

# Hydrolysis Reaction of Poly(ethylene terephthalate) Using Ionic Liquids as Solvent and Catalyst

Fusheng Liu, Xiao Cui, Shitao Yu, Zhuo Li, Xiaoping Ge

College of Chemical Engineering, Qingdao University of Science and Technology, Qingdao 266042, China

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**ABSTRACT:** The hydrolysis of poly(ethylene terephthalate) (PET) was studied using ionic liquid 1-*n*-butyl-3-methylimidazolium chloride ([Bmim][Cl]) as solvent and acid-functionalized ionic liquid 1-methyl-3-(3-sulfopropyl)-imidazolium hydrogen sulfate ([HSO<sub>3</sub>-pmim][HSO<sub>4</sub>]) as catalyst. The effects of temperature, time, and dosages of solvent and catalyst on hydrolysis results were examined. Under the optimum conditions of m(PET) : m(H<sub>2</sub>O) : m([Bmim][Cl]) : m([HSO<sub>3</sub>-pmim][HSO<sub>4</sub>]) = 3 : 4 : 6 : 0.6, reaction temperature 170°C and time 4.5 h, the conversion

of PET and the yield of terephthalic acid (TPA) were almost 100% and ≥88%, respectively. After easily separated from the product, the ionic liquids could be reused eight times without obvious decrease in the conversion of PET and yield of TPA. Hence, an environmental friendly strategy for chemical recycling of PET was developed. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 3561–3565, 2009

**Key words:** polyester; recycling; ionic liquid; hydrolysis; degradation

## INTRODUCTION

Over the last decades, polyester, poly(ethylene terephthalate), PET, consumption has tremendously increased because of its ever-increasing use in fiber manufacturing and packaging. With the rapid increase of production and consumption of PET, the problem about the treatment of waste PET is now an important issue in the global conservation of carbon resources and in the protection of petroleum resources from depletion.<sup>1</sup> There are two main methods for recycling of waste PET, which are physical and chemical ones. The physical method reuses waste PET to produce some plastic products which are of poor quality. The chemical one can recycle waste PET to produce monomers or chemical reagents.<sup>2</sup> Chemical recycling method is advantageous because it can reproduce virgin plastic products.

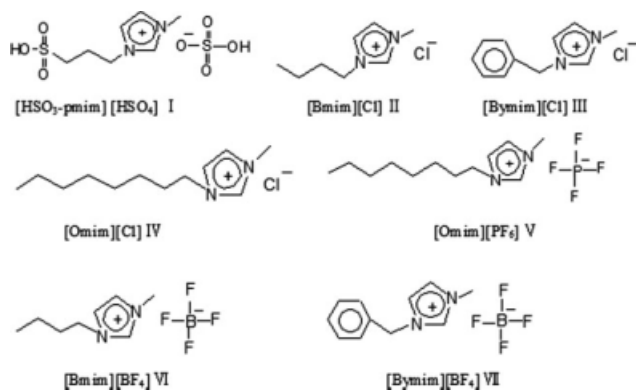
For the purpose of chemical recycling of waste PET, there have been reported a number of degradation methods,<sup>3–6</sup> among which hydrolysis of PET is an important one. However, due to the insolubility of PET in water, the hydrolysis of PET require severe conditions such as long reaction time, high temperature and pressure, and in presence of a high

amount of concentrated acids or bases<sup>7–12</sup> or even under supercritical conditions.<sup>13</sup> Large quantities of catalyst such as H<sub>2</sub>SO<sub>4</sub> or NaOH used in traditional hydrolysis of PET cannot be reused and can result in other disadvantages such as equipment corrosion, tedious workup procedure, and environmental problem. Although supercritical method can overcome some of aforementioned shortcomings, it has its own disadvantages such as severe conditions (350°C, 20–50 MPa), its application is limited. Therefore, it is necessary to explore a new approach for hydrolysis of PET.

The room temperature ionic liquid, a kind of environmental friendly solvent and catalyst, because of its adjustable physical and chemical properties, got broad attention of scholars from various fields such as synthesis, catalysis, separation, and electrochemistry.<sup>14</sup> Especially, since Cole et al.<sup>15</sup> first published an article about a functionalized ionic liquid (FIL) with strong Brønsted acidity, the research and application of various FILs have received more and more attention.<sup>16,17</sup> Among them, there were many articles on the subject of FIL used as acidic catalysts in different reactions.<sup>18,19</sup> To the best of our knowledge, no article about ionic liquid used in hydrolysis of PET has been published. In this article, we prepared several ionic liquids (Fig. 1) and used them in hydrolysis of PET. The results showed that using 1-butyl-3-methylimidazolium chloride as solvent and 1-methyl-3-(3-sulfopropyl)-imidazolium hydrogen sulfate as catalyst for hydrolysis of PET, they were of better catalytic activity and reusability.

Correspondence to: F. Liu (636390@public.qd.sd.cn).

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**Figure 1** Structures of ionic liquids prepared and used in this article.

## EXPERIMENTAL

### Chemicals and instruments

PET powder of 0.1–0.3 mm was prepared from commercial PET pellets ( $\text{Ø}2.5 \text{ mm} \times 3 \text{ mm}$ ,  $M_w = 30,000$ ). *n*-Methylimidazole (MIM, 99%), 1,3-Propane sulfone (1,3-PS, 99%), *n*-butylchloride, and other chemicals (AR) were commercially available and used without further purification.

The IR spectra were recorded by a Nicolette 510P FTIR spectrometer in the range of  $4500 \text{ cm}^{-1}$  to  $400 \text{ cm}^{-1}$ . NMR spectra were recorded on a BRUKER AV500 spectrometer and calibrated with tetramethylsilane (TMS) as the internal reference.

### Synthesis of ionic liquids

#### Synthesis of 1-*n*-butyl-3-methylimidazolium chloride

A mixture of 1-methylimidazole and *n*-butylchloride in a 1 : 1.2 molar ratio were reacted with stirring at  $70^\circ\text{C}$  for 72 h. Excess of *n*-butylchloride was distilled off at  $70^\circ\text{C}$  under reduced pressure (10 mmHg) over 2 h to obtain [Bmim][Cl] (yield 95%). 1-benzyl-3-methylimidazolium chloride ([Bymim][Cl]) and 1-*n*-octyl-3-methylimidazolium chloride ([Omim][Cl]) were prepared with a similar procedure. [Bmim][BF<sub>4</sub>], [Omim][PF<sub>6</sub>], and [Bymim][BF<sub>4</sub>] were synthesized according to the Refs.<sup>20–23</sup>. [Bmim][Cl]: IR (KBr disk,  $\text{cm}^{-1}$ ):  $\nu$ 3145, 3076, 2962, 2873, 1570, 1465, 1382, 1170, 1109, 855, 757, 653, 623. <sup>1</sup>H-NMR (500 MHz, D<sub>2</sub>O, ppm):  $\delta$  8.68 (s, 1H), 7.35 (s, 1H), 7.00 (s, 1H), 4.07 (t, 2H), 3.76 (s, 3H), 1.72 (t, 2H), 1.20 (m, 2H), 0.81(t, 3H). <sup>13</sup>C-NMR (500 MHz, D<sub>2</sub>O, ppm):  $\delta$  135.79, 123.40, 122.14, 49.22, 31.20, 35.52, 18.68, 12.54. The earlier data are the same as or similar to those reported in literature.<sup>20</sup>

#### Preparation of 1-methyl-3-(3-sulfopropyl)-imidazolium hydrogen sulfate ([HSO<sub>3</sub>-pmim][HSO<sub>4</sub>])

1,3-PS was dissolved in toluene, equivalent mole 1-methylimidazole was dropped slowly in an ice bath under vigorous stirring. The mixture was slowly heated to room temperature and stirred for 2 h after the dropping. Then the mixture was filtered to obtain white precipitate. The precipitate was washed three times with ethyl acetate and dried for 6 h at  $80^\circ\text{C}$ , giving 3-(1-methylimidazolium-3-yl)propane-1-sulfonate (MIM-PS) (yield 96.7%) as a white powder. MIM-PS was dissolved in water and equal-mole sulfuric acid was dropped slowly at room temperature under vigorous stirring. The mixture was slowly heated up to  $90^\circ\text{C}$  and stirred for 2 h, then the water was removed at  $90^\circ\text{C}$  under vacuum (6–10 mmHg), a light yellow viscous liquid [HSO<sub>3</sub>-pmim][HSO<sub>4</sub>] (yield 98%) was obtained. MIM-PS: <sup>1</sup>H-NMR (500 MHz, D<sub>2</sub>O):  $\delta$  2.26 (m, 2H), 2.86 (t, 2H), 3.83 (s, 3H), 4.30 (t, 2H), 7.38 (s, 1H), 7.46 (s, 1H), 8.70 (s, 1H). <sup>13</sup>C-NMR (125 MHz, D<sub>2</sub>O):  $\delta$  24.79, 35.46, 46.97, 47.41, 121.85, 123.5, 135.82. IR (KBr):  $\nu$ 3450, 3154, 3110, 1640, 1575, 1195, 1043, 746, 622, 532. [HSO<sub>3</sub>-pmim][HSO<sub>4</sub>]: <sup>1</sup>H-NMR (500 MHz, D<sub>2</sub>O):  $\delta$  2.11 (m, 2H), 2.71 (t, 2H), 3.71 (s, 3H), 4.16 (t, 2H), 7.25 (s, 1H), 7.32 (s, 1H), 8.53 (s, 1H). IR (LF):  $\nu$ 3437, 3157, 2970, 1722, 1653, 1574, 1230, 1172, 1029, 853, 582. The earlier data are the same as or similar to those reported in literature.<sup>20</sup>

### Hydrolysis of PET

Weighed amounts of PET ( $w_1$ ), water, and ionic liquids were added in an autoclave with a stirrer and a thermometer. The mixture was heated up to the given temperature for certain time. The reaction mixture was diluted with an equal volume of water and a precipitate was obtained and filtered. The obtained filtrate was distilled under vacuum to remove water and ethanediol, the residue which is mainly ionic liquids was reused directly as solvent and catalyst. The filter cake which is mainly composed of terephthalic acid (TPA) and unreacted PET was treated with sodium hydroxide solution to dissolve TPA and the unreacted PET ( $w_2$ ) was removed by filtration. The obtained solution is then acidified to  $\text{pH} = 2\text{--}3$  with sulfuric acid to precipitate TPA. Filtered and dried to obtain TPA product ( $w_3$ ). Conversion of PET and yield of TPA were calculated by following formula: Conversion of PET =  $[(w_1 - w_2)/w_1] \times 100\%$ . Yield of TPA =  $(w_3/w) \times 100\%$ , where  $w$  is the weight of TPA which should be obtained theoretically.

## RESULTS AND DISCUSSION

## Effect of ionic liquid solvent on hydrolysis results of PET

Table I shows the effect of ionic liquid solvent on hydrolysis results of PET. According to Table I, using ionic liquids [Bmim][Cl], [Bymim][Cl] or [Omim][Cl] as reaction medium (Table I entries 2, 4, and 6), the conversions of PET were much higher than that of without ionic liquid as solvent (Table I entry 1) and the yield of product also increased accordingly. Especially, [Bmim][Cl] (Table I entry 2) exhibited an outstanding performance for hydrolysis of PET. This is because the ionic liquids can improve the dissolubility of PET in the reaction system. It is difficult for PET to dissolve in water, so the reaction result was poor when no ionic liquid solvent was used. Moreover, we can see from Table I that the cations and anions of ionic liquids have significant effect on hydrolysis results of PET. When the anion is the same, with the increase of volume/size of the cation, the PET conversion and TPA yield were decreased. It is also found that when the anion of ionic liquid is [Cl], the conversion and yield are much better (Table I entries 2, 4, and 6) than when the anion is [BF<sub>4</sub>] (Table I entries 3 and 5) or [PF<sub>6</sub>] (Table I entry 7), especially when using [Bymim][BF<sub>4</sub>] as solvent (Table I entry 5), the hydrolysis results of PET were even poorer than without ionic liquid as solvent (Table I entry 1). It is suggested that when the anion is [Cl], the dissolubility of PET in the ionic liquid is better than that when the anion is [BF<sub>4</sub>] or [PF<sub>6</sub>]. Because [Bymim][BF<sub>4</sub>] cannot improve the dissolubility of PET in the reaction system but dilute the concentration of catalyst, the hydrolysis results of PET was even poorer than without ionic liquid as solvent. The results showed that [Bmim][Cl] was an excellent solvent for hydrolysis of PET.

**TABLE I**  
Effect of Ionic Liquid Solvent on Hydrolysis Results of PET<sup>a</sup>

Entry	Ionic liquid	Ionic liquid dosage (g)	PET conversion (%)	TPA yield (%)
1	–	0	21.1	12.9
2	[Bmim][Cl]	6	100	88.7
3	[Bmim][BF <sub>4</sub> ]	6	29.5	20.6
4	[Bymim][Cl]	6	58.6	53.3
5	[Bymim][BF <sub>4</sub> ]	6	12.6	8.2
6	[Omim][Cl]	6	45.1	35.8
7	[Omim][PF <sub>6</sub> ]	6	32.2	24.8

<sup>a</sup> PET 3 g, H<sub>2</sub>O 4 g, [HSO<sub>3</sub>-pmim][HSO<sub>4</sub>] 0.6 g, *t* = 4.5 h, *T* = 170°C.

**TABLE II**  
Effect of Catalyst on Hydrolysis Results of PET<sup>a</sup>

Entry	Solvent	Catalyst	PET conversion (%)	TPA yield (%)
1	[Bmim][Cl]	H <sub>2</sub> SO <sub>4</sub>	86.6	75.6
2	[Bmim][Cl]	[HSO <sub>3</sub> -pmim][HSO <sub>4</sub> ]	100	88.7
3	[Bmim][Cl]	–	84.1	73.6
4	H <sub>2</sub> O	–	10.5	7.2

<sup>a</sup> PET 3 g, H<sub>2</sub>O 4 g, solvent 6 g, catalyst 2 mmol, *t* = 4.5 h, *T* = 170°C.

## Effect of catalyst on hydrolysis results of PET

Table II shows the effect of catalyst on hydrolysis results of PET. When compared with the traditional catalyst sulfuric acid, the acid-FIL [HSO<sub>3</sub>-pmim][HSO<sub>4</sub>] exhibited better catalytic performance when using [Bmim][Cl] as reaction medium. This is because the ionic liquid [HSO<sub>3</sub>-pmim][HSO<sub>4</sub>] can play a role of solvent in addition to the role of catalyst. Moreover, a good hydrolysis result of PET was obtained when using [Bmim][Cl] as solvent and without any acidic catalyst (Table II entry 3), which is almost equivalent to that obtained using [Bmim][Cl] as solvent and H<sub>2</sub>SO<sub>4</sub> as catalyst (Table II entry 1). However, when using H<sub>2</sub>O as solvent and without any acidic catalyst, the hydrolysis result of PET was poor (Table II entry 4). It is well-known that the hydrolysis of PET can take place in neutral medium and proceed significantly faster in the molten state than in the solid one,<sup>24</sup> therefore, it usually runs at temperature higher than 240°C. In this article, we carried out the hydrolysis of PET only at 170°C at which PET cannot be in the molten state, so the PET conversion is only about 10% in absence of [Bmim][Cl] and acidic catalyst. The reason that hydrolysis result of PET can be significantly improved by using [Bmim][Cl] as solvent is that [Bmim][Cl] can improve the dissolving of PET in reaction mixture to some extent.

## Effect of PET particle size on hydrolysis results

Table III shows the effect of PET particle size on hydrolysis results. According to Table III, the size of

**TABLE III**  
Effect of PET Particle Size on Hydrolysis Results<sup>a</sup>

Particle size of PET	PET conversion (%)	TPA yield (%)
Ø2.5 mm × 3 mm	13.8	10.0
0.40 mm	86.1	71.6
0.15 mm	100	88.2

<sup>a</sup> PET 3 g, H<sub>2</sub>O 4 g, [Bmim][Cl] 6 g, [HSO<sub>3</sub>-pmim][HSO<sub>4</sub>] 0.6 g, *t* = 4.5 h, *T* = 170°C.

**TABLE IV**  
Effect of Reaction Conditions on Hydrolysis Results of PET<sup>a</sup>

Entry	Temperature (°C)	Solvent (g)	Catalyst (g)	PET conversion (%)	TPA yield (%)
1	150	6	0.6	18.6	7.6
2	160	6	0.6	78.5	66.8
3	170	6	0.6	100	88.8
4	170	1.5	0.6	90.5	80.6
5	170	3	0.6	96.5	85.8
6	170	6	0.4	95.6	84.8
7	170	6	0.2	89.0	78.9

<sup>a</sup> PET 3 g, H<sub>2</sub>O 4 g, reaction time 4.5 h, the solvent is [Bmim][Cl] and catalyst is [HSO<sub>3</sub>-pmim][HSO<sub>4</sub>].

PET particle was of a significant influence on hydrolysis results. With decreasing of the particle size, both the PET conversion and TPA yield increased greatly. Under the given conditions, when the particle size was Ø2.5 mm × 3 mm, PET conversion is only 13.8%. However, when the particle size became 0.15 mm, the hydrolysis of PET almost finished and TPA yield reached to 88.2%. This is because PET is a macromolecule and the dissolving of PET in reaction mixture was very slow. That is to say, the solubility of PET is the hydrolysis reaction rate determining step. Therefore, the smaller the particle size of PET, the more quicker the dissolving and hydrolysis of PET occur. On the other hand, PET with decreased particle size have increased surface area available for the reaction. Thus, the reaction rate is increased and greater PET conversion and TPA yield can be obtained.

#### Effect of reaction conditions on hydrolysis results of PET

Three different reaction temperatures were examined at 150, 160, and 170°C. The effect of temperature on PET conversion and TPA yield was shown in Table IV (Entries 1, 2, and 3). A great increase in PET conversion and TPA yield with increasing reaction temperature was observed. When temperature is 150°C, the PET conversion is only 18.6% after 4.5 h. However, under the given conditions, when the temperature was increased to 170°C, the hydrolysis of PET almost finished and the TPA yield was over 88%. The effects of the dosages of [Bmim][Cl]

and [HSO<sub>3</sub>-pmim][HSO<sub>4</sub>] on hydrolysis results of PET were also shown in Table IV. It can be seen that with the increasing of both [Bmim][Cl] dosage (Entries 4, 5, and 3) and [HSO<sub>3</sub>-pmim][HSO<sub>4</sub>] dosage (Entries 7, 6, and 3), PET conversion and TPA yield were gradually increased. Under the given conditions, when the dosages of [Bmim][Cl] and [HSO<sub>3</sub>-pmim][HSO<sub>4</sub>] were 6 g and 0.6 g, respectively, the hydrolysis of PET almost finished and the TPA yield was over 88%.

#### Reusability results of [Bmim][Cl] and [HSO<sub>3</sub>-pmim][HSO<sub>4</sub>]

The ionic liquids were easily separated from the reaction mixture and reused directly as solvent and catalyst. The reusability of the ionic liquids for the hydrolysis of PET was examined and the results were showed in Table V. The results showed that the ionic liquid system was reused for eight times without obvious decrease in its catalytic activity. The main factor which affects the reuse performance of ionic liquid is its stability under the reaction temperature and reaction fluid surroundings. The good reusability of the ionic liquid system was attributed to the stable covalent bond between the cation of ionic liquid and the alkyl sulfonic acid group, which played the main role of catalysis in the reactions. The DSC-TG data of [HSO<sub>3</sub>-pmim][HSO<sub>4</sub>] indicated that the ionic liquid was thermally stable when temperature was below 330°C.<sup>25</sup> Therefore, the ionic liquid system has excellent reusable performance in the hydrolysis of PET.

#### CONCLUSION

The kind of ionic liquids used as solvent was a significant influence on hydrolysis results of PET. Among the ionic liquids examined, [Bmim][Cl] is an excellent reaction medium. When compared with traditional catalyst sulfuric acid, acid-FIL [HSO<sub>3</sub>-pmim][HSO<sub>4</sub>] exhibited better catalytic activity. A great increase in PET conversion and TPA yield was observed when the reaction temperature increased from 150 to 170°C. Under the optimum conditions of m(PET) : m(H<sub>2</sub>O) : m([Bmim][Cl]) : m([HSO<sub>3</sub>-pmim][HSO<sub>4</sub>]) = 3 : 4 : 6 : 0.6, reaction temperature 170°C and time 4.5 h, the conversion of PET and the

**TABLE V**  
Reusability Results of [Bmim][Cl] and [HSO<sub>3</sub>-pmim][HSO<sub>4</sub>]<sup>a</sup>

Cycle	1	2	3	4	5	6	7	8
PET conversion (%)	100	100	100	100	100	100	100	100
TPA yield (%)	88.6	87.6	88.5	88.0	88.4	88.7	88.4	88.2

<sup>a</sup> PET 3 g, H<sub>2</sub>O 4 g, [Bmim][Cl] 6 g, [HSO<sub>3</sub>-pmim][HSO<sub>4</sub>] 0.6 g, *t* = 4.5 h, *T* = 170°C.

yield of TPA were almost 100% and  $\geq 88\%$ , respectively. After easily separated from the product, the ionic liquids could be reused eight times without obvious decrease in the conversion of PET and yield of TPA. Therefore, an environmental friendly approach for the hydrolysis of PET is provided.

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