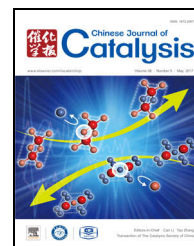


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## Article

# Synthesis of isosorbide-based polycarbonates via melt polycondensation catalyzed by quaternary ammonium ionic liquids

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## ABSTRACT

A series of quaternary ammonium ionic liquids (ILs) were synthesized and employed as catalysts for the production of poly(isosorbide carbonate) (PIC) from diphenyl carbonate and isosorbide via a melt polycondensation process. The relationship between the anions of the ILs and the catalytic activities was investigated, and the readily-prepared IL tetraethylammonium imidazolate (TEAL) was found to exhibit the highest catalytic activity. After optimizing the reaction conditions, a PIC with a weight-average molecular weight ( $M_w$ ) of 25600 g/mol was obtained, in conjunction with an isosorbide conversion of 92%. As a means of modifying the molecular flexibility and thermal properties of the PIC, poly(aliphatic diol-co-isosorbide carbonate)s (PAIC)s were successfully synthesized, again using TEAL, and polymers with  $M_w$  values ranging from 29000 to 112000 g/mol were obtained. <sup>13</sup>C NMR analyses determined that the PAIC specimens had random microstructures, while differential scanning calorimetry demonstrated that each of the PAICs were amorphous and had glass transition temperatures ranging from 50 to 115 °C. Thermogravimetric analyses found  $T_{d-5\%}$  values ranging from 316 to 332 °C for these polymers. Based on these data, it is evident that the incorporation of linear or cyclohexane-based diol repeating units changed the thermal properties of the PIC.

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## 1. Introduction

Polycarbonate (PC) is an excellent engineering plastic widely used for various industrial applications owing to its unique properties, including high tensile strength, impact resistance, and good transparency [1,2]. Currently, one of the most important and widely commercialized PCs is bisphenol A PC (BPAPC) [3,4]. However, bisphenol A is a toxic, petroleum-derived chemical [5,6], and so much effort has been devoted

to replacing this compound with bio-based monomers [7–9]. Isosorbide (1,4:3,6-dianhydro-D-sorbitol) is a well-known potential replacement and has the advantages of rigidity, chirality and low toxicity [10,11]. Moreover, it is the only carbohydrate-based bicyclic monomer currently commercially available [12] and so could represent an ideal renewable monomer for polymer synthesis [13]. To date, isosorbide has been widely used for the synthesis of polyesters [14–16], polyurethanes [17–19], poly(ester-co-carbonate)s [20,21] and PCs

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[22–26]. The large-scale production of poly(isosorbide carbonate) (PIC) via the melt polycondensation of isosorbide with dimethyl carbonate (DMC) or diphenyl carbonate (DPC) has also been investigated recently [5,27–29].

Isosorbide has some associated challenges such as its higher hydrophilic and lower acidity than that of bisphenol A, so the synthesis of PIC is complex [10]. The production of high molecular weight PIC requires suitable catalysts for the melt polycondensation process because of the severe reaction conditions. To date, basic catalysts have been found to be the most efficient for PIC synthesis [5,30,31]. Li et al. [29] synthesized a PIC by melt polycondensation of isosorbide with DMC, using lithium acetylacetonate as the catalyst. Shin et al. [5] reported that cesium carbonate exhibited superior catalytic activity during the synthesis of a PIC by melt polycondensation with DPC. Although inorganic bases have been used for this reaction [32,33], they tend to have several drawbacks, including unsatisfactory activities, difficult separations and branching. More recently, basic ionic liquids (ILs) have been shown to be promising substitutes for inorganic bases [34–39]. As an example, Park et al. [40] demonstrated the transesterification of ethylene carbonate with methanol catalyzed by 1-alkyl-3-methylimidazolium ILs.

In recent years, many researchers have paid much attention to the functionalized ILs by designing the structures of cations or anions according to practical requirements and special purposes [41–46]. In the present work, we designed and synthesized several basic ILs and investigated the effects of the anions on the catalytic activities of these compounds during the synthesis of a PIC via the melt polycondensation of DPC with isosorbide. The results demonstrate that the readily synthesized IL tetrabutylammonium imidazolate (TEAI) shows the highest activity, producing a PIC with a weight-average molecular weight ( $M_w$ ) of 25600 g/mol in conjunction with an isosorbide conversion of 92%. In addition, the molecular flexibility and thermal properties of the PIC were modified by synthesizing poly(aliphatic diol carbonate)s (PAIC)s through combining isosorbide and various aliphatic diols (diethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol and 1,4-cyclohexanedimethanol). The PIC and PAICs samples were characterized by  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopy, gel permeation chromatography (GPC), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

## 2. Experimental

### 2.1. Materials and measurements

Isosorbide (98%) was purchased from Alfa Aesar, while 1,4-cyclohexanedimethanol (*cis+trans*, 99%), 1,5-pentanediol (97%), 1,6-hexanediol (98%), 1,3-propanediol ( $\geq 99.5\%$ ), imidazole (99%), 1,2,4-triazole (99%), sodium dicyanamide (96%), diethylene glycol ( $>99\%$ ), tetramethylammonium hydroxide solution (TMAH, 25% aqueous solution), tetrabutylammonium hydroxide solution (TEAH, 25% aqueous solution), tetrapropylammonium hydroxide solution (TPAH, 1.0 mol/L aqueous solution) and diphenyl carbonate (99%) were

purchased from Shanghai Aladdin Bio-chem Technology. The remaining reagents, 1,4-butanediol, silver nitrate, benzoic acid, tetrabutylammonium hydroxide solution (TBAH, 10% aqueous solution), acetic acid, lactic acid, isopropyl alcohol, dichloromethane, phosphorus oxide, sodium hydroxide and tetraethylammonium bromide, were purchased from Sinopharm Chemical Reagent.

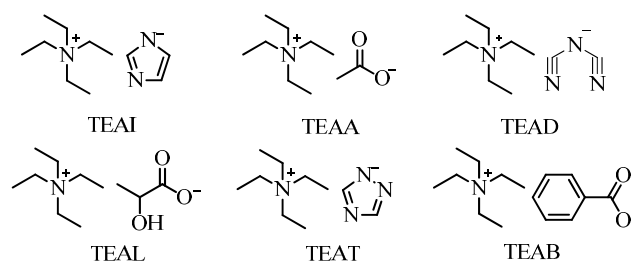
$^1\text{H}$  NMR spectra were recorded in deuterated water ( $\text{D}_2\text{O}$ ) or deuterated chloroform ( $\text{CDCl}_3$ ) with tetramethylsilane (TMS) as the internal reference, using a Bruker Avance III-600 spectrometer. GPC was employed to estimate the  $M_w$  and polydispersity ( $\text{PDI} = M_w/\text{number-average molecular weight } (M_n)$ ), using an Agilent PL-GPC 50 system at 30 °C, with chloroform as the eluent (1.0 mL/min) and generating a calibration curve with polystyrene standards. The glass transition temperature ( $T_g$ ) of each polymer was determined by DSC using a DSC 1 instrument (Mettler Toledo) at a heating rate of 10 °C/min with a nitrogen gas purge (50 mL/min). TGA data were acquired with a NETZSCH STA449F3 thermogravimetric analyzer under a nitrogen flow rate of 20 mL/min, heating samples (2.0–3.0 mg) from 50 to 600 °C at a rate of 10 °C/min. Fourier transform infrared (FT-IR) spectra were recorded using a Thermo Nicolet 380 spectrophotometer.

### 2.2. Synthesis of the quaternary ammonium IL catalysts

The structures of the quaternary ammonium IL catalysts synthesized in this study are shown in Scheme 1, and the methods used to obtain these compounds are described below.

Tetraethylammonium imidazolate (TEAI) was prepared using a modification of a reported procedure [47]. Imidazole (0.68 g, 0.01 mol) was added to a solution of NaOH (0.40 g, 0.01 mol) in isopropyl alcohol (20 mL) followed by refluxing for 30 min. Tetraethylammonium bromide (3.09 g, 0.01 mol) was then added at room temperature and the resulting mixture was refluxed for a further 6 h. The solid portion of the reaction mixture was removed by filtration, the solvent was evaporated under vacuum, and the residue (TEAI) was dried at 60 °C under vacuum over 2 d. Yield: 1.87 g (95%);  $^1\text{H}$  NMR (600 MHz,  $\text{D}_2\text{O}$ , 298 K): 7.62 (s, 1H), 7.00 (d, 2H), 3.08–3.11 (q, 8H), 1.10–1.13 (m, 12H).

The synthetic method for tetraethylammonium 1,2,4-triazolate (TEAT) was the same as that used to obtain TEAI, except that 1,2,4-triazole (0.69 g, 0.01 mol) was added to the NaOH solution. Yield: 1.90 g (96%);  $^1\text{H}$  NMR (600 MHz,  $\text{D}_2\text{O}$ , 298 K): 8.02 (s, 2H), 3.10–3.14 (q, 8H), 1.12–1.15 (m, 12H).



**Scheme 1.** Structures of the quaternary ammonium ionic liquids synthesized in this work.

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