Polymer Bulletin 60, 191–198 (2008)
DOI 10.1007/s00289-007-0855-9

Polymer Bulletin

Direct Polyamidation in Molten Tetrabutylammonium bromide: Novel and Efficient Green Media

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Received: 26 July 2007 / Revised version: 7 October 2007 / Accepted: 7 October 2007

Summary

This is the first report of application of molten ionic liquid (**MIL**) for the synthesis of polyamides (**PA**s) from the reaction of dicarboxylic acids with diisocyanates. A fairly inexpensive and readily accessible **MIL**, tetrabutylammonium bromide (**TBAB**) was used for the synthesis of polymers. Therefore, polycondensation of terephthalic acid with various commercially available diisocyanates was performed in molten **TBAB** with or without dibutyltin dilaurate (**DBTDL**) as a catalyst. The polymerization reaction gave similar results in the presence or absence of **DBTDL**, indicating that, the catalyst was not needed in this process. Various **PA**s were obtained with high yields and moderate inherent viscosities ranging from 0.36 to 0.71 dL/g. This method was compared with the polymerization reaction in conventional solvent and in the presence of **DBTDL** as a catalyst. In the case of using **TBAB**, higher yields and inherent viscosities were obtained. This process is safe and green since toxic and volatile organic solvent such as *N*-methylpyrrolidone (NMP) was eliminated.

Keywords

polyamidation, molten ionic liquid, tetrabutylammonium bromide, diisocyanates route, green media, terephthalic acid, green chemistry

Introduction

As the introduction of cleaner technologies has become a major concern throughout both academy and industry, the search for alternatives to the unsafe volatile solvents has become a high priority. Due to worsening of the environment, green chemistry has been receiving progressively more interest since the 1990's. Highly polar conventional solvents which have been used in polycondensation, such as *N,N'*-dimethylformamide (DMF), *N,N'*-dimethylacetamide (DMAc), pyridine, *N*-methylpyrrolidone (NMP) and chlorinated solvents are volatile, most of them flammable, toxic, quite hazardous and harmful. Hence, there is a great require for the advancement of new methodologies for polymerization using environmentally eco-friendly media which could replace the traditional solvents and give adequate solubility to polymerization.

Recently, water and ionic liquids (**IL**)s have been identified and are fascinating attention as benign solvents for organic as well as polymer synthesis. In contrast to conventional solvents, **IL**s do not produce volatile organic compounds due to their insignificant vapor pressure [1,2]. **IL**s made of organic cations and suitable anions have attracted much recent consideration as solvents for chemistry because of the fact that they have melting points close or near to room temperature. The most of **IL**s are clear and colorless viscous liquid. **IL**s possess a unique array of physico-chemical properties that make them appropriate in numerous task-specific uses in which conventional solvents are non-applicable or inadequately effective. Such properties comprise: high electrical conductivity, high thermal stability, large electrochemical window, low nucleophilicity and capability of providing weekly coordinating or non-coordinating environment, very good solvents properties for an extensive diversity of organic, inorganic, organometallic and polymeric compounds [3]. In some cases, the solubility of certain solutes in **IL**s can be several orders of magnitude higher than that in traditional solvents. Moreover, by fine-tuning the structure, these properties can be tailor-designed to gratify the definite application requirements. It has been reported that these solvents can be readily removed and recycled [4-6]. As well as being used as reaction solvents, a current report has shown that they can be used as reagents for many syntheses. Due to the above reasons, room temperature ionic liquid (**RTIL**)s are enthusiastically being investigated as possible "green" solvents to substitute classical volatile organic solvents in a variety of processes, including industrially essential chemical process [7,8]. Lately **IL**s have also gain rising attention for application in polycondensation reactions [9-13]. However, the high cost of most **RTIL**s and apprehension about their toxicity has led researchers to discover the use of more benign salts in the molten state as useful alternatives. Recently, molten tetrabutylammonium bromide (**TBAB**) was used as a low toxic and cost-effective **IL** in a number of useful synthetic transformations [3, 14-18].

Polyamides (**PA**)s are crystalline polymers that have excellent properties, such as toughness, rigidity, wear resistance, corrosion resistance, and so on, for common applications [19]. **PA**s are usually prepared by the polymerization reactions of diacids or diacid chlorides with diamines or diacids with diisocyanates in conventional volatile organic solvents which are environmentally hazardous.

Herein we wish to demonstrate that the replacement of volatile organic solvents by **MIL** would be an efficient, and environmentally friendly green route for the production of **PA**s from the polymerization of terephthalic acid (**TPA**) with different diisocyanates and compared it with conventional method.

Experimental

Materials

Reagents were purchased from Fluka Chemical (Buchs, Switzerland), Aldrich Chemical (Milwaukee, WI) and Riedel-deHaen AG (Seelze, Germany). DMAc, dimethyl sulfoxide (DMSO), DMF, and NMP were dried over BaO and then were distilled under reduced pressure.

Apparatus

Proton nuclear magnetic resonance ^{1}H-NMR (500 MHz) spectrum was recorded on a Bruker, Avance 500 instrument (Bruker, Rheinstetten, Germany). Proton resonances are designated as singlet (s), and multiplet (m). Fourier transform infrared (FT-IR) spectra were recorded on Jasco-680 (Jasco-Japan) spectrophotometer. Spectra of solids were obtained with KBr pellets. Vibration bands were reported in wavenumber (cm^{-1}). The band intensities are classified as weak (w), medium (m), strong (s) and broad (br). Inherent viscosities were measured by a standard procedure using a Cannon-Fenske routine viscometer (Cannon-Mainz, Germany). Thermal Gravimetric Analysis (TGA) data for polymers were taken on a Perkin Elmer Thermal Gravimetric Analyzer (Germany) under a nitrogen atmosphere at a heating rate of 10°C/min, by the Institute of Polymer and Petrochemical of Iran (IPPI). Elemental analyses were also performed by IPPI.

Polymer Synthesis

1) Method I: A typical preparation of **PA1** is as follow: A mixture of **TPA** (0.166 g, 1 mmol) and **TBAB** (0.853 g, 2.65 mmol) was ground until a powder was formed. Then was transferred into a 25-mL round-bottom flask and 4,4'-methylenebis(phenyl isocyanate) (**MDI**) (3) (0.25 g, 1 mmol) 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 70/30 methanol/water mixture. The white solid was filtered off and dried to give 0.362 g (85%) of **PA1**.

2) Method II: typical preparation of **PA**s in NMP as a solvent is as follow:
A mixture of NMP (0.2 mL) and **TPA** (0.166 g, 1 mmol) in a round-bottom flask was heated at 70°C. Hexamethylene diisocyanate (**HMDI**) (1) (0.16 mL, 1 mmol) was added to this mixture under nitrogen atmosphere, and the mixture was stirred for 1 h at this temperature, 10 h at 80-100°C and 1 h at 100-110°C. The viscous solution was precipitated in 30 mL of 70/30 methanol/water mixture. The solid was filtered off and dried to give 0.297 g (78%) of **PA1**. The above polymerization was repeated, in the presence of dibutyltin dilaurate (**DBTDL**) as a catalyst. The other **PA**s were prepared with a similar procedure using the other diisocyanates, toluylene-2,6-diisocyanate (80/20) (**TDI**) (**2**) and isophorone diisocyanate (**IPDI**) (**4**).

PA1I: IR (KBr, cm^{-1}): 3334 (m, br), 2931 (w), 2856 (w), 1686 (s), 1620 (w), 1574 (m), 1509 (w), 1424 (m), 1286 (s), 1135 (w), 1112 (w), 781 (m), 732 (m).

PA2I: IR (KBr, cm^{-1}): 3285 (m, br), 2960 (m, sh), 2952 (m, sh), 1654 (s), 1600 (m), 1529 (s), 1409 (w), 1280 (s), 1136 (w), 1112 (w), 781 (m). ^{1}H-NMR (500 MHz, DMSO-d_6, δ, ppm): 2.04 (s, br, 3H, CH_3), 7.08-8.30 (m, br, Ar-H), 10.00-10.40 (m, br, N-H).

PA3I: IR (KBr, cm^{-1}): 3372 (m, br), 2924 (w), 1685 (s), 1597 (m), 1541 (m, sh) 1509 (s), 1411 (m), 1285 (m), 1112 (w), 781 (w), 731 (w).

PA4I: IR (KBr, cm^{-1}): 3381 (m, br), 2935 (m, sh), 2924 (m, sh), 1682 (s), 1560 (m), 1209 (w), 1424 (m), 1384 (w), 1286 (s), 1112 (w), 942 (w), 781 (m), 732 (m).

Elemental analysis. Calcd. For polymer **PA1I** ($C_{14}H_{18}N_2O_2$): C, 68.27%; H, 7.37%; N, 11.37%. Found: C, 65.41%; H, 8.21%; N, 10.18%. Correction: C, 67.86%; H, 7.90%; N, 10.56% (for moisture content = 3.75).

Moisture Content (%) = $\frac{(W - W_0)}{W_0} \times 100$, W = weight of polymer sample after standing at room temperature and W_0 = weight of polymer sample after dried in vacuum at 100°C for 10 h. Corrected value for C and N = Found value × $\frac{(100 + moisture\ content)}{100}$, and Corrected value for H = Found value × $\frac{(100 - moisture\ content)}{100}$.

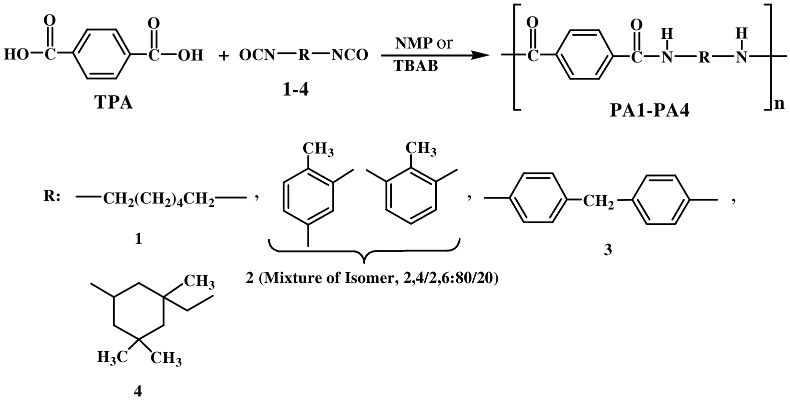
Elemental analysis. Calcd. For polymer **PA2I** ($C_{15}H_{12}N_2O_2$): C, 71.42%; H, 4.79%; N, 11.10%. Found: C, 69.63%; H, 5.60%; N, 10.51%. Correction: C, 71.09%; H, 5.48%; N, 10.73% (for moisture content = 2.10).

Elemental analysis. Calcd. For polymer **PA3I** ($C_{21}H_{14}N_2O_2$): C, 77.29%; H, 4.32%; N, 8.58%. Found: C, 74.73 %; H, 5.34%; N, 7.87%. Correction: C, 77.19%; H, 5.16%; N, 8.06% (for moisture content = 3.30).

Elemental analysis. Calcd. For polymer **PA4I** ($C_{18}H_{24}N_2O_2$): C, 71.67%; H, 8.05%; N, 9.33%. Found: C, 68.73 %; H, 8.47%; N, 8.48%. Correction: C, 71.24%; H, 8.16%; N, 8.79% (for moisture content = 3.65).

Results and Discussion

As extension of our studies on the application of green chemistry principles in polymerization, we wish to report a simple, safe and efficient method for the polymerization of **TPA** with readily accessible diisocyanates in molten **TBAB** as homogenizer. The **PA**s based on **TPA** were synthesized by one step high temperature method (Scheme 1). The polymerization reaction was carried out in molten **TBAB** in the presence and in the absence of **DBTDL**. The results are comparative; this indicates that **DBTDL** was not required in this polycondensation reaction. Therefore, molten **TBAB** acts both as solvent and catalyst in this process. It is worth to mention that the reaction mixture was homogenous throughout the polymerization. The resulting **PA**s were obtained in high yields, good inherent viscosities and thermal stability. The data are summarized in Table 1. In order to compare the efficiency of this novel method of polymerization (method I) with conventional polymerization method (method II) the above reactions were performed in polar organic solvent such as NMP in the presence and in the absence of **DBTDL** as a catalyst with graduate heating. We obtained better yields and viscosities with method I, indicating that polymerization in molten **TBAB** was more efficient. It is interesting to mention that, in method II, NMP was used as a solvent which is volatile, and will cause a change in the concentration of reaction mixture during polymerization process and lead to the formation of polymers with lower inherent viscosity. On the other hand **DBTDL** was required to be used in this method; otherwise the resulting **PAs** had lower yields and comparable inherent viscosities (Table 2). In method I, molten **TBAB** was used as a solvent which is green, safe, and **DBTDL** was eliminated which also lowers the cost and pollution. Thus, **TBAB** act both as effective solvent and catalyst to mediate clean polymerization reactions to yield the desired **PA**s. When polymerization reaction was performed in molten **TBAB**, viscous solutions were formed and the resulting polymers were never precipitated, whereas precipitation was observed during of conventional method in NMP as a solvent. The resulting polymers from **TDI** and **IPDI** are soluble in many organic solvents such as DMF, DMSO, DMAc, NMP and in H_2SO_4, but the polymers from **HMDI** and **MDI** are slightly soluble in these solvents and readily soluble in H_2SO_4.



Scheme 1. Polycondensation reactions of **TPA** with diisocyanates in NMP and molten **TBAB**.

Table 1. Reaction conditions for the polymerization of monomer **TPA** with diisocyanates **1**, **2**, **3** and **4** in molten **TBAB** (method I)

Diisocyanate	Polymer	Catalyst	Yield (%)	η_{inh} (dL/g)	Non-Solvent
HMDI	**PA1AI**	-	75	0.40[a]	CH_3OH/H_2O
TDI	**PA2BI**	-	89	0.41[b]	CH_3OH
MDI	**PA3CI**	-	85	0.71[a]	CH_3OH
IPDI	**PA4DI**	-	73	0.25[b]	CH_3OH/H_2O
HMDI	**PA1EI**	DBTDL[c]	78	0.39[a]	CH_3OH/H_2O
TDI	**PA2FI**	DBTDL	94	0.43[b]	CH_3OH
MDI	**PA3GI**	DBTDL	89	0.75[a]	CH_3OH
IPDI	**PA4HI**	DBTDL	75	0.32[b]	CH_3OH/H_2O

[a] Measured at a concentration of 0.5 g/dL in concentrated sulfuric acid at 25°C.
[b] Measured at a concentration of 0.5 g/dL in DMF at 25°C.
[c] Dibutyltin dilaurate.

Structural Characterization of Polymer

The formation of **PA**s was confirmed by FT-IR and ^{1}H-NMR spectroscopies and elemental analysis. The FT-IR spectra of **PA**s show the characteristic absorptions of amide groups occurred around 3300 and 1650 cm^{-1}, peculiar to N-H and carbonyls stretching of amide, respectively. The ^{1}H-NMR spectrum (500 MHz) of polymer **PA2** showed peaks that confirm its chemical structure (Figure 1). In the ^{1}H-NMR spectrum of this polymer, appearance of the two isomer (isomers 2,4 and 2,6) diisocyanate **2** in the polymer chain indicates two different amide groups around 10.04 and 10.36 ppm. The absorption of aromatic protons appeared in the range of 7.08-8.30 ppm. The absorption of the CH_3 protons appeared at 2.04 ppm as a singlet. Since polymers from **MDI** and **HMDI** do not have sufficient solubility in DMSO, we were not able to run ^{1}H-NMR for these polymers.

Table 2. Reaction conditions for the polymerization of monomer **TPA** with diisocyanates **1**, **2**, **3** and **4** in NMP (method II)

Diisocyanate	Polymer	Catalyst	Yield (%)	η_{inh} (dL/g)	Non-Solvent
HMDI	**PA1AII**	-	78	0.38[a]	CH_3OH/H_2O
TDI	**PA2BII**	-	72	0.38[b]	CH_3OH
MDI	**PA3CII**	-	77	0.51[a]	CH_3OH
IPDI	**PA4DII**	-	74	0.21[b]	CH_3OH/H_2O
HMDI	**PA1EII**	DBTDL[c]	88	0.40[a]	CH_3OH/H_2O
TDI	**PA2FII**	DBTDL	85	0.40[b]	CH_3OH
MDI	**PA3GII**	DBTDL	87	0.57[a]	CH_3OH
IPDI	**PA4HII**	DBTDL	85	0.28[b]	CH_3OH/H_2O

[a] Measured at a concentration of 0.5 g/dL in concentrated sulfuric acid at 25°C.
[b] Measured at a concentration of 0.5 g/dL in DMF at 25°C.
[c] Dibutyltin dilaurate.

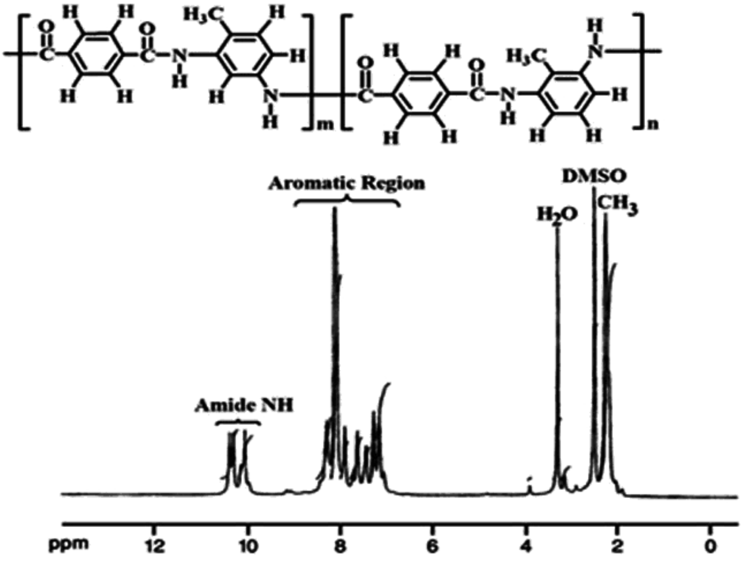


Figure 1. ^{1}H NMR (500 MHz) spectrum of **PA2** in DMSO-d_6 at R.T.

Thermal properties

The thermal behavior of **PA3GI** and **PA3GII** was measured by thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) analysis at a heating rate of 10°C min^{-1} in a nitrogen atmosphere. The temperatures of 5% and 10% weight loss together with char yield at 650°C for **PA3GI** and **PA3GII** were 290°C, 315°C and

14%, 340°C, 460°C and 40%, respectively. Figures 2 and 3 show thermograms of **PA3GI** and **PA3GII**, respectively. **PA3GI** show higher thermal stability than **PA3GII**, this can be explained in terms of higher inherent viscosity of **PA3GI**.

Table 3. Thermal Properties of **PA3GI** and **PA3GII**

Polymer	T_5 (°C)[a]	T_{10} (°C)[b]	Char Yield (%)[c]
PA3GI	340	460	40
PA3GII	290	315	14

[a] Temperature at which 5% weight loss was recorded by TGA at heating rate of 10°C/min in N_2.
[b] Temperature at which 10% weight loss was recorded by TGA at heating rate of 10°C/min in N_2.
[c] Percentage weight of material left undecomposed after TGA analysis at maximum temperature 650°C in N_2.

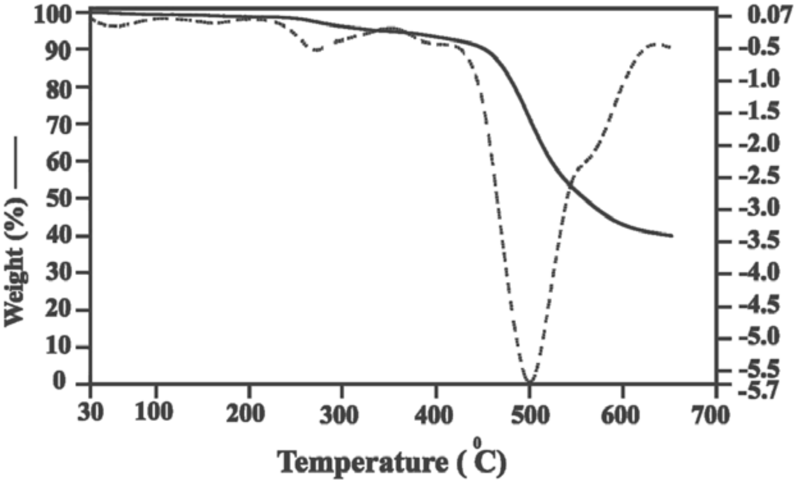


Figure 2. TGA/DTG of **PA3GI** with a heating rate of 10°C/min in a nitrogen atmosphere.

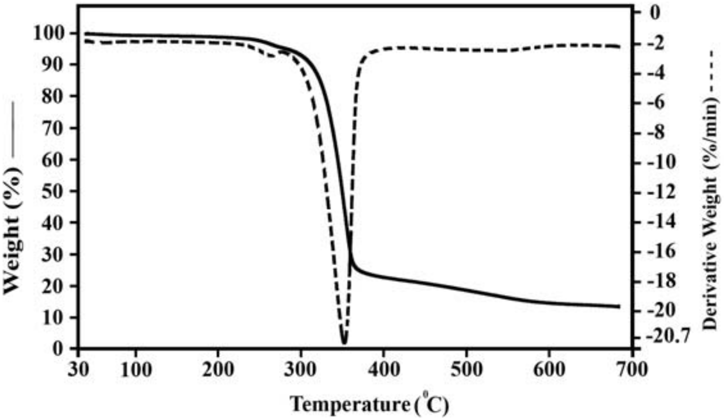


Figure 3. TGA/DTG of **PA3GII** with a heating rate of 10°C/min in a nitrogen atmosphere.

Conclusion

In summary, molten **TBAB** may act as a simple, cheap and safe medium for polymerization reactions. The reported procedure for the polycondensation of **TPA** with various diisocyanates under green conditions demonstrates the potential of molten **TBAB**, a benign readily available **IL,** as an efficient catalyst and has much promise for further applications. Moreover, this methodology offers significant improvements with regard to yield of products, inherent viscosities, thermal stability, cost efficiency and green aspects avoiding toxic catalysts and solvents. In this study, we substituted NMP (harmful solvent) with **TBAB**. Since **DBTDL** did not have any catalytic effect on this polycondensation reaction, we may presume that the molten **TBAB** can act both as solvent and catalyst.

Acknowledgements. We wish to express our gratitude to the Research Affairs Division Isfahan University of Technology (IUT), Isfahan, for partial financial support. Further financial support from Center of Excellency in Sensors and Green Chemistry Research (IUT) is gratefully acknowledged. We also extend our thanks to Miss. Z. Rafiee for her helpful discussion.

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