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Fe-containing magnetic ionic liquid as an effective catalyst for the glycolysis of poly(ethylene terephthalate)

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ABSTRACT

The depolymerization of poly(ethylene terephthalate) (PET) in ethylene glycol could be catalyzed by imidazolium-based Fe-containing ionic liquid, 1-butyl-3-methylimidazolium tetrachloroferrate ([bmim]-$FeCl_4$). This magnetic ionic liquid exhibits higher catalytic activity for the glycolysis of PET, compared with $FeCl_3$ or ionic liquid, 1-butyl-3-methylimidazolium chloride ([bmim]Cl). Investigation also shows that the onset reaction temperature of the glycolysis process catalyzed by [bmim]$FeCl_4$ is much lower, being 140 °C. The proposed mechanism indicates that the high catalytic activity of [bmim]$FeCl_4$ is attributed to the synergic effect of its cation and anion.

1. Introduction

The amount of plastic production has been increasing significantly year by year, with uses including fiber, packing, container, building materials, etc. [1]. Plastics offer a tremendous convenience for our life. However, the proliferation of plastic uses has raised waste disposal issues. In recent years, disposal of waste materials has come into focus as an environmental problem that affects everyone. Poly(ethylene terephthalate) (PET) resin, a common form of plastics, has excellent characteristic features such as thermal stability, clarity, transparency, light, and processability. The amount of PET consumption has rising each year, used for producing fibers, textiles, video and audio tapes, food packing and containers [2]. With the increasing of PET consumption, its recycling has received considerable attention for the ecological and economic considerations.

Glycolysis of PET is one of the most widely studied processes for PET degradation. This process is carried out most frequently using ethylene glycol [3,4], diethylene glycol [5,6], propylene glycol [5,7], and dipropylene glycol [6]. The glycolysis reaction is very sluggish when performed without a catalyst. Traditionally, the glycolysis of PET is catalyzed by metal acetates [3,8], titanium-phosphate [9], solid superacids [10], metal oxides such as copper oxide [11], etc. These catalysts show high catalytic activity, with good yield of the bis(hydroxyethyl) terephthalate (BHET) monomer [3]. However, it is difficult to separate the catalysts from the depolymerized products. Thus, the property of the products would be influenced. In our previous study, we have found that ionic liquids could catalyze the depolymerization of PET in ethylene glycol [12]. But long reaction time and large amount of catalyst were required for high conversion of PET in the glycolysis catalyzed by ionic liquids such as 1-butyl-3-methylimidazolium chloride ([bmim]Cl). Recently, we have found that magnetic ionic liquid (MIL) has good catalytic activity for the glycolysis of PET.

Magnetic ionic liquid is basically a kind of ionic liquid (IL). The only difference between IL and MIL is that MIL is magnetic. MILs have the unusual properties of ILs, including extremely low volatility, high thermal stability, nonflammability, high ionic conductivity, etc. Besides, they show a strong response to a magnetic field. Hayashi et al. have found that 1-butyl-3-methylimidazolium tetrachloroferrate ([bmim]$FeCl_4$) is nearly paramagnetic, having a large magnetic susceptibility of 40.6×10^{-6} emu/g [13]. It is also reported that magnetic ionic liquids could be separated from other solvents by a combination of magnetic field and conventional methods such as filtration, ultracentrifugation, and adsorption [14]. [Bmim]$FeCl_4$ has already been used in synthesis [15–17], catalysis [18], etc. However, there is no report on the use of MIL in the catalysis of depolymerization of PET.

In the present study, [bmim]$FeCl_4$ was synthesized and used to catalyze the depolymerization of PET in ethylene glycol. This magnetic ionic liquid shows better catalytic activity than metal salt, $FeCl_3$, or ionic liquid, [bmim]Cl.

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2. Experimental

2.1. Materials

PET pellets (2.0 × 2.5 × 2.7 mm) were supplied by Jindong Commercial Co., Ltd., Jiangsu Province, China. Their average molecular weight was measured in a 60:40 (w/w) phenol/1,1,2,2-tetrachloroethane solution at 25 °C. The average molecular weight of bottle grade PET was found to be 2.63×10^4 g/mol, and that of carbonated beverage grade PET was 3.12×10^4 g/mol. Analytical grade ethylene glycol, phenol, 1,1,2,2-tetrachloroethane, methylimidazole, 1-chlorobutane, acetone, anhydrous ferric trichloride and dichloromethane were obtained from Sinopharm Chemical Reagent Beijing Co., Ltd., China. The materials were used without any further treatment.

2.2. Synthesis of ionic liquids

In the present study, we prepared [bmim]$FeCl_4$ by mixing crystal powder of [bmim]Cl with anhydrous $FeCl_3$. Crystalline [bmim]Cl was prepared according to the standard procedure [18,19] followed by repeated recrystallization from acetone. By mixing equimolar amounts of [bmim]Cl and $FeCl_3$ at 30 °C for 3 h, a dark brown liquid was obtained as a result of an exothermic solid-state reaction. The obtained ionic liquid was extracted with small portions of dichloromethane. The dichloromethane was evaporated and finally the resulting clear brown liquid was dried in a vacuum oven at 60 °C for 24 h.

2.3. General procedure for the glycolysis of PET

A 50 mL round-bottom three-necked flask equipped with a thermometer and a reflux condenser was loaded with 5.0 g of PET, 20.0 g of ethylene glycol, and a certain amount of catalyst. The glycolysis reactions were carried out under atmospheric pressure at reaction temperatures ranging from 140 °C to 178 °C for glycolysis times of 3–7 h. The flask was immersed in an oil bath at a specific temperature for the required time.

When the glycolysis reaction is completed, the undepolymerized PET pellets were quickly separated from the liquid phase before the products precipitated. Then an excess amount of cold distilled water was used to wash the undepolymerized PET pellets, and the water was then mixed with the product fraction. The undepolymerized PET was collected, dried, and weighed. The conversion of PET is defined by Eq. (1):

$$\text{Conversion of PET} = \frac{W_0 - W_1}{W_0} \times 100\% \tag{1}$$

where W_0 represents the initial weight of PET and W_1 represents the weight of undepolymerized PET. Meanwhile, the glycolysis product mixture was vigorously agitated (cold distilled water would dissolve the remaining ethylene glycol, catalyst, and the monomer) and then filtered. The collected filtrate was concentrated to about 150 mL by vacuum evaporation at 50 °C. The concentrated filtrate was stored in a refrigerator at 0 °C for 24 h. White crystalline flakes were formed in the filtrate, then separated and dried. This was the bis(hydroxyethyl) terephthalate (BHET) monomer. The fraction insoluble in cold water was a mixture of the dimer and oligomers. (The products were analyzed by HPLC, NMR, MS and DSC.) The selectivity of BHET monomer is defined by Eq. (2):

$$\text{Selectivity of BHET} = \frac{\text{moles of BHET}}{\text{moles of depolymerized PET units}} \times 100\% \tag{2}$$

3. Results and discussion

The obtained [bmim]$FeCl_4$ was characterized by Electrospray Ionization-Mass Spectrum (ESI-MS) and Raman spectroscopy. The negative ion ESI-MS spectrum of [bmim]$FeCl_4$ is shown in Fig. 1. It is clear from the mass spectrum that the peak up to m/e 197.8 with intensity almost 100% was obtained. This peak is related to the presence of $[FeCl_4]^-$. While, the appearance of the peak at m/e 199.8 might be caused by the existence of chloride isotope, which also indicates the presence of $[FeCl_4]^-$ in this ionic liquid.

Fig. 2 compares the Raman spectrum of [bmim]$FeCl_4$ with that of [bmim]Cl. The spectrum of [bmim]$FeCl_4$ shows a strong band at 330 cm^{-1}. This band is assigned to the totally symmetric Fe–Cl

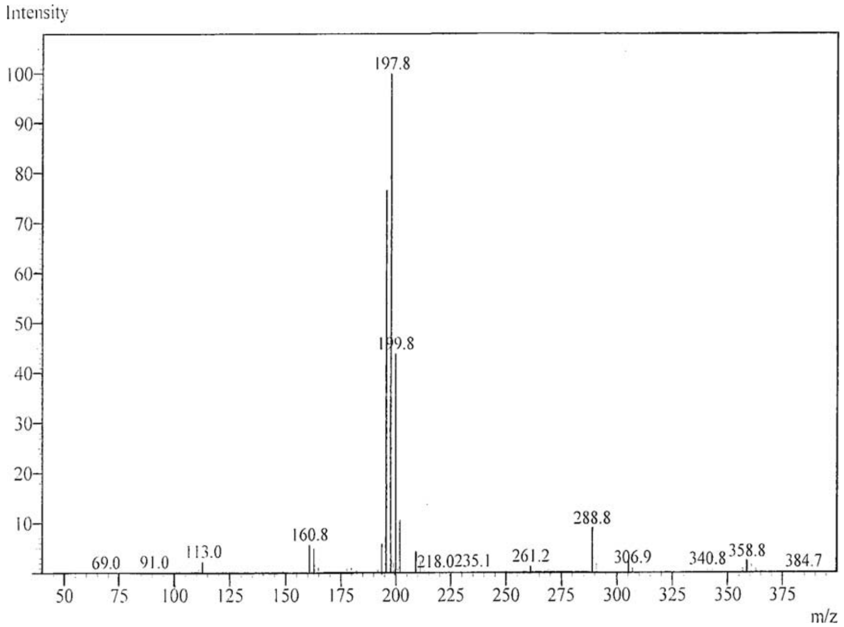


Fig. 1. Negative ion ESI-MS spectrum of [bmim]$FeCl_4$.

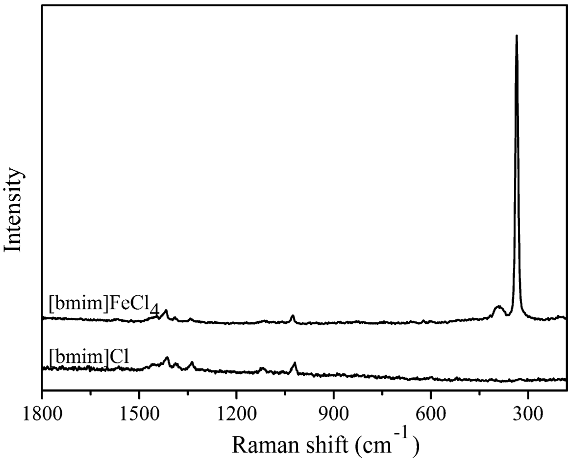


Fig. 2. Raman spectra of [bmim]$FeCl_4$ and [bmim]Cl.

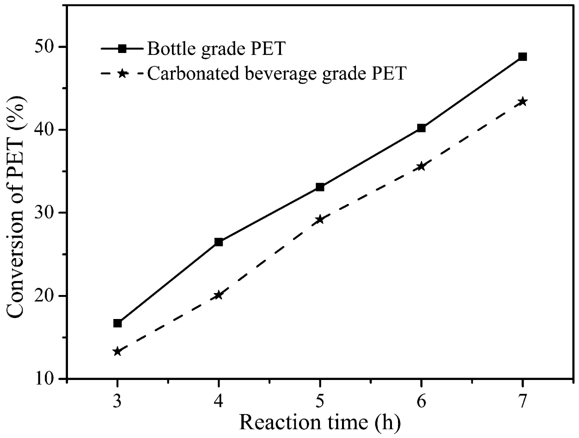


Fig. 3. The glycolysis conversions of bottle grade PET and carbonated beverage grade PET as a function of reaction time (1 atm, 160 °C, 0.5 g [bmim]$FeCl_4$).

Table 1
Catalytic activity of different catalysts on the glycolysis of PET.[a]

Temperature (°C)	[bmim]$FeCl_4$ (%)		$FeCl_3$ (%)		[bmim]Cl (%)	
	C[b]	S[b]	C	S	C	S
140	1.8	9.9	0	0	0	0
150	16.5	76.4	0	0	0	0
160	55.1	69.5	4.2	2.3	0	0
170	88.6	62.8	47.2	30.1	1.2	1.2
178	100	59.2	79.3	52.8	5.1	5.7

[a] Reaction conditions: 1 atm, 4 h, 1.00 g [bmim]$FeCl_4$, 0.48 g $FeCl_3$, 0.52 g [bmim]Cl.

[b] C: conversion of PET; S: selectivity of BHET.

stretch vibration of $[FeCl_4]^-$ [20]. The absorption bands from 900 to 1500 cm^{-1} are very similar to those of [bmim]Cl, which are assigned to the vibrations of the $[bmim]^+$ cation. Thus, the characteristic results indicate that the synthesized ionic liquid is [bmim]$FeCl_4$.

The catalytic performances of different catalysts are shown in Table 1. It indicates that [bmim]$FeCl_4$ is an effective catalyst for the glycolysis of PET. It is clear from Table 1 that in the experimental region, the conversion of PET and the selectivity of BHET monomer from the catalysis by [bmim]$FeCl_4$ are the highest. When the glycolysis of PET is catalyzed by [bmim]$FeCl_4$, the reaction starts to occur at 140 °C. However, the glycolysis of PET catalyzed by $FeCl_3$ could only proceed when reaction temperature is higher than 160 °C, and the onset reaction temperature of this glycolysis process catalyzed by [bmim]Cl is 170 °C. It is reported that the glycolysis of PET catalyzed by traditional catalysts, such as metal acetates, could not proceed when the reaction temperature is 150 °C [21,22]. Therefore, [bmim]$FeCl_4$ has the best low-temperature catalytic activity for the depolymerization of PET in ethylene glycol, and the glycolysis process catalyzed by [bmim]$FeCl_4$ is more energy-efficient. Table 1 also shows that when the glycolysis reaction is catalyzed by [bmim]$FeCl_4$, the conversion of PET increases as the reaction temperature rises. The selectivity of BHET monomer reaches a maximum value (76.4%) when the temperature is set at 150 °C, while, Xi et al. [23] have found that the highest selectivity of BHET in the catalysis by zinc acetate is about 80% at reaction temperature of 196 °C. Thus, the selectivity of BHET from the glycolysis catalyzed by [bmim]$FeCl_4$ at 150 °C is comparable to that from the catalysis by traditional catalysts at higher reaction temperature.

A comparison of the glycolysis reactions of bottle grade PET and carbonated beverage grade PET is shown in Fig. 3. It indicates that the depolymerization of bottle grade PET as well as that of carbonated beverage grade PET could be effectively catalyzed by [bmim]$FeCl_4$. Thus, it may be concluded that [bmim]$FeCl_4$ could catalyze the depolymerization of different kinds of PET. It is also clear from Fig. 3 that the conversion of PET increases with the increasing of reaction time from 3 h to 7 h. While, conversion of carbonated beverage grade PET is lower than that of bottle grade PET, which might be caused by the higher average molecular weight of carbonated beverage grade PET.

Fig. 4 presents the effects of the amount of catalyst on the conversion of PET and selectivity of BHET. It shows that the glycolysis conversion increases with the amount of [bmim]$FeCl_4$. When more ionic liquid was added, more cations and anions in [bmim]$FeCl_4$ would interact with the active centers of the reactants (shown in the following Scheme). Thus, more amount of PET would be glycolyzed and the conversion of PET increases. The selectivity of BHET monomer has a maximum value when the amount of [bmim]$FeCl_4$ is about 0.5 g, then it decreases with the amount of catalyst. Presumably, when more [bmim]$FeCl_4$ is used, BHET monomer is produced in a short time. Then, as the glycolysis reaction proceeds, BHET would polymerize into dimer or oligomers, which results in decrease of the amount of BHET monomer. Therefore, when large amount of [bmim]$FeCl_4$ is used, the reaction time should be shortened in order to obtain more BHET monomer.

The mechanisms of glycolysis of PET catalyzed by different catalysts are illustrated in Schemes 1 and 2. When $FeCl_3$ or [bmim]Cl

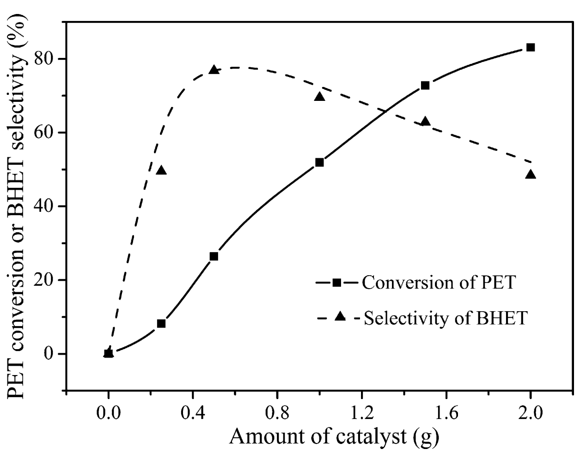
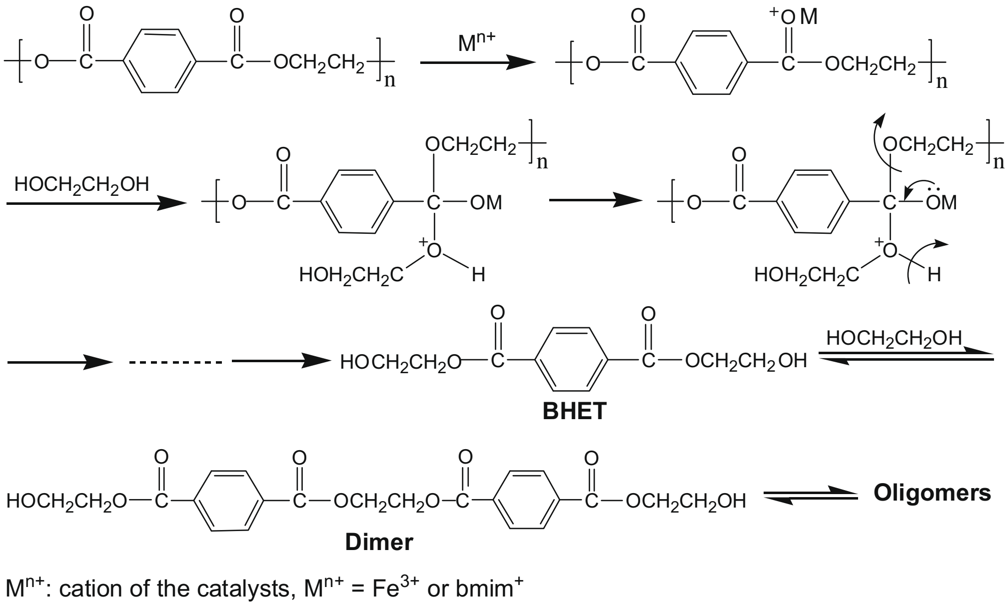
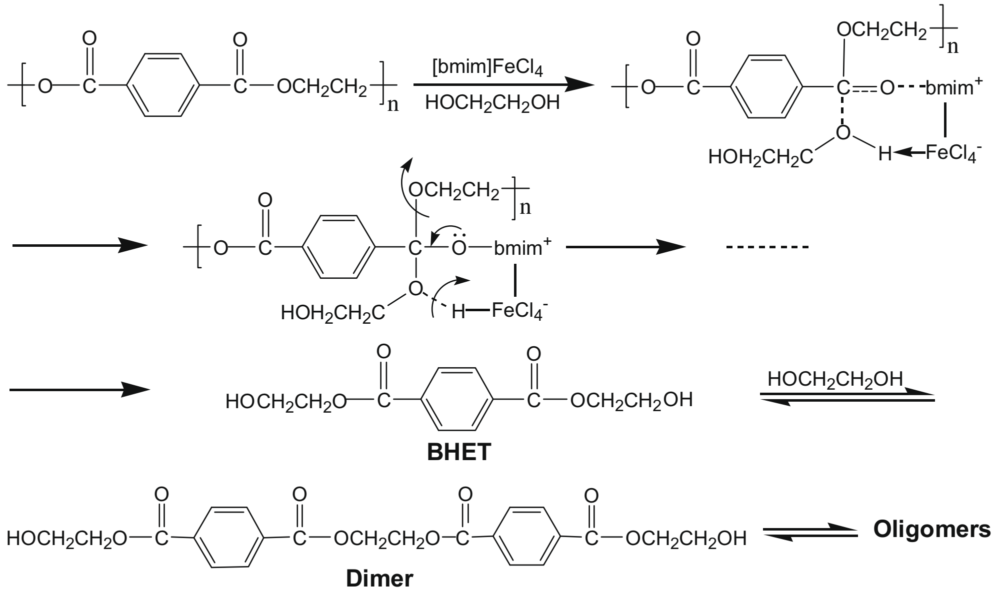


Fig. 4. Effects of the amount of catalyst on the conversion of PET and selectivity of BHET (1 atm, 160 °C, 4 h, bottle grade PET).



Scheme 1. Mechanism of the glycolysis of PET catalyzed by $FeCl_3$ or [bmim]Cl.



Scheme 2. Mechanism of the glycolysis of PET catalyzed by $[bmim]FeCl_4$.

was added, this process is a Lewis acid catalytic reaction. 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 in ethylene glycol leaves. Then the electrons on the oxygen in –OM transfer, forming C═O. The acyl-oxygen cleaves, and the $–OCH_2CH_2–$ group leaves, combining with H^+ to form $HOCH_2CH_2–$. These transfer processes repeat, and BHET monomer is formed. With proceeding of the reaction, BHET would further polymerize into dimer or oligomers. However, when $[bmim]FeCl_4$ was used, it is assumed that there exits synergic effect between the cation and anion of this catalyst [24]. The cation of this ionic liquid, $[bmim]^+$, interacts with the carbonyl oxygen (C═O) in the ester of PET. Meanwhile, the anion of the catalyst, $[FeCl_4]^-$, interacts with the hydrogen in the hydroxyl group of ethylene glycol, resulting in the oxygen of ethylene glycol more negative and easier to attack the carbon cation of the ester group. Thus, the synergic effect makes the depolymerization of PET much easier, and the catalytic activity of $[bmim]FeCl_4$ is higher than those of $FeCl_3$ and [bmim]Cl.

4. Conclusions

In summary, it was demonstrated that $[bmim]FeCl_4$ could behave as the efficient and eco-friendly catalyst for the depolymerization of PET in ethylene glycol. Comparison of the catalytic effects of $[bmim]FeCl_4$, $FeCl_3$, and [bmim]Cl indicates that the catalytic activity of $[bmim]FeCl_4$ is the highest. Investigation also shows that the onset reaction temperature of the glycolysis process catalyzed by [bmim]$FeCl_4$ is much lower, being 140 °C. Results also indicate that this ionic liquid could catalyze the depolymerization of different kinds of PET. The amount of catalyst used in this reaction influences the PET conversion and BHET selectivity distinctly. With the increase of the amount of [bmim]$FeCl_4$, the conversion increases apparently, and the selectivity of BHET reaches a maximum value when about 0.5 g of ionic liquid was used. The proposed mechanism indicates that the synergic effect of the cation and anion in [bmim]$FeCl_4$ makes the attack of oxygen in ethylene glycol on the carbon cation of the ester group much easier. The magnetic ionic liquid, [bmim]$FeCl_4$, might have the potential to substitute traditional compounds to catalyze the depolymerization of PET in industrial production.

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