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Synthesis of New Polyureas Derived from 4-(4′-*N*-trimellitylimidophenyl)-1,2,4-triazolidine-3,5-dione

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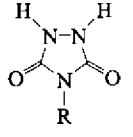
ABSTRACT

4-(4′-Aminophenyl)-1,2,4-triazolidine-3,5-dione (**1**) was reacted with trimellitic anhydride (**2**) in refluxing DMF (*N,N*-dimethylformamide) and gave 4-(4′-*N*-trimellitylimidophenyl)-1,2,4,-triazolidine-3,5-dione (NTMPTD) (**3**) in high yield and purity. This compound was characterized by IR, ^{1}H NMR and elemental analysis. Solution polycondensation reactions of monomer **3** with hexamethylene diisocyanate (HMDI) and isophorone diisocyanate (IPDI) were performed in DMSO in the presence of pyridine as a catalyst and lead to the formation of novel aliphatic polyureas. The polymerization reaction with tolylene-2,4-diisocyanate (TDI) gave novel aromatic polyurea. These novel polyureas have inherent viscosities in a range of 0.11–0.21 dLg^{-1} in DMF at 25 °C. Some structural characterization and physical properties of these novel polymers are reported.

Key Words: polyurea, step-growth polymerization, inherent viscosity, 4-(4′-*N*-trimellitylimidophenyl)-1,2,4-triazolidine-3,5-dione

INTRODUCTION

4-Substituted urazoles (R= alkyl and aryl) are five-membered heterocyclic compounds of the following structure:



R= Alkyl or Aryl

These compound possess two N–H protons. These protons are rather acidic. The urazole derived from the ene reaction of triazolinediones with alkenes and polydienes has one N–H proton, which seems to be very acidic. The acidity of this proton has been measured and is quite acidic with pKa of 4.71, which is almost the same as that of acetic acid [1]. 4-Substituted urazoles have potential to undergo *N*-acylation. These compounds 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

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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 synthesis of novel polymers via *N*-alkylation and *N*-acylation reactions [4,5]. Polymerization of compound 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 dLg^{-1} [7]. Copolymerization of 4-cyclohexylurazole (CHU) with aliphatic diacid chlorides gave soluble polyamides [8]. We have also reported the reaction of PHU with diisocyanates [9]. The resulting novel polyureas have inherent viscosities in a range of 0.04–0.23 dLg^{-1}

The purpose of this investigation was to examine the step-growth polymerization reactions of NTMPTD as a monomer with diisocyanates. In the present paper we report on the successful polycondensation reaction where NTMPTD as a novel monomer is used for the synthesis of aliphatic and aromatic polyureas.

EXPERIMENTAL

Apparatus

Proton nuclear magnetic resonance (^{1}H NMR, 90 MHz) spectra were recorded on a Varian EM-390 instrument. Tetramethylsilane (TMS) was used as an internal reference. IR Spectra were recorded on Shimadzu 435 IR spectrophotometer. Spectra of solids were carried out using KBr pellets. Vibrational transition frequencies are reported in wavenumber (cm^{-1}). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br). Inherent viscosities were measured by a standard procedure using a Cannon Fensk Routine Viscometer (Germany). Thermal gravimetric analysis (TGA) data for polymers were taken on a Mettler TGA-4000 in nitrogen atmosphere at a rate of 10 °C/min. Elemental analyses were performed by Tarbiat Modarres University, Tehran, Iran.

Reagents and Monomer

Reagents were purchased from Fluka Chemical Co., Alderich Chemical Co. and Riedel-deHaen AG.

Preparation of 4-(4′-*N*-trimellitylimidophenyl)-1,2,4,-triazolidine-3,5-dione (NTMPTD) (3)

In a 25 mL round-bottom flask, 4-(4′-aminophenyl)-1,2,4-triazolidine-3,5-dione **(1)** (1.50 g, 7.81×10^{-3} mol) and trimellitic anhydride **(2)** (1.50 g, 7.81×10^{-3} mol) were dissolved in 10 mL of DMF. The solution was stirred for 0.5 h at room temperature then it was refluxed for 24 h. The reaction mixture was cooled in an ice bath, filtered, and washed with 20 mL of water to give 2.28 g (80%) of white solid with mp>320 °C; IR (KBr): 3350–2800 (s, br), 1780 (m, sh), 1760 (m, sh), 1710 (s, sh), 1650 (s, br), 1515 (s), 1470 (m, br), 1375 (s), 1278 (s), 1240 (s), 1215 (s), 1165 (m), 1115 (m), 1085 (s), 880 (m), 840 (w), 795 (m), 765 (m), 725 (m), 690 (m, sh), 595 (m), 525 (w) cm^{-1}. ^{1}H NMR (DMSO, TMS): δ 7.63 (s, 4H), 8.10 (d, 2H, J = 7.5 Hz), 8.35 (s, 1H), 8.48 (d, 2H, J = 7.5 Hz), 10.6 (br, 2H). Elemental analysis calculated for $C_{17}H_{10}N_6O_4$: C, 56.74%; H, 2.75% and N, 15.30%. Found: C, 56.10%; H, 2.50% and N, 15.40%.

Polymerization of NTMPTD with HMDI

In a 25 mL round-bottom flask was placed HMDI **(4)** (0.1021 g , 6.07×10^{-4} mol) and pyridine (0.1 mL, 1.21×10^{-3} mol). In a 10 mL beaker, NTMPTD **(3)** (0.2223 g, 6.07×10^{-4} mol) was dissolved in 1.4 mL of hot DMSO. The solution was cooled to room temperature and it was added to the flask. The solution was stirred for 24 h at room temperature, then for 24 h at 85 °C. The viscous solution was precipitated in 50 mL of methanol. The solid was filtered off, dried to give 0.23 g (71%) of gray polyurea PU1. Inherent viscosity (0.5 dLg^{-1} DMF, 25 °C) = 0.21; IR(KBr): 3300 (s), 2930 (s), 2860 (m), 1770 (m), 1710 (s, br), 1660 (s, br), 1615 (s), 1570 (s, br), 1515 (s), 1475 (m), 1430 (m), 1375 (s), 1250 (m), 1215 (m), 1170 (m), 1120 (m), 1085 (m), 1010 (w), 930 (w), 840 (w), 780 (m, br), 725 (m), 695 (w), 600 (w), 525 (w) cm^{-1}. Thermal analysis: T_5 133 °C, T_{10} 227 °C, char yield at 600 °C: 20.0%. Elemental analysis calculated for $C_{25}H_{22}N_6O_8$: C, 56.18%; H, 4.18% and N, 15.72%.

Found: C, 56.21%; H, 5.40% and N, 15.82%.

Polymerization of NTMPTD with IPDI

In a 25 mL round-bottom flask was placed IPDI **(5)** (0.1247 g , 5.61×10^{-4} mol) and pyridine (0.09 mL, 1.12×10^{-3} mol). In a 10 mL beaker, NTMPTD (0.2055 g, 5.61×10^{-4} mol) was dissolved in 1.4 mL of hot DMSO. The solution was cooled to room temperature and it was added to the flask. The solution was stirred for 24 h at room temperature, then for further 24 h at 85 °C. The viscous solution was precipitated in 50 mL of methanol. The solid was filtered off, dried to give 0.19 g (58%) of gray polyurea PU2. Inherent viscosity (0.5 dLg^{-1} DMF, 25 °C) = 0.11; IR(KBr): 3350 (s, br), 2940 (s), 2900 (s), 1710 (s, sh), 1640 (s, br), 1540 (s, br), 1510 (s), 1460 (m), 1370 (s, br), 1280 (m), 1240 (s, sh), 1120 (w), 1090 (m), 930 (w), 835 (w), 775 (m, br), 725 (m), 695 (w), 600 (w), 520 (w) cm^{-1}. Thermal analysis: T_5 127 °C, T_{10} 220 °C, char yield at 600 °C: 30.0%. Elemental analysis calculated for $C_{29}H_{28}N_6O_8$: C, 59.18%; H, 4.79% and N, 14.28%. Found: C, 59.98%; H, 4.91% and N, 13.35 %.

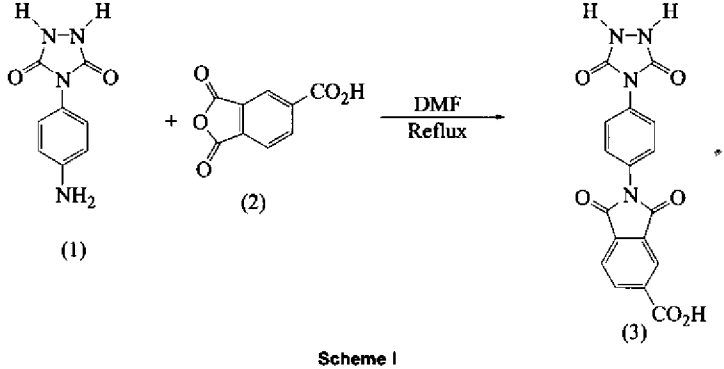
Polymerization of NTMPTD with TDI

TDI **(6)** (0.1300 g , 7.46×10^{-4} mol) and pyridine (0.12 mL, 1.49×10^{-3} mol) and NTMPTD (0.2734 g, 7.46×10^{-4} mol) in hot DMSO were polymerized like above. The viscous solution was precipitated in 50 mL of methanol. The solid was filtered off, dried to give 0.37 g (92%) of gray polyurea PU3. Inherent viscosity (0.5 dLg^{-1} DMF, 25 °C) = 0.16; IR(KBr): 3600–2900 (s, br), 1780–1620 (s, br), 1605 (s), 1515 (s), 1475 (s), 1285 (m), 1245 (s), 1220 (s), 1180 (m), 1120 (m), 1090 (m), 1020 (m), 950 (w), 930 (w), 860 (w), 835 (w), 720 (m), 690 (m), 595 (m), 525 (w) cm^{-1}. Thermal analysis: T_5 120 °C, T_{10} 207 °C, char yield at 600 °C: 36.7%. Elemental analysis calculated for $C_{26}H_{16}N_6O_8$: C, 57.78%; H, 2.98% and N, 15.55%. Found: C, 55.65%; H, 3.84% and N, 15.00%.

RESULTS AND DISCUSSION

Monomer Synthesis

Recently we synthesized 4-(4′-aminophenyl)-1,2,4-triazolidine-3,5-dione **(1)** starting from 4-nitrobenzoic acid in 5 steps [10]. The compound **1** was reacted with trimellitic anhydride **(2)** in refluxing DMF (*N,N*-dimethylformamide) and gave 4-(N-trimellitylimido)-1,2,4,-triazolidine-3,5-dione (NTMPTD) **(3)** in high yield and purity (Scheme I). The structure of this novel monomer was confirmed by IR, ^1H NMR and elemental analysis. The IR spectrum of **(3)** showed a broad peak between 3350–2800 cm^{-1} for the N–H and OH stretching and peaks at 1780, 1760, 1710 and 1650 cm^{-1} for the carbonyl groups. The ^1H NMR spectrum of **(3)** showed a singlet at 7.63 ppm for the aromatic protons of phenyl urazole, a doublet at 8.10, a singlet at 8.35 and another doublet at 8.48 ppm for aromatic protons of trimellitylimido group and a broad singlet at 10.6 ppm for the N–H protons.



(1) (2) (3)

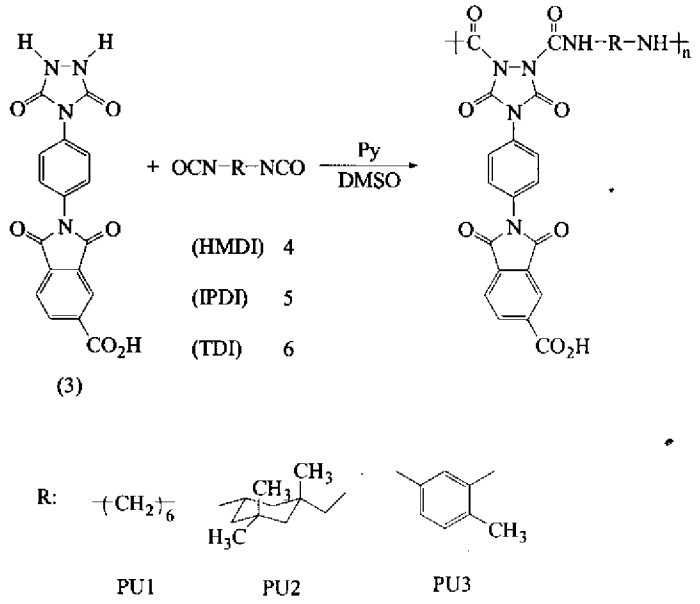
Scheme I

Polymerization Reactions

Since 4-(4′-*N*-trimellitylimidophenyl)-1,2,4,-triazolidine-3,5-dione (NTMP-TD) **(3)** as a new monomer was synthesized in good yield and purity we became interested to examine the step-growth polymerization reactions of NTMPTD as a monomer with diisocyanates. In the present paper we report on the successful polycondensation reaction where NTMPTD as a novel monomer is used for the synthesis of soluble polyureas. Thus HMDI **(4)**, IPDI **(5)** and TDI **(6)** were selected as diisocyanates. The reaction of monomer **3** with these diisocyanates was performed via solution polymerization. The reactions were carried out in DMSO solution in the presence of pyridine as a catalyst and the resulted polyureas PU1-PU3 were obtained as gray solids in good yield (Scheme II).

The resulting polymers were characterized by IR, ^{1}H NMR, elemental analysis, and TGA. The IR spectrum of polymer PU1 showed a strong peak at 3300 cm^{-1} for the acid group which covers the N–H stretching, a strong peak at 2930 cm^{-1} for the aliphatic C–H bonds, a medium peak at 2860 cm^{-1} for the aromatic C–H bonds, also three peaks at 1770,1710 and 1680 cm^{-1} for the carbonyl groups. These peaks are characteristic pattern for the urazole moiety. The elemental analysis results are also in good agreement with the structure of PU1. The low solubility of the PU1 precluded any NMR measurement.

The IR spectrum of polymer PU2 showed a strong broad peak at 3350 cm^{-1} for the acidic hydroxyl group which covers the N–H stretching, a strong peak at 2940 cm^{-1} for the aliphatic C–H bonds, a strong peak at 2900 cm^{-1} for the aromatic C–H bonds, also a strong broad peak with two shoulders at 1710 cm^{-1} for the carbonyl groups. These peaks are characteristic pattern for the urazole moiety. 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 low solubility of the PU2



Scheme II

precluded any NMR measurement.

The IR spectrum of polymer PU3 showed a strong broad peak at 3600–2900 cm^{-1} which covers the area for the N–H, aromatic C–H and aliphatic C–H bonds, and a strong broad peak at 1780–1620 cm^{-1} for the carbonyl groups. The ^1H NMR spectrum of PU3 showed a singlet at 2.15 ppm for the toluene methyl group, a broad singlet at 5.5 ppm for the N–H protons of end group, a singlet at 7.7 ppm, a doublet at 8.2 ppm, a singlet at 8.4 ppm and another doublet at 8.5 ppm for aromatic protons. The elemental analysis results are also in good agreement with calculated percentages for carbon, hydrogen and nitrogen contents in polymer repeating unit of PU3.

Thermal Properties

The thermal behaviour of polyureas PU1, PU2 and PU3 were measured by thermogravimetric analysis (TGA) at a rate of 10 °C/min in nitrogen atmosphere. An examination of the data reveals that all of the above polyureas are thermally stable up to 120 °C in nitrogen atmosphere. The polymers PU1, PU2 and PU3 show 5% weight loss at 133, 127 and 120 °C, respectively.

CONCLUSION

The novel monomer NTMPTD **(3)** was synthesized from 4-(4′-aminophenyl)urazole. This compound is an interesting monomer for the polycondensation reactions. The compound **3** contains trimellitimide acid and urazole moieties. This compound has two acidic N–H groups, which are rather acidic. Thus compound **3** can act as a bifunctional monomer and its polymerization reaction with aliphatic and aromatic diisocyanates gave novel polyureas. Furthermore, these polymers have COOH and NH as well as C=O functional groups and they can readily form H-bonding and make a physical network. On the other hand, presence of these functional groups will make these polymers cross-linkable. The resulting polymers do not have good thermal stability, but it has the potential to be converted to the thermally stable materials via cross-linking processes.

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