

A Novel and Green Method for Polycondensation Reaction of 4-Substituted Phenylurazoles with Different Diisocyanates Under Solvent-Free Conditions

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ABSTRACT: In this investigation, a new method for step-growth polymerization reactions of 4-phenylurazole (PHU) and 4-(4-methoxyphenyl)urazole (MPU) with various diisocyanates were developed under solvent-free conditions. The reaction of these monomers with hexamethylene diisocyanate (HMDI), isophorone diisocyanate (IPDI), and toluylene-2,4-diisocyanate (TDI) were performed in the presence or absence of dibutyltin dilaurate (DBTDL) as a catalyst. The results of polymerization revealed that DBTDL did not have considerable effect on the polymerization process. The resulting polyureas showed good yields and moderate inherent viscosities ranging of 0.17–0.30 dL/g in *N,N*-dimethylformamide (DMF) at 25°C. They are soluble in most polar organic solvents. All of the above polymers were characterized

by ¹H-NMR, FTIR spectroscopy, and thermogravimetric analysis (TGA). This method was compared with the polymerization reaction in *N,N*-dimethylacetamide as a solvent via solution polymerization. Under solvent-free conditions, higher yields and inherent viscosities were obtained. In addition, in this method we do not need to use any solvents and the polymerization reaction can be classified as a green and environmentally friendly method. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3462–3466, 2008

Key words: solid state polymerization; polycondensation; polyureas; inherent viscosity; 4-phenylurazole; 4-(4-methoxyphenyl)urazole; thermogravimetric analysis (TGA); green chemistry

INTRODUCTION

Research work on polymerization under solid state conditions was begun in 1954 with a series of publications by Mersobian et al.^{1–3} Solid state polymerization (SSP) has certain advantages which render its application very attractive. SSP polymers often have improved properties, because monomer cyclization and other side reactions are limited, or even avoided.^{4–8} Only linear chains seem to be formed,⁹ and usually SSP products show greater heat stability in the molten state than samples prepared in the melt; on the other hand, their monomer and oligomers content is so low because of which there is no necessity for it to be removed. Furthermore, the increase in the molecular weight during SSP is accompanied by increased crystallinity and crystal perfection,^{10,11} while drying the polymer, which is important because moisture content may influence

processability in the manufacture of yarns.¹² In addition, there is virtually no environmental pollution, because no solvent is required, and the method can be a continuous operation.¹³ SSP process could be more economical than an all melt-polymerization process.¹⁴ However, at SSP low temperatures,¹⁵ the chain building reactions are slow compared to polymerization in the melt,^{16,17} because of the reduced mobility of the reacting species, and the slow diffusion of the by-products. Agglomeration of the reacting particles has also been reported during SSP, especially at high reaction temperatures, and is related to a low softening point of the reacting mass and to condensate retention in the system.^{18–20} Because of aforementioned advantages of this method of polymerization, recently a number of methods have developed in which polymers was prepared without use of solvent such as supercritical carbon dioxide,^{11,21} polymerization of functional monomers on solid support,²² photoinitiated chemical vapor deposition (piCVD), which is an evolutionary CVD technique for depositing polymeric thin films in one-step without using any solvents²³ and the polymerization reaction in the water as a solvent.²⁴

Urazole derivatives are very interesting five-membered heterocyclic compounds which contain three nitrogen atoms and two carbonyl groups. Since, the

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4-position of the urazole group can readily be substituted with a wide variety of the functional groups, and either aliphatic or aromatic substitution, one can achieve the important properties such as supramolecular aggregation by hydrogen bonding, optically active,²⁵ and liquid crystal polymers.²⁶ They have two N—H protons, which are acidic.²⁷ 4-Substituted urazole was converted into 1-acyl derivatives by an acylation reaction with a series of carboxylic acid anhydrides.²⁸ A simplified procedure for the *N*-acylation of oxazolidin-2-one chiral auxiliaries has also been reported.²⁹ They are synthesized in five steps from corresponding carboxylic acids and in two steps from corresponding isocyanates.³⁰ Urazole is an important chemical reagent in the laboratory and in industry. Industrially urazole is used in the manufacture of automobile air bags, as a blowing agent in plastics, in the production of herbicides,³¹ antifungal compounds, and in polymeric materials.^{32–37} It is also used in the production of antitumor drugs³⁸ and as a stabilizer in milk. Urazole is used as a laboratory reagent for synthesizing novel heterocyclic^{39,40} and organometallic compounds.

Polyureas are a class of polymers which has a —NH—CO—NH— functional group; they can make hydrogen bonds from different sides. A number of processes have been used to prepare polyureas, but the best method is from 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. They are polyamide of carbonic acid and are tough, high melting, and suitable for fiber applications.⁴¹ They can be tailor made to obtain properties which lead to multi-purpose applications such as coating systems for waterproofing and corrosion protection.⁴² Polyureas have been used for many applications, including the encapsulation of pharmaceuticals, inks, dyes, and the modification of wool fibers by interfacial grafting techniques.⁴³

As part of our continuing efforts in developing heterocyclic polymers containing urazole units,⁴⁴ the present study describes the synthesis of a series of polyureas under solvent-free polycondensation reaction that can be classified as green method for polymerization reaction.

EXPERIMENTAL

Materials and equipments

Reagents were purchased from Fluka Chemical (Buchs, Switzerland), Aldrich Chemical (Milwaukee, WI), and Riedel-deHaen AG (Seelze, Germany). 4-Phenylurazole (PHU) and 4-(4-methoxyphenyl)urazole (MPU) were synthesized according to published procedure.^{45,46} Proton nuclear magnetic resonance

(¹H-NMR, 500 MHz) spectra were recorded in DMSO-*d*₆ solution using a Bruker (Germany) Avance 500 instrument at Sharif University of Technology, Tehran, Iran. Multiplicities of proton resonance were designated as singlet (s) and multiplet (m). FTIR spectra were recorded on a Nicolet Impact 400_D 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). All melting points were taken with a Gallenham melting point apparatus. Inherent viscosities were measured by standard procedure using a Cannon Fenske Routine viscometer. Thermal gravimetric analysis (TGA)/derivative of thermaogravimetric (DTG) data for polymers were taken on TGA-PerkinElmer (Pyris 1) in a nitrogen atmosphere at a heating rate of 10°C/min by the Research Institute of Polymer and Petrochemical of Iran (IPPI).

Solvent free polymerization of PHU and MPU with diisocyanates

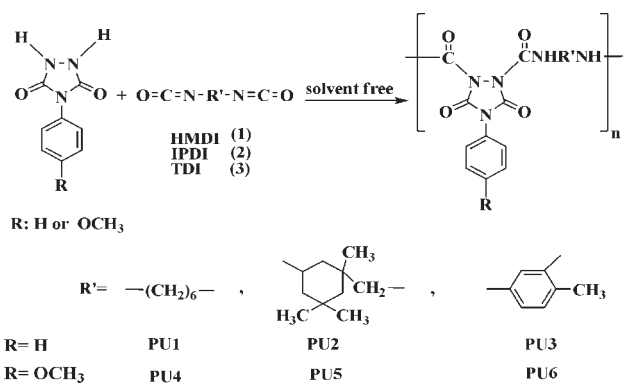
A typical preparation of PU1AI was as follows:

PHU (0.1012 g, 5.7×10^{-4} mol) was pulverized until a powder was formed. It was transferred into a 25-mL round-bottomed flask, hexamethylene diisocyanate (HMDI) 1 (0.0962 g, 5.8×10^{-4} mol) was added and heated. Then the mixture was stirred for 12 h at 120°C. The white solid was precipitated in a mixture of 30 mL of 50/50 methanol/water. The white solid was obtained, filtered off, and dried to give 0.195 g (92%) of PU1AI. The above method of polymerization reaction was repeated in the presence of dibutyltin dilaurate (DBTDL) as a catalyst. The other polyureas were prepared with similar procedure.

PU1AI: m.p. 117–120°C; FTIR (KBr, cm⁻¹): 3347 (m), 2934 (m), 2857 (w), 1735 (s), 1597 (w), 1533 (m), 1500 (m), 1457 (w), 1417 (s), 1263 (m), 1208 (m), 1063 (w), 763 (m), 689 (w), 617 (w). ¹H-NMR (500 MHz, DMSO-*d*₆): δ 1.28–1.49 (m, 8H, CH₂), 3.08–3.33 (m, 4H, CH₂), 7.48–7.98 (m, 5H, Ar-H), 8.1 (s, br, N—H) ppm.

PU2BI: m.p. 137°C; FTIR (KBr, cm⁻¹): 3413 (m), 3069 (w), 2954 (m), 1788 (w), 1747 (s), 1668 (m), 1618 (w), 1531 (m), 1502 (m), 1458 (w), 1414 (s), 1308 (w), 1249 (m), 1212 (m), 1065 (w), 922 (w), 753 (m), 722 (w), 618 (m), 504 (w). ¹H-NMR (500 MHz, DMSO-*d*₆): δ 0.85–1.12 (m, 11H, CH₃, CH₂), 1.24–1.29 (m, 4H, CH₂), 3.04 (m, 2H, CH₂), 3.69 (m, 1H, CH), 7.41–7.60 (m, 5H, Ar-H), 7.91 (s, br, N—H) ppm.

PU3BI: m.p. 138°C; FTIR (KBr, cm⁻¹): 3365 (m), 2953 (m), 1742 (s), 1647 (w), 1534 (m), 1501 (m), 1458 (w), 1414 (s), 1309 (w), 1213 (m), 1063 (w), 1024 (w), 765 (m), 689 (w). ¹H-NMR (500 MHz, DMSO-*d*₆): δ 2.11–2.18 (m, 3H, CH₃), 7.11–7.96 (m, 8H, Ar-H), 8.21 (s, br, N—H) ppm.



Scheme 1 Polycondensation reactions of PHU and MPU with various diisocyanates such as HMDI (1), IPDI (2), and TDI (3).

PU4AI: m.p. 188–190°C; FTIR (KBr, cm⁻¹): 3347 (m), 3081 (w), 2935 (s), 2857 (w), 1736 (s), 1610 (w), 1590 (w), 1513 (s), 1419 (m), 1302 (w), 1249 (s), 1179 (m), 1106 (w), 1025 (m), 832 (m), 755 (w), 576 (m). ¹H-NMR (500 MHz, DMSO-*d*₆): δ 1.31–1.49 (m, 8H, CH₂), 2.71–3.23 (m, 4H, CH₂), 3.80 (s, 3H), 7.04 (d, 2H, Ar-H), 7.38 (d, 2H, Ar-H), 7.86 (s, br, N—H) ppm.

PU5BI: m.p. 161°C; FTIR (KBr, cm⁻¹): 3318 (m), 3071 (w), 2925 (s), 2854 (m), 1753 (s), 1674 (ms), 1615 (w), 1557 (w), 1514 (s), 1365 (m), 1254 (s), 1173 (m), 1144 (w), 1029 (m), 943 (w), 831 (m), 761 (m), 689 (w), 524 (w), 472 (w). ¹H-NMR (500 MHz, DMSO-*d*₆): δ 0.82–1.19 (m, 11H, CH₃, CH₂), 1.24–1.62 (m, 4H, CH₂), 3.02–3.32 (m, 2H, CH₂), 3.71 (m, 1H, CH), 3.81 (s, 3H, CH₃), 7.03 (m, 2H, Ar-H), 7.36 (d, 2H, Ar-H), 7.87 (s, br, N—H) ppm.

PU6AI: m.p. 282–283°C; FTIR (KBr, cm⁻¹): 3382 (m), 3084 (w), 2956 (m), 2925 (s), 1738 (s), 1710 (m), 1658 (m), 1539 (m), 1514 (s), 1467 (w), 1418 (m), 1302 (m), 1251 (s), 1173 (m), 1060 (w), 1027 (w), 832 (m), 608, (m), 529 (w). ¹H-NMR (500 MHz, DMSO-*d*₆): δ 2.11–2.25 (m, 3H, CH₃), 3.65–3.80 (s, 3H, CH₃), 7.06–7.40 (m, 4H, Ar-H), 8.17 (s, br, N—H) ppm.

TABLE I
Reaction Conditions for the Solvent-Free Polymerization of PHU with Different Diisocyanates

Polymer	Diisocyanate	Catalyst	Yield (%)	η_{inh} (dL/g) ^a	Color
PU1AI	HMDI	–	72	0.29	W ^b
PU1BI	HMDI	DBTDL	76	0.27	W
PU2AI	IPDI	–	81	0.23	W
PU2BI	IPDI	DBTDL	82	0.24	W
PU3AI	TDI	–	83	0.30	W
PU3BI	TDI	DBTDL	87	0.28	Off-W

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

^b W = White.

TABLE II
Reaction Conditions for the Polymerization of PHU with Diisocyanates using DMAC as a Solvent

Polymer	Diisocyanate	Catalyst	Yield (%)	η_{inh} (dL/g) ^a	Color
PU1AII	HMDI	–	78	0.18	Off-W
PU1BII	HMDI	DBTDL	69	0.17	W ^b
PU2AII	IPDI	–	81	0.19	W
PU2BII	IPDI	DBTDL	76	0.16	W
PU3AII	TDI	–	83	0.20	W
PU3BII	TDI	DBTDL	80	0.19	Off-W

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

^b W = White.

RESULTS AND DISCUSSION

Polymer synthesis

From a technological point of view, the use of an organic solvent in large-scale production is not very friendly. So, in this investigation we tried to eliminate *N,N*-dimethylacetamide (DMAC) and performed the polymerization reaction under solvent free conditions to report a simple, safe, and efficient method for the reaction of PHU and MPU with readily accessible diisocyanates such as HMDI (1), isophorone diisocyanate (IPDI) 2, and toluylene-2,4-diisocyanate (TDI) 3 and compare this method with conventional solution polymerization.

The polyureas based on 4-substituted phenylurea were synthesized by one-step high temperature method (Scheme 1). The polymerization reaction was carried out under solvent free conditions in the presence or absence of DBTDL as a catalyst. The comparison of these results indicates that DBTDL is not required in this polycondensation reaction, because the inherent viscosities and the yields of polymers did not differ so much, and as a matter of fact, by eliminating DBTDL both cost and pollution will be descended. The resulting polyureas were obtained in high yields, moderate inherent viscosities, and thermal stability. The results are shown in Tables I–III.

TABLE III
Reaction Conditions for the Solvent-Free Polymerization of MPU with Different Diisocyanates

Polymer	Diisocyanate	Catalyst	Yield (%)	η_{inh} (dL/g) ^a	Color
PU4AI	HMDI	–	83	0.23	W ^b
PU4BI	HMDI	DBTDL	85	0.24	W
PU5AI	IPDI	–	90	0.17	W
PU5BI	IPDI	DBTDL	91	0.19	W
PU6AI	TDI	–	86	0.29	Off-W
PU6BI	TDI	DBTDL	90	0.27	Off-W

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

^b W = White.

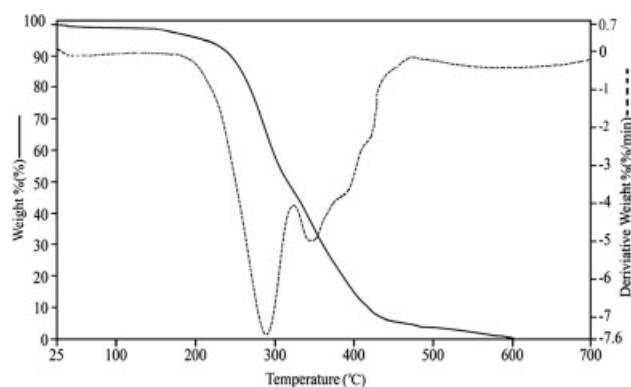


Figure 1 TGA/DTG thermogram of PU1AI in a nitrogen atmosphere and heating rate of 10°C/min.

To compare the efficiency of this novel method of polymerization (method I) with conventional solution polymerization (method II),^{46,47} the polymerization reaction of these monomers were carried out via two different methods. The good yields and inherent viscosities were obtained by method I, so the polymerization reaction under solvent free conditions is more efficient than polymerization reaction in DMAc (method II). Since DMAc is volatile, the concentration of reaction mixture during polymerization process may be changed and these will results to lower molecular weight polymers. Furthermore, the use of solvent increases the needed time, energy, and cost of the reaction.

Polymer characterization

FTIR study

The structures of these polymers were confirmed by means of FTIR spectroscopy. The FTIR spectra of all polymers showed absorptions around 3413–3347 cm^{-1} (N—H). Main absorption bands at range 1770–1600 cm^{-1} 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.

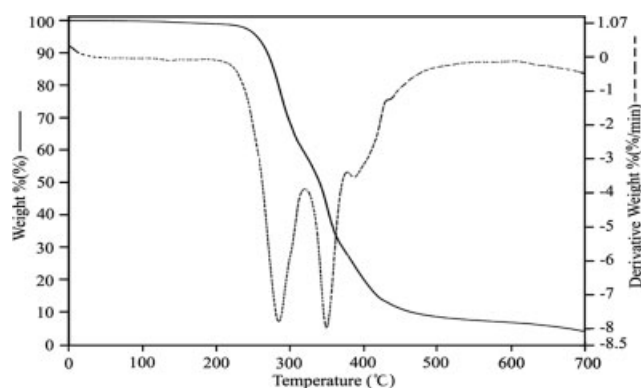


Figure 2 TGA/DTG thermogram of PU2BI in a nitrogen atmosphere and heating rate of 10°C/min.

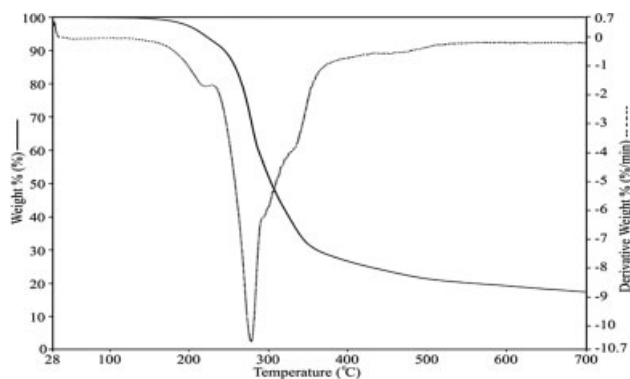


Figure 3 TGA/DTG thermogram of PU3BI in a nitrogen atmosphere and heating rate of 10°C/min.

¹H-NMR study

The ¹H-NMR spectra of PU1–PU6 resulting from monomers of PHU and MPU showed all peaks for aliphatic, aromatic protons, and N—H amidic group that confirm their chemical structures.

Solubility of polyureas

The resulting polymers are completely soluble in polar organic solvents such as *N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidinone, dimethyl sulfoxide, DMAc, and in H₂SO₄, but insoluble in solvents such as water, methanol, acetone, cyclohexane, and chloroform.

Thermal properties

The thermal behavior of PU1AI, PU2BI, and PU3BI were measured by thermogravimetric analysis (TGA) and derivative of thermogravimetric (DTG) analysis at a heating rate of 10°C/min in a nitrogen atmosphere. An examination of the data reveals that all polyureas are thermally stable up to 230°C in a nitrogen atmosphere. Figures 1–3 show thermograms of PU1AI, PU2BI, and PU3BI, respectively. The temperatures of 5 and 10% weight loss together with char yield at 600°C for PU1AI, PU2BI, and PU3BI are 230°C, 254°C, and 0%, 261°C, 270°C, and 6% and 236°C, 255°C, and 20%, respectively, (Table IV). The thermal behavior of these polyureas were also compared with polyureas synthesized by conventional method; the polymers, PU1BII and PU2BII show 5% weight loss at 240 and 200°C, respectively.

CONCLUSIONS

From this investigation, it is clear that solvent-free polycondensation reaction is a simple, cheap, and safe technique for polymerization reactions. The present work has shown that 4-substituted phenylur-

TABLE IV
Thermal Properties of PU1AI, PU2BI, and PU3BI

Polymer	Decomposition Temperature (°C)		Char Yield (%) ^c
	T ₅ ^a	T ₁₀ ^b	
PU1AI	230	254	–
PU2BI	261	270	6
PU3BI	236	255	20

^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 maximum temperature 600°C in a nitrogen atmosphere.

azoles are interesting monomers for the formation of polyureas under solvent free conditions. The reported procedure of the polymerization reaction on these monomers with various diisocyanates under green conditions, absence of solvent and catalyst demonstrates the potential of this method has much promise for further applications. Moreover, this methodology offers significant improvements with regard to yield of products, inherent viscosities, thermal stability, simplicity in operation, cost efficiency, and green aspects avoiding toxic catalysts and solvents. The resulting polymers are soluble in most polar organic solvents, and can be used as thermoplastic materials.

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