

# Degradation of poly(ethylene terephthalate) using ionic liquids

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The degradation of poly(ethylene terephthalate) (PET) was successfully achieved using ionic liquids. The products were separated according to their solubilities in boiling water. Average molecular weights of the main product were determined by gel permeation chromatography (GPC). The physicochemical properties of the product have been characterized by scanning electron microscopy equipped with an energy dispersive X-ray analyzer (SEM/EDX), X-ray diffractometer, infrared spectrometric analyzer, differential scanning calorimeter, and thermogravimetric analysis instrument. The influences of experimental parameters, such as the reaction time, reaction temperature, and addition of different catalysts on the solubility of PET were investigated. A study on the recycling of the ionic liquid shows that ionic liquid could be used repeatedly. Moreover, the solubility of PET in the recycled ionic liquid is higher than that in fresh ionic liquid. Further study shows that the increase of solubility in the recycled ionic liquid is attributable to the presence of a minor amount of water. A mechanism of the degradation of PET in 1-butyl-3-methylimidazolium chloride ([bmim]Cl) was proposed. In addition, the kinetics of this reaction was investigated. Results show that this degradation process is a first-order kinetic reaction and the activation energy is 232.79 kJ mol<sup>-1</sup>.

## 1. Introduction

Poly(ethylene terephthalate) (PET) is widely used in the manufacture of video and audio tapes, X-ray films, food packaging and especially of soft-drink bottles due to its excellent properties.<sup>1</sup> The interest in PET recycling is continuously growing because of ecological and economic considerations. Among the methods of polymer recycling, chemical recycling, which is applied in the case of postconsumer condensation polymers, draws great interest.

To date, several processes for PET depolymerization have been put forward, such as the methanolysis process with methanol,<sup>2</sup> glycolysis processes with ethylene glycol or other glycols,<sup>3,4</sup> and hydrolysis under the promotion of acidic or basic conditions.<sup>5,6</sup> PET could be effectively depolymerized into monomers or oligomers by these methods, however, there exist disadvantages in these processes. Methanolysis is usually carried out at relatively high pressure and temperature, moreover, it involves the volatilization of methanol. The main drawback of the glycolysis process is that the reaction products are not discrete chemicals but the bis(hydroxyethyl) terephthalate (BHET) monomer along with higher oligomers, which are difficult to purify with conventional methods.<sup>3</sup> Hydrolysis of PET under acidic or basic conditions gives terephthalic acid (TPA), along with corrosion and pollution problems.<sup>7</sup> Therefore,

a green solvent for the depolymerization of PET needs to be developed.

Ionic liquids, being considered as desirable green solvents, have attracted enormous research interest because of their unique features, such as the advantages of optimization of compound characteristics through a broad selection of anion and cation combinations, thermal stability, non-volatility, electrochemical stability, and low flammability.<sup>8–10</sup> In the last decade, ionic liquids have been widely used in extraction,<sup>11</sup> catalysis,<sup>12</sup> electrochemistry,<sup>13</sup> and organic synthesis.<sup>14,15</sup> It has also been reported that ionic liquids could be used in the research of polymers. In 2002, Swatloski *et al.*<sup>16</sup> firstly reported that ionic liquids can be used to dissolve cellulose. It was found that 1-butyl-3-methylimidazolium chloride ([bmim]Cl) dissolved cellulose in relatively high concentrations, *e.g.* 10 wt% by heating.<sup>16</sup> Later, a novel ionic liquid, 1-allyl-3-methylimidazolium chloride ([amim]Cl), was reported to be effective in producing regenerated cellulose by a non-polluting process.<sup>17</sup> And chloroaluminate(III) ionic liquids could be used in the catalytic cracking of polyethylene to light alkanes.<sup>18</sup> Kamimura *et al.*<sup>19</sup> have employed quaternary ammonium ionic liquids to depolymerize polyamide plastics, and the caprolactam monomer was obtained. However, we have found no report on the use of ionic liquids in the degradation of PET. The special properties of ionic liquids make them suitable for this process. Thus, the development of ionic liquids in this field appears encouraging.

In this study, we have found that ionic liquids could be used in the degradation of PET under moderate reaction conditions. Average molecular weights of the main degradation product were determined by gel permeation chromatography (GPC). The main product has been characterized for morphology and elemental composition by scanning electron microscopy equipped

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with an energy dispersive X-ray analyzer (SEM/EDX). The properties of the product were also characterized by means of X-ray diffraction (XRD), infrared spectroscopy (IR), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). The effects of experimental conditions on the solubility of PET in ionic liquid were also illustrated. Moreover, the recycling of the ionic liquid, mechanism of this degradation process, and kinetics of this reaction were investigated.

## 2. Experimental

### 2.1 Materials

PET pellets ( $2.0 \times 2.5 \times 2.7$  mm) were supplied by Jindong Commercial Co. Ltd, Jiangsu Province, China. Their average molecular weight, measured in a 60 : 40 (w/w) phenol/1,1,2,2-tetrachloroethane solution at 25 °C, was found to be  $2.63 \times 10^4$  g mol<sup>-1</sup>. Phenol and 1,1,2,2-tetrachloroethane (99% purity) were obtained from Sinopharm Chemical Reagent Beijing Co., Ltd., China. Reagents for synthesizing ionic liquids were purchased from J & K Chemical Ltd., China. The materials were used without any further treatment. Ionic liquids were synthesized according to the procedures described in the literature.<sup>20</sup>

### 2.2 General procedure

In each experiment, the PET pellets and ionic liquids, with a weight ratio of 1 : 4, were charged into a 50 mL round-bottom flask equipped with a thermometer and a reflux condenser. The degradation reactions were carried out under atmospheric pressure at reaction temperatures ranging from 120 °C to 200 °C for reaction times of 6–10 h. The flask was immersed in an oil bath at a specific temperature for the required time.

When each reaction finished, the contents of the reactor were allowed to cool to room temperature. Then an excess amount of distilled water was added into the reactor and used to wash the residual PET pellets. The residual PET was collected, dried and weighed. The solubility of PET ( $S_{\text{PET}}$ ) in ionic liquid is defined by eqn (1):

$$S_{\text{PET}} = \frac{W_1 - W_2}{W_0} \times 100\% \quad (1)$$

where  $W_0$  represents the weight of ionic liquid,  $W_1$  represents the initial weight of PET, and  $W_2$  represents the weight of residual PET.

The degradation products were precipitated after water was added, and a simple separation of the products was carried out. The products were boiled in 1500 mL distilled water with vigorous stirring, and then filtered. The collected filtrate in this step was concentrated to about 300 mL by heating at the boiling point. The concentrated filtrate was stored in a refrigerator at 0 °C for 24 h. White powder was formed in the filtrate, then filtered and dried. This was the main degradation product. The fraction insoluble in boiling water is a minor proportion of the degradation products, and it was not studied further.

### 2.3 Characterization

The average molecular weights of the main degradation product were determined by GPC (Waters-515) equipped with a

differential refraction detector and an ultrastyrigel column. The GPC analysis was performed using tetrahydrofuran (THF) as the mobile phase at a flow rate of 1.0 mL min<sup>-1</sup>. Calibration of GPC was carried out with standard polystyrene samples. A JSM-6301F scanning electron microscopy integrated with an X-ray energy dispersive analyzer was used for morphological and elemental analysis of the product. The X-ray diffraction (XRD) patterns were collected on an X-ray diffractometer (X'Pert, PRO) operated at 40 kV and 10 mA with nickel filtered Cu K $\alpha$  radiation ( $\lambda = 1.54060$  Å). IR spectra of the main degradation product and PET material were measured on a 25PC FT-IR spectrograph by KBr method. DSC scans of the main product and PET material were obtained using DSC-2910 by heating from room temperature to 500 °C at a heating rate of 10 °C min<sup>-1</sup> in an atmosphere of nitrogen with a flow rate of 25 mL min<sup>-1</sup>. A thermogravimetric analyzer (TGA-2050) was used to measure the weight loss of the main product and PET material in an atmosphere of nitrogen with a flow rate of 25 mL min<sup>-1</sup> over a temperature range from room temperature to 500 °C at a heating rate of 10 °C min<sup>-1</sup>. <sup>1</sup>H NMR spectra of the recycled ionic liquid were recorded with a Bruker ARX-400 Advance Spectrometer operating at 400 MHz. The spectra were obtained in DMSO solution.

## 3. Results and discussion

### 3.1 Solubility of PET in different ionic liquids

We synthesized the same kind of ionic liquids used in the dissolution of cellulose and catalytic cracking of polyethylene, and they were used in the degradation of PET. The solubility of PET in these ionic liquids is summarized in Table 1.

The results show that PET dissolved readily in 1-butyl-3-methylimidazolium chloroaluminate(III) ([bmim]AlCl<sub>4</sub>), and the solubility could reach 7.5 wt%. The solubility of PET in ionic liquids that contain Cl<sup>-</sup>, Br<sup>-</sup>, CF<sub>3</sub>COO<sup>-</sup>, and CH<sub>3</sub>COO<sup>-</sup> is also good. However, PET did not dissolve in ionic liquids containing BF<sub>4</sub><sup>-</sup> or PF<sub>6</sub><sup>-</sup>, which is in accordance with the result that cellulose could not dissolve in [bmim]BF<sub>4</sub> or [bmim]PF<sub>6</sub>.<sup>16</sup> [bmim]Cl, which has higher decomposition temperature and is much more stable than [bmim]AlCl<sub>4</sub>, [bmim]CF<sub>3</sub>COO, and [bmim]CH<sub>3</sub>COO, is chosen as the solvent to dissolve PET for our further study.

**Table 1** Solubility of PET in different ionic liquids<sup>a</sup>

Ionic liquid <sup>b</sup>	Reaction temperature/°C <sup>c</sup>	Solubility of PET (wt%)
[bmim]Cl	180	2.7
[bmim]Br	180	1.8
[emim]Br	180	1.6
[bmim]BF <sub>4</sub>	180	insoluble
[bmim]PF <sub>6</sub>	180	insoluble
[bmim]CF <sub>3</sub> COO	120	1.9
[bmim]CH <sub>3</sub> COO	150	3.4
[bmim]AlCl <sub>4</sub>	150	7.5

<sup>a</sup> Reaction conditions: 1 atm, 8 h, no catalyst. <sup>b</sup> emim: 1-ethyl-3-methylimidazolium; the molar ratio of [bmim]Cl to AlCl<sub>3</sub> for the synthesis of [bmim]AlCl<sub>4</sub>: 1/1.5. <sup>c</sup> Reaction temperature: dependent on the decomposition temperatures of ionic liquids.

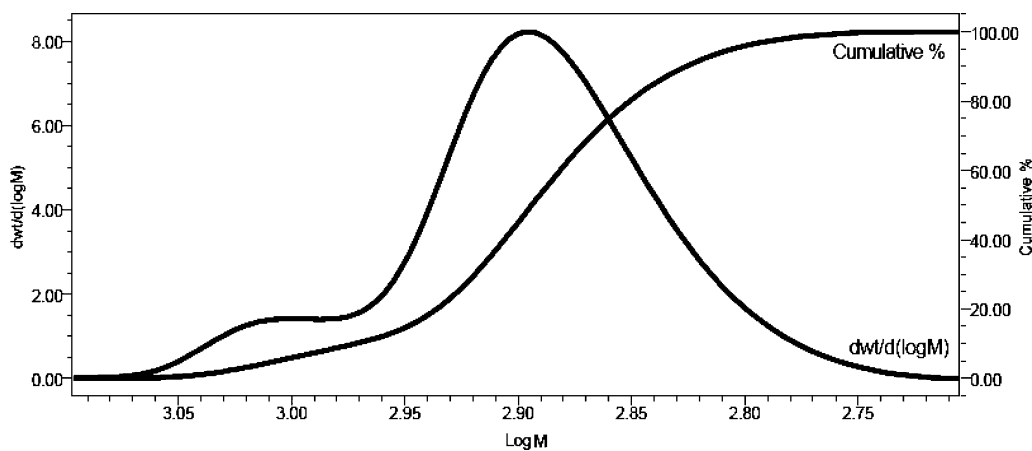


Fig. 1 GPC curves of the main product in the degradation of PET.

### 3.2 GPC analysis

The average molecular weights (number-average molecular weight ( $M_n$ ) and weight-average molecular weight ( $M_w$ )) of the main degradation product were determined by GPC, and the results are shown in Fig. 1. After placing of the data in a molecular weight distribution curve, the  $M_n$  and  $M_w$  of this product are shown to be  $777 \text{ g mol}^{-1}$  and  $790 \text{ g mol}^{-1}$ , respectively. The cumulative curve in Fig. 1 shows that the average molecular weight of about 75% of the product is in the range of  $710 \text{ g mol}^{-1}$  to  $890 \text{ g mol}^{-1}$ . The average molecular weight of the product is two orders of magnitude smaller than that of the fresh PET ( $2.63 \times 10^4 \text{ g mol}^{-1}$ ). Therefore, the ionic liquid is a kind of effective solvent for the degradation of PET.

### 3.3 Characterization of the main product

The elemental composition of the main product was analyzed by an X-ray energy dispersive spectrometer, and the result is presented in Fig. 2. The energy dispersive X-ray spectrum indicates the presence of C and O (Au was sprayed onto the surface of the product before the measurement) in this fraction. Thus, it could be concluded that the main product in the

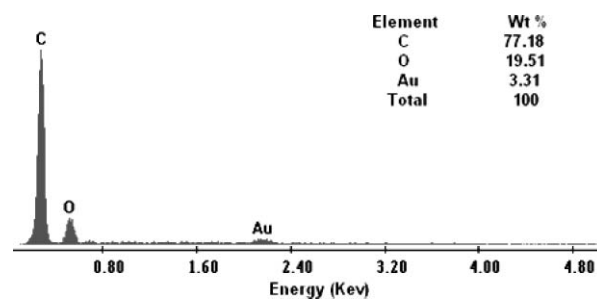


Fig. 2 The energy dispersive X-ray spectrum of the main degradation product.

degradation of PET using [bmim]Cl is mainly composed of elements C and O (hydrogen could not be detected by this method). This indicates that the elements in [bmim]Cl, such as N and Cl, were not transferred onto the degradation product, that is to say, no chemical reaction occurred between PET and the ionic liquid [bmim]Cl during this process.

Scanning electron micrographs (SEM) revealing the morphology of the main degradation product are shown in Fig. 3. The image in Fig. 3(a) clearly displays that the main product has a spherical shape, with different size spheres from  $8 \mu\text{m}$

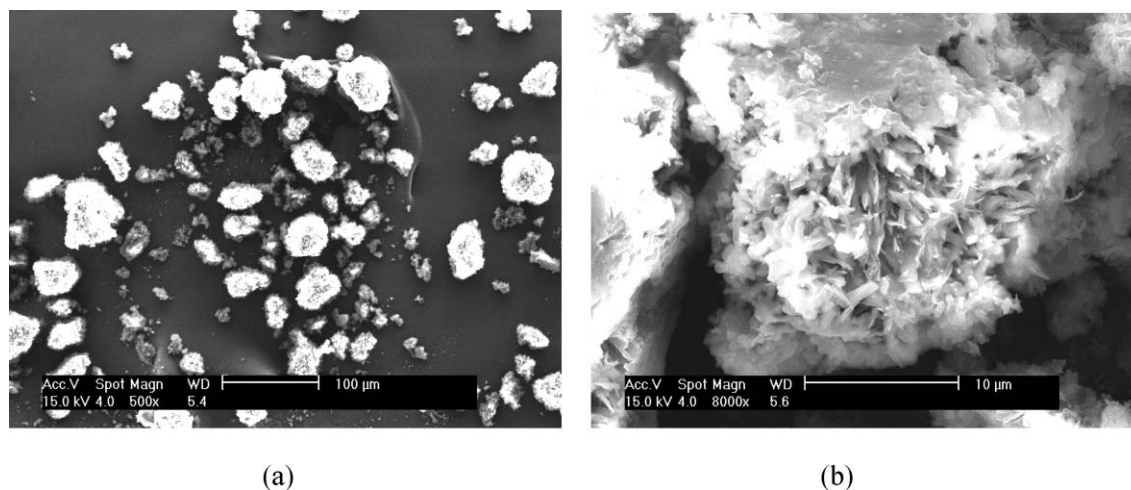
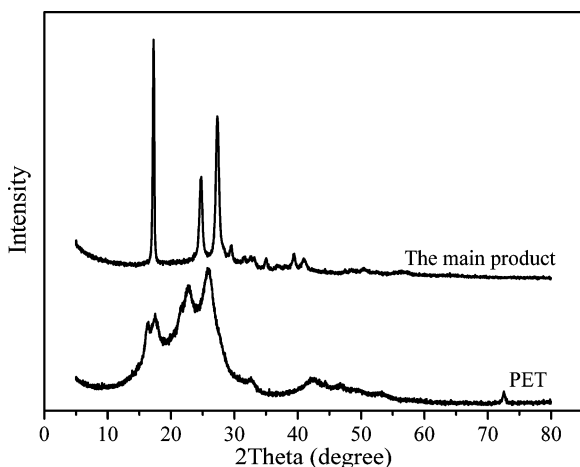


Fig. 3 SEM images of the main degradation product.

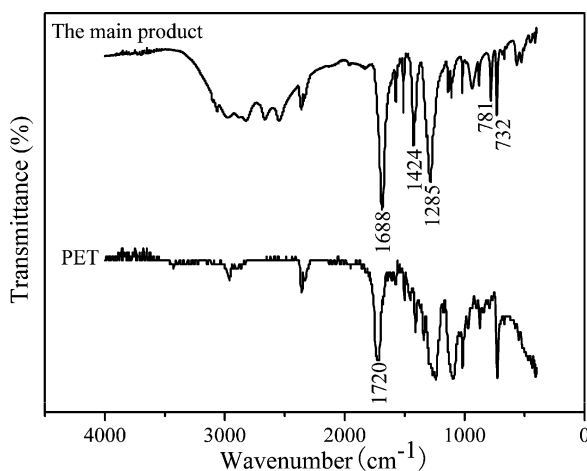
to 70  $\mu\text{m}$ . While, an enlarged image presented in Fig. 3(b) indicates that the product has a rosette structure. Compared with the smooth surface of the PET material (reported in our previous work),<sup>21</sup> the morphology of the degradation product has changed significantly.

Fig. 4 shows the XRD profile of the main degradation product 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  $2\theta = 16.1^\circ$ ,  $17.5^\circ$ , and  $22.6^\circ$ . Fig. 4 also indicates that the product exhibits a high degree of crystallinity, but its crystalline structure is different from that of PET. The typical diffraction peaks of the main product are at  $2\theta = 17.3^\circ$ ,  $25.0^\circ$ , and  $27.3^\circ$ .



**Fig. 4** XRD patterns of the main degradation product and the PET material.

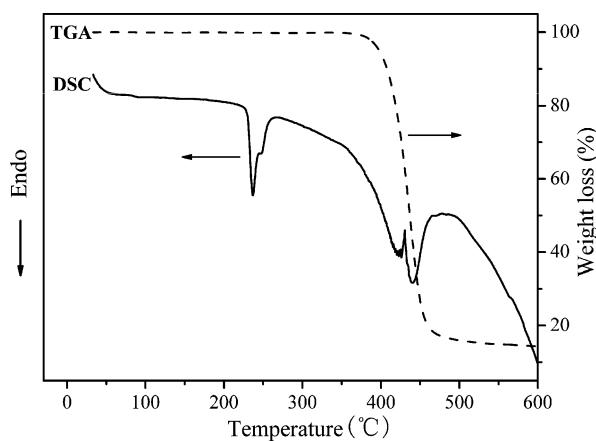
The IR spectra of the main degradation product and the PET material are given in Fig. 5. It can be seen that the two spectra are quite similar, and no new peaks appear in the spectrum of the degradation product, which indicates that no new chemical bonds are formed during this process. The absorption bands in the IR spectrum of the product at  $700\text{--}800\text{ cm}^{-1}$  and  $1424\text{ cm}^{-1}$  are assigned to the vibration of the



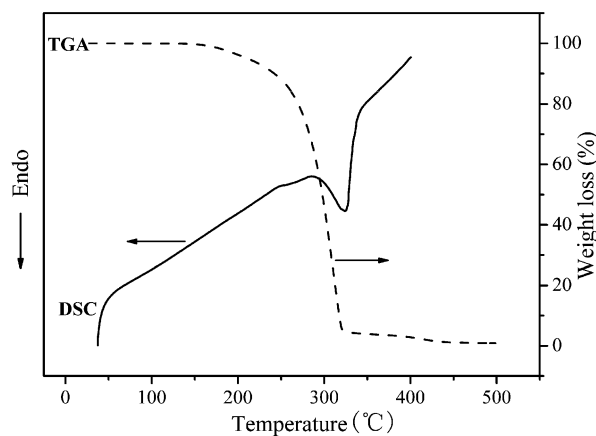
**Fig. 5** IR spectra of the main degradation product and the PET material.

benzene ring. And the strong absorption peaks at  $1688\text{ cm}^{-1}$  and  $1285\text{ cm}^{-1}$  indicate the presence of  $\text{C}=\text{O}$  and  $\text{C}-\text{O}$ , respectively. Compared with the absorption band of the carbonyl at  $1720\text{ cm}^{-1}$  for the PET material, that of  $\text{C}=\text{O}$  for the product shifted to a lower wavenumber. This might indicate that the carbonyl bond becomes weaker and the  $\text{C}-\text{O}$  bond in the ester group breaks during the degradation process.

The DSC and TGA curves of the PET material and the main degradation product are illustrated in Fig. 6. The TGA curve of PET shows significant weight loss at  $397^\circ\text{C}$ . This weight loss is attributed to the thermal decomposition of PET material.<sup>22</sup> The DSC thermogram of PET shows an endothermic peak centered at about  $235^\circ\text{C}$ , which is related to the melting of PET material.<sup>3</sup> The TGA curve of the degradation product exhibits a lower onset temperature ( $203^\circ\text{C}$ ) for decomposition. While, the DSC scan for the product exhibits only an endothermic peak in the decomposition region. Thus, it could be considered that the product has decomposed before it melts. From results of the thermal analysis, it could be concluded that the degradation product is more easily decomposed than PET.



(a)



(b)

**Fig. 6** DSC and TGA curves of the PET material (a) and the main degradation product (b).

### 3.4 Influence of reaction conditions

**3.4.1 Influence of reaction time.** Fig. 7 presents the influence of reaction time on the solubility of PET in [bmim]Cl. It is observed that with the increasing of reaction time from 6 h to 10 h, the solubility of PET in the ionic liquid increases linearly. When the reaction time is extended to 10 h, the solubility of PET could reach 4.0 wt% at a reaction temperature of 180 °C.

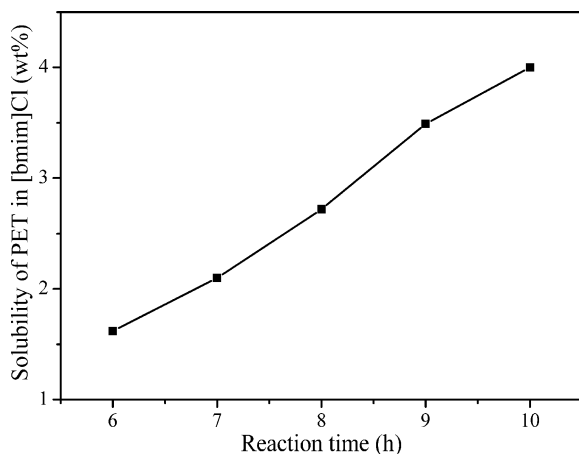


Fig. 7 Effect of reaction time on the solubility of PET in [bmim]Cl (1 atm, 180 °C, no catalyst).

**3.4.2 Influence of reaction temperature.** The effect of reaction temperature on the solubility of PET in [bmim]Cl is shown in Fig. 8. It displays that the solubility of PET in [bmim]Cl is very close to 0 when the reaction temperature is below 160 °C. Subsequently, with increasing reaction temperature, the solubility of PET apparently increases, and it reaches 17.5 wt% when the temperature is set at 200 °C. The rate of degradation is also enhanced as the reaction temperature rises. Comparing the influence of reaction temperature on the solubility of PET in [bmim]Cl with that of reaction time, it is clear that reaction temperature is a more critical factor in this process.

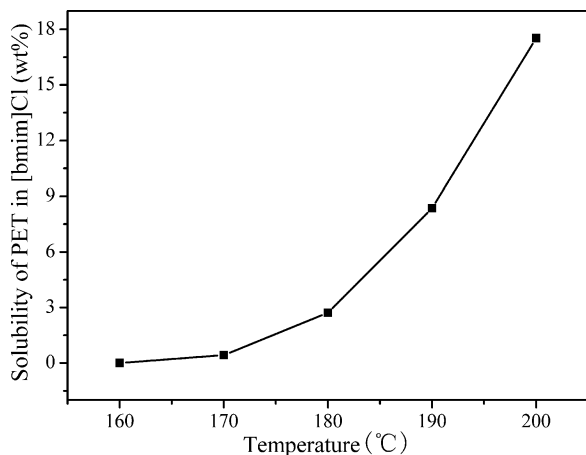


Fig. 8 Effect of reaction temperature on the solubility of PET in [bmim]Cl (1 atm, 8 h, no catalyst).

**3.4.3 Influence of the addition of catalyst.** To study the effect of addition of different kinds of catalysts on this reaction

process, experiments were carried out at atmospheric pressure, 180 °C, 8 h, with a catalyst concentration of 1.0% based on the weight of PET, and the results are shown in Fig. 9. It indicates that the addition of zinc acetate ( $\text{Zn}(\text{CH}_3\text{COO})_2$ ), tetrabutyl titanate ( $\text{Ti}(\text{OC}_4\text{H}_9)_4$ ), and solid superacid ( $\text{SO}_4^{2-}/\text{TiO}_2$ ) restrains the dissolution of PET in ionic liquid. However, the addition of concentrated sulfuric acid has no influence on the solubility of PET in [bmim]Cl. Presumably, zinc acetate, tetrabutyl titanate, and solid superacid could not dissolve in [bmim]Cl. Additionally, ionization did not exist in concentrated sulfuric acid. Thus, when these substances were used, Lewis acids or protonic acids, which play an important role in this process (shown in Section 3.6), could not be formed in the reaction system, and this degradation process would not be accelerated. In addition, zinc acetate, tetrabutyl titanate, and solid superacid could be considered as impurities in the ionic liquid. The presence of a minor amount of impurity would influence the properties of the ionic liquid and further cause the decrease of solubility of PET in [bmim]Cl. In order to increase the solubility of PET in ionic liquid, an effective catalyst for this process should be developed.

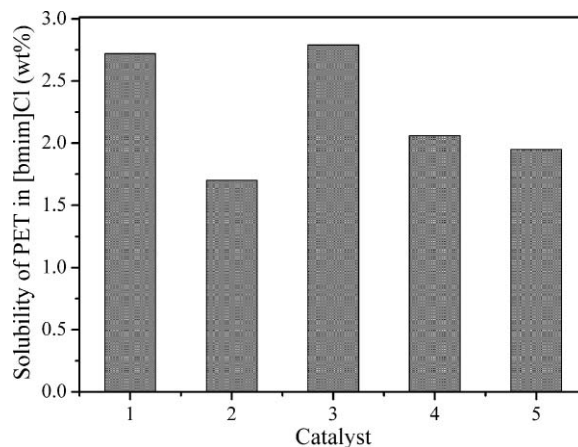


Fig. 9 Effect of the addition of different kinds of catalysts on the solubility of PET in [bmim]Cl (1 – none; 2 –  $\text{Zn}(\text{CH}_3\text{COO})_2$ ; 3 –  $\text{H}_2\text{SO}_4$ ; 4 –  $\text{Ti}(\text{OC}_4\text{H}_9)_4$ ; 5 –  $\text{SO}_4^{2-}/\text{TiO}_2$ ).

### 3.5 Recycling of the ionic liquid

From the viewpoint of environmental conservation and economics of the process, recycling use of the solvent ionic liquid is absolutely required after the degradation of PET.

In our study, after the main product was filtered from the liquid phase, the residual ionic liquid in the filtrate was recovered by vacuum evaporation at 70 °C, and then it was stored in a vacuum oven for 48 h. We examined the solubility of PET in the recycled ionic liquid, and the result is presented in Fig. 10. It shows that the recycled [bmim]Cl worked efficiently when it was used six times. Moreover, the solubility of PET in the recycled ionic liquid is even higher than that in fresh ionic liquid. The recycled ionic liquid was also analyzed by  $^1\text{H}$  NMR spectroscopy, and the spectrum is presented in Fig. 11. Comparing the  $^1\text{H}$  NMR spectrum of the recycled ionic liquid with that of the fresh [bmim]Cl,<sup>23</sup> it is clear that there is no obvious change of the chemical shifts of [bmim]Cl after the

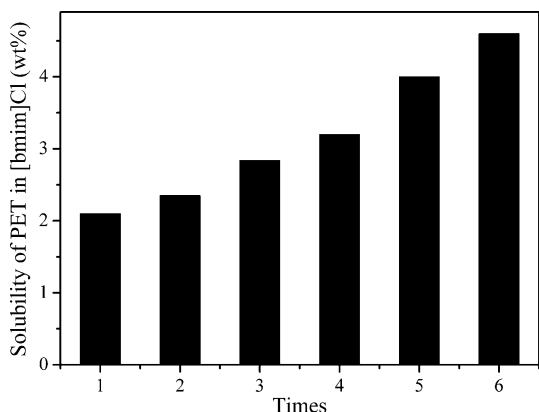


Fig. 10 Recycling use of [bmim]Cl (1 atm, 180 °C, 7 h, no catalyst).

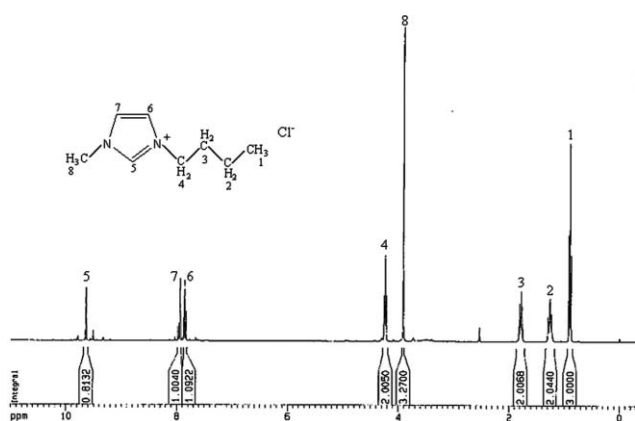


Fig. 11 <sup>1</sup>H NMR spectrum of [bmim]Cl after being reused six times.

sixth recycling, which indicates that this ionic liquid underwent virtually no decomposition throughout the reaction.

The physicochemical properties of ionic liquids have been shown to be very sensitive to water,<sup>24</sup> reactions in ionic liquids can be strongly influenced by the moisture content. It is assumed that the increase of solubility of PET in recycled ionic liquid is caused by the presence of a minor amount of water which is difficult to remove during the recycling process. In order to study the influence of the presence of water in [bmim]Cl on the solubility of PET, experiments were carried out under atmospheric pressure at 180 °C with reaction time of 8 h. The results are shown in Fig. 12. It indicates that with the increasing of water content in [bmim]Cl from 0 to 2.0%, the solubility of PET increases. In fresh [bmim]Cl, the solubility was only 2.7 wt%. Then it dramatically reached 8.3 wt% when the water content in the ionic liquid increased to 2.0%. This result is quite different from the conclusion that the presence of water in [bmim]Cl significantly decreases the solubility of cellulose.<sup>16</sup> From the point of view of the recycling and reuse process, it could be concluded that ionic liquid is a recyclable solvent for the degradation of PET.

### 3.6 Mechanism of this process

It is reported that the chloride ion in [bmim]Cl plays important role in the dissolution of cellulose. The corresponding solvation

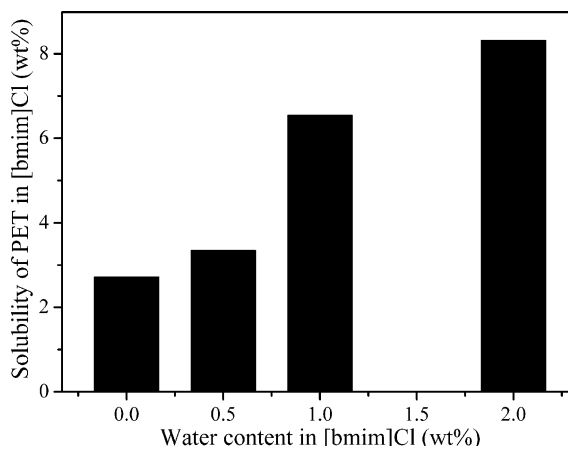
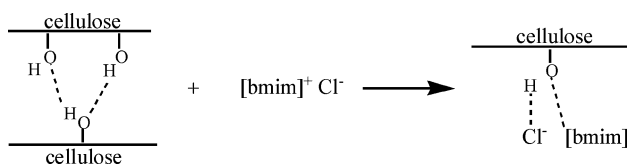
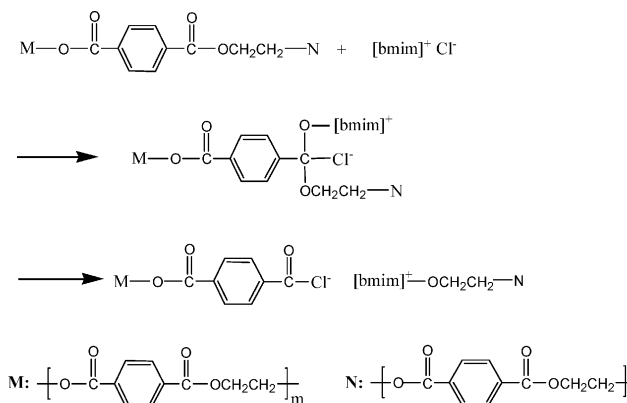


Fig. 12 Effect of water content in [bmim]Cl on the solubility of PET.

mechanism, as shown in Scheme 1, is proposed to involve the interaction of chloride ions with the hydroxyl protons in this carbohydrate, resulting in the breakage of the extensive hydrogen bonding network in cellulose and dissolution of cellulose in ionic liquid.<sup>16,17,25</sup> As to the degradation of PET in [bmim]Cl, a similar mechanism is proposed, which is shown in Scheme 2. The hydrogen in the cation of the ionic liquid interacts with the carbonyl oxygen O=C in the ester, forming a hydrogen bond. Meanwhile, the chloride ion in [bmim]Cl attacks the carbon atom of the ester group. Then a tetrahedral intermediate is formed. These two interactions result in the breakage of the C–O bond as well as the decrease of average molecular weight of PET, and further cause the dissolution of PET in [bmim]Cl.



Scheme 1 Mechanism of the dissolution of cellulose in [bmim]Cl.



Scheme 2 Possible mechanism of the degradation of PET in [bmim]Cl.

As to the effect of water in this process, it could be considered that a Lewis acid or protonic acid was formed in the reaction system when water was present in [bmim]Cl. This assumption could be confirmed by the pH variation of [bmim]Cl with the

increase of water content in it, as shown in Fig. 13. This figure indicates that the pH value of the ionic liquid [bmim]Cl decreases with an increase of water content, and it reaches a constant value when the water content is higher than 15%. When [bmim]Cl with a certain amount of water was used to dissolve PET, the formed acid would protonate the carbonyl oxygen and thus make the carbonyl group more susceptible to nucleophilic attack. Meanwhile, the attack of  $\text{Cl}^-$  on the carbon in the ester is easier and the solubility of PET increases. Therefore, acidic conditions are beneficial to the degradation of PET in ionic liquid. The high solubility of PET in [bmim]AlCl<sub>4</sub> might also be caused by the acidity of this ionic liquid, as in the synthesis of [bmim]AlCl<sub>4</sub>, the molar ratio of [bmim]Cl to AlCl<sub>3</sub> was 1 : 1.5 and the obtained ionic liquid is acidic at this ratio.

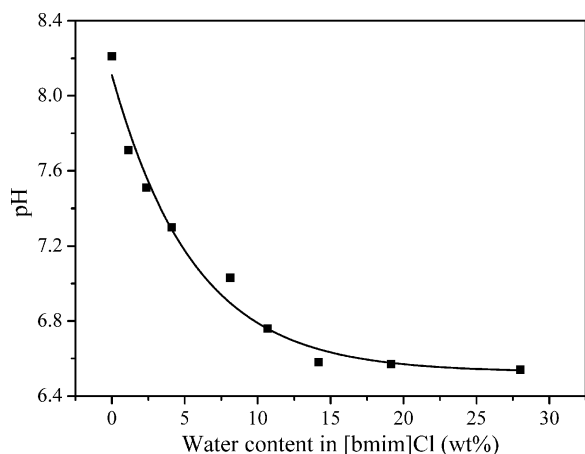


Fig. 13 Effect of water content on the pH value of [bmim]Cl.

### 3.7 Kinetics of this reaction

The kinetic study of degradation of PET in [bmim]Cl was undertaken on the basis of degraded PET and residual PET. The velocity constant of degradation of PET in ionic liquid was calculated by eqn (2):

$$k = \frac{1}{t} \ln \frac{1}{1-x} \quad (2)$$

where  $x$  represents the degree of conversion of PET at reaction time  $t$ , and  $k$  represents the velocity constant of the process.

The effect of reaction temperature on the rate of degradation of PET in [bmim]Cl is presented in Fig. 14, and the linear regression results of the data in Fig. 14 are shown in Table 2. The linear correlative coefficients in Table 2 are all higher than 0.99, indicating that  $\ln \frac{1}{1-x}$  is proportional to reaction time at different temperatures, and that this process is a first-order kinetic reaction. That is to say, the rate of degradation of PET in the ionic liquid is proportional to the PET concentration, while it is independent of the concentration of ionic liquid. The straight lines in the graph of  $\ln \frac{1}{1-x}$  vs. time give the slope values of 0.00387 h<sup>-1</sup>, 0.02794 h<sup>-1</sup>, and 0.06387 h<sup>-1</sup>, respectively. Thus, the velocity constants of 0.00387 h<sup>-1</sup>, 0.02794 h<sup>-1</sup>, and 0.06387 h<sup>-1</sup> are recorded for this degradation reaction at temperatures of 170 °C, 180 °C, and 190 °C, respectively.

Table 2 Linear regression results of the data in Fig. 14

Reaction temperature/°C	Regressive equation	Linear correlative coefficient
170	$y = -0.01742 + 0.00387x$	0.993
180	$y = -0.10469 + 0.02794x$	0.997
190	$y = -0.12064 + 0.06387x$	0.994

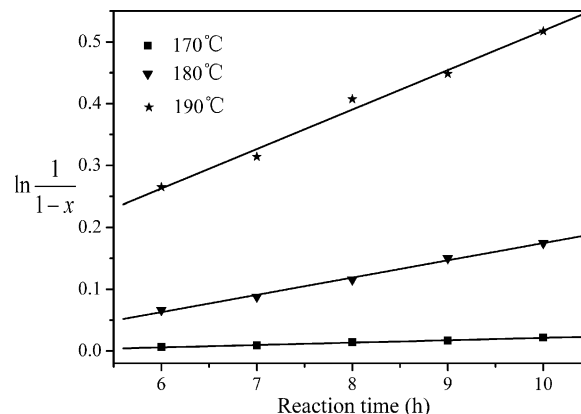


Fig. 14 Effect of reaction temperature (170 °C, 180 °C, and 190 °C) on the rate of degradation of PET in [bmim]Cl.

According to the relationship of rate constant with reaction temperature, the Arrhenius plot of the rate constant of the degradation of PET in [bmim]Cl is shown in Fig. 15. The activation energy ( $E_a$ ) for this process calculated from the slope is 232.79 kJ mol<sup>-1</sup> and the Arrhenius constant ( $A$ ) calculated from the intercept is  $1.54 \times 10^{25}$ . The kinetic equation is shown as follows:

$$r = 1.54 \times 10^{25} \exp\left(-\frac{232790}{RT}\right) c_{\text{PET}}$$

The activation energy for this reaction is higher than the values for the methanolysis, hydrolysis and glycolysis processes (49.9–85 kJ mol<sup>-1</sup>),<sup>2,26,27</sup> which are catalyzed by substances such as metal acetates. To reduce the activation energy for the degradation of PET in [bmim]Cl, the development of an effective catalyst is required.

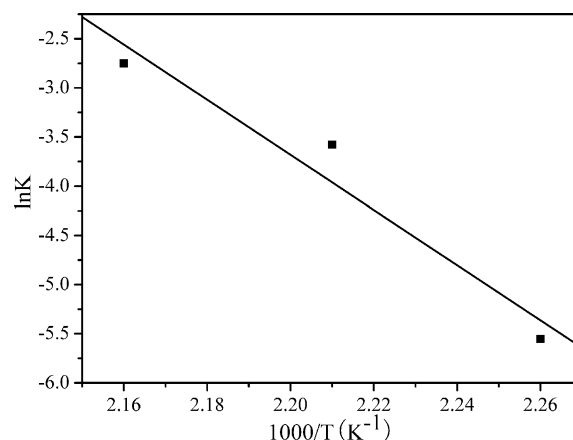


Fig. 15 Arrhenius plot of rate constant of the degradation of PET in [bmim]Cl.

#### 4. Conclusions

The degradation of poly(ethylene terephthalate) (PET) using ionic liquids proceeds easily under relatively lower pressure and temperature, with no emission of toxic substances. Another attractive feature of this reaction is that the products are easily separated from the ionic liquid by addition of water and filtration, enabling the ionic liquid to be reused in further reactions. In [bmim]Cl, the main product with a number-average molecular weight of 777 g mol<sup>-1</sup> and weight-average molecular weight of 790 g mol<sup>-1</sup> was obtained. Characterizations of the main degradation product, such as SEM/EDX, XRD, IR, DSC, and TGA, show that no chemical reaction occurred between PET and the ionic liquid, indicating that this process only referred to the breakage of the chemical bonds. This study also shows that reaction temperature is a critical factor in the degradation of PET in ionic liquids. Investigation into recycling of the ionic liquid in this process shows that the ionic liquid could be reused, with no decrease of solubility of PET in the recycled ionic liquid. The proposed mechanism of this degradation process reveals the interactions between PET and the ionic liquid. In addition, the kinetics of this reaction was investigated. Results indicate that the degradation of PET in [bmim]Cl is a first-order kinetic reaction and the activation energy is 232.79 kJ mol<sup>-1</sup>. In summary, as a kind of environmentally friendly and recyclable substance, ionic liquids have the potential to substitute traditional organic solvents in the degradation of PET.

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