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Tetrabutylammonium bromide: An efficient, green and novel media for polycondensation of 4-(4-dimethylaminophenyl)-1,2,4-triazolidine-3,5-dione with diisocyanates

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Abstract

This is the first report of application of molten ionic liquid (MIL) for the synthesis of heterocyclic polyureas. An inexpensive and readily available MIL, tetrabutylammonium bromide (TBAB) was used for the synthesis of polymers. Therefore, polycondensation of 4-(4-dimethylaminophenyl)-1,2,4-triazolidine-3,5-dione (DAPTD) with various commercially available diisocyanates was performed in molten TBAB with or without dibutyltin dilurate (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 polyureas were obtained with high yields and moderate inherent viscosities ranging from 0.26 to 0.38 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 was safe and green since toxic and volatile solvent such as *N*,*N*-dimethylacetamide (DMAc) was eliminated.

Keywords: Polyureas; Step-growth polymerization; Inherent viscosity; 4-(4-Dimethylaminophenyl)-1,2,4-triazolidine-3,5-dione; Tetrabutylammonium bromide; Thermogravimetric analysis (TGA)

1. Introduction

In chemical industries as well as research laboratories, solution polycondensation reactions are performed in volatile organic solvents (VOS) such as *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc), *N*-methylpyrrolidone (NMP), pyridine, triethylamine, chlorinated hydrocarbons and so on. These solvents are volatile, most of them flammable, toxic, and harmful. Thus, removing organic solvents in polymer synthesis is very important in the drive towards environmentally friendly technologies. In a search for more efficient and at the same time more environmentally green processes chemists have recently turned their interest to the new class of potential solvents namely to ionic

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liquids (ILs) and have become a part of the so-called 'green chemistry' [1–4].

ILs are a new class of solvents which have interesting properties such as non-volatility, good thermal stability, high ionic concentration, nonflammability and can dissolve most of organic as well as inorganic compounds. Recently, ILs are attracting more attention due to their significant role in controlling the reaction as a catalyst. It is important that ILs are the chemicals that can be applied as solvents and catalysts in green chemistry processes [5–10]. Lately ILs have also gained increasing attention for application in polymer synthesis [11–15]. Various polyimides, polyamides, polyhydrazides and poly[naphthoylene-bis-(benzimidazole)]s are effectively formed in ILs without any added catalyst [16,17]. These results allow to assume ILs can activate some polycondensation reactions.

However, high cost of most of the common room temperature ILs and uncertainty regarding the toxicity of some of them has led to the use of more benign salts in the molten state as practical alternatives. Recently, molten TBAB has been used as an efficient catalyst in a number of useful synthetic transformations [18–22]. These reactions catalyzed by molten TBAB are in general, very fast and clean. Molten TBAB has been demonstrated as an efficient catalyst for Michael addition in a solventless system. Considering these elegant discoveries of addition activity of IL, we envisage that other types of addition could also be catalyzed by IL.

The most of ILs are clear and colorless viscous liquid. ILs possess a unique array of physico-chemical properties that make them suitable in numerous task-specific applications in which conventional solvents are non-applicable or insufficiently effective. Such properties include: high thermal stability, high electrical conductivity, large electrochemical window, low nucleophilicity and capability of providing weekly coordinating or non-coordinating environment, very good solvents properties for a wide variety of organic, inorganic and organometallic compounds: in some cases, the solubility of certain solutes in ILs 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 satisfy the specific application requirements [23]. As a result, ILs are very popular materials and they enjoy a plethora of applications in various domains of physical sciences [24,25].

ILs are a class of salts consisting of cation–anion pair that has a very low melting point. There is no reliable way to predict the precise melting point of organic salts, and identification of new room-temperature ILs is a somewhat hit and miss affair. Definition of an IL is open to some debate amongst researchers in the area, but most in the are use of three: (1) An ionic compound that melts below 100 °C (b.p. of H_2O). (2) An ionic compound that has a melting point at or below ambient temperatures. These are often called room temperature ionic liquids (RTILs). (3) Molten IL that melts up 100 °C. However, IL's liquid range is up to −50 to 250 °C.

In most of their applications, the stability of ILs, at least at a certain extent, is crucial for optimum process performance. Several studies have indicated that, although not 100% inert, certain ILs incorporating 1,3-dialkyl imidazolium cations are generally more resistant than traditional solvents under certain harsh process conditions, such as those occurring in oxidation, photolysis and radiation processes.

High quality ILs incorporating $[bmim]^+$ cation and a variety of anions, such as $[PF_6]^-$, $[BF_4]^-$, $[CF_3SO_3]^-$, $[CF_3CO_2]^-$ and $[(CF_3SO_2)_2N]^-$ have been reported to be colorless, even though they are not 100% pure. The color of less pure ILs generally ranges from yellowish to orange. The formation of the color has been attributed to the use of raw materials with color or excessive heating during the synthesis of imidazolium salt. A number of precautions for synthesis of colorless ILs have been described, and a procedure for removal of color from impure ILs using acidic alumina and activated charcoal has also been proposed.

The water content has an influence on the viscosity of the ILs. Viscosity measurement indicates that ILs became less viscous with increasing water content. Hydrolysis problems can also occur.

The degree of polarity can be varied by adapting the length of the 1-alkyl chain (in 1,3-substituted imidazolium cations), and the counterion. Long-chain ILs salts have attracted some interest due to their liquid-crystalline (LC) properties. The anion chemistry has a large influence on the properties of ILs. Though little variation in properties might be expected between same-cation salts of these species, the actual differences can be dramatic: for example, $[bmim]PF_6^-$ is immiscible with water, whereas $[bmim]BF_4^-$ is water-soluble [23].

The toxicological studies available have shown that ILs are rather non-toxic substances (LD50 is 1400 mg/kg). Of course as the alkyl chain length increased, the lethality of the ILs increased [26,27].