74	0.20	70	0.18
6	[1,3-Hep$_2$im]Br[f]	69	0.18	61	0.17
7	[1,3-All$_2$im]Br[g]	89	0.46	94	0.42
8	[1,3-Bz$_2$im]Br[h]	86	0.24	73	0.29
9	TBAB	88	0.36	78	0.31

[a] Pr = Propyl.

[b] Isopr = Isopropyl.

[c] Bu = Butyl.

[d] Pent = Pentyl.

[e] Hex = Hexyl.

[f] Hep = Heptyl.

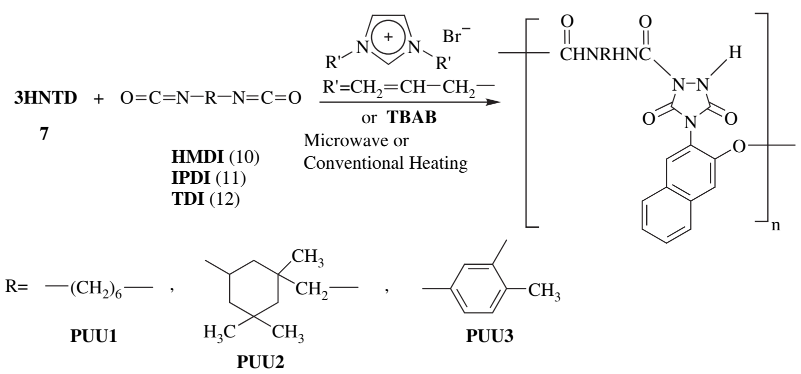
[g] All = Allyl.

[h] Bz = Benzyl.

[i] Using microwave irradiation (**HMDI** = **3HNTD** = 4.45×10^{-4} mol, **RTIL**s = 0.20 g or **TBAB** = 0.30 g, power level = 70%, $t = 60 + 30 + 30$ s).

[j] Using conventional heating (**HMDI** = **3HNTD** = 5.21×10^{-4} mol, **RTIL**s = 0.30 g or **TBAB** = 0.30 g, $T = 120$ °C, 12 h).

[k] Measured at a concentration of 0.5 g/dL in DMF at 25 °C.



Scheme 4. Polycondensation reaction of **3HNTD** with diisocyanates in **RTIL**s and molten **TBAB** under microwave irradiation and conventional heating.

(DBTDL). No significant difference was observed when the reaction was performed by using DBTDL; indicate that it is not required in this polycondensation reaction. Thus, **IL**s may act as both solvent and catalyst in this process (Table 3).

3.4. Polymer characterization

The structure of polymers was implemented by means of elemental analysis, FTIR and ^{1}H NMR (500 MHz) spectroscopies. The elemental analysis results were in good agreement with calculated percentages for carbon, hydrogen and nitrogen contents in **PUU**s repeating unit. The FTIR spectra of polymers show peak around 3300 cm^{-1} for the N−H bond. Main absorption bands at 1770–1650 cm^{-1} range were attributed to the carbonyl groups. The two absorption bands at 2900 and 2850 cm^{-1} are related to the corresponding C−H stretching vibration. The ^{1}H NMR spectra of polymers (Figs. 4 and 5) showed all peaks for aliphatic and aromatic protons which confirmed their structures.

3.5. UV absorption characteristics

The UV–vis spectra of the **3HNTD** (**7**), model compounds **8** and **9**, **PUU**s were recorded in *N*,*N*-dimethylformamide (DMF). It is apparent that the wavelength of maximum absorption is related to the naphthalene group in the aforementioned compounds. All of these compounds show almost similar UV–vis spectra pattern. These macromolecules exhibited maximum ultraviolet–visible absorption at 275 and 331 nm

Table 3
Synthesis and some physical properties of **PUU1–PUU3**s under microwave irradiation (*method I*) and conventional heating (*method II*)

Polymer	Diisocyanate	Method	Cat.	**IL**	Yield (%)	η_{inh}[b] (dL/g)
PUU1AI	HMDI	I	–	[1,3-All$_2$im]Br	89	0.46
PUU1BI	HMDI	I	–	TBAB	88	0.36
PUU1CI	HMDI	I	DBTDL[a]	[1,3-All$_2$im]Br	91	0.42
PUU1DI	HMDI	I	DBTDL	TBAB	86	0.35
PUU2AI	IPDI	I	–	[1,3-All$_2$im]Br$^-$	92	0.24
PUU2BI	IPDI	I	–	TBAB	91	0.21
PUU2CI	IPDI	I	DBTDL	[1,3-All$_2$im]Br	94	0.22
PUU2DI	IPDI	I	DBTDL	TBAB	89	0.24
PUU3AI	TDI	I	–	[1,3-All$_2$im]Br	82	0.26
PUU3BI	TDI	I	–	TBAB	87	0.31
PUU3CI	TDI	I	DBTDL	[1,3-All$_2$im]Br	85	0.27
PUU3DI	TDI	I	DBTDL	TBAB	81	0.26
PUU1AII	HMDI	II	–	[1,3-All$_2$im]Br	94	0.42
PUU1BII	HMDI	II	–	TBAB	78	0.31
PUU1CII	HMDI	II	DBTDL	[1,3-All$_2$im]Br	85	0.32
PUU1DII	HMDI	II	DBTDL	TBAB	89	0.33
PUU2AII	IPDI	II	–	[1,3-All$_2$im]Br	90	0.23
PUU2BII	IPDI	II	–	TBAB	88	0.20
PUU2CII	IPDI	II	DBTDL	[1,3-All$_2$im]Br	88	0.22
PUU2DII	IPDI	II	DBTDL	TBAB	86	0.19
PUU3AII	TDI	II	–	[1,3-All$_2$im]Br	80	0.28
PUU3BII	TDI	II	–	TBAB	79	0.32
PUU3CII	TDI	II	DBTDL	[1,3-All$_2$im]Br	76	0.22
PUU3DII	TDI	II	DBTDL	TBAB	74	0.21

[a] Dibutyltin dilaurate.

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

Table 4
Comparison of some physical properties of the **PUU1**–**PUU3**s synthesized by *method I* and *method II*, under optimum conditions

Polymer	Diisocyanate	Yield[a] (%)	$\eta_{inh}{}^{a}$ (dL/g)	Yield[b] (%)	$\eta_{inh}{}^{b}$ (dL/g)
PUU1A	HMDI	89	0.46	94	0.42
PUU1B	HMDI	88	0.36	78	0.31
PUU2A	IPDI	92	0.24	90	0.23
PUU2B	IPDI	91	0.21	88	0.20
PUU3A	TDI	82	0.26	80	0.28
PUU3B	TDI	87	0.31	79	0.32

[a] *Method I*: polycondensation of **3HNTD** with diisocyanates using [1,3-All$_2$im]Br and **TBAB**, respectively, in the optimum conditions under microwave irradiation.

[b] *Method II*: polycondensation of **3HNTD** with diisocyanates using [1,3-All$_2$im]Br and **TBAB**, respectively, in the optimum conditions under conventional heating.

in DMF solution. The absorption spectrum of 4.60×10^{-6} M, DMF solution of the **PUU1** is shown in Fig. 6.

3.6. Fluorescence characteristics

Polymers with fluorescent properties have been investigated in recent years [39,40]. These polymers include chromophores in the backbone and polymers having chromophores as a pendant group. They are used as fluorescent labels and photoharvesters. The fluorescence spectra of the monomer, model compounds, **PUU1**, **PUU2** and **PUU3** were recorded in DMF. For example, in the case of the monomer, the compound was excited at 260 nm, and emission fluorescence wavelengths were observed at 361 and 427 nm, respectively. All of these compounds show almost similar fluorescence spectra pattern. Because of these **PUU**s have naphthalene functional group; they have potential to be used as photolabeling and photoresponsive materials. The fluorescent intensity of **PUU3** is higher than that of **PUU1** and **PUU2**. It can be probably due to the rigidity enhancement of this polymer in compared with other two polymers.

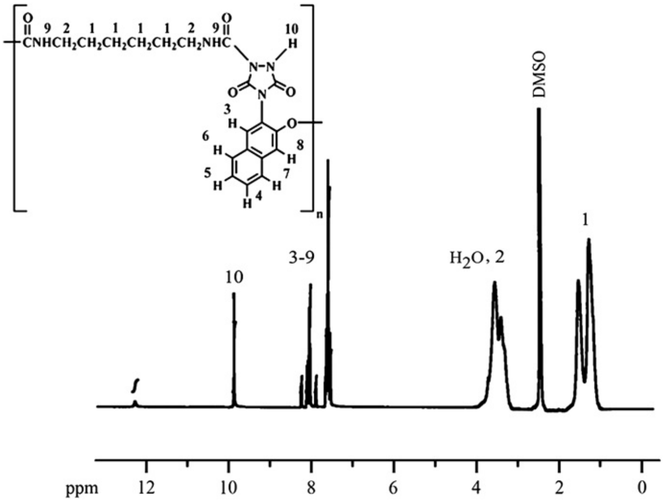


Fig. 4. ^{1}H NMR (500 MHz) spectrum of **PUU1** in DMSO-d_6 at room temperature.

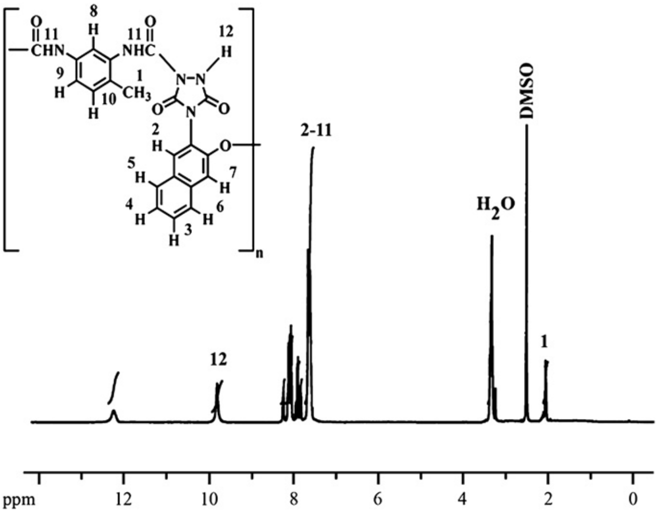


Fig. 5. ^{1}H NMR (500 MHz) spectrum of **PUU3** in DMSO-d_6 at room temperature.

3.7. Solubility of **PUU**s

All of the polymers are soluble in organic solvents such as DMF, DMAc, dimethyl sulfoxide, *N*-methyl-2-pyrrolidone and in H_2SO_4, and are insoluble in solvents such as water, methanol, acetone, cyclohexane and chloroform.

3.8. Thermal properties

In order to understand the thermal properties, the thermal behavior of **PUU**s were measured by thermogravimetric analysis (TGA) and derivative of thermogravimetric (DTG) analysis at a heating rate of 10 °C/min in a nitrogen atmosphere. Figs. 7 and 8 show TGA results of **PUU1AI** and **PUU3CI**, respectively. They clearly indicate that there is no weight loss when they are heated from room temperature to 300 °C. The 5 and 10% weight loss (T_5, T_{10}) of the polymers

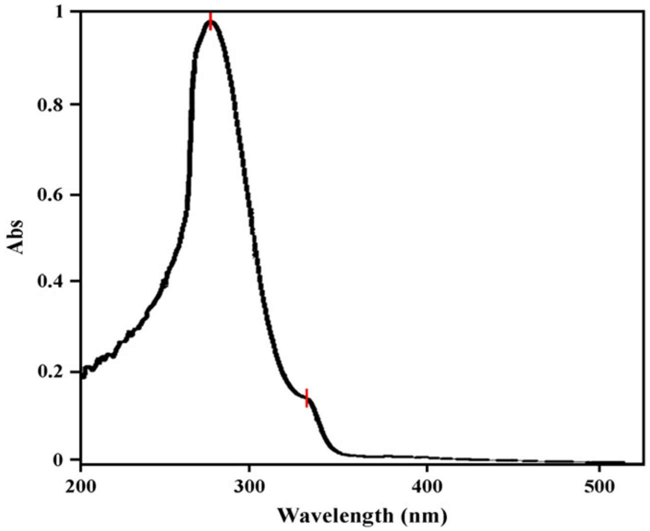


Fig. 6. Absorption spectrum of **PUU1** in DMF solution 4.60×10^{-6} M.

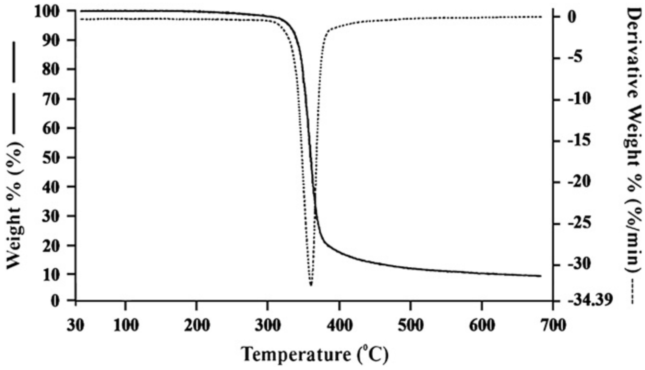


Fig. 7. TGA/DTG of **PUU1AI** with a heating rate of 10 °C/min in a nitrogen atmosphere.

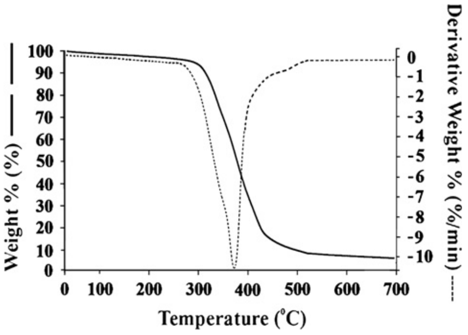


Fig. 8. TGA/DTG of **PUU3CI** with a heating rate of 10 °C/min in a nitrogen atmosphere.

and residue at 600 °C (char yield) were used as criterions for their thermal stability. The temperatures of 5 and 10% weight loss together with char yield at 600 °C for all **PUU**s were calculated from their thermograms and listed in Table 5. It seems that symmetric, linear diisocyanate, **HMDI** has shown higher thermal stability than unsymmetric diisocyanates **IPDI** and **TDI**. This could explain that higher inherent viscosity resulting from **HMDI** could be responsible for its higher thermal stability. The DSC analyses for **PUU1AI**, **PUU2AI** and **PUU3CI** show T_g around 111, 148 and 153 °C, respectively. The thermoanalysis data of polymers are summarized in Table 5.

Table 5
Thermal Properties of **PUU1AI**, **PUU2AI** and **PUU3CI**

Polymer	Decomposition temperature		Char yield (%)[c]	T_g[d]
	T_5 (°C)[a]	T_{10} (°C)[b]		
PUU1AI	317	331	10	111
PUU2AI	200	240	3	148
PUU3CI	287	313	10	153

[a] Temperature at which 5% weight loss was recorded by TGA at a heating rate of 10 °C/min in a nitrogen atmosphere.

[b] Temperature at which 10% weight loss was recorded by TGA at a heating rate of 10 °C/min in a nitrogen atmosphere.

[c] Percentage weight of material left undecomposed after TGA analysis at a maximum temperature of 600 °C in a nitrogen atmosphere.

[d] Glass transition temperature was recorded at a heating rate of 20 °C/min in a nitrogen atmosphere.

4. Conclusions

In summary, we developed a facile and green procedure to accelerate polycondensation of **3HNTD** with diisocyanates by using microwave irradiation in conjunction with **IL**s. In this study, advantages of both of the **IL** and microwave irradiation have been utilized. This methodology offers significant improvements for the synthesis of polymers with regard to yield of products, simplicity in operation, and green aspects by avoiding toxic catalysts and volatile solvents. This approach also requires only a few seconds of reaction time in compare to several hours needed under conventional heating conditions. Therefore, microwave technique makes the synthesis of **PUU**s not only faster but also 'greener', and much more convenient.

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References

[1] Kemperman GJ, Horst BT, Goor DV, Roeters T, Bergwerff J, Eem RV, et al. Eur J Org Chem 2006;3169–74.
[2] Ranu BC, Jana R. Adv Synth Catal 2005;347:1811–8.
[3] Moon BS, Lee KC, An GI, Chi DY, Yang SD, Choi CW, et al. J Labelled Compd Radiopharm 2006;49:287–93.
[4] Welton T. Chem Rev 1999;99:2071–83.
[5] Weng J, Wang C, Li H, Wang Y. Green Chem 2006;8:96–9.
[6] Carlin RT, Wilkes JS. J Mol Catal 1990;63:125–9.
[7] Kobryanskii VM, Arnautov SA. J Chem Soc Chem Commun 1992; 727–8.
[8] Lozinskaya EI, Shaplov AS, Vygodskii YaS. Eur Polym J 2004;40: 2065–75.
[9] Mallakpour S, Kowsari E. J Polym Sci Part A Polym Chem 2005;43: 6545–53.
[10] Uyama H, Takamoto T, Kobayashi S. Polym J 2002;34:94–6.
[11] Zhang H, Hong K, Mays JW. Macromolecules 2002;35:5738–41.
[12] Biedron T, Kubisa P. Macromol Rapid Commun 2001;22:1237–42.
[13] Ramesh C, Mahender G, Ravindranath N, Das B. Green Chem 2003;5:68–70.
[14] Perreux L, Loupy A. Tetrahedron 2001;57:9199–223.
[15] Wiesbrock F, Hoogenboom R, Schubert US. Macromol Rapid Commun 2004;25:1739–64.
[16] Zinck P, Barbier-Baudry D, Loupy A. Macromol Rapid Commun 2005;26:46–51.
[17] Mallakpour S, Rafiemanzelat F. J Appl Polym Sci 2004;93:1647–59.
[18] Liao L, Liu L, Zhang C, Gong S. Macromol Rapid Commun 2006;27: 2060–4.
[19] Mallakpour S, Kowsari E. Iranian Polym J 2006;15:239–47.
[20] Peng Y, Song G. Catal Commun 2007;8:111–4.
[21] Legeay JC, Eyndeb JJV, Bazureau JP. Tetrahedron 2005;61:12386–97.
[22] Jikihara T, Matsuya K, Ohta H, Suzuki S, Wakabayashi O. US Patent 4,249,934; 1981; Jpn Chem Abstr 1981;95:62219 y.
[23] Mallakpour S, Rafiee Z. Polym Bull 2006;56:293–303.
[24] Mallakpour S, Rafiee Z. J Appl Polym Sci 2007;103:947–54.
[25] Hall IH, Wong OT, Simlot R, Miller MC, Izydore R. Anticancer Res 1992;12:1355–62.

[26] Boldi AM, Johnson CE, Eissa HO. Tetrahedron Lett 1999;40:619–22.
[27] Izydore RA, Hall IH. US Patent 4,866,058, 1990. Chem Abstr 1990;112:151876 x.
[28] Ovadia D, Peleg N, Bracha P. US Patent 4,087,534, 1978. Chem Abstr 1978;89:109513 h.
[29] Von Bredow B, Brechbuehler H. Ger Offen 2,343,347; 1974. Chem Abstr 1974;80:140210 s.
[30] Giesecke H, Merten R, Rottmaier L. Ger Offen 3,027,612; 1982. Chem Abstr 1982;96:182879 f.
[31] Oikawa M, Ebina C, Inui N, Nagasaki H, Yago, S. JP 04,249,552; 1993. Chem Abstr 1993;118:61373 a.
[32] Rottmaier L, Merten R. Ger Offen 3,106,944; 1982. Chem Abstr 1982;97:198209 u.
[33] Zolfigol MA, Torabi M, Mallakpour SE. Tetrahedron 2001;57:8381–4.
[34] Mallakpour SE. J Chem Educ 1992;69:238–41.
[35] Sarwade BD, Wadgaonkar PP, Mahajan SS. J Polym Sci Part A Polym Chem 1989;27:3263–9.
[36] Akcelrud L. Prog Polym Sci 2003;28:875–962.
[37] Wang CS, Leu TS. Polymer 2000;41:3581–91.
[38] Cassebaum H. Chem Ber 1957;90:2876–88.
[39] Itoh Y, Inoue M. Eur Polym J 2000;36:2605–10.
[40] Simasa ER, Akcelrud L. J Lumin 2003;105:69–79.