

## 1-Allyl-3-methylimidazolium Halometallate Ionic Liquids as Efficient Catalysts for the Glycolysis of Poly(ethylene terephthalate)

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**ABSTRACT:** Series of 1-allyl-3-methylimidazolium halometallate ionic liquids (ILs) were synthesized and used to degrade poly(ethylene terephthalate) (PET) as catalysts in the solvent of ethylene glycol. One important feature of these new IL catalysts is that most of them, especially [amim][CoCl<sub>3</sub>] and [amim][ZnCl<sub>3</sub>], exhibit higher catalytic activity under mild reaction condition, compared to the traditional catalysts [e.g., Zn(Ac)<sub>2</sub>], the conventional IL catalysts (e.g., [bmim]Cl), Fe-containing magnetic IL catalysts (e.g., [bmim][FeCl<sub>4</sub>]), and metallic acetate IL catalysts (e.g., [Deim][Zn(OAc)<sub>3</sub>]). For example, using [amim][ZnCl<sub>3</sub>] as catalyst, the conversion of PET and the selectivity of bis(hydroxyethyl) terephthalate (BHET) reach up to 100% and 80.1%, respectively, under atmospheric pressure at 175°C for only 1.25 h. Another important feature is that BHET can be easily separated from the catalyst and has a high purity. Finally, based on the experimental phenomena, *in situ* infrared spectra, and experimental results, the possible mechanism of degradation with synthesized IL is proposed. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** catalysts; degradation; ionic liquids; polyesters

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### INTRODUCTION

Recycling and reusing plastic is of critical importance with the ever-growing energy and resource demands, environmental concerns, and economic benefits, together with the diminishing fossil fuel reserves.<sup>1–3</sup> As one of the important multipurpose plastics, poly(ethylene terephthalate) (PET) is widely used to produce products, such as bottles, fibers, and packaging due to its excellent mechanical properties, chemical stability, safety, light weight, transparency, and air-tightness,<sup>4,5</sup> which resulted in a continuously growing stream of PET material.<sup>6</sup> The global PET consumption has exceeded 50 million tons in 2009 and still increases markedly. Thus, effectively recycling PET wastes has been regarded as one of the most important ways of resolving problem of the “white pollution” and saving resources.<sup>7,8</sup>

At present, there are two major PET recycling methods, mainly physical and chemical methods. The former is most commonly practiced and involves sorting, crushing, washing, and drying PET wastes before melt-processing to produce a new material, which causes downgraded properties and limited their further applications, because organometallic catalysts used to synthesize

PET remain permanently in the fabricated item.<sup>9,10</sup> The latter can recycle the PET wastes to yield original monomers, from which the virgin plastic products are reproduced.<sup>11</sup> Considering the quality of the recycled products, chemical methods are more prospective and have been widely studied. Many chemical methods, such as methanolysis,<sup>12</sup> glycolysis,<sup>13</sup> hydrolysis,<sup>14</sup> and ammonolysis,<sup>15,16</sup> have been reported, and among which glycolysis has attracted more attention because of less volatile solvents and easily continuous production; moreover, the bis(hydroxyethyl) terephthalate (BHET) product obtained from glycolysis reaction can be used directly to synthesize PET products. With glycolysis method, the metal acetates (e.g., zinc acetate, manganese acetate, cobalt acetate, and lead acetate), metal chlorides, metal oxide, solid super acids, titanium phosphate, and sodium carbonate are served as catalysts with high-degradation efficiency of PET wastes,<sup>17–23</sup> but these catalysts require higher temperature and pressure, and the main product is difficultly separated from the catalysts. Thus, developing new catalysts that can effectively degrade the PET wastes into high-pure monomer BHET under the relatively mild condition is significantly important.

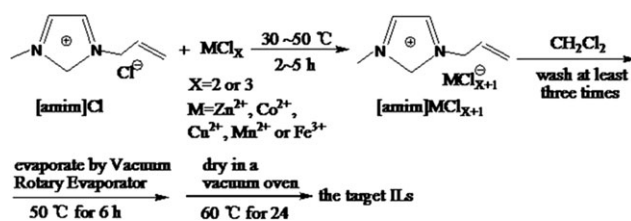
Ionic liquids (ILs),<sup>24–28</sup> as promising catalysts,<sup>29</sup> have been reported that they could be used in the degradation of polymer. Gu et al.<sup>30</sup> first found that chloroaluminate ILs can be used in the depolymerization of polycarbonate as catalysts. Our previous research showed that many conventional ILs can be used for the degradation of PET and then found that Fe-containing magnetic IL demonstrated better low-temperature catalytic activity than FeCl<sub>3</sub> and [bmim]Cl.<sup>31,32</sup> However, the main monomer product is very easy to be stained by Fe-containing ILs and needs to be washed by a large amount of deionized water, which not only increases the water consumption but also causes the loss of monomers. Moreover, the conversion of PET and the selectivity of BHET are relatively lower, only 88.6% and 62.8% at 170°C for 4 h. Subsequently, Zhou et al.<sup>33</sup> found that metallic acetate ILs displayed effective catalysis of PET degradation and can be easily separated from product, while the conversion of PET and the selectivity of BHET are still not high, only 98.05% and 70.9% at 180°C for 2.5 h. Dawsey et al.<sup>34</sup> and Zhang et al.<sup>35</sup> found that 1-allyl-3-methylimidazolium chloride ([amim]Cl) has better solubility than [bmim]Cl, because the [amim]<sup>+</sup> has a smaller ion size due to three carbon atoms and a double bond in N-substituted methimidazonium cation of [amim]Cl compared to [bmim]Cl, which suggests that the small size [amim]<sup>+</sup> favors the attack on oxygen atom of cellulose hydroxyl, and, moreover, the electron-deficient structure caused by alkyl group also enhances the interaction between cation of IL and oxygen atoms of hydroxide group in cellulose. These inspire us to try to explore novel 1-allyl-3-methylimidazolium halometallate ILs to be the catalysts of the degradation of PET to overcome the disadvantages mentioned earlier.

Herein, five kinds of 1-allyl-3-methylimidazolium halometallate ILs were synthesized, characterized by electrospray ionization-mass spectrum (ESI-MS) and FTIR spectrum, and used to degrade PET as catalysts in ethylene glycol (EG). Among them, [amim][ZnCl<sub>3</sub>] and [amim][CoCl<sub>3</sub>] exhibit higher catalytic activity. The structure and purity of the main degradation product were determined by gas chromatography-mass spectrometer (GC-MS), nuclear magnetic resonance (NMR) spectroscopy, ultra performance liquid chromatography (UPLC), ESI-MS, and elemental analyzer. The physical properties of the product were characterized by means of X-ray diffraction (XRD), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). Moreover, the possible mechanism of the degradation process with the new catalysts was proposed based on the SEM, *in situ* IR, and experimental results.

## EXPERIMENTAL

### Reagents and Materials

PET pellets (2.0 × 2.5 × 2.7 mm—30 mesh) were purchased by Jindong Commercial Co., Jiangsu Province, China. The average molecular weight was measured in a 60 : 40 (w/w) phenol/1,1,2,2-tetrachloroethane solution at 25°C and estimated to be 2.63 × 10<sup>4</sup> g mol<sup>-1</sup>. [amim]Cl and [bmim]Cl were supplied by Henan Lihua Pharmaceutical Co., China. The other reagents for the preparation of ILs and degradation of PET, such as manganese dichloride (MnCl<sub>2</sub>), anhydrous ferric trichloride (FeCl<sub>3</sub>), cobalt dichloride (CoCl<sub>2</sub>), copper chloride (CuCl<sub>2</sub>), zinc



Scheme 1. Synthesis process of ILs.

chloride (ZnCl<sub>2</sub>), dichloromethane, and EG, were purchased from Sinopharm Chemical Reagent Beijing Co., China. The reagents and materials were used without any further treatment. ILs were synthesized according to the literatures.<sup>31,36–38</sup>

### Preparation of Ionic Liquid Catalysts

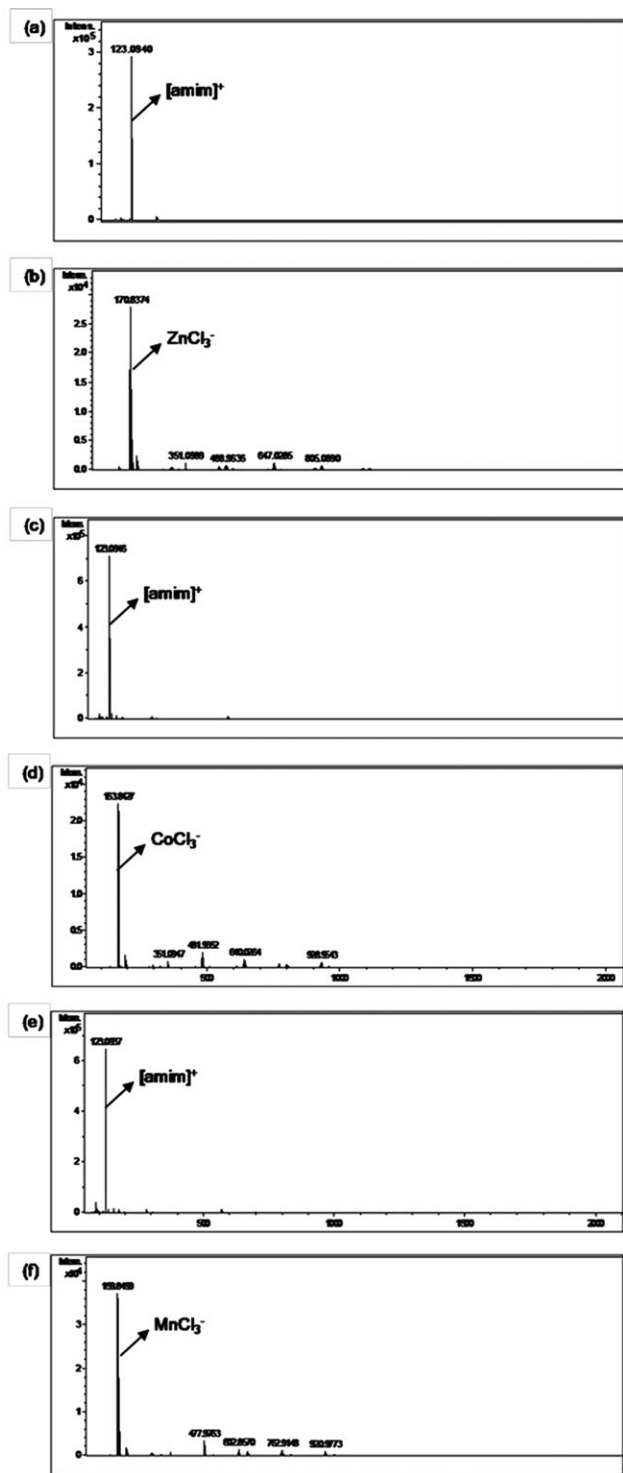
In the present study, we prepared five kinds of 1-allyl-3-methylimidazolium halometallate ILs by mixing crystal powder of [amim]Cl with anhydrous MnCl<sub>2</sub>, FeCl<sub>3</sub>, CoCl<sub>2</sub>, CuCl<sub>2</sub>, and ZnCl<sub>2</sub>. By mixing the equimolar ratio of [amim]Cl and metal chloride at reaction temperatures ranging from 30 to 50°C for reaction times of 2–5 h until the clear, homogeneous, and transparent liquids appear, the crude ILs are obtained. The crude ILs are extracted with small amount of dichloromethane at least three times. The residual dichloromethane in ILs is evaporated by vacuum rotary evaporator at 50°C for 6 h, and finally, the purified colorful ILs are dried in a vacuum oven at 60°C for 24 h. The preparation method of [bmim][FeCl<sub>4</sub>] was consistent with that of [amim][FeCl<sub>4</sub>], only using [bmim]Cl instead of [amim]Cl. The synthesis process of ILs was shown in Scheme 1.

### General Procedure of PET Degradation

The PET pellets, IL, and EG with a certain weight ratio are, respectively, charged into a 50-mL round-bottomed three-necked flask equipped with a thermometer and a reflux condenser. The degradation reaction is performed under atmospheric pressure at 175°C for reaction times ranging from 1.25 to 3 h. The flask is immersed in an oil bath at a specific temperature for the required time. When the reaction finishes, the reaction mixture is cooled to room temperature. Then a little distilled water is added into the reactor repeatedly for several times to separate the undepolymerized pellets from the product. The collected PET pellets are dried at 70°C, and the conversion of PET ( $C_{PET}$ ) is calculated by eq. (1):

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

where  $W_0$  represents the initial weight of PET and  $W_1$  represents the weight of undepolymerized PET. Then the degradation products are separated according to the reported methods in the same or similar reaction system in literature.<sup>10,19,26,31–33</sup> The degradation products are agitated after about 900 mL cold-distilled water is added and then filtered (the remaining EG, catalyst, and monomer will dissolve into the distilled water). The collected filtrate in this step is concentrated to about 70 mL by vacuum rotary evaporator at about 50°C. The concentrated filtrate is stored in a refrigerator at 0°C for 12 h and



**Figure 1.** ESI-MS spectra of the synthesized ILs: (a) positive mode of [amim][ZnCl<sub>3</sub>]; (b) negative mode of [amim][ZnCl<sub>3</sub>]; (c) positive mode of [amim][CoCl<sub>3</sub>]; (d) negative mode of [amim][CoCl<sub>3</sub>]; (e) positive mode of [amim][MnCl<sub>3</sub>]; (f) negative mode of [amim][MnCl<sub>3</sub>].

then a lot of white needle-like crystals, that is, the main degradation product. Many characterizations show that it is a BHET monomer. The selectivity of BHET ( $S_{\text{BHET}}$ ) is calculated by eq. (2):

$$S_{\text{BHET}} = \frac{\text{moles of BHET}}{\text{moles of depolymerized PET units}} \times 100\% \quad (2)$$

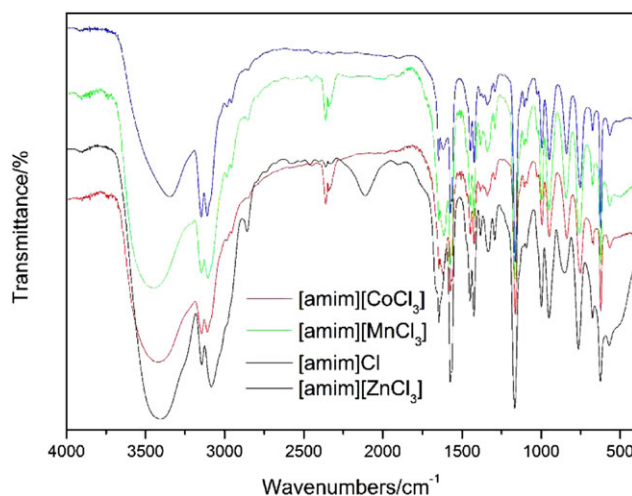
### Characterization

Mass spectra of ILs and the main product are performed through a microTOF (Bruker, Germany) instrument with ESI. FTIR spectra of ILs were obtained using a Nicolet 380 (Thermo Fisher Scientific, America) spectrometer. The main product is analyzed by GC-MS spectra using a 6890N Network GC System and a 5975B inert MSD (Agilent, America), NMR spectra using ECA-600 (JEOL, Japan) in *d*<sub>6</sub>-DMSO solution, UPLC spectrum using a ACQUITY UPLC with TUV detector and BET C<sub>18</sub> (Waters, America), and elementary analysis using a Vario EL cube (Elementar, Germany). XRD spectra of the main product and PET material are tested by a D<sub>8</sub> Focus (Bruker, Germany). DSC scan of the main products is 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, and DTG-60H (SHIMADZU, Japan) is used to measure the weight loss of the product and PET material under nitrogen atmosphere during a temperature range from room temperature to 700°C and also at a heating rate of 10°C/min.

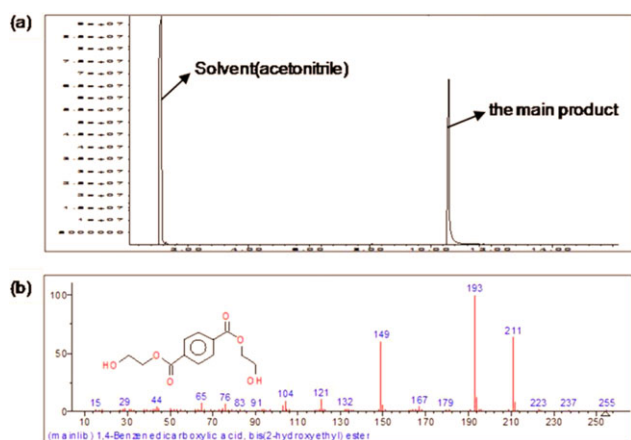
## RESULTS AND DISCUSSION

### Characterization of the Synthesized Ionic Liquids

The structure of the synthesized ILs was confirmed by ESI-MS and FTIR spectra.<sup>31,33,39,40</sup> The ESI-MS spectra of [amim][ZnCl<sub>3</sub>], [amim][CoCl<sub>3</sub>], and [amim][MnCl<sub>3</sub>] were conducted both in positive and negative mode and shown in Figure 1. The same peak at *m/e* 123.09 in Figure 1(a,c,e) with intensity almost 100% is obtained in positive mode, which is caused by the presence of [amim]<sup>+</sup>. In negative mode in Figure 1(b,d,f), ZnCl<sub>3</sub><sup>-</sup>, CoCl<sub>3</sub><sup>-</sup>, and MnCl<sub>3</sub><sup>-</sup> brought about the only peak at *m/e* 170.84, 163.84, and 159.45, respectively. Figure 2 compared the FTIR spectra of the synthesized ILs with that of [amim]Cl. The absorption bands of [amim][ZnCl<sub>3</sub>], [amim][CoCl<sub>3</sub>], and [amim][MnCl<sub>3</sub>] from 4000 to 400 cm<sup>-1</sup> were similar to those of [amim]Cl, which were assigned to the vibrations of



**Figure 2.** FTIR spectra of the synthesized ILs and [amim]Cl. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



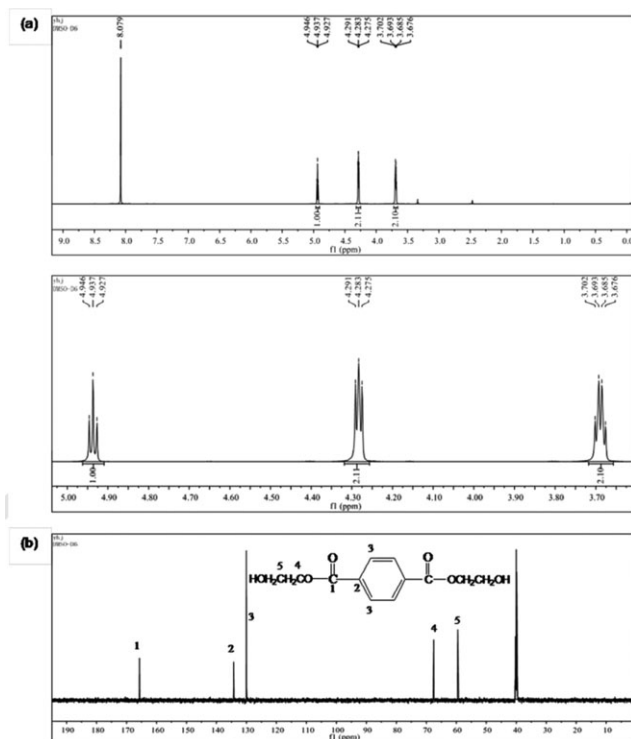
**Figure 3.** GC–MS spectra of the main product: (a) GC spectrum of the main product and (b) MS spectrum of the main product. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

characteristic peaks of  $[\text{amim}]^+$ . The results further confirmed that the synthesis of the target ILs.

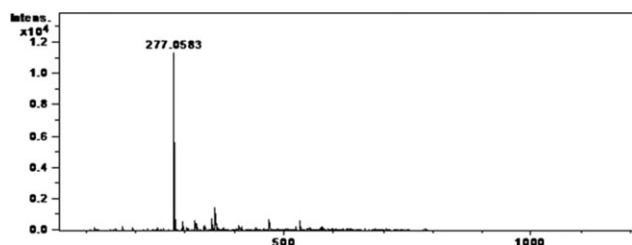
The synthesis of  $[\text{amim}][\text{CuCl}_3]$  and  $[\text{amim}][\text{FeCl}_4]$  is followed by the same procedure as for  $[\text{amim}][\text{ZnCl}_3]$ ,  $[\text{amim}][\text{CoCl}_3]$ , and  $[\text{amim}][\text{MnCl}_3]$  described earlier, and the difference is  $\text{CuCl}_2$  and  $\text{FeCl}_3$  is used instead of  $\text{ZnCl}_2$ ,  $\text{CoCl}_2$ , and  $\text{MnCl}_2$ .

#### Qualitative Analysis of the Main Degradation Product

To identify the structure of the main product in the degradation of PET in EG catalyzed by  $[\text{amim}][\text{ZnCl}_3]$ , a series of characterization instruments, such as GC–MS, NMR, ESI–MS, HPLC, and



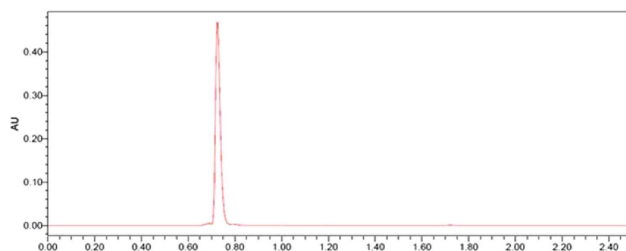
**Figure 4.** NMR patterns of the main product (a)  $^1\text{H-NMR}$  patterns of the main product and (b)  $^{13}\text{C-NMR}$  patterns of the main product.



**Figure 5.** ESI–MS spectrum of the main product.

element analysis, are performed. The GC–MS spectra show that the main product is BHET at 10.594 min, and the product has high purity, because there is no extra peak except solvent peak at 1.144 min (acetonitrile) in Figure 3.  $^1\text{H-NMR}$  spectrum is reproduced in Figure 4(a) for illustration. The single signal at  $\delta$  8.1 ppm indicates the presence of the four aromatic protons of the benzene ring. The triplet at 4.3 ppm and the quartet at 3.7 ppm represent the methylene protons of  $\text{COO-CH}_2$  and  $\text{CH}_2\text{-OH}$ , respectively. The triplet at  $\delta$  4.9 ppm is the characteristic of the protons of the hydroxyl. Moreover, the information of  $^{13}\text{C-NMR}$  is in accordance with those predicted in  $^1\text{H-NMR}$ , shown in Figure 4(b). It is clear from the ESI–MS in Figure 5 that the peak up to  $m/e$  277 with intensity almost 100% is obtained. This peak is related to the main product ionized by  $\text{Na}^+$  (in electrospray ionization, the fraction could be ionized by  $\text{H}^+$ ,  $\text{Na}^+$ , or  $\text{K}^+$ ). Thus, the molecular weight of the main product is 254 g/mol, which is the same as the molecular weight of BHET. The only peak in the UPLC spectrum from Figure 6 indicates that the purity of the main product obtained in our research is high. Element analysis results of the main product are compared to the theoretical values of BHET in Table I. It can be clearly seen that the measured value of every element in the main product is completely consistent with the theoretical value of BHET, and there is chlorine-free in the main product, which indicates that the main product is pure and can be well-separated from catalyst. Therefore, it is certain that BHET with high purity can be obtained by the present method in this work.

Some physical properties of BHET obtained are studied by XRD, DSC, and TGA and are shown in Figure 7. Figure 7(a) shows the XRD pattern of BHET in comparison with that of the PET material. PET exhibits a typical diffraction pattern due to the crystalline structure of this polyester, with broader diffraction peaks at  $2\theta = 16.4^\circ$ ,  $17.7^\circ$ , and  $23.0^\circ$ . The diffraction peaks of BHET become narrower and are of higher relative intensity than that of PET, which illustrates that BHET obtained



**Figure 6.** UPLC spectrum of the main product. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table I.** Element Analysis Results of the Main Product

BHET	C (%)	H (%)	O (%)	Cl (%)
Measured value	56.76	5.73	37.84	0
Theoretical value	56.69	5.51	37.80	-

by this method has a high crystallinity, and its crystalline structure is different from that of PET. In the DSC curve in Figure 7(b), there is a sharp endothermic peak; furthermore, the melting onset temperature and peak temperature of BHET are 110.19 and 111.12°C, respectively. The TGA curves of the PET material and BHET are illustrated in Figure 7(c). The TGA curve of PET wastes shows significant weight loss at 410°C. This weight loss is attributed to the thermal decomposition of PET.<sup>19,26</sup> The TGA curve of BHET exhibits two clear weight losses. The first one is about 42% at onset temperature 241°C because of the thermal decomposition of BHET. The other one is about 53% at onset temperature 413°C, because the thermal decomposition of PET is polymerized by BHET.<sup>19</sup>

### Comparison of PET Degradation in Different Ionic Liquid Catalysts

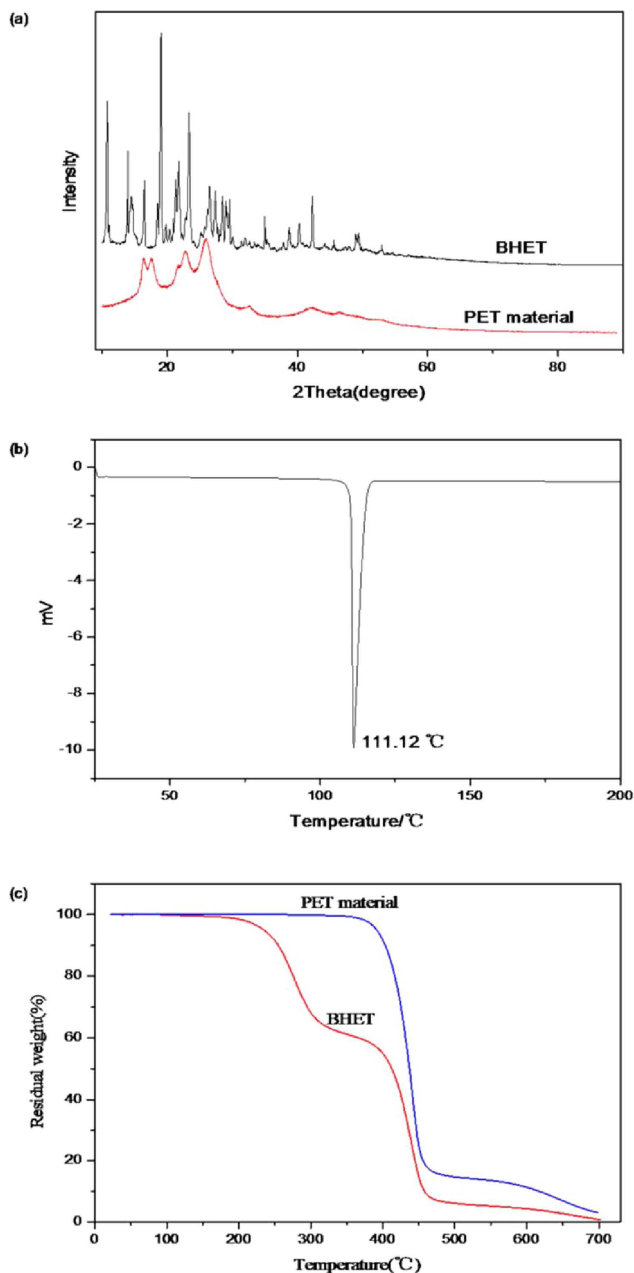
The result of the degradation of PET in EG catalyzed by the synthetic 1-allyl-3-methylimidazolium halo-metallate ILs is summarized in Table II. It is obviously indicated that most synthetic IL catalysts exhibit high-catalytic activity for PET degradation. Especially, using [amim][CoCl<sub>3</sub>] and [amim][ZnCl<sub>3</sub>] as catalysts, the conversion of PET and selectivity of BHET are both higher under mild reaction conditions than conventional ILs and Fe-containing magnetic IL reported in the literatures, and also the reaction time is shortened greatly. For example, using [amim][ZnCl<sub>3</sub>] as a catalyst, the conversion of PET and the selectivity of BHET reach up to 100% and 80.1%, respectively, under atmospheric pressure at 175°C for only 1.25 h, which are obviously higher than that catalyzed by [bmim]Cl, [bmim][H<sub>2</sub>PO<sub>4</sub>], [bmim][HSO<sub>4</sub>], [bmim]OH, [bmim]Br, [bmim][FeCl<sub>4</sub>], [Deim][Zn(OAc)<sub>3</sub>], and [Deim][Co(OAc)<sub>3</sub>]<sup>10,31–33</sup> and far higher than that of the case without catalyst (1.6 and 4.7%, respectively). Thus, it is concluded that the catalytic performance of the new IL catalysts used in this work is much better. At the same time, the catalysts have an advantage of energy consumption, because the degradation reaction occurred in the relative mild conditions with a higher reaction rate compared to traditional metal salt catalysts,<sup>17–23</sup> common IL catalysts, Fe-containing magnetic IL catalysts, and metallic acetate IL catalysts.

### Recycling of the Residual EG and Catalyst

Considering the environmental conservation and economics of the process, recycling of the residual EG and the catalyst is carried out. After BHET was filtered from the liquid phase, the residual EG and catalyst in the filtrate were recovered by vacuum evaporation at 65°C, stored in a vacuum oven at 60°C for 6 h, and then supplied a certain amount of EG until the weight is equal to the initial weight of fresh EG and catalyst. The conversion of PET and the selectivity of BHET in the recycled EG and [amim][ZnCl<sub>3</sub>] were examined, and the result is listed in Table III. It shows that the degradation efficiency does not reduce in the sixth recycling of catalyst and residual EG.

### The Degradation Mechanism of PET Catalyzed by [amim][ZnCl<sub>3</sub>]

There have been some debates on the mechanism of the degradation of PET. Researchers<sup>26,31,41,42</sup> agreed that the degradation of PET resulted from the disconnection of the ester group in PET. And some study found that the degradation of PET occurred in the amorphous phase and at the chain folds on the crystal surface.<sup>43,44</sup> In this process, the PET pellets are getting smaller and smaller until disappearance, the speed that PET pellets become smaller and disappear accelerated significantly at the middle and late of reaction, and SEM images showed that



**Figure 7.** (a) XRD spectra of BHET and PET material; (b) DSC curves of BHET; (c) TGA curves of PET material and BHET. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table II.** Comparison of PET Degradation with Different Catalysts

Source	Catalyst	Temperature (°C)	Time (h)	C <sub>PET</sub> (%)	S <sub>BHET</sub> (%)
This work <sup>a</sup>	-	175	3	1.6	4.7
	[amim][MnCl <sub>3</sub> ]	175	1.5	100	74.6
	[amim][FeCl <sub>4</sub> ]	175	3	100	71.4
	[amim][CoCl <sub>3</sub> ]	175	1.25	100	79.5
	[amim][CuCl <sub>3</sub> ]	175	3	10.8	77.3
	[amim][ZnCl <sub>3</sub> ]	175	1.25	100	80.1
	[amim]Cl	175	1.25	4.8	11.4
	ZnCl <sub>2</sub>	175	1.25	94.1	76.2
	[bmim]Cl	175	1.25	3.7	9.8
	[bmim][FeCl <sub>4</sub> ]	175	1.25	19.7	48.3
Ref. <sup>24b</sup>	[bmim][FeCl <sub>4</sub> ]	178	4	100	59.2
Ref. <sup>25c</sup>	[bmim][H <sub>2</sub> PO <sub>4</sub> ]	175	8	6.9	-
	[bmim][HSO <sub>4</sub> ]	170	8	0.5	-
	[3a-C <sub>3</sub> P(C <sub>4</sub> ) <sub>3</sub> ][Gly]	180	8	100	-
	[3a-C <sub>3</sub> P(C <sub>4</sub> ) <sub>3</sub> ][Ala]	180	8	100	-
	[bmim]Cl	180	8	44.7	-
Ref. <sup>8d</sup>	[bmim]Br	180	8	98.7	-
	[bmim]OH	190	2	100	71.2
Ref. <sup>33e</sup>	[bmim][HCO <sub>3</sub> ]	190	2	82.8	14.1
	[Deim][Zn(OAc) <sub>3</sub> ]	180	1.5	100	67.10
	[Deim][Cu(OAc) <sub>3</sub> ]	180	2	100	58.64
	[Deim][Mn(OAc) <sub>3</sub> ]	180	3.75	100	51.30
	[Deim][Co(OAc) <sub>3</sub> ]	180	1.5	100	56.65
	[Deim][Ni(OAc) <sub>3</sub> ]	180	1.75	100	54.13

<sup>a</sup>Reaction conditions: atmospheric pressure, 5.0 g PET, 20 g EG, and 0.5 g catalyst.

<sup>b</sup>Reaction conditions: atmospheric pressure, 5.0 g PET, 20 g EG, and 1.0 g catalyst.

<sup>c</sup>Reaction conditions: atmospheric pressure, 5.0 g PET, 20 g EG, and 1.0 g catalyst.

<sup>d</sup>Reaction conditions: 2.0 g PET, 20 g EG, and 1.0 g catalyst.

<sup>e</sup>Reaction conditions: atmospheric pressure, 3.0 g PET, 20 g EG, and 0.5 g catalyst.

the surfaces of undepolymerized PET pellets are covered by more and more obvious cracks with the reaction time increasing in Figure 8. The phenomena indicate that the degradation of PET takes place on the surfaces of PET pellets, which conformed the reports from literatures,<sup>43,44</sup> and the reaction rate is accelerated with the exposed areas increased due to more and more cracks.

The catalytic activities of these synthesized ILs follow the order: [amim][ZnCl<sub>3</sub>] > [amim][CoCl<sub>3</sub>] > [amim][MnCl<sub>3</sub>] > [amim][FeCl<sub>4</sub>] > [amim][CuCl<sub>3</sub>] > [amim][Cl] (see Table II), from which we can see that the metal anions play an important role in the PET degradation process when the cation is the same [amim]<sup>+</sup>. And it is shown that the catalytic activity of [amim][FeCl<sub>4</sub>] is higher than that of [bmim][FeCl<sub>4</sub>], and there is the same tendency when catalysts are [amim]Cl and [bmim]Cl (Table II). The higher catalytic activity of [amim]<sup>+</sup> results from the smaller size of [amim]<sup>+</sup> than that of [bmim]<sup>+</sup> by the structure comparison of [amim]<sup>+</sup> and [bmim]<sup>+</sup>, and the electron-deficient structure is caused by alkyl group that can enhance the interaction between cation of IL and oxygen of ester in PET.<sup>34,35</sup> So, the cation is important to the PET degradation.

To verify the role of catalyst, *in situ* IR spectra of the EG and the solution of [amim][ZnCl<sub>3</sub>] and EG were tested and given in Figure 9. It can be seen that the peak of hydroxyl vibration in EG shows an obvious redshift from 3378 to 3420 cm<sup>-1</sup> with the increase in temperature. But the peak of hydroxyl vibration in EG does not obviously change in the IR spectra of only EG

**Table III.** Recycling of the Residual EG and [amim][ZnCl<sub>3</sub>]

Recycling times	Conversion of PET (%)	Selectivity of BHET (%)
0 <sup>a</sup>	100	80.2
1 <sup>a</sup>	100	80.7
2 <sup>a</sup>	100	80.4
3 <sup>a</sup>	100	80.2
4 <sup>a</sup>	100	80.4
5 <sup>a</sup>	100	80.3
6 <sup>a</sup>	100	80.1

<sup>a</sup>Reaction conditions: atmospheric pressure, 5.0 g PET, 20 g EG, 0.5 g catalyst, 175°C, and 1.25 h.

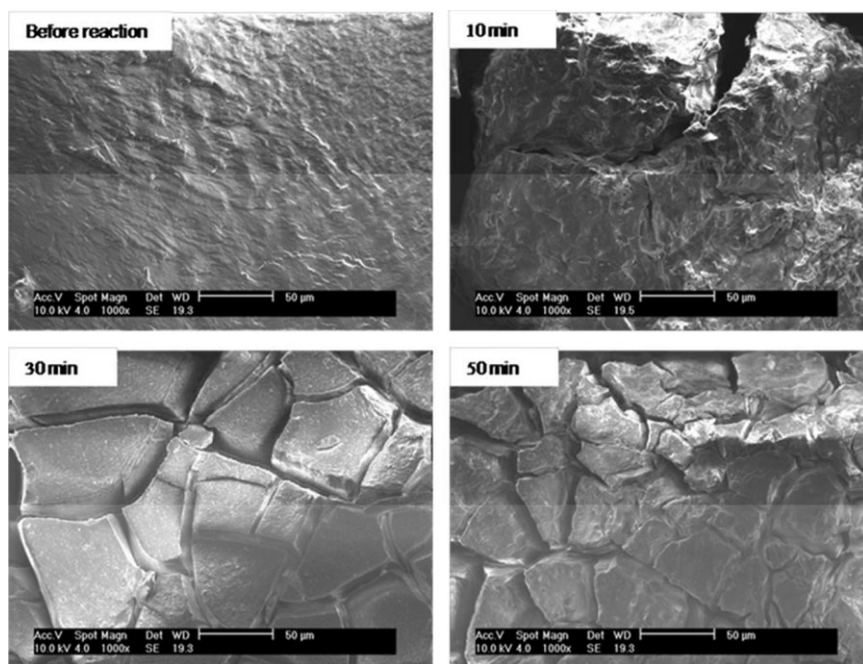


Figure 8. SEM images of the residual PET pellets at different reaction times.

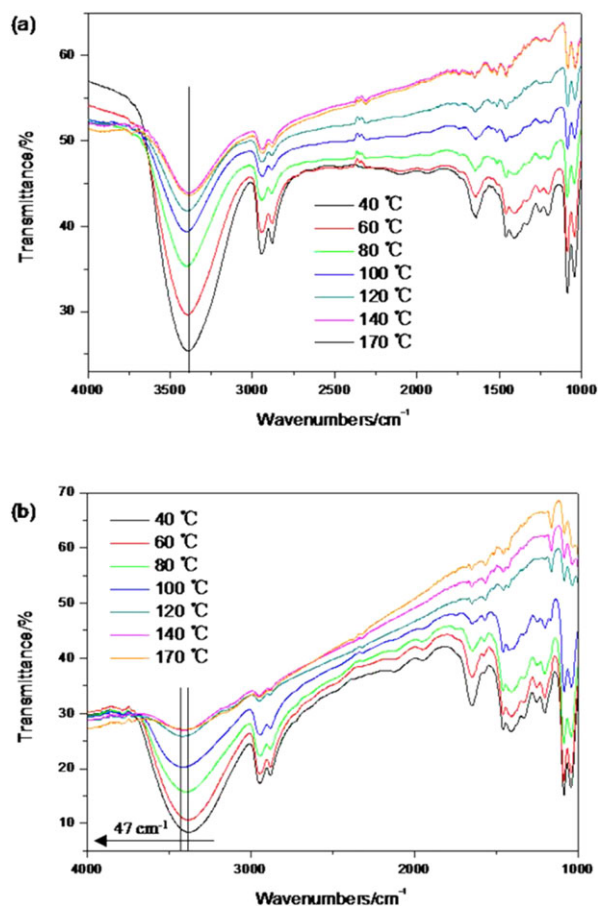
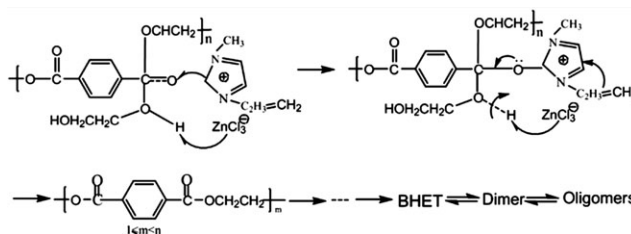


Figure 9. *In situ* IR spectra: (a) *in situ* IR spectra of reactant EG; (b) *in situ* IR spectra of EG and catalyst [amim][ZnCl<sub>3</sub>]. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

shown in Figure 9(b) when the temperature increased. Apparently, there is an interaction between EG and catalyst that can activate the hydroxyl in EG to enhance the degradation of PET.<sup>45</sup> The high-catalytic activity is mainly attributed to the synergic effect between cation and anion of the IL catalyst. The catalytic activity of [amim][ZnCl<sub>3</sub>] is higher than that of ZnCl<sub>2</sub> or [amim]Cl (Table II), which indirectly verifies the synergic effect from the other view. In the synergic effect, the role of anion is more important than that of the cation by the comparison of the catalytic activity of different ILs.

According to the experimental phenomena, *in situ* IR spectra, and experimental results, the possible mechanism is proposed in Scheme 2. [ZnCl<sub>3</sub>]<sup>-</sup> interacts with the hydrogen of the hydroxyl in EG, and [amim]<sup>+</sup> interacts with the oxygen in the ester of PET. Then the oxygen in EG attacks the carbon cation of the ester group in PET more easily and the electron-deficient structure caused by alkyl group also enhances the interaction between cation of IL and oxygen of ester in PET and finally results in the disconnection of the long molecule chain of PET. The higher catalytic activity is attributed to the synergic effect between cation and anion of the IL catalyst, and the electron-deficient structure caused by the alkyl group.



Scheme 2. The proposed mechanism for the degradation of PET catalyzed by [amim][ZnCl<sub>3</sub>].

## CONCLUSIONS

1-Allyl-3-methylimidazolium halometallate ILs can effectively degrade PET as catalysts in EG, and [amim][ZnCl<sub>3</sub>] and [amim][CoCl<sub>3</sub>] exhibit higher catalytic activity. The conversion of PET and the selectivity of BHET are both higher than that catalyzed by common IL catalysts, Fe-containing magnetic IL catalysts, and metallic acetate IL catalysts. In addition, the degradation method catalyzed by [amim][ZnCl<sub>3</sub>] and [amim][CoCl<sub>3</sub>] has the advantage. The main product BHET can be separated from catalysts easily, the obtained BHET has a high purity, and the reaction rate is faster than that catalyzed by conventional IL catalysts and Fe-containing magnetic IL catalysts. These all show that [amim][ZnCl<sub>3</sub>] and [amim][CoCl<sub>3</sub>] are excellent catalysts. Moreover, based on *in situ* IR, SEM, and experimental results, the possible mechanism of this degradation process was proposed. The degradation reaction mainly takes place on the surface of PET pellets, and the high-catalytic activity is attributed to the synergistic effect of [ZnCl<sub>3</sub>]<sup>-</sup> and [amim]<sup>+</sup> and the electron-deficient structure caused by alkyl group.

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