Research Article

Metal-Containing Ionic Liquids: Highly Effective Catalysts for Degradation of Poly(Ethylene Terephthalate)

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Poly(ethylene terephthalate) (PET) waste from local market was depolymerized by ethylene glycol (EG) in the presence of metal-containing ionic liquids, and the qualitative analysis showed that the bis(hydroxyethyl)terephthalate (BHET) was the main product in this process. Compared with other metal-containing ionic liquids, [Bmim]ZnCl3 was considered the best catalyst in the glycolysis of PET. When the reaction temperature was 180°C, the conversion of PET reached 97.9% and the BHET yield was 83.3% within 5 h. At the same time, [Bmim]ZnCl3 could be reused for six times without obvious decrease in the yield of BHET. Additional, the effects of waste PET’s source and size were investigated.

1. Introduction

Poly(ethylene terephthalate) (PET), a high volume thermoplastic polyester, is extensively used in diverse application textiles, high strength fibers, photographic films, soft-drink bottles, and others [1, 2]. However, PET is also one of the largest components of the postconsumer plastics waste in landfills. Therefore, in the past few years, the interest in recycling PET was continuously growing because of ecological and economic considerations [3–5]. It is well known that three methods, hydrolysis, glycolysis, and aminolysis, have been developed for the chemical recycling of PET [1, 6–9]. Since the bis-2-hydroxyethyl terephthalate (BHET) monomer can be produced by the glycolysis of PET waste in ethylene glycol (EG) and it has been widely used in the production of unsaturated polyesters, rigid or flexible polyurethanes, and other fine chemicals, the glycolysis of PET has attracted much attention recently [1, 10, 11]. But the glycolysis of PET is very sluggish in the absence of catalysts; various kinds of catalysts have been explored for this reaction, such as metal acetate, metal chloride, metal oxides, solid superacids, and titanium-phosphate [12–16]. These traditional catalysts are efficient, but they are noxious to environment and difficult to separate from the reaction mixture which would influence the property of the products.

Recently, ionic liquids (ILs) have been noticed by many researchers because of ILs’ unique feature, such as a strong solvent power for organic and inorganic compounds, thermal stability, nonvolatility, electrochemical stability, and low flammability [17]. In 2009, Liu et al. [18] reported that the hydrolysis of PET was carried out with using [Bmim]Cl as a solvent and [HSO3Pmim]HSO4 as a catalyst. In the same year, Wang et al. [19] reported the solubility of PET in different ionic liquids, such as [Bmim]Cl, [Bmim]Br, [Emim]Br, [Bmim]BF4, [Bmim]PF6, [Bmim]CH3COO, [Bmim]CF3COO, and [Bmim]AlCl4. Their research showed that PET dissolved readily in [Bmim]AlCl4, and the solubility of PET in ionic liquids, which contained Cl−, Br−, CH3COO−, and CF3COO− as an anion, was also good. More recently, Wang and coworkers also found [20] that the glycolysis of PET in EG was catalyzed by ionic liquids, and the conversion of PET reached 100% when [3a-C3P(C4)4][Gly]
and [3a-C₃P(C₆H₅)₃][Ala] were used as catalysts. But this kind of ionic liquids was very expensive. In the presence of [Bmim][Cl] and [Bmim][Br], the conversion of PET is 44.7% and 98.7%, respectively, but the dosage of catalyst was very high (20 wt%). Therefore, it is necessary to explore a new ionic liquid catalyst with high catalytic activity for the glycolysis of PET under mild reaction conditions.

In the present work, we prepared and characterized the metal-containing ionic liquids. Its catalytic activity was evaluated in the glycolysis of PET. A systematic investigation was conducted on the effects of reaction parameters and different PET products on the conversion of PET and the yield of BHET.

2. Experimental

2.1. Materials. PET flakes were prepared from drinking water bottles which were made by PepsiCo, Nongfu Spring Group Co. Ltd., nine-three oil Group Co. Ltd., and Tingyi (Cayman Islands) Holding Corporation Tingyi. The bottles’ labels left. White crystalline powder of BHET was purified by recrystallization from water and dried in an oven at 90°C and then weighed for determining the yield of BHET. The main products of depolymerization were characterized by FT-IR, ¹H NMR, and Differential Scanning Calorimetry (DSC).

2.2. Prepared Catalysts

2.2.1. Synthesis of 1-Methyl-3-butylimidazolium Chloride ([Bmim][Cl]). The ionic liquid, 1-methyl-3-butylimidazolium chloride ([Bmim][Cl]), was synthesized according to the previous literature [21].

[Bmim][Cl] was synthesized by refluxing the 1-methylimidazole with a large excess of the chlorobutane for 24 h. The excess chlorobutane was removed by evaporation and crude product was recrystallized from acetonitrile/ethyl acetate. The resulting white precipitate was isolated by filtration and then dried in vacuo for 24 h.

2.2.2. Synthesis of Metal-Containing Ionic Liquids. Equimolar amounts of [Bmim][Cl] and metal chloride (ZnCl₂, MnCl₂, PbCl₂, FeCl₂, NiCl₂, AlCl₃, and CuCl₂) were mixed for 8–24 h at room temperature in dichloromethane. Then, the dichloromethane was evaporated. Then, these metal-containing ionic liquids were dried in a vacuum oven at 70°C for 24 h and the metal-containing ionic liquids were obtained (Scheme 1).

2.2.3. Glycolysis of PET. The PET waste was treated with ethylene glycol under reflux in the presence of different catalysts for 5 h. At the end of the reaction, distilled water was added in excess to the reaction mixture with vigorous agitation. The glycolyzed product was obtained as a residue after filtration. The filtrate contained unreacted EG, BHET, and soluble oligomer. White crystals of BHET were obtained by first concentrating the filtrate and then chilling it. The glycolyzed residue was then boiled with water to extract any BHET left. White crystalline powder of BHET was purified by recrystallization from water and dried in an oven at 90°C and then weighed for determining the yield of BHET.

3. Results and Discussions

3.1. Analysis of Main Depolymerized Product. Purified main product was characterized by FT-IR, ¹H NMR, and DSC. From Figure 1, it can be clearly seen that the FT-IR spectrograph contained a –OH band at 3347 cm⁻¹ and 1135 cm⁻¹, a C=O stretching at 1716 cm⁻¹, an alkyl C–H at 2873 cm⁻¹ and 2954 cm⁻¹, and an aromatic C–H at 1456–1504 cm⁻¹. These results indicated that the product was BHET [22]. The proton NMR spectrum of the product was shown in Figure 2; the peak at δ 8.12 ppm was assigned the four aromatic protons ascribed to the protons of hydroxyl in the BHET. The results of NMR spectrum were also accord very well to the ¹H NMR spectrum of BHET in the literature [23]. The DSC of depolymerization showed (Figure 3) reasonably sharp single endothermic peak at 112°C, which agreed well with the known melting point of BHET which was reported in the literature [24]. The results of FT-IR, ¹H NMR, and DSC indicated that the main product was BHET.

3.2. Depolymerization of PET in the Presence of Catalysts. In the presence of 1 wt% metal-containing ionic liquids, the
glycolysis of PET was carried out in ethylene glycol, and the results were shown in Figure 4. From Figure 4, it can be seen that the conversion of PET was 5.9% in the absence of a catalyst, but no BHET was detected. When the [Bmim]CuCl$_3$ was used as a catalyst, the conversion of PET was increased to 12.1%, but the products were the oligomer and the trace of BHET. Similar results were obtained when the [Bmim]AlCl$_4$ and [Bmim]SnCl$_3$ were used as catalysts. When the metal ion was changed to Ni or Fe in the metal-containing ionic liquids, the conversion of PET was increased, yet the yield of BHET was very low. It was surprising that the 33.6% conversion of PET was given and the yield of BHET was increased to 20.7% when the metal-containing ionic liquid [Bmim]PbCl$_3$ was used as the catalyst. When the Pb$^{2+}$ was changed to Mn$^{2+}$ or Zn$^{2+}$, the excellent conversion of PET and yield of BHET were obtained. In the presence of [Bmim]ZnCl$_3$, the 97.9% conversion of PET was given, and the BHET was yielded to 83.3%. It was probably due to the Lewis acid of ionic liquid [Bmim]ZnCl$_3$. Form the results of glycolysis, [Bmim]ZnCl$_3$ was considered as the suitable catalyst.

3.3. Optimized Reaction Conditions of Glycolysis in the Presence of Zinc-Containing Ionic Liquid

3.3.1. Effect of Reaction Time on the Glycolysis of PET. In the presence of [Bmim]ZnCl$_3$, the effects of reaction time were investigated (Figure 5). From Figure 5, it can be seen that the conversion of PET was increased when the reaction time was prolonged. When the reaction time was 6 h, the conversion of PET was achieved 100%. The yield of BHET was increased with prolonging reaction time from 1 h to 5 h, and then the yield of BHET was decreased slightly when the reaction was prolonged.
Table 1: The catalytic effect of [Bmim]ZnCl\textsubscript{3} under different temperatures\textsuperscript{a}.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temperature (°C)</th>
<th>Conversion (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>180</td>
<td>97.9</td>
<td>83.3</td>
</tr>
<tr>
<td>2</td>
<td>175</td>
<td>75.5</td>
<td>58.9</td>
</tr>
<tr>
<td>3</td>
<td>170</td>
<td>50.6</td>
<td>39.4</td>
</tr>
<tr>
<td>4</td>
<td>165</td>
<td>30.6</td>
<td>23.1</td>
</tr>
<tr>
<td>5</td>
<td>160</td>
<td>21.5</td>
<td>14.5</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Reaction conditions: PET 2 g; [Bmim]ZnCl\textsubscript{3} 1 wt%; reaction time 5 h.

3.3.2. Effect of Reaction Temperature on the Glycolysis of PET. The glycolysis reaction was carried in different temperatures and the results have been shown in Table 1.

From Table 1, it can be seen that the conversion of PET and the yield of BHET were increased with increasing the reaction temperature. When the reaction was performed at 160 °C, the conversion of PET was 21.5% and the BHET was yielded to 14.5% (Table 1, entry 5). With increasing the temperature to 180 °C, the conversion of PET was achieved 97.9%, and the 83.3% BHET was given (Table 1, entry 1). To our best knowledge, this result was the best in the glycolysis of PET in EG.

3.3.3. Reusing Ability of Zinc-Containing Ionic Liquid. In the literature \cite{25}, ZnCl\textsubscript{2} was found to be a good catalyst for the glycolysis of PET, but ZnCl\textsubscript{2} could not be reused because it was sensitive to water. When zinc-containing ionic liquid was prepared from [Bmim]Cl and ZnCl\textsubscript{2}, it was stable in water and could be reused \cite{26}. At the same time, the thermal stability [Bmim][ZnCl\textsubscript{3}] was determined (Figure 6). Figure 6 showed the TG curve of ionic liquid catalyst [Bmim][ZnCl\textsubscript{3}] and it can be seen that the initiative decomposition temperature of [Bmim][ZnCl\textsubscript{3}] was 318.4 °C. It could be inferred that [Bmim][ZnCl\textsubscript{3}] showed a good thermal stability in this process.

In order to investigate the stability of [Bmim][ZnCl\textsubscript{3}], the reusability of [Bmim][ZnCl\textsubscript{3}] was examined in the glycolysis. After the glycolysis, the oligomer, and monomer were separated from the reaction mixture, and [Bmim][ZnCl\textsubscript{3}] was obtained by distillation and directly reused for subsequent reaction and the results were shown in Figure 7. It was shown that the catalyst could be reused for six times without obvious decrease in the yield of BHET. Therefore, [Bmim][ZnCl\textsubscript{3}] has excellent reusable performance in glycolysis of PET under the given conditions.

3.3.4. Effect of Raw Material on the Glycolysis of PET. In order to investigate the effects of different raw materials, a comparison of the glycolysis reaction of different PET products in local market was carried out and the results were shown in Table 2. It indicates that the depolymerization of waste bottle, which is all of PET products, could be effectively catalyzed by [Bmim][ZnCl\textsubscript{3}]. It is also clear from Table 3 that yield of BHET was 66.8% with waste bottle of edible oil, which might be because thickness of edible oil bottle was deeper than that of other products of PET in this paper.
Scheme 2: Mechanism of the glycolysis of PET in the presence of metal-containing ionic liquids.

3.3.5. Effect of PET Size on the Glycolysis. Table 3 showed the effect of PET size on reaction results. According to Table 3, the size of PET was a significant influence on reaction results. With decreasing of the size, both the PET conversion and BHET yield were increased greatly. Under the given conditions, when the PET size was 4 mm$^2$, PET conversion and BHET yield were 88.8% and 64.8%. However, when decreasing the size from 4 mm$^2$ to 1 mm$^2$, the glycolysis of PET arrived at 97.9% and BHET yield reached 83.3%. It was because PET was a macromolecule material and dissolving of PET in EG was very slow, and decreasing the size of PET was beneficial for increasing available surface area for the reaction [27]. Furthermore, the solubility of PET was the rate determining step in the glycolysis reaction. Therefore, the dissolving and glycolysis of PET in EG were accelerated when its size was decreased.

3.3.6. Reaction Mechanism of the Glycolysis. Based on the results of this study, a reasonable catalytic cycle was proposed for the glycolysis over the metal-containing ionic liquids catalyst (Scheme 2). The cation in the catalyst interacts with the carbonyl oxygen (C=O) in the ester, and then the oxygen in the hydroxyl of ethylene glycol attacks the carbon cation of the ester group, forming a tetrahedral intermediate. Afterwards, the hydrogen leaves the ethylene glycol. Then, the electrons on the oxygen in –OM transfer form C=O. The acyl-oxygen cleaves, and the –OCH$_2$CH$_2$– group leaves, combining with H$^+$ to form HOCH$_2$CH$_2$–. These transfer processes repeat, and BHET monomer is formed.

Table 3: The effects of size on the glycolysis of PET$^a$.

<table>
<thead>
<tr>
<th>Size of PET (mm$^2$)</th>
<th>Conversion (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>100</td>
<td>81.4</td>
</tr>
<tr>
<td>1</td>
<td>97.9</td>
<td>83.3</td>
</tr>
<tr>
<td>2</td>
<td>95.5</td>
<td>74.6</td>
</tr>
<tr>
<td>3</td>
<td>93.7</td>
<td>69.3</td>
</tr>
<tr>
<td>4</td>
<td>88.8</td>
<td>64.8</td>
</tr>
</tbody>
</table>

$^a$Reaction conditions: PET 2 g; [Bmim]ZnCl$_3$ 1 wt%; reaction time 5 h; reaction temperature 180°C.

4. Conclusions

Metal-containing ionic liquids as [Bmim]ZnCl$_3$, [Bmim]MnCl$_3$, [Bmim]PbCl$_3$, [Bmim]FeCl$_3$, [Bmim]NiCl$_2$, [Bmim]SnCl$_3$, [Bmim]AlCl$_4$, and [Bmim]CuCl$_3$ were prepared and the different catalytic activity in the glycolysis of PET was shown. In the presence of [Bmim]ZnCl$_3$, the conversion of PET was achieved 97.9% and the BHET was yielded to 83.3% under the optimized reaction conditions. And at the same time, the influences of the source and the size of PET waste were investigated. Moreover, [Bmim]ZnCl$_3$ could be reused six times without obvious decrease in yield of BHET.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References


