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Effective catalysis of poly(ethylene terephthalate) (PET) degradation by metallic acetate ionic liquids*

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Abstract: Poly(ethylene terephthalate) (PET) is widely used for beverage bottles, electrical and electronic instruments, household wares, and so on. As a consequence of dramatically increasing consumption, recycling of post-consumer PET products has become an important environmental opportunity for sustainable usage in society. In this paper, we investigated the use of chlorine-free metallic acetate ionic liquids (ILs) as catalysts for the degradation of PET because of their lower toxicity, corrosivity, and cost. 1,3-Diethylimidazolium triaceticzincate ([deim][Zn(OAc)₃]) behaved as the best in this group. The synthesized ILs and the major product, characterized by a variety of techniques and factors affecting glycolysis, were examined. Under optimum conditions, conversion of PET reached 98.05 %, and the selectivity of the bis(hydroxyethyl) terephthalate (BHET) monomer was 70.94 %. A probable mechanism for the glycolysis of PET catalyzed by [deim][Zn(OAc)₃] was given. In our opinion, catalysis accounted for the synergic effect of the cation and anion of the IL.

Keywords: ionic liquids; poly(ethylene terephthalate) (PET); degradation; bis(hydroxyethyl terephthalate) (BHET).

INTRODUCTION

Plastics or polymer recycling is of great importance for various reasons, including conservation of oil, reduction of greenhouse gas emissions, saving of landfill space, and the economic benefits of reuse [1]. As one versatile plastic material, poly(ethylene terephthalate) (PET) is odorless, tasteless, and nontoxic and is further characterized by light weight, high strength, air tightness, and high transparency. Hence, it is widely used for fibers, films, electrical insulation materials, and beverage bottles, particularly for packaging of carbonated drinks, mineral water, and edible oil in the food industry. These different uses generate a continuously growing stream of waste material, resulting in great interest in the scope for recycling PET [2]. While used PET beverage bottles are all a waste, according to statistics on the production and processing of polyester, PET accounts for 8 % by weight and 12 % by volume of the

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world's solid waste [3]. From 2000 to 2010, the world demand for PET increased from 27.6 to 56.0 million tons. This proliferation of PET poses serious environmental and economic threats and necessitates recycling [4]. Physical recovery, including separation, crushing, washing, drying, and regranulation of used PET products, causes downgraded properties and limited applications [5]. By contrast, chemical methodology offers a more effective approach to recycling PET polyester. Chemical recycling leads to the generation of raw materials, which can be reused to manufacture polymer as a secondary valueadded product, therefore, it is the most acceptable option, according to the principles of sustainable development [6].

Current chemical recycling methods for PET are divided by depolymerization agent as follows: (1) hydrolysis; (2) methanolysis; (3) glycolysis; (4) other methods [7]. Corrosion and pollution may be brought about during hydrolysis under acidic or basic conditions [8,9]. Unlike supercritical methanolysis and thermal degradation, glycolysis requires smaller amount of reactants, as well as lower temperatures and pressures [10–14]. Depending on reaction conditions, the products of glycolysis are very complex. Zinc acetate as catalyst in glycolysis has been much studied, owing to its outstanding activation of this reaction [15–21]. Other salts, such as metal (Co, Pb, and Mn) acetates [22–24], metal (Zn, Li, Mg, and Fe) chlorides [25], titanium phosphate [26], and sodium carbonate [27], have also been investigated. However, these salts are difficult to separate, which may adversely affect quality of the products [28].

Ionic liquids (ILs) have emerged as a key substitution of traditional organic solvents in chemical processes, in order to achieve more environmentally benign conditions [29]. ILs displayed a range of unique properties arising from variations in cationic and anionic components, such as nonflammability, negligible volatility, high conductivity, and a wide electrochemical window [30]. These properties are responsible for their reputation as environmentally friendly solvents and catalysts and growing attention in various fields, such as synthesis, catalysis, separation, and electrochemistry [31]. Deng et al. first studied chloroaluminate ILs as catalysts in depolymerization of polycarbonate in 2002 [31], whereafter increasing attention has been devoted to degradation of various types of polymers by ILs. More recently, our team has researched the use of ILs in depolymerization of PET [28,32,33]. ILs not only fully display catalytic effectiveness in the degradation, but also can be used as solvents in such processes. However, the ILs employed are chlorine-containing, such as 1-butyl-3-methylimidazolium chloride ([bmim]Cl), 1-butyl-3-methylimidazolium tetrachloroferrate ([bmim]FeCl₄), and some other chloroaluminate ILs. Especially, [bmim]Cl, one of the most common ILs, promises excellent application both as catalyst in glycolysis and solvent.

The aim of this investigation was to synthesize metallic acetate ILs, then apply them as catalysts to depolymerize PET, in order to avoid the negative impact on the environment and health brought about by chlorine-containing IL catalysts. This group of ILs is easy to synthesize and is chlorine-free, namely, they are less toxic, less erosive than many other ILs used to catalyze the degradation of PET. In the present experiments, we studied 1,3-diethylimidazolium triaceticzincate ($[deim][Zn(OAc)_3]$), 1,3-diethylimidazolium triaceticcobaltate ($[deim][Co(OAc)_3]$), 1,3-diethylimidazolium triaceticcickelate ($[deim][Ni(OAc)_3]$), and 1,3-diethylimidazolium triaceticcuprate ($[deim][Cu(OAc)_3]$), but have found that $[deim][Zn(OAc)_3]$ showed better catalytic activity than the others. The main variables of the glycolysis process (time, addition of catalyst, temperature, amount of PET) have been optimized, giving special attention to the search for alternative, eco-friendly, active catalysts for degradation of PET.

EXPERIMENTAL

Material

PET pellets $(2.0 \times 2.5 \times 2.7 \text{ mm})$ were purchased from Jindong Commercial Co. Ltd., Jiangsu Province, China. Their average molecular weight was measured in a 60:40 (w/w) phenol/1,1,2,2-tetra-

chloroethane solution at 25 °C. Analytical-grade formadehyde solution, acetic acid, glyoxal solution, ethylamine solution, ethylene glycol (EG), acetone, anhydrous zinc acetate $[Zn(OAc)_2]$, anhydrous copper acetate $[Cu(OAc)_2]$, anhydrous manganese acetate $[Mn(OAc)_2]$, anhydrous cobalt acetate $[Co(OAc)_2]$, anhydrous nickel acetate $[Ni(OAc)_2]$, and dichloromethane were obtained from Sinopharm Chemical Reagent Beijing Co., Ltd., China. The materials were used without further treatment.

Characterization

ILs and main product were analyzed by ¹H NMR spectra, which were recorded on ECA-600 (JEOL, Japan) in d₆-acetone solution and Fourier transform-infrared (FT-IR) using a Nicolet 380 (Thermo Fisher Scientific, USA) spectrometer. Mass spectrum of ILs was performed through a micrOTOF (Bruker, Germany) instrument with electrospray ionization (ESI). Elementary analysis of the product was tested by Vario EL cube (elementar, Germany) and X-ray diffraction (XRD) curve was examined by a D8 Focus (Brucker, Germany). Differential scanning calorimetry (DSC) scan of the main product was obtained using DSC1 (Mettler-Toledo, Switzerland) by heating from room temperature to 200 °C at a rate of 10 °C/min in an atmosphere of nitrogen. DTG-60H (SHIMADZU, Japan) was used to measure the weight loss of the product in a nitrogen atmosphere during a temperature range from room temperature to 500 °C, also at a heating rate of 10 °C/min.

Synthesis of ionic liquids

Synthesis of 1,3-diethylimidazolium acetate ([deim]OAc) [34]

Formadehyde solution was placed in a round-bottom flask. (Temperature inside the flask was kept around 4 °C.) Then ethylamine solution, acetic acid, and glyoxal solution were added at low temperatures in order. After each addition, the mixture was heated for a period of time at 70 °C, respectively, whereafter the product was extracted with diethyl ether until the extractant phase was colorless. Water and diethyl ether were removed by a rotary evaporator, and the product was further dried in vacuum at 60 °C for 24 h. The product was determined by ¹H NMR.

Synthesis of 1,3-diethylimidazolium triaceticzincate ([deim][Zn(OAc)₃])

In the present study, we prepared $[deim][Zn(OAc)_3]$ by mixing equimolar amount of $Zn(OAc)_2$ with [deim]OAc, which was synthesized following the procedure above, at 40 °C for 3 h. The obtained IL was extracted with a small portion of dichloromethane. Dichloromethane was evaporated by rotary evaporator, and the resulting crystalline IL was dried in a vacuum oven at 60 °C for 24 h.

Electrospray ionization-mass spectrometry (ESI-MS) has been conducted both in negative and positive mode on the synthetic $[\text{deim}][\text{Zn}(\text{OAc})_3]$. The peak at m/e 241.0 with intensity almost 100 % was obtained in negative mode, which is caused by the presence of $[\text{Zn}(\text{OAc})_3]^-$. In addition, the other peaks, which are much weaker than the $[\text{Zn}(\text{OAc})_3]^-$ peak, indicate the existence of little $[\text{Zn}_2(\text{OAc})_5]^{3-}$ and $[\text{Zn}_3(\text{OAc})_7]^{4-}$. In positive mode, $[\text{deim}]^+$ brought about the peak at m/e 125.1 with 100 % intensity.

Synthesis of other ionic liquids

The synthesis of $[deim][Cu(OAc)_3]$, $[deim][Mn(OAc)_3]$, $[deim][Co(OAc)_3]$, and $[deim][Ni(OAc)_3]$ followed the same procedure as for $[deim][Zn(OAc)_3]$ described above, although $Cu(OAc)_2$, $Mn(OAc)_2$, $Co(OAc)_2$, and $Ni(OAc)_2$ was used instead of $Zn(OAc)_2$.

Glycolysis of PET

A 50-mL round-bottom three-necked flask equipped with a thermometer and a reflux condenser was loaded with various amounts of PET, 20.0 g of EG, and a certain amount of catalyst. The glycolysis

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reactions were carried out under atmospheric pressure at reaction temperatures ranging from 160 to 190 °C for glycolysis times of 1–4 h. The flask was immersed in an oil bath at a specific temperature for the required time. When the reaction was completed, un-depolymerized PET pellets were quickly separated from the liquid phase before the products precipitated. Then the un-depolymerized PET pellets were washed by excess distilled water and the products, which includes monomer, dimer, and oligomers, were mixed with water. Un-depolymerized PET was collected, washed, dried, and weighed. Conversion of PET (C_p) is defined by eq. 1

$$C_{\rm P} = \frac{W_0 - W_1}{W_0} \times 100 \ \% \tag{1}$$

where C_P represents the conversion of PET, W_0 represents the initial weight of PET, and W_1 represents the weight of un-depolymerized PET. Meanwhile, the glycolysis product mixture was vigorously agitated (remaining EG, catalyst, and the monomer would be dissolved in distilled water) and filtered. The collected filtrate was concentrated to about 150 mL by vacuum evaporation at 70 °C. The concentrated filtrate was stored in a refrigerator at 0 °C for 24 h. White crystalline flakes formed in the filtrate, then they were separated and dried. This was the bis(hydroxyethyl) terephthalate (BHET) monomer, which was the main product. The fraction insoluble in cold water was a mixture of dimer and oligomers. Selectivity of BHET (S_B) monomer is defined by eq. 2

$$S_{\rm B} = \frac{n_{\rm B}}{n_{\rm Theo,B}} \times 100 \ \% \tag{2}$$

where $S_{\rm B}$ represents the selectivity of BHET, $n_{\rm B}$ stands for moles of specific BHET products, and $n_{\rm theo,B}$ represents the moles of depolymerized PET units.

RESULTS AND DISCUSSION

Selection of catalysts

The catalytic effect of synthesized ILs on the glycolysis of PET was investigated, and the results are summarized in Table 1. Because of the less glycolysis time and higher selectivity of BHET than others, $[deim][Zn(OAc)_3]$ is considered as the best catalyst. This group of ILs all possess excellent catalytic properties for the degradation of PET. All the glycolysis times are below 4 h, and the selectivities of BHET monomer are higher than 50 %. In particular, when $[deim][Zn(OAc)_3]$ is used as the catalyst, it takes only 1.5 h to depolymerize the PET grains completely (PET size is 40–60 mesh).

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IL	Time (h)	$S_{\rm B}(\%)$		
[Deim][Zn(OAc) ₃]	1.50	67.10		
[Deim][Cu(OAc) ₃]	2.00	58.64		
[Deim][Mn(OAc) ₃]	3.75	51.30		
[Deim][Co(OAc) ₃]	1.50	56.65		
[Deim][Ni(OAc) ₃]	1.75	54.13		

 Table 1 Catalytic effect of different ILs on the glycolysis of PET*.

*Reaction conditions: *C*_P is 100 %, PET size is 40–60 mesh, 0.5 g IL, 20.0 g EG, 3 g PET, 180 °C.

Influences of reaction conditions

Influence of reaction time

The influence of glycolysis time on the reaction is presented in Figs. 1 and 2. It can be seen, $C_{\rm P}$ rises as reaction time increases. From 1 h to 2.5 h, $C_{\rm P}$ increases drastically from 38.66 to 98.05 %, while it changes mildly after the reaction exceeds 2.5 h. $S_{\rm B}$ also increases linearly before 2.5 h and reaches a climax at 2.5 h, then $S_{\rm B}$ begins to drop. This phenomenon may result from the repolymerization of BHET monomers just generated during the degradation process. Composition of BHET monomers also increases with reaction time. But the change of this indicator is not as obvious as $C_{\rm P}$ and $S_{\rm B}$, which increases only from 78.49 to 94.77 % during the entire process.



Fig. 1 Influence of reaction time on $C_{\rm P}$ and $S_{\rm B}$ (0.5 g IL, 3 g PET, 20 g EG, 180 °C).



Fig. 2 Influence of reaction time on product composition (0.5 g IL, 3 g PET, 20 g EG, 180 °C).

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Influence of the addition of catalyst

As shown in Figs. 3 and 4, the addition of catalyst has a strong impact on $C_{\rm P}$ and $S_{\rm B}$. Both of them show a trend from ascent to descent. $C_{\rm P}$ peaks at 98.72 % when the amount of catalyst is 1.0 g. But $C_{\rm P}$ develops steadily after [deim][Zn(OAc)₃] is more than 0.5 g because the increase of catalyst accelerates the reaction and shortens the equilibration time. The decreases of $C_{\rm P}$ and $S_{\rm B}$ are also attributed to the repolymerization. In Fig. 4, the composition of BHET dwindles with the increased addition of catalyst, which is another proof of the repolymerization. The results above might lead to the conclusion that [deim][Zn(OAc)₃] is an excellent catalyst for the degradation of PET. Using only 0.125 g, $C_{\rm P}$ achieves 69.32 %, $S_{\rm B}$ is 53.71 %, and the percentage of BHET is even 91.15 %.



Fig. 3 Influence of addition of catalyst on $C_{\rm P}$ and $S_{\rm B}$ (3 g PET, 20 g EG, 180 °C, 2.5 h).



Fig. 4 Influence of addition of catalyst on product composition (3 g PET, 20 g EG, 180 °C, 2.5 h).

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Influence of temperature

Figures 5 and 6 enable us to conclude that temperature plays an extremely important role in this degradation process. When the temperature is below 170 °C, the reaction processes very slowly. $S_{\rm B}$ is just 0.8 % at 160 °C and $S_{\rm B}$ is 5.61 % at 170 °C after 2.5 h. As temperature increases from 170 to 180 °C, $C_{\rm P}$ picks up from 41.63 to 98.05 % strikingly and $S_{\rm B}$ even soars to 70.94 %. However, $S_{\rm B}$ begins to decline as the temperature increases to 190 °C. In Fig. 6, the products present an opposite composition below and above 170 °C. When the temperature is below 170 °C, there are very few BHET monomers, 5.43 % at 160 °C and 36.51 % at 170 °C. But BHET develops into the main product at 175 °C, accounting for 92.70 %.



Fig. 5 Influence of temperature on $C_{\rm P}$ and $S_{\rm B}$ (0.5 g IL, 3 g PET, 20 g EG, 2.5 h).



Fig. 6 Influence of temperature on product composition (0.5 g IL, 3 g PET, 20 g EG, 2.5 h).

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Influence of the addition of PET

Figures 7 and 8 show the active degradation takes place within the PET range of 1.0-7.0 g. Figure 7 demonstrates that under the reaction condition of 0.5 g IL, 20 g EG, 180 °C, 2.5 h, when the dosage of PET is 3.0 g, C_P and S_B approach the climax. Then they both begin to decline. S_B even drops from 70.94 to 40.52 %. In Fig. 8, the composition of BHET has an obvious variation. After PET is more than 3.0 g, the percentage of BHET monomers shrinks with the increasing amount of PET. When the PET added is 7.0 g, the product is a half-and-half mixture of BHET and dimer, oligomer. Under the given reaction conditions, the appropriate PET added is 3.0 g. When the amount is more than 3.0 g, PET cannot be degraded completely. The depolymerized part is almost dimer and oligomers, and the portion of BHET is very low.



Fig. 7 Influence of the addition of PET on $C_{\rm p}$ and $S_{\rm B}$ (0.5 g IL, 20 g EG, 180 °C, 2.5 h).



Fig. 8 Influence of the addition of PET on product composition (0.5 g IL, 20 g EG, 180 °C, 2.5 h).

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Qualitative analysis of the main product

Composition

Elementary analysis of the separated BHET is shown in Table 2, and it is very similar to the theoretical values (56.74 % C, 5.5 % H, and 37.76 % O) [35]. Besides, the result indicates that there is no N element of [deim]⁺, which means the Il did not remain in the BHET products.

Table 2 Data of elementary analysis of BHET.ElementaryCOH

37.82

5.69

56.49

Figure 9 gives the IR spectras of the BHET product and PET material. Compared with the PET material, there is no new peak in the spectra of BHET, which means no new chemical bond is formed. In the spectra of BHET, the absorption peaks at 1689 and 700–800 cm⁻¹ demonstrate benzene ring. The two peaks at 1282 cm⁻¹ are attributed to the vibration of the C–O–C bond. The C=O bond causes the 1715 cm⁻¹ peak. The strong peak at 3447 cm⁻¹ and two attached peaks at 2931 and 2879 cm⁻¹ indicate the alcoholic group. The sharp crest at 3447 cm⁻¹ is much sharper than that of the PET spectra, resulting from the increasing O–H bond of the HOCH₂CH₂– group.



Fig. 9 IR spectra of the BHET product and PET material.

¹H NMR and ¹³C NMR were performed to confirm main product is BHET. There are four kinds of H and five kinds of C theoretically. In ¹HNMR spectra, the signal at around δ 8.1 ppm indicates the presence of the four aromatic protons of the benzene ring. Signals at 4.4 and 3.9 ppm represent the methylene protons of COO–CH₂ and CH₂–OH. The peak at δ 4.1 ppm is characteristic of the protons of the hydroxyl. Moreover, the information of ¹³C NMR is in accordance with those predicted in ¹HNMR.

The XRD spectra of BHET product are demonstrated in Fig. 10, which indicates that the product shows a high degree of crystallinity and the typical diffraction peaks are at $2\theta = 6.96^{\circ}$, 16.53° , 23.40° , which are very close to the investigation of V. M. Castano [35], and his results are demonstrated in Table 3.



Fig. 10 XRD patterns of the BHET product.

Table 3	XRD	results	[35].
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20	d (nm)	Relative intensity (%)
16.400	0.5380	100.00
35.193	0.2548	56.40
21.900	0.4056	45.70
6.900	1.2893	31.40
16.450	0.5390	30.24
20.895	0.4249	12.40
30.041	0.2973	10.05
38.865	0.1985	4.13

Thermal analysis of the products

In the DSC curve, there is a sharp endothermic peak. Furthermore, the melting onset temperature and peak temperature of BHET are 108.98 and 110.54 °C, respectively, which agree well with the information in the literature (105 and 109 °C) [32].

Two times of weight loss emerged in the thermogravimetric analysis (TGA) curve. The first one starts at about 200 °C, which resulted from the thermo decomposition of the BHET product. During the heating process of TGA analysis, BHET repolymerizes to PET again. The second weight loss begins from 400 °C or so and may be caused by the decomposition of the regenerated PET [24].

All of the above spectras confirm the BHET structure of the main product, with a high degree of purity.

Possible mechanism of the glycolysis of PET

There had been a heated debate on the mechanism of degradation of PET. In this investigation, when the reaction proceeded over 2.5 h, it accelerated significantly and the surfaces of un-depolymerized PET pellets were covered by lots of cracks. These phenomena indicated that the reaction took place on the surfaces of PET pellets. In addition, as the reaction continued, the pellets were getting smaller and smaller. With the aggrandizement of cracks on the surfaces and increasing exposed areas, the reaction accelerated. This assumption comforms to the idea that D. R. Kint [36] and S. Mishra [37] presented,

the reaction rate was inversely proportional to particle size and surfaces roughened. The research of A. Launary [38] and H. Kurokawa [39] pointed out that degradation occured in the amorphous phase and at chain folds on the crystal surface. Furthermore, in Chin-Yu Kao's experiment, the results of gel permeation chromatography (GPC) analysis indicated that the deploymerization of PET in the absence of catalyst included three steps. Firstly, the chain scission occurred at a tie molecule connecting PET crystals and the chain length was shortened to about 1/3. Secondly, the shortened chain was cut down to oligomers and the deploymerization took place at random positions on the polymer chain. Finally, the oligomers were contracted to monomers under the promotion of catalyst [40].

Figure 11 gives the supposed pathway of glycolysis of PET catalyzed by $[deim][Zn(OAc)_3]$. We tentatively put forward the synergistic effect of cation and anion. The imidazole ring with a positive charge attacked the C=O bond, while the carboxyl group of the anion combined with hydrogen in the hydroxyl group of EG. The break of C–O in PET resulted from the attack of the anion, which made the oxygen in hydroxyl group of EG more negative and easier to associated with the carbon cation next to benzene. In this case, EG molecular and carbon connected, a new ester group formed, and the chain of PET cleaved. Depolymerization of PET proceeded step by step, and oligomers, dimers, and monomers generated sequentially. With the process of the reaction, more and more BHET monomers emerged and they might polymerize into dimers or oligomers again for the chemical equilibrium.



Fig. 11 Mechanism of the glycolysis of PET catalyzed by [deim][Zn(OAc)₂].

CONCLUSION

In our investigation, several kinds of chlorine-free metallic acetate ILs, which have the excellent properties of low toxicity, corrosivity, and cost, facilitated the glycolysis of PET, and [deim][Zn(OAc)₃] behaved as the best catalyst. The synthesized ILs and main product were characterized by several sorts of techniques. It turned out that the main product is BHET monomer, which can be recycled for synthesis of fresh PET. Detailed study of the properties of BHET product also illustrated its purity. The effects of reaction parameters, such as the glycolysis time, amount of catalyst, reaction temperature, and addition of PET on C_P , S_B , and distribution of the products have been researched. C_P is enhanced with the increase of these factors, but S_B has a maximum for variation of glycolysis time owing to the chemical balance. The optimum condition we chose was 0.5 g catalyst, 3.0 g PET, 180 °C, and 2.5 h. Under that condition, C_P is 98.05 % and S_B comes up to 70.94 %. In the glycolysis of PET catalyzed by [deim][Zn(OAc)₃] was proposed, indicating the synergistic effect of cation and anion. Taken together with our data, this effect proved the suitability of chlorine-free metallic acetate ILs as an environmen-

tally friendly and efficient catalyst for the depolymerization of PET, which unfolds a promising perspective for chlorine-free industry.

SUPPLEMENTARY INFORMATION

Supplementary Information is available online (http://dx.doi.org/10.1351/PAC-CON-11-06-10).

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