Catalyst screening for the melt polymerization of isosorbide-based polycarbonate

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\textbf{A B S T R A C T}

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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\textbf{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...
PC by melt polymerization with dimethyl carbonate (DMC) and lithium acetylatedonate 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 an azeotrope (K2CO3, 99.995%), 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 \(^1\)H and \(^{13}\)C 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 \(\text{Ti(OCH(CH}_3)_2)\text{O}, 99.999\%), lanthanum acetylatedonate \(\text{La(acac)}_3\), hydrate, lithium carbonate \(\text{Li}_2\text{CO}_3, 99\%), sodium carbonate \(\text{Na}_2\text{CO}_3, 99.999\%), potassium carbonate \(\text{K}_2\text{CO}_3, 99.995\%), and cesium carbonate \(\text{Cs}_2\text{CO}_3, 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 \(10.48\text{ g}, 0.0717 \text{ mol}\), DPC \(15 \text{ g}, 0.0700 \text{ mol}\), and a catalyst \(5 \text{ mg}, 500 \text{ ppm based on ISB}\) were charged into a 100-\(\text{mL}\) 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 \(^\circ\)C and stirred continuously for 30 min until the reagents presented a uniform melt. The temperature was then gradually increased to 200 \(^\circ\)C and maintained for 30 min to remove phenol. In the polymerization stage, the temperature was gradually increased to 220 \(^\circ\)C and maintained for 30 min under vacuum (100 Torr); then, the temperature was further increased to 240 \(^\circ\)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 \(^1\)H and \(^{13}\)C 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 \(^\circ\)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.

### 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, \(\text{Ti(OCH(CH}_3)_2)\text{O}, \text{LiOH}, \text{La(acac)}_3\), and \(\text{Cs}_2\text{CO}_3\), as per previous reports [23, 25]. \(\text{Ti(OCH(CH}_3)_2)\text{O}\) and \(\text{LiOH}\) are representative Lewis acid and base catalysts for polycondensation, especially for polyester, and \(\text{La(acac)}_3\) showed good reactivity for BPA and DPC polymerization in the work of Betiku et al. [23] Based on patent claims and our preliminary results, \(\text{Cs}_2\text{CO}_3\) was also tested as a catalyst for ISB and DPC polymerization [27].

**Table 1** summarizes the results of typical transesterifications. Catalysts such as \(\text{Ti(OCH(CH}_3)_2)\text{O}\) and \(\text{LiOH}\) are not effective for the transesterification of ISB and DPC in the melt, whereas \(\text{La(acac)}_3\) induces formation of a high-molecular-weight polymer from ISB and DPC, as observed in the reaction between BPA and DPC. Interestingly, \(\text{Cs}_2\text{CO}_3\) generates a polymer with the highest molecular weight among these catalysts, and the \(T_g\) of the resulting polymer was 164 \(^\circ\)C. The \(T_g\) of the ISB-based PCs were determined from DSC thermograms (see Fig. S3 in the ESI). Based on the

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(M_g (\text{g/mol}))</th>
<th>(M_w (\text{g/mol}))</th>
<th>PDI</th>
<th>(T_g (\ ^\circ\text{C}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium isopropoxide</td>
<td>5,960</td>
<td>9,100</td>
<td>1.51</td>
<td>120</td>
</tr>
<tr>
<td>Lithium hydroxide 14,100</td>
<td>19,900</td>
<td>1.64</td>
<td>154</td>
<td></td>
</tr>
<tr>
<td>Lanthanum acetylatedonate 21,800</td>
<td>30,500</td>
<td>1.40</td>
<td>158</td>
<td></td>
</tr>
<tr>
<td>Cesium carbonate 26,700</td>
<td>39,500</td>
<td>1.48</td>
<td>164</td>
<td></td>
</tr>
</tbody>
</table>

**Table 1** Molecular weights and glass transition temperatures of ISB-based PCs prepared by melt polymerization with different catalysts (catalyst amount was 500 ppm).
observed molecular weight and $T_g$, Cs$_2$CO$_3$ is a good catalyst for the melt polymerization of ISB and DPC. Considering the weak polarization of the DPC carbonyl group and the low nucleophilicity of the hydroxyl group in ISB, the Cs$^+$ ion appears to fortify the polarization of the DPC carbonyl group by forming metal-carbonyl coordination.

To understand the alkaline metal ion effect in greater detail, four different alkali metal carbonate catalysts were tested, and the results are given in Table 2. Among the four different alkali metal carbonates, Cs$_2$CO$_3$ yields a polymer with the highest molecular weight and a relatively narrow PDI value. A narrow PDI implies that Cs$_2$CO$_3$ can suppress the side reactions caused by severe reaction conditions.

To understand Tables 1 and 2, kinetics studies on the transesterification of ISB and DPC with different catalysts were performed, and the catalytic activities of these catalysts were calculated.

**Catalytic activity analysis**

Catalytic activity significantly influences the equilibrium constant for the transesterification reaction and the reaction time. Consequently, the choice of catalyst is crucial for the success of this polymerization reaction. In this study, catalytic activities were determined by monitoring the condensate generated during the transesterification reaction and calculated according to the following equation, as suggested by Ignatov et al. [25]

$$ k' t = \frac{[P]}{[A]^n [P][A]_0} $$

$$ k = \frac{k'}{|\text{Cat}|} (\text{mL}^2/\text{mol}^2 \text{min}) $$

where $k'$ is the effective reaction rate constant; $t$ is the reaction time, $[P]$ is the concentration of phenol at time $t$, $[A]_0$ is the initial concentration of a monomer, $k$ is the catalytic reactivity, and $|\text{Cat}|$ is the initial concentration of the catalyst.

Fig. 1 shows the catalytic activities determined for four different catalysts. The catalytic activity ($k$) of LiOH is 133.1, and that of Cs$_2$CO$_3$ is 1899.3. Based on Table 1 and Fig. 1, high-molecular-weight PC was obtained when a catalyst with a large catalytic activity was used. Furthermore, by removing as much phenol as possible in 50 min, the resulting polymers exhibit high molecular weights. This means that a high initial rate results in a high degree of polymerization. The initial reaction rate of Cs$_2$CO$_3$ is higher than that of the other catalysts, per its catalytic reactivity value. After 50 min, the catalytic activities become constant for all catalysts (see Fig S4 in the ESI). Therefore, a long reaction time has little effect on the phenol volume, and the initial rate is more important for phenol removal and the degree of polymerization. Although LiOH seems to have a high catalytic activity (Fig. 1), its $k$ value is lower than those of the other catalysts when considering the catalyst concentration.

Fig. 2 shows the catalytic activities of several alkali metal carbonates towards the ISB-based PC melt polymerization. Among the alkali metal carbonates, Cs$_2$CO$_3$ shows the best catalytic activity. In terms of cationic radius and electronic polarizability, the Cs$^+$ ion stands out against the other alkali metal ions [28,29]. It is also known that the Cs$^+$ ion has the lowest degree of solvation and ion-pairing when compared with analogous alkali metal ions. In the ISB and DPC polymerization system, Cs$_2$CO$_3$ will dissociate to...
yield a free Cs+ ion, which has the highest reactivity in nucleophilic substitution reactions. Due to the high polarizability of the Cs+ ion, the carbonyl group of DPC is easily polarized and becomes more susceptible to an attack by secondary hydroxyl groups on ISB (see Scheme 1). OH stretching band observed at around 3500 cm\(^{-1}\) in FTIR spectrum means resulting polymer has hydroxyl groups as its end groups (see Fig. S5 in the ESI).

Catalyst solubility is also integral when attempting to understand catalytic activity. Because Cs₂CO₃ has superior solubility in aprotic polar solvents [28,29], it is expected that Cs₂CO₃ will have good solubility in the hydrophilic molten mixture of ISB and DPC. Higher solubility leads to greater accessibility to the monomers and thus to a higher reactivity.

**Effect of cesium carbonate content**

Although Cs₂CO₃ exhibits good catalytic activity, it causes discoloration as its concentration increases. To avoid this problem, the molecular weight and color of synthesized PCs were monitored while varying the amount of Cs₂CO₃. Table 3 shows that there are no remarkable changes in the molecular weight and \(T_g\) of ISB-based PC, despite a decrease in the catalyst to 0.2 ppm. When the concentration of Cs₂CO₃ was less than 10 ppm, the Cs₂CO₃ was added as an aqueous solution to ensure homogeneous mixing. Fig. 3 shows that the color of the polymer solution changes to light brown from dark brown as the amount of Cs₂CO₃ decreases to 10 ppm.

In addition, the polymer solution becomes a brighter and more transparent yellow when 99.8% purity ISB and 99.9% purity DPC are used instead of 98% purity ISB and 99% purity DPC. In our work, 0.2 ppm Cs₂CO₃ can produce a high-molecular-weight (\(M_w=32,600\)) and high-\(T_g\) (164 °C) ISB-based PC, and its color is also markedly improved, as displayed in Fig. 1(e). Thin film cast from 20 wt% of ISB-based PC (Fig. 1(e)) solution has 40 μm

![Scheme 1. Polymerization mechanism of ISB-based PC with Cs₂CO₃ catalyst.](image)

**Table 3**  
Cesium carbonate volume effects on the melt polymerization of ISB and DPC.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(M_w) (g/mol)</th>
<th>(M_m) (g/mol)</th>
<th>PDI</th>
<th>(T_g) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5000</td>
<td>21,300</td>
<td>37,200</td>
<td>1.72</td>
<td>165</td>
</tr>
<tr>
<td>1000</td>
<td>19,800</td>
<td>31,600</td>
<td>1.60</td>
<td>161</td>
</tr>
<tr>
<td>500</td>
<td>26,700</td>
<td>39,500</td>
<td>1.48</td>
<td>164</td>
</tr>
<tr>
<td>50</td>
<td>18,800</td>
<td>33,000</td>
<td>1.84</td>
<td>163</td>
</tr>
<tr>
<td>10</td>
<td>17,200</td>
<td>32,100</td>
<td>1.93</td>
<td>163</td>
</tr>
<tr>
<td>0.2*</td>
<td>18,300</td>
<td>32,600</td>
<td>1.79</td>
<td>164</td>
</tr>
</tbody>
</table>

* Aqueous solution.
thickness and 91% transmittance at 550 nm (see Fig. S6 in the ESI).

Conclusions

An ISB-based PC was successfully synthesized by melt polymerization using ISB and DPC. Depending on the catalyst, the ISB-based PC displayed $M_w$ values that ranged from 9100 to 39,500 g/mol, and our results showed that Cs$_2$CO$_3$ was the most effective in achieving a high-molecular-weight polymer. This result is believed to be due to the large electronic polarizability of the Cs$^+$ ion and the good solubility of Cs$_2$CO$_3$. In our work, 0.2 ppm Cs$_2$CO$_3$ was sufficient to produce a high-molecular-weight ($M_w = 32,600$) and high-$T_g$ (164 °C) ISB-based PC. Discoloration, which is critical to the melt polymerization of ISB-based PC, was influenced not only by the Cs$_2$CO$_3$ concentration but also by the purities of ISB and DPC.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jiec.2016.03.007.

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