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Solid-State Polymerization of 4-(4-Dimethylamino-phenyl)-urazole with Diisocyanates

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Summary

In the present study, the solid-state thermal polymerization of 4-(4-dimethylaminophenyl)-1,2,4-triazolidine-3,5-dione (**DAPTD**) with diisocyanates such as hexamethylene diisocyanate, isophorone diisocyanate and toluylene-2,4-diisocyanate as a new method for synthesis of polyureas are described. The influence of reaction parameters, such as presence of catalyst in the starting material and ratio of **DAPTD** to diisocyanate were investigated. Polycondensation was successfully preceded without any solvent, which is used in conventional method. The resulting polyureas were obtained in high yields with inherent viscosities ranging from 0.14 to 0.25 dL/g. This method was also compared with two other polycondensation methods for the polymerization reactions which were reported before: conventional solution method and a method using tetrabutylammonium bromide as a molten ionic liquid media.

Keywords

solid-state polymerization, polyureas, 4-(4-dimethylaminophenyl)-1,2,4-triazolidine-3,5-dione; green chemistry; diisocyanates

Introduction

With condensation polymers, such as polyamides (PA)s and polyesters (PE)s, one of the routes to high molecular weight products has been through solid state polymerization (SSP) [1,2]. Starting materials are heated to a temperature higher than the glass transition temperature (T_g), but lower than the onset of melting (T_m) so as to make the end groups mobile enough to react and the by-products are removed by passing inert gas through the reacting mass or by maintaining reduced pressure [3-10]. SSP has certain advantages which make its application striking. The most important commercial benefits of SSP focus on the use of easy and inexpensive equipment, and on evading some of the limitations of conventional polymerization processes. SSP polymers often have improved properties, because monomer cyclization and other side reactions are limited, or even avoided, due to the low SSP operating temperatures. Only linear chains seem to be formed, and usually SSP products show greater heat stability in the molten state than samples prepared by the melt polymerization technique; on the other hand, their monomer and oligomers content is so low, that there is no essential need for it to be removed. Furthermore, the increase in the molecular weight during SSP is accompanied by increased crystallinity and crystal perfection [5]. In addition, there is practically no environmental pollution, because no solvent is required, and the process can be a continuous operation.

Polyureas are very tough materials with high hardness and good chemical resistance. They can be tailor-made to gain properties which lead to versatile applications such as coating systems for waterproofing and corrosion protection [11]. A number of methods have been used to prepare polyureas, but the best method is the reaction of diamines with diisocyanates. This reaction is a step-growth addition reaction of amine across the carbon-nitrogen double bond and there is no by-product. Polyureas have been used for many applications including encapsulation of pharmaceutical, ink, dyes and the modification of wool fibers by interfacial grafting techniques [12].

This article is concerned with the preparation and characterization of the resulting polyureas (**PU**)s from polycondensation of 4-(4-dimethylaminophenyl)-1,2,4-triazolidine-3,5-dione (**DAPTD**) as a heterocyclic monomer with different diisocyanates under SSP conditions. The products prepared by SSP were characterized by ^{1}H NMR, FTIR, UV-Vis, fluorescence, elemental analysis and TGA techniques, and were compared with those synthesized in organic solvent and the homogeneous molten state using tetrabutylammonium bromide (**TBAB**).

Experimental

Materials

Reagents were purchased from Fluka Chemical (Buchs, Switzerland), Aldrich Chemical (Milwaukee, WI) and Riedel-deHaen AG (Seelze, Germany). **DAPTD** was prepared from 4-dimethylaminobenzoic acid in five steps according to our previous work [13].

Equipments

Proton nuclear magnetic resonance ^{1}H-NMR (500MHz) spectra were recorded on a Bruker (Germany), Avance 500 instrument. 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 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 standard procedure using a Cannon Fenske Routine viscometer at a concentration of 0.5 g dL^{-1} in *N,N*-dimethylformamide (DMF) at 25°C. Fluorescence and UV-Vis spectra were recorded on a spectrofluorometer, JASCO, FP-750 and UV/VIS/NIR spectrophotometer, JASCO, V-570, respectively. Thermal Gravimetric Analysis (TGA) data for polymers were taken on a Stanton-650 TGA under N_2 atmosphere by the Research Institute of Polymer and Petrochemical of Iran (IPPI). Elemental analyses were performed by Research Institute of petroleum Industry, Tehran, I.R. Iran.

PUs Synthesis

Polymerization of DAPTD with diisocyanates (1:1 DAPTD to diisocyanate) under SSP conditions

General procedure for preparation of **PU**s: as an example for preparation of **PU1BI**, 0.0895 g (5.32×10^{-4} mol) of hexamethylene diisocyanate (**HMDI**) (**1**),

0.1172 g (5.32×10^{-4} mol) of **DAPTD** and 0.05 g (7.92×10^{-5} mol) of dibutyltin dilaurate (DBTDL) were stirred at 120°C under nitrogen atmosphere for 12 h. The reaction mixture at the beginning is a viscous solution then it will turn to a white solid and stay as a solid during reaction period. The white solid was precipitated in 30 mL of 50/50 methanol/water, was filtered off and dried to give 0.196 g (95%) of **PU1BI**.
The other polymers **PU2**s and **PU3**s were prepared by the same procedure using isophorone diisocyanate (**IPDI**) (**2**) and toluylene-2,4-diisocyanate (**TDI**) (**3**) as diisocyanates, respectively. The above polymerization was repeated, in the absence of **DBTDL** as a catalyst. The polymers were also prepared by the same procedure with molar ratios of 1:1.1 and 1:1.2, **DAPTD** to diisocyanate, respectively.

Polymerization of DAPTD with diisocyanates in molten TBAB
A typical preparation of **PU1II** was as follow:
A mixture of **DAPTD** (0.1016 g, 4.61×10^{-4} mol) and **TBAB** (0.3000 g, 9.23×10^{-4} mol) was ground until a powder was formed. Then was transferred into a 25-mL round-bottomed flask and **HMDI** (**1**) (0.0776 g, 4.61×10^{-4} mol) was added to the mixture and was heated until homogeneous solution was formed. The solution was stirred for 12 h at 120°C. The viscous solution was precipitated in 30 mL of 50/50 methanol/water mixture. The white solid was filtered off, dried to give 0.156 g (87%) of **PU1II**. The above polymerization was repeated in the presence of DBTDL as a catalyst. The other **PU**s were prepared with similar procedures.

Polymerization of DAPTD with diisocyanates in conventional solvent
A typical preparation of **PU1III** was as follow:
Method I: Into a 25-mL round-bottom flask **DAPTD** (0.1038 g, 4.71×10^{-4} mol) and DBTDL (0.05 g, 7.92×10^{-5} mol) were added to a solution of **HMDI** (**1**) (0.0793 g, 4.71×10^{-4} mol) in 0.5 mL of *N,N*-dimethylacetamide (DMAc). The solution was stirred for 6 h at room temperature, 12 h at 60°C and then 24 h at 85°C. During of this period 0.6 mL of DMAc was added. The viscous solution was precipitated in 30 mL of methanol. The solid was filtered off, dried to give 0.167 g (91%) of **PU1III**. The above polymerization was repeated in the presence of triethylamine and pyridine as a catalyst, respectively.
Method II: The above polymerization was repeated, but the reaction mixture was refluxed in DMAc for one, 3 and 6 min. in the presence of different catalysts.
The other **PU**s were prepared with analogous procedures.

PU1AI: FTIR(KBr): 3307 (m), 2925 (m), 2932 (m), 2855 (m), 1789 (m), 1735 (s), 1676 (m), 1543 (s), 1502 (m), 1418 (s), 1078 (s), 764 (m), 739 (m), 688 (m), 647 (m), 465 (m) cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d$_6$, δ, ppm): 1.25-1.46 (m, br, 8H, CH_2), 2.96 (s, 6H, CH_3), 3.15 (m, br, 4H, CH_2), 6.87 (s, br, 2H, Ar-H), 7.27 (s, br, 2H, Ar-H), 7.91 (s, br, N-H). ANAL. Calcd for $C_{18}H_{24}N_6O_4$: 55.6% C; 6.2% H; 21.6% N. Found: 53.9% C; 6.6% H; 21.0% N. UV (DMF): λ_{max} (ε) = 269 (78006), 311 nm (34262 L. mol^{-1}. cm^{-1}).

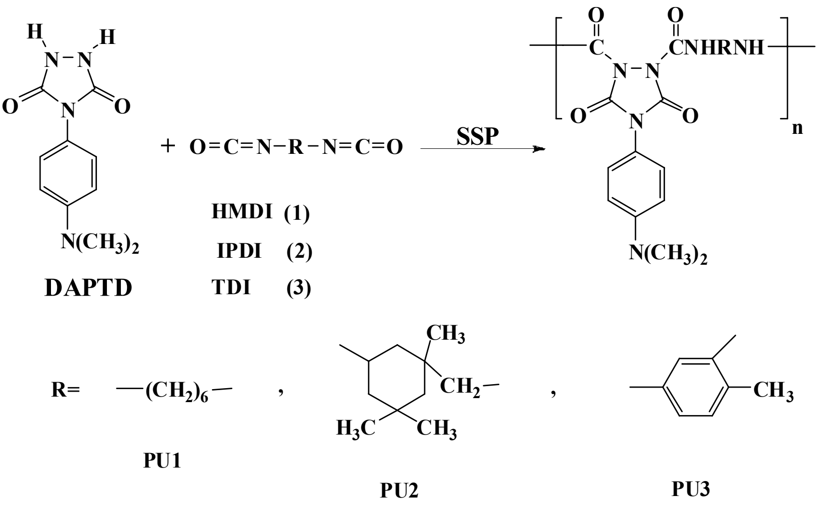
PU2AI: FTIR(KBr): 3368 (m), 2954 (s), 2925 (s), 2854 (m), 1786 (m), 1705 (s), 1637 (s), 1560 (s), 1502 (m), 1459 (m), 1413 (m), 1386 (m), 1063 (m), 1306 (m), 1243 (m), 1151 (w), 1071 (w), 880 (w), 766 (w), 721 (w), 689 (w), 645 (w) cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d$_6$, δ, ppm): 0.83-1.11 (m, br, 11H, CH_3, CH_2), 1.19-1.48 (m, br, 4H, CH_2), 2.73 (m, br, 2H, CH_2), 2.95 (s, 6H, CH_3), 3.64 (m, br, 1H, CH), 5.60-5.81

(m, br), 7.02-7.68 (m, 6H, Ar-H, N-H). UV (DMF): λ_{max} (ε) = 264 (46798), 308 nm (5688 L. mol^{-1}. cm^{-1}).

PU3AI: FTIR(KBr): 3298 (m), 3100 (w), 2925 (m), 2860 (m), 1738 (m), 1706 (s), 1656 (s), 1600 (s), 1540 (s), 1500 (s), 1416 (s), 1217 (s), 1058 (m), 1025 (m), 1006 (m), 933 (m), 911 (m), 874 (m), 815 (m), 762 (m), 688 (m), 645 (m), 536 (m), 505 (m), 454 (m) cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d$_6$, δ, ppm): 2.22 (m, br, 3H, CH_3), 2.97 (s, br, 6H, CH_3), 6.90-7.52 (m, br, Ar-H), 7.62-8.22 (m, br, Ar-H, N-H). UV (DMF): λ_{max} (ε) = 262 (98486), 296 nm (13105 L. mol^{-1}. cm^{-1}).

Results and Discussion

Because of the abundant demand for various types polymer, it is increasingly important that an environmentally friendly synthesis is developed. In an attempt to devise a solvent-free synthesis of polymers, SSP of the polymer was explored. From a technological viewpoint, the use of an organic solvent in large-scale production is not very affable. So we carried out the polymerization reaction under solvent-free conditions in order to description a safe, straightforward and efficient method for polymerization reaction. In this work, **PU**s were prepared by SSP of **DAPTD** and diisocyanates, as shown in Scheme 1.



Scheme 1. Polycondensation reactions of **DAPTD** with diisocyanates under **SSP** conditions.

Polymerization was carried out by the heating of the monomers via one step high temperature method. Polycondensation proceeded in the solid state at the selected temperature in the presence and in the absent of DBTDL as a catalyst. Regarding the catalytic experiments, the effectiveness of DBTDL in the **PU**s preparation was also proved. The highest inherent viscosity was attained in the presence of DBTDL as a catalyst. Although the reaction was practically completed in a few hours, it was extended for a period of 12 h to ensure a completion of the reaction. To study the effect of monomers ratio on the polymerization process, a series of experiments was carried out by changing the ratio of the two starting components: **DAPTD** and diisocyanates. From these data it is clear that no significant changes have been observed in yields and inherent viscosities. In Tables 1, 2 and 3 all the experimental recipes are summarized. All of the polymers precipitated in a fiber-like form when the mixture of methanol and water were poured into resulting polymer.

Table 1. Reaction conditions for the polymerization of monomer **DAPTD** with **HMDI** (**1**) under SSP conditions

Polymer	Ratio **DAPTD** to Diisocyanate	Catalyst	Yield (%)	η_{inh} (dL/g)[b]
PU1AI	1:1	-	89	0.19
PU1BI	1:1	DBTDL[a]	95	0.25
PU1CI	1:1.1	-	86	0.16
PU1DI	1:1.1	DBTDL	91	0.22
PU1EI	1:1.2	-	86	0.18
PU1FI	1:1.2	DBTDL	82	0.23

[a]Dibutyltin dilaurate. [b]Measured at a concentration of 0.5 g/dL in DMF.

Table 2. Reaction conditions for the polymerization of monomer **DAPTD** with **IPDI** (**2**) under SSP conditions

Polymer	Ratio **DAPTD** to Diisocyanate	Catalyst	Yield (%)	η_{inh} (dL/g)[b]
PU2AI	1:1	-	93	0.14
PU2BI	1:1	DBTDL[a]	92	0.18
PU2CI	1:1.1	-	85	0.16
PU2DI	1:1.1	DBTDL	86	0.20
PU2EI	1:1.2	-	81	0.14
PU2FI	1:1.2	DBTDL	83	0.17

[a]Dibutyltin dilaurate. [b]Measured at a concentration of 0.5 g/dL in DMF.

The characterization of the polymers structure was implemented with FT-IR, ^{1}H NMR and elemental analysis. All of the polymers were characterized by absorption peak for the amide N-H groups around 3300 cm^{-1}. The absorption bands appeared around 2900 and 2850 cm^{-1} are related to the corresponding aliphatic C-H stretching vibration. Main absorption bands at 1790-1650 cm^{-1} range were attributed to the carbonyl groups.

The ^{1}H-NMR spectra of polymers showed all peaks for aliphatic and aromatic as well as end group N-H protons. The elemental analysis result for **PU1AI** is also in good agreement with calculated percentages for carbon, hydrogen and nitrogen contents in polymer repeating unit.

The UV-Vis spectra of the **PU1AI**, **PU2AI** and **PU3AI** were recorded in DMF. It is apparent that the wavelength of maximum absorption is related to the dimethylaminophenyl group in the compounds. All of these compounds show almost similar UV-Vis spectra pattern.

Fluorescence spectra of the **PU**s were recorded in DMF. Fluorescence wavelengths are observed within 504 and 540 nm. All of these compounds show almost similar fluorescence spectra pattern. The fluorescent intensity of these compounds is almost medium. The fluorescent intensity **PU3AI** is larger than other two polymers, probably due to the rigidity enhancement of this polymer in comparison with other two polymers. These fluorescent characteristic of polymers are due *N,N*-dimethylaminophenyl chromophore [14].

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

Table 3. Reaction conditions for the polymerization of monomer **DAPTD** with **TDI** (**3**) under SSP conditions

Polymer	Ratio **DAPTD** to Diisocyanate	Catalyst	Yield (%)	η_{inh} (dL/g)[b]
PU3AI	1:1	-	84	0.15
PU3BI	1:1	DBTDL[a]	92	0.19
PU3CI	1:1.1	-	88	0.20
PU3DI	1:1.1	DBTDL	93	0.21
PU3EI	1:1.2	-	91	0.20
PU3FI	1:1.2	DBTDL	86	0.22

[a]Dibutyltin dilaurate. [b]Measured at a concentration of 0.5 g/dL in DMF.

We have previously reported that the **DAPTD** and diisocyanates provide polymers during the solution polymerization with inherent viscosities and yields in the range of 0.08-0.23 dL/g and 71-91%, respectively [13] and in TBAB with inherent viscosities and yields in the range of 0.26 to 0.38 dL/g and 82-92%, respectively [15]. The resulting **PU**s by SSP method are obtained in high yields, moderate inherent viscosities. It is interesting to mention that in SSP method higher yields and inherent viscosities were obtained compare to conventional method. Results from comparative polymerization methods for polymers are given in Table 4.

Table 4. Comparative SSP runs of **DAPTD** and diisocyanates and conventional method

Polymer	Cat.	Yield (%)[b]	η_{inh} (dL/g)[b]	Yield (%)[c]	η_{inh} (dL/g)[c]
PU1A	-	89	0.19	-	-
PU1B	DBTDL[a]	95	0.25	91	0.19
PU2A	-	93	0.14	-	-
PU2B	DBTDL	92	0.18	87	0.15
PU3A	-	84	0.15	-	-
PU3B	DBTDL	92	0.19	83	0.08

[a]Dibutyltin dilaurate. [b]SSP conditions, [c]conventional method in DMAc solution (gradual heating at different temperatures).

Thermal Properties

The thermal behavior of **PU1BI** and **PU3FI** were measured by thermaogravimetric analysis (TGA) at a rate of 10°C/min in a nitrogen atmosphere. Typical TGA curves of two representative polymers are shown in Figures 1 and 2. An examination of the data reveals that **PU1BI** and **PU3FI** are thermally stable up to 200°C. The temperatures of 5% and 10% weight loss together with char yield at 600°C for this **PU**s were calculated from their thermograms. The TGA traces of **PU1BI** exhibited a two-step degradation including a significant break, followed by a small weight loss while, **PU3FI** showed one-step decomposition. It can be explained according to their different structure. In

Figure 1 the first weight loss is due to the decomposition of aliphatic linkages and the second weight loss is due to the rest of the molecule. It seems that symmetric, linear diisocyanate, **HMDI** has shown slightly higher thermal stability than unsymmetric diisocyanate **TDI**. This could be explained in terms of higher inherent viscosity resulting from **HMDI** but, its weight residue at 600°C is lower (Table 5). The thermoanalyses data of **PU1BI** and **PU3FI** are summarized in Table 5.

Table 5. Thermal Properties of **PU1BI** and **PU3FI**

	Decomposition Temperature (°C)		
Polymer	T_5 [a]	T_{10} [b]	Char Yield (%) [c]
PU1BI	200°C	225°C	5%
PU3FI	175°C	220°C	23%

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

[b] Temperature at which 10% weight loss was recorded by TGA at heating rate 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.

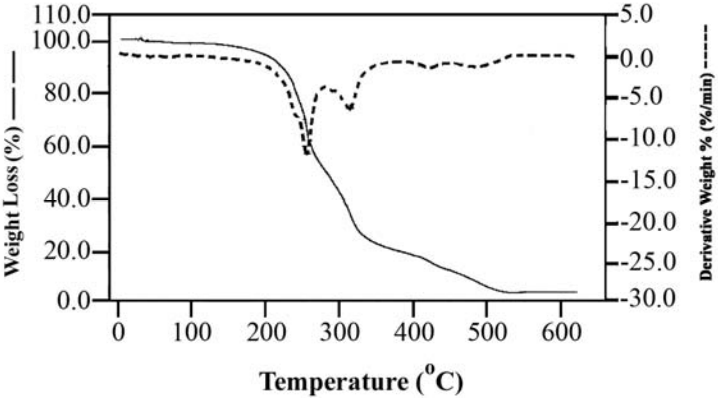


Figure 1. TGA/DTG of **PU1BI** with a heating rate of 10°C/min in a nitrogen atmosphere.

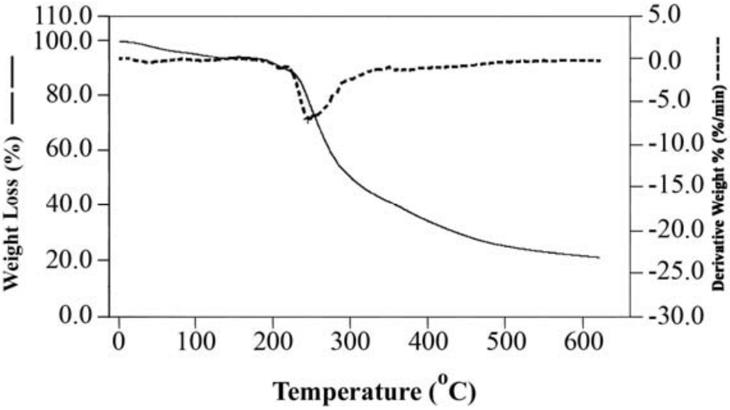


Figure 2. TGA/DTG of **PU3FI** with a heating rate of 10°C/min in a nitrogen atmosphere.

Conclusions

In this study we have presented an inexpensive, simple and secure technique for preparation of **PU**s. Aliphatic-aromatic **PU**s having urazole moiety could be synthesized with high yields and moderate molecular weights from the thermal polycondensation of the **DAPTD** and diisocyanates by SSP method. We obtained higher yields and viscosities of polymers from SSP method compared with solution polycondensation. The SSP has been investigated from various research viewpoints. It is a solvent-free process and in future it will become more important as an environmentally friendly polymerization technique. It is also very important to mention that in this method no solvent will be used, therefore not only we do not have environmental pollution, but also it decreases the cost of process drastically.

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