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Polymerization of 4-(4-tetrabromophthalimidophenyl)-1,2,4-triazolidin-3,5-dion with diisocyanates

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ABSTRACT

The reaction of 4-(4-aminophenyl)urazole (1) with tetrabromophthalic anhydride (2) in a mixture of pyridine and acetic acid (3:2) as a solvent led to the related amic acid. The amic acid was heated in the same solvent mixture to give 4-(4-tetrabromo-phthalimidophenyl)-1,2,4-triazolidine-3,5-dione (3). Solution polycondensation reactions of monomer (3) with hexamethylene diisocyanate (HMDI) and isophorone diisocyanate (IPDI) were performed in DMF 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 0.17-0.25 dLg⁻¹ in DMF at 25°C. Some structural characterization and physical properties of these novel polymers are reported. © 2012 Trade Science Inc. - INDIA

KEYWORDS

Polyurea;
4-(4-tetrabromophthalimidophenyl)-1,2,4-triazolidine-3,5-dione.;
Step-growth polymerization;
Urazole.

INTRODUCTION

Urazoles (1,2,4-triazolidine-3,5-diones) are very significant chemical reagents in the laboratory as well as in industry. Industrially urazoles are used as a stabilizer in milk, and in the production of anti-tumor drugs^[1]. They are also utilized in polymeric materials^[2-3], in the production of automobile air bags, as a blowing agent in plastics, in the manufacture of antifungal compounds, and herbicides^[4]. Urazoles have been used as a laboratory reagent for preparation of novel organometallic and heterocyclic compounds^[5]; for example triazolo[1,2-a]indazole-triones have been

prepared via a three-component method, by using homogeneous^[6], or heterogeneous^[7] catalysts. Some urazole derivatives were found to be potent cytotoxic agents in murrain and human cancer cell lines. Other pharmaceutical properties of urazole derivatives are hypolipidemic activity via lowering serum, cholesterol, and triglyceride levels^[8], pesticides^[9] and insecticides^[10]. Preparations of thermoplastics, production of heat resistant coatings^[11], tire rubbers with high gripability^[12] and melamine resins^[13], are among the applications in the field of polymerization of urazole derivatives. Urazoles could also be oxidized to the corresponding triazolinedione derivatives using various

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oxidizing reagents such as silica chloride/ NaNO_2 ^[14], silica sulfuric acid/ NaNO_2 ^[15], Ph_3BiCO_3 ^[16], KMnO_4 / Al_2O_3 ^[17], 1,4-diazabicyclo[2.2.2]octane, 1,4-bis(oxide)-bis(hydrogen peroxide)/ MCl ^[18], NO^+ crown $\text{H}(\text{NO}_3)_2$ ^{-[19]}, $\text{Ca}(\text{OCl})_2$ ^[20], $\text{K}_2\text{Cr}_2\text{O}_7$ / AlCl_3 ^[21], silica sulfuric acid/ KClO_3 ^[22], silica chloride/oxone^[22], 1,3-dihalo-5,5-dimethylhydantoin^[23], periodic acid, and oxone[®]/ KBr ^[24]. The resulted products of these reactions, triazolinediones, are very active species toward cycloaddition and ene reactions^[25-27]. Triazolinediones, also used as an initiator in the radical addition reactions^[28].

The synthesis and characterization of the macromolecules restrain heterocyclic rings in the main chain has been the topic of considerable interest, because of their relatively good thermal stability and some attractive novel properties^[29].

EXPERIMENTAL

Apparatus

Proton nuclear magnetic resonance ($^1\text{H-NMR}$, 500 MHz) spectra were recorded by Sharif University, Tehran, Iran. Tetramethylsilane (TMS) was used as an internal reference. Peak multiplicities are assigned as singlet (s), doublet (d), triplet (t), and multiplet (m). IR spectra were recorded on Shimadzu 470 IR spectrophotometer. Spectra of solids were carried out using KBr disks. 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). Inherent viscosities were measured by a standard procedure using a Cannon Fensk Routine Viscometer. Thermal gravimetric analysis (TGA) data for polymers were taken by Amir-Kabir University, Tehran, Iran, in nitrogen atmosphere at a rate of $10^\circ\text{C}/\text{min}$. Elemental analyses were performed by Ferdossi University, Mashhad, I.R. Iran.

Reagents and Monomer

Reagents were purchased from Fluka Chemical Co., Aldrich Chemical Co. and Merk Co. 4-(4-aminophenyl)urazole was synthesized according to our previous report^[30].

Preparation of 4-(4-tetrabromophthalimidophenyl)-1,2,4-triazolidine-3,5-dione (3).

In a 25 mL round bottom flask, was placed 4-(4-aminophenyl)-1,2,4-triazolidine-3,5-dione (1) (0.200 g, 1.04×10^{-3} mol), tetrabromophthalic anhydride (2) (0.48 g, 1.04×10^{-3} mol) and a mixture of acetic acid and pyridine ($\text{AcOH}:\text{Py}=3:2$) as solvent. The reaction mixture was stirred for 4 h in room temperature, then refluxed for 1 h. Hydrochloric acid solution (30%) was added drop wise to $\text{pH}=2$. The yellow solid was filtrated off, and washed with hot ethanol. (0.46 g, 76%). mp $370\text{-}372^\circ\text{C}$. IR (KBr): 3455 (w), 3100 (w), 1770 (m), 1720 (s, br), 1520 (s), 1440 (m), 1380 (s), 1340 (m), 1270 (m), 1170 (m), 1125 (m), 905 (w), 830 (w), 775 (w), 740 (w), 670 (m), 640 (w) cm^{-1} . $^1\text{H-NMR}$ (DMSO-d_6 , TMS) 7.6 (d, 2H, $J=9$ Hz), 7.7 (d, 2H, $J=9$ Hz), 10.6 (br, 2H), ppm. ANAL. Calcd for $\text{C}_{16}\text{H}_6\text{N}_4\text{O}_4\text{Br}_4$: C, 30.48%; H, 1.79%; N, 8.89%. Found: C, 30.48%; H, 1.65%; N, 8.74%.

Polymerization of 4-(4-tetrabromophthalimidophenyl)-1,2,4-triazolidine-3,5-dione (3) with hexamethylene diisocyanate

In a 10 mL round bottom flask, 4-(4-tetrabromophthalimidophenyl)-1,2,4-triazolidine-3,5-dione (3) (0.1778 g, 3.056×10^{-4} mol) was added to a solution of hexamethylene diisocyanate (0.0514 g, 3.056×10^{-4} mol) and pyridine (1 drop) in 0.5 mL of N,N -dimethylformamide (DMF). The solution was stirred for 13 h in room temperature. 0.5 mL of DMF was added and the solution was stirred for 24 h in 60°C , then for 24 h in 85°C . The viscose gel was precipitated in 50 mL of methanol. The yellow solid (0.20 g, 71%) was filtrated. mp 344°C . Inherent viscosity (0.5 g/dL DMF, 25°C) = 0.22 dLg^{-1} . Thermal analysis: T_5 215°C , T_{10} 235°C . Carbon yield (600°C) 8%; IR (KBr): 3300 (m), 3105 (w), 2920 (m), 2850 (m), 1765 (m), 1705 (s, br), 1650 (s), 1620 (m), 1540 (m), 1515 (s), 1440 (m, sh), 1380 (s), 1335 (m), 1270 (m), 1170 (m), 1140 (w), 1120 (m), 1095 (w), 1015 (w), 920 (w), 900 (w), 835 (w), 770 (m), 740 (m), 660 (s) cm^{-1} . ANAL. Calcd for $\text{C}_{24}\text{H}_{18}\text{N}_6\text{O}_6\text{Br}_4$: C, 35.76%; H, 2.25%; N, 10.43%. Found: C, 35.18%; H, 1.91%; N, 10.15%.

Polymerization of 4-(4-tetrabromophthalimidophenyl)-1,2,4-triazolidine-3,5-dione (3) with isophorone diisocyanate

In a 10 mL round bottom flask, 4-(4-

tetrabromophthalimidophenyl)-1,2,4-triazolidine-3,5-dione (3) (0.1209 g, 2.078×10^{-4} mol) was added to a solution of isophorone diisocyanate (0.04620 g, 2.078×10^{-4} mol) and pyridine (1 drop) in 0.5 mL of DMF. The solution was stirred for 12 h in room temperature, for 24 h in 60 °C, and then for 24 h in 85 °C. The viscous gel was precipitated in 50 mL of methanol. The yellow solid (0.12 g, 67%) was filtrated. mp $\sim 279^\circ\text{C}$. Inherent viscosity (0.5 g/dL DMF, 25°C) = 0.19 dLg⁻¹. Thermal analysis: T₅ 230°C, T₁₀ 270°C. Carbon yield (600°C) 15%; IR (KBr): 3300 (w), 3100 (w), 2900 (m), 1770 (m), 1705 (s, br), 1650 (s), 1540 (m), 1515 (s), 1435 (m), 1380 (s), 1335 (m), 1270 (m), 1220 (w), 1170 (m), 1140 (w), 1120 (m), 1095 (w), 1060 (w), 1015 (w), 940 (w), 920 (w), 900 (w), 835 (w), 770 (m), 740 (m), 660 (s) cm⁻¹. ANAL. Calcd for C₂₈H₂₄N₆O₆Br₄: C, 39.10%; H, 2.81%; N, 9.77%. Found: C, 38.27%; H, 2.85%; N, 10.42%.

Polymerization of 4-(4-tetrabromophthalimidophenyl)-1,2,4-triazolidine-3,5-dione (3) with tolylene diisocyanate

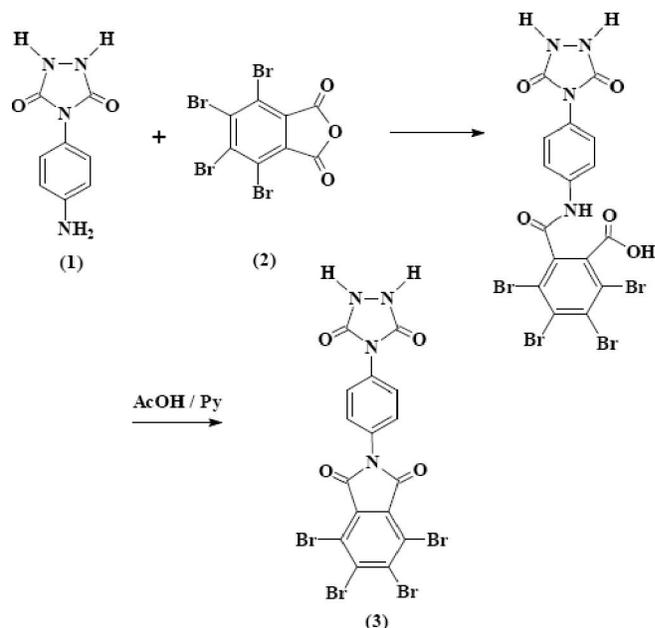
In a 10 mL round bottom flask, 4-(4-bromophthalimidophenyl)-1,2,4-triazolidine-3,5-dione (3) (0.1717 g, 2.951×10^{-4} mol) was added to a solution of tolylene diisocyanate (0.0514 g, 2.951×10^{-4} mol) and pyridine (1 drop) in 0.5 mL of DMF. The reaction mixture was stirred for 12 h in room temperature, then for 24 h in 60 °C. 0.5 ml of DMF was added and the reaction mixture was stirred for 24 h in 85 °C. The viscous gel was precipitated in 50 mL of methanol. The yellow solid (0.21 g, 75%) was filtrated on a buchner funnel. mp $>390^\circ\text{C}$. Inherent viscosity (0.5 g/dL DMF, 25°C) = 0.20 dLg⁻¹; Thermal analysis: T₅ 190°C, T₁₀ 252°C. Carbon yield (600°C) 20%; IR (KBr): 3250 (w, br), 3100 (w), 2900 (w), 1765 (m), 1715 (s), 1650 (s), 1515 (s), 1440 (w), 1375 (s), 1335 (m), 1270 (w), 1215 (w), 1170 (m), 1020 (m), 1015 (w), 895 (w), 830 (w), 770 (w), 740 (w), 690 (w), 660 (w), 640 (w) cm⁻¹. ANAL. Calc. for C₂₅H₁₂N₆O₆Br₄: C, 44.37%; H, 1.79%; N, 12.42%. Found: C, 43.96%; H, 2.03%; N, 12.40%.

RESULTS AND DISCUSSION

Monomer synthesis

4-(4-Aminophenyl)-1,2,4-triazolidine-3,5-dione

(1) was reacted with tetrabromo-phthalic anhydride (2) in a mixture of pyridin/acetic acid (2:3) in room temperature. The resulted amic acid was heated to reflux for 12 hours, condensing to 4-(4-tetrabromophthalimidophenyl)-1,2,4-triazolidine-3,5-dione (3) in high yield (Scheme 1).



Scheme 1 : Synthesis of the 4-(4-tetrabromo phthalimido phenyl)-1,2,4-triazolidine-3,5-dione

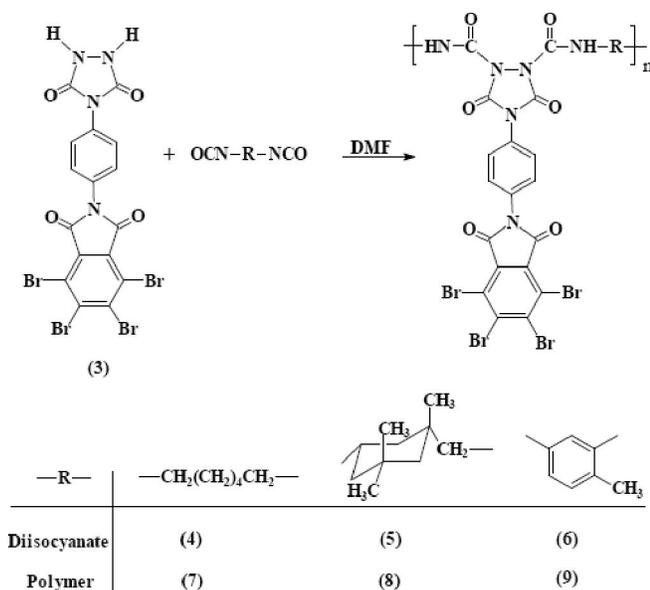
The compound (3) was characterized by IR, ¹H-NMR and elemental analysis. The IR spectrum of (3) showed a peak at 3455 cm⁻¹ for the stretching vibration of the N-H bonds, and a peak at 3100 cm⁻¹ for the stretching vibration of the aromatic C-H bonds. The strong peak at 1720 cm⁻¹ covers the carbonyl related area of both the urazolic and the imidic carbonyl groups. The strong peak at 1520 is related to stretching vibrations of the aromatic carbon-carbon double bonds. The strong peak at 1380 cm⁻¹ is also related to stretching vibrations of the carbon-bromide bonds. The ¹H-NMR spectrum of (3) showed a pair of doublets at 7.6 and 7.7 ppm for the aromatic protons. The broad peak related to the N-H protons is at 10.6 ppm. Elemental analysis results for carbon, hydrogen, and nitrogen is also in good agreement with the calculated amounts, thus confirm the structure of the compound (3).

Polymerization reactions

Since various derivatives of 1,2,4-triazolidine-3,5-dione have been reacted with aliphatic and aromatic

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diisocyanates to produce related polyureas^[31], we decided to perform this type of reaction for the formation of the novel tetrabromophthalimido-phenyl urazole containing 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 DMF solution in the presence of pyridine as a catalyst and the resulted polyureas (7-9) were obtained as yellow solids in high yields (Scheme 2).



Scheme 2 : Synthesis of the polymers

The resulting polymers were characterized by IR, elemental analysis, and TGA.

The IR spectrum of the polymer (7) showed a peak at 3300 cm⁻¹ for stretching vibration of the amide N-H bounds, two peaks at 3105 and 2920 cm⁻¹ for stretching vibration of the aromatic and the aliphatic C-H bounds respectively. The peaks at 1765, 1705, and 1650 cm⁻¹ are the specific characteristic of the urazolic carbonyls which covers the main chain carbonyl groups. The strong peak at 1515 is related to stretching vibrations of the aromatic carbon-carbon double bonds. The strong peak at 1380 cm⁻¹ is also related to stretching vibrations of the carbon-bromide bonds. The elemental analysis results also are in good agreement with the calculated percentages for carbon, hydrogen and nitrogen contents in polymer repeating unit.

The IR spectrum of the polymer (8) showed a peak at 3300 cm⁻¹ for stretching vibration of the amide N-H

bounds. The peaks appeared at 3100 and 2900 is attributed to stretching vibration of the aromatic C-H bounds and the aliphatic C-H bounds of the isophorone moiety, respectively. The peaks at 1770, 1705, and 1650 cm⁻¹ are the specific characteristic of the urazolic carbonyls which covers the main chain carbonyl groups. The strong peak at 1515 is related to stretching vibrations of the aromatic carbon-carbon double bonds. The strong peak at 1380 cm⁻¹ is also related to stretching vibrations of the carbon-bromide bonds. The elemental analysis results are in good agreement with the calculated percentages for carbon, hydrogen and nitrogen contents in polymer repeating unit.

The IR spectrum of the polymer (9) showed a peak at 3250 cm⁻¹ for stretching vibration of the N-H bound. The peaks appeared at 3100 and 2900 is attributed to stretching vibration of the aromatic C-H bounds and the aliphatic C-H bounds of the tolylene groups. The peaks at 1765, 1715, and 1650 cm⁻¹ are the specific characteristic of the urazolic carbonyls which covers the main chain carbonyl groups. Also the strong peak at 1515 is attributed to stretching vibrations of the aromatic carbon-carbon double bonds. The strong peak at 1375 cm⁻¹ is also related to stretching vibrations of the carbon-bromide bonds. The elemental analysis results are in good agreement with the calculated percentages for carbon, hydrogen and nitrogen contents in polymer repeating unit.

The polymers (7), (8) and (9) are soluble in polar organic solvents such as DMF, DMSO and DMAc, and are insoluble in solvents such as water, methanol, acetone, cyclohexane and chloroform.

Thermal properties

The thermal behavior of the polymers 7, 8 and 9 was measured by thermogravimetric analysis (TGA) at a rate of 10°C/min in nitrogen atmosphere. An examination of the data for the polymer 7 reveals that this polyurea is thermally stable up to 200°C in nitrogen atmosphere. This polymer shows 5% and 10% weight loss at 215 and 235°C respectively. The polymer 8 shows 5% weight loss at 230°C and 10% weight loss at 270°C. Also an examination of the data for the polymer 9 shows that this polyurea shows 5% and 10% weight loss at 190 and 252°C respectively.

CONCLUSION

This investigation has shown that 4-(4-bromophthalimidophenyl)-1,2,4-triazolidine-3,5-dione (3) is an interesting monomer for the polycondensation reactions. This compound can act as a bifunctional monomer and its polymerization reaction with aliphatic and aromatic diisocyanates gave the novel polyureas (7-9).

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