



Catalyst screening for the melt polymerization of isosorbide-based polycarbonate



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ABSTRACT

Isosorbide, a renewable sugar-diol, is used to make isosorbide-based polycarbonates by melt polymerization with diphenyl carbonate. To make high-molecular-weight and optically clear isosorbide-based polycarbonates, several catalysts are selected from well-known promoters of polycondensation, and their catalytic activities are evaluated. Among those chosen, cesium carbonate shows the highest catalytic activity, and its optimum concentration is determined by taking into account the molecular weight, glass transition temperature and discoloration of the resulting polycarbonates. In this study, a small amount of cesium carbonate (0.2 ppm) is sufficient to produce a high-molecular-weight ($M_w = 32,600$) isosorbide-based polycarbonate with a high glass transition temperature (164 °C) that shows the least discoloration. Furthermore, in the case of melt polymerization, the purities of isosorbide and diphenyl carbonate also play an important role in the discoloration of isosorbide-based polycarbonates.

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Introduction

Isosorbide (ISB), which can be produced from renewable resources such as glucose, has been regarded as a promising monomer for polycondensation [1–3] because of its attractive rigidity, chirality and non-toxicity [4,5]. Therefore, ISB has been used for the synthesis of polyesters [6–8], polyurethanes [9–11], poly(ester-co-carbonate)s [12,13] and polycarbonates [14–19]. As far as polycarbonates (PC) are concerned, ISB is an excellent candidate to replace petroleum-based bisphenol A (BPA), which causes chronic toxicity problems [20]. In addition, ISB can offer excellent optical properties such as high clarity, UV stability and low birefringence and can impart rigidity to the polymer backbone to induce an enhanced glass transition temperature (T_g) [21,22]. Therefore, ISB-based PCs have superior optical properties compared to the conventional BPA-based PCs and high resistance to heat and humidity. ISB-based PCs also have outstanding scratch resistance. Despite these advantages, it is difficult to polymerize

ISB-based PCs because ISB is highly hydrophilic and its acidity is lower than that of BPA.

Several attempts have been made to produce PC with ISB by solution and melt polymerizations. Solution polymerization has mainly been attempted because it can precisely control chemical reaction heat and viscosity and can prevent auto-acceleration reactions. However, solution polymerization requires phosgene and chlorinated solvents, which are not environmentally benign, and additional processing is needed for their removal [18]. Conversely, melt polymerization is environmentally friendly compared with solution polymerization; therefore, it has recently attracted more interest from industry. However, melt polymerization demands severe reaction conditions for the removal of condensates, which is necessary to obtain a high-molecular-weight polymer. Because severe reaction conditions occasionally induce undesirable side reactions (e.g., degradation and colorization of the resulting polymers), catalysts that can easily shift the reaction equilibrium towards polymer formation under mild conditions become important. There are several papers on catalysts for melt polymerization of ISB. Betiku et al. reported several catalysts for the synthesis of a poly(isosorbide carbonate) and lactide copolymer by melt and solvent-assisted transesterifications [23]. Li et al. made an ISB-based

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PC by melt polymerization with dimethyl carbonate (DMC) and lithium acetylacetonate as a catalyst [24]. Ignatov et al. reported the activities of different classes of transesterification catalysts for BPA and diphenyl carbonate (DPC) melt transesterification [25], and Woo et al. reported that melt polymerization of BPA and DPC in a semi-batch reactor [26]. However, there are few papers on catalyst use for the melt polymerization of ISB and DPC.

In this paper, we sought to synthesize high-molecular-weight and high- T_g PC by melt polymerization of ISB and DPC. DPC is chosen as a carbonyl source instead of DMC because DMC forms azeotrope with methanol. This makes it difficult to remove methanol from DMC and interrupts reaction equilibrium shift to the polymer formation. Although DPC contains a carbonyl group connected to two phenols, the transesterification of DPC and ISB scarcely occurs because of the less reactive hydroxyl group on ISB. To determine the proper catalyst, we tested several complexes, including two representative base catalysts for polycondensation, alkali metal carbonates, and lanthanum acetylacetonate [La(acac)₃], which shows good performance in the melt polymerization of BPA and DPC. Their catalytic activities for ISB and DPC melt polymerization were evaluated, and the most promising catalyst was proposed based on these results. ISB-based PCs were characterized by ¹H and ¹³C NMR spectroscopy; their average molecular weights and T_g s were measured by gel permeation chromatography (GPC) and differential scanning calorimetry (DSC). We also investigated the effect of catalyst quantity and identified the optimum catalyst content for melt polymerization of ISB and DPC.

Experimental

Materials

Isosorbide (ISB, 98%) and diphenyl carbonate (99%) were purchased from Sigma-Aldrich. Lithium hydroxide (LiOH, 98%), titanium isopropoxide [Ti(OCH(CH₃)₂)₄, 99.999%], lanthanum acetylacetonate [La(acac)₃, hydrate], lithium carbonate (Li₂CO₃, 99%), sodium carbonate (Na₂CO₃, 99.999%), potassium carbonate (K₂CO₃, 99.995%), and cesium carbonate (Cs₂CO₃, 99.995%) were also purchased from Sigma-Aldrich. All reagents were used without further purification.

Preparation of ISB-based PCs

ISB-based PCs were synthesized by a one-step melt polymerization method, where transesterification and polymerization occurred in the same reactor (see Fig. S1 in the ESI). Under a nitrogen atmosphere, ISB (10.484 g, 0.0717 mol), DPC (15 g, 0.0700 mol), and a catalyst (5 mg, 500 ppm based on ISB) were charged into a 100-mL reactor for polymerization that was equipped with a mechanical stirrer, a nitrogen inlet, and a Dean-Stark type condenser (for vacuum). In the transesterification stage, the reaction mixture was heated to 180 °C and stirred continuously for 30 min until the reagents presented a uniform melt. The temperature was then gradually increased to 200 °C and maintained for 30 min to remove phenol. In the polymerization stage, the temperature was gradually increased to 220 °C and maintained for 30 min under vacuum (100 Torr); then, the temperature was further increased to 240 °C and maintained for 1 h under high vacuum (<5 Torr). Before characterization, all ISB-based PCs were purified by dissolving in dichloromethane, followed by precipitation from methanol. The ¹H and ¹³C NMR spectra of synthesized ISB-based PC are displayed in Fig. S2 in the ESI.

Catalytic activity measurements

First, 53.5 g (0.25 mol) of DPC and 35.78 g (0.25 mol) of ISB were introduced into a round-bottomed double-necked flask under a nitrogen blanket. The flask was then immersed in an oil bath and heated until the temperature was stabilized at 165 °C. Then, an appropriate amount of catalyst was added to the reaction melt and magnetically stirred. Small amounts of the reaction melt (0.2–0.3 mL) were sampled throughout the reaction and then poured into small ampoules, sealed and stored immediately in a refrigerator. The concentrations of phenol in the samples obtained at different reaction times were determined by gas chromatography, and biphenyl was used as an internal standard.

Characterizations

The ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE 600 NMR spectrometer using deuterated chloroform (CDCl₃) and tetramethylsilane (TMS) as an internal reference. The number-average (M_n) and weight-average (M_w) molecular weights and their distribution (M_w/M_n) were estimated by high-temperature chromatography (PL-GPC220) using *m*-cresol as an eluent and polystyrene as a standard. The glass transition temperatures (T_g s) of the polymers were measured using a differential scanning calorimeter (DSC Q20 TA Instruments) at a heating rate of 10 °C/min with a nitrogen gas purge (50 mL/min). The concentrations of phenol in samples from different reaction times were determined by gas chromatography (Shimadzu QP 2010 ultra). Samples were diluted in dichloromethane, and biphenyl was used as an internal standard.

Results and discussion

Catalyst screening for ISB-based PC

The relatively low nucleophilicity of the hydroxyl group in ISB makes it difficult to attack the carbonyl group of DPC, which means that the transesterification of DPC and ISB scarcely occurs in the absence of a catalyst. We chose four different catalysts, namely, Ti(OCH(CH₃)₂)₄, LiOH, La(acac)₃ and Cs₂CO₃, as per previous reports [25]. Ti(OCH(CH₃)₂)₄ and LiOH are representative Lewis acid and base catalysts for polycondensation, especially for polyester, and La(acac)₃ showed good reactivity for BPA and DPC polymerization in the work of Betiku et al. [23]. Based on patent claims and our preliminary results, Cs₂CO₃ was also tested as a catalyst for ISB and DPC polymerization [27].

Table 1 summarizes the results of typical transesterifications. Catalysts such as Ti(OCH(CH₃)₂)₄ and LiOH are not effective for the transesterification of ISB and DPC in the melt, whereas La(acac)₃ induces formation of a high-molecular-weight polymer from ISB and DPC, as observed in the reaction between BPA and DPC. Interestingly, Cs₂CO₃ generates a polymer with the highest molecular weight among these catalysts, and the T_g of the resulting polymer was 164 °C. The T_g s of the ISB-based PCs were determined from DSC thermograms (see Fig. S3 in the ESI). Based on the

Table 1
Molecular weights and glass transition temperatures of ISB-based PCs prepared by melt polymerization with different catalysts (catalyst amount was 500 ppm).

Catalyst	M_n (g/mol)	M_w (g/mol)	PDI	T_g (°C)
Titanium isopropoxide	5,960	9,100	1.51	120
Lithium hydroxide	14,100	19,900	1.64	154
Lanthanum acetylacetonate	21,800	30,500	1.40	158
Cesium carbonate	26,700	39,500	1.48	164

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