

Article

The Glycolysis of Poly(ethylene terephthalate) Waste: Lewis Acidic Ionic Liquids as High Efficient Catalysts

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Abstract: Poly(ethylene terephthalate) waste from a local market was depolymerized by ethylene glycol (EG) in the presence of Lewis acidic ionic liquids [Bmim]ZnCl₃ and the qualitative analysis showed that bis(hydroxyethyl) terephthalate was the main product. Compared with ionic liquid [Bmim]Cl, the Lewis acidic ionic liquids showed highly catalytic activity in the glycolysis of poly(ethylene terephthalate) PET. Significantly, the conversion of PET and the yield of bis(hydroxyethyl) terephthalate were achieved at 100% and 83.8% with low catalyst ([Bmim]ZnCl₃) loading (0.16 wt %). Investigation also showed that the catalytic activity of [Bmim]ZnCl₃ was higher than that of [Bmim]MnCl₃. Catalyst [Bmim]ZnCl₃ can be reused up to five times and ¹H-NMR results show that the recovered catalyst is similar to the fresh one. A mechanism of the glycolysis of PET catalyzed by [Bmim]ZnCl₃ was proposed.

Keywords: poly(ethylene terephthalate); glycolysis; Lewis acidic ionic liquid; bis(hydroxyethyl) terephthalate

1. Introduction

Poly(ethylene terephthalate), commonly known as PET, is used extensively in the manufacture of fibers, photographic films and soft drinks bottled. PET production offer a tremendous convenience in our lives and daily life would be quite different without them. However, the amount of PET waste is increasing drastically and a recycling process must be established for the preservation of resources and the protection of the global environment [1].

Glycolysis of PET is one of the most widely studied processes for PET depolymerization [2–5]. However, it is very sluggish in the absence of a catalyst. Traditionally, the glycolysis of PET was carried out in the presence of metal acetates [6,7], titanium-phosphate [8], solid superacids [9], metal oxides such as NiO, Fe₂O₃ or TiO₂ [10], *etc.* However, these catalysts are toxic and/or corrosive and/or resulting in severe pollution. Therefore, the development of an environmentally benign and highly efficient catalyst for the glycolysis of PET is still important work.

Recently, ionic liquids, being considered as desirable green solvents and/or catalysts, have attracted enormous research interest because of their unique features, such as advantages of thermal stability, electrochemical stability, low flammability, and structural adjustability of the cation and the anion. It has been reported that ionic liquids were used as solvents and/or catalysts in polymer depolymerization [11,12]. In 2009, Wang [13] found that ionic liquids could catalyze the depolymerization of PET in ethylene glycol. However, long reaction time and high dosage of a catalyst were required for high conversion of PET in the presence of 1-methyl-3-butylimidazolium chloride ([Bmim]Cl). In our previous research [14], the basic ionic liquid, 1-methyl-3-butylimidazolium hydroxyl ([Bmim]OH), was synthesized and used as a catalyst for glycolysis of PET. In the present research, the basic ionic liquid [Bmim]OH, the 100% conversion of PET and the 71.2% yield of bis(hydroxyethyl) terephthalate (BHET) were obtained. However, the optimum dosage of ionic liquid was high and it achieved at 5 wt %.

More recently, Lewis acidic ionic liquids become an important topic. In 2004, Xia found ionic liquid catalytic activity in the cycloaddition of carbon dioxide. Moreover, epoxides were increased by adding Lewis acid to ionic liquid because the Lewis acidic ionic liquids were formed *in situ* [15]. In the cross-condensation of aldehyde and ketone, the yield of α,β -unsaturated ketones was more than 99% when the Lewis acidic ionic liquids were used as catalysts [16]. Herein, Lewis acidic ionic liquids were prepared and used to catalyze the glycolysis of PET in ethylene glycol (EG). The components and Lewis acidity of ionic liquids were characterized and the reaction conditions were optimized. Under the optimal reaction conditions, the Lewis acidic ionic liquid showed highly catalytic activity and high selectivity.

2. Experimental Section

2.1. Materials and Instruments

Commercial PET soft-drink bottles were procured from a local market. The bottles, after removing caps and labels, were washed, dried and cut into 1 mm $\times$ 1 mm flakes for glycolysis experiments. Their average molecular weight was measured in a 50:50 (w/w) phenol/1,1,2,2-tetrachloroethane solution at 25 °C, and the results showed that the average molecular weight of PET, which was used in

the experiments, was $1.81 \times 10^4 \text{ g} \cdot \text{mol}^{-1}$. Others chemicals were commercially available and were used without further purification.

The components of Lewis acidic ionic liquids were characterized by electrospray ionization mass spectrometry (ESI-MS) MicroTOF-QII mass instrument (Bruker, Karlsruhe, Germany) and Avance AV400 spectrometer instrument (Bruker), and their acidity were determined on the V80 FT-IR spectrometer (Bruker) in the range of 4000 to 400 cm^{-1} with using pyridine as a monitor molecular. ^1H -NMR spectra of the main product was recorded on a Avance III 400 MHz Nuclear Magnetic Resonance Spectroscopy (Bruker) and calibrated with tetramethylsilant (TMS) (Sigma-aldrich, Shanghai, China) as the internal standard.

2.2. Synthesis of Lewis Acidic Ionic Liquids

The ionic liquid, 1-methyl-3-butylimidazolium chloride ([Bmim]Cl), was synthesized according to the previous literature [17].

The mixture of equimolar amounts of [Bmim]Cl and ZnCl_2 were stirred for 8 h at room temperature in dichloromethane. Then the dichloromethane was evaporated and the ionic liquid [Bmim] ZnCl_3 was obtained as the colorless viscous liquid. Then the [Bmim] ZnCl_3 was dried in a vacuum oven at 70°C for 24 h.

The ionic liquid [Bmim] MnCl_3 was prepared with a similar procedure, and it was a pea green viscous liquid.

2.3. Glycolysis of PET Waste

A 50 mL round-bottom three-necked flask, equipped with a thermometer and a reflux condenser, was loaded certain amount of PET, ethylene glycol (EG), and a catalyst. The glycolysis reactions were carried out under atmospheric pressure at 190°C . When the glycolysis reaction was finished, the undepolymerized PET pellets were quickly separated from the liquid phase before the products was precipitated. Then an excess amount of cold distilled water was used to wash the undepolymerized PET pellets, and then the water was mixed with the product fraction. The undepolymerized PET was collected, dried, and weighed. The ionic liquid was separated from the reaction mixture and used the next time directly.

The conversion of PET is defined by Equation (1):

$$\text{Conversion Percentage of PET} = \frac{w_0 - w_1}{w_0} \times 100\% \quad (1)$$

where w_0 represents the initial weight of PET and w_1 represents the weight of undepolymerized PET. Meanwhile, the glycolysis product mixture was vigorously agitated (cold distilled water would dissolve the remaining ethylene glycol, ionic liquids, and the monomer) and filtered. The flocculate that could not be solved in cold water was a mixture of the oligomer. Floccules oligomer was separated from the mixture and not be studied further in this paper. The collected filtrate was concentrated to about 40 mL and then was stored in a refrigerator at 0°C for 24 h. White crystalline flakes were formed in the filtrate, and it was separated and dried. This white crystalline was the main product of glycolysis and its yield was defined by Equation (2):

$$\text{Yield (\%)} = \frac{\text{Actual production}}{\text{Theoretical production}} \times 100\% \quad (2)$$

3. Results and Discussion

3.1. Characterization of Ionic Liquids and Product

3.1.1. Determination of the Component of Ionic Liquids

The components of the ionic liquids were characterized by ESI-MS, and the results were shown in Figure 1. From Figure 1a,c, the positive mode ESI mass spectrum showed a base peak at $m/z = 138.9$ and it was corresponded to the $[\text{Bmim}]^+$ cation of the ionic liquids. In Figure 1b, the minus mode ESI mass spectrum of $[\text{Bmim}]\text{ZnCl}_3$ showed the peak up to m/e 170.5 with intensity almost 100% and it indicated that the anion of Zn^{2+} -containing ionic liquid was ZnCl_3^- . The peaks at m/e 161.6 and 159.6, which were caused by the existence of chloride isotope, were shown in Figure 1d and they suggested that the MnCl_3^- was the main component in the Mn^{2+} -containing ionic liquid.

Figure 1. Electrospray ionization (ESI)-Mass spectrum of catalysts in PET glycolysis: (a) Cation of $[\text{Bmim}]\text{ZnCl}_3$; (b) Anion of $[\text{Bmim}]\text{ZnCl}_3$; (c) Cation of $[\text{Bmim}]\text{MnCl}_3$; and (d) Anion of $[\text{Bmim}]\text{MnCl}_3$.

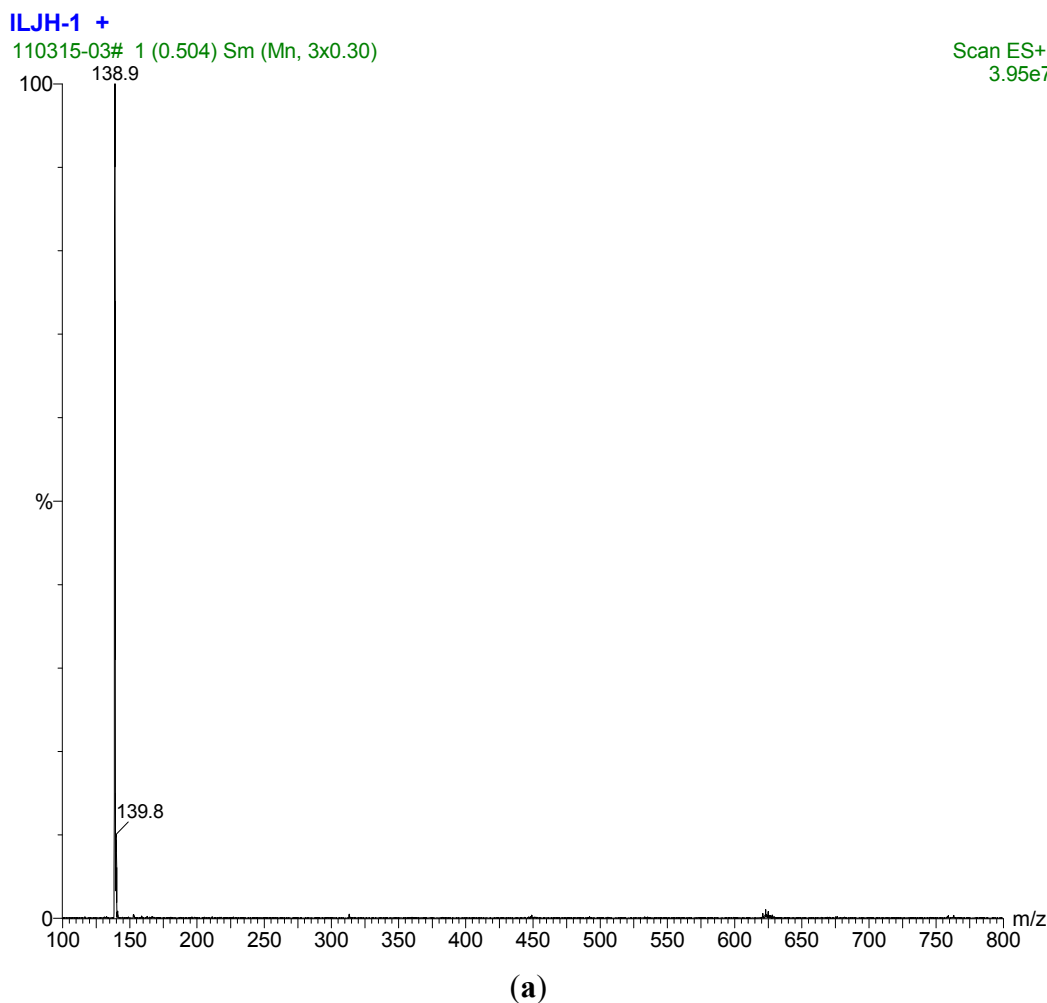


Figure 1. Cont.

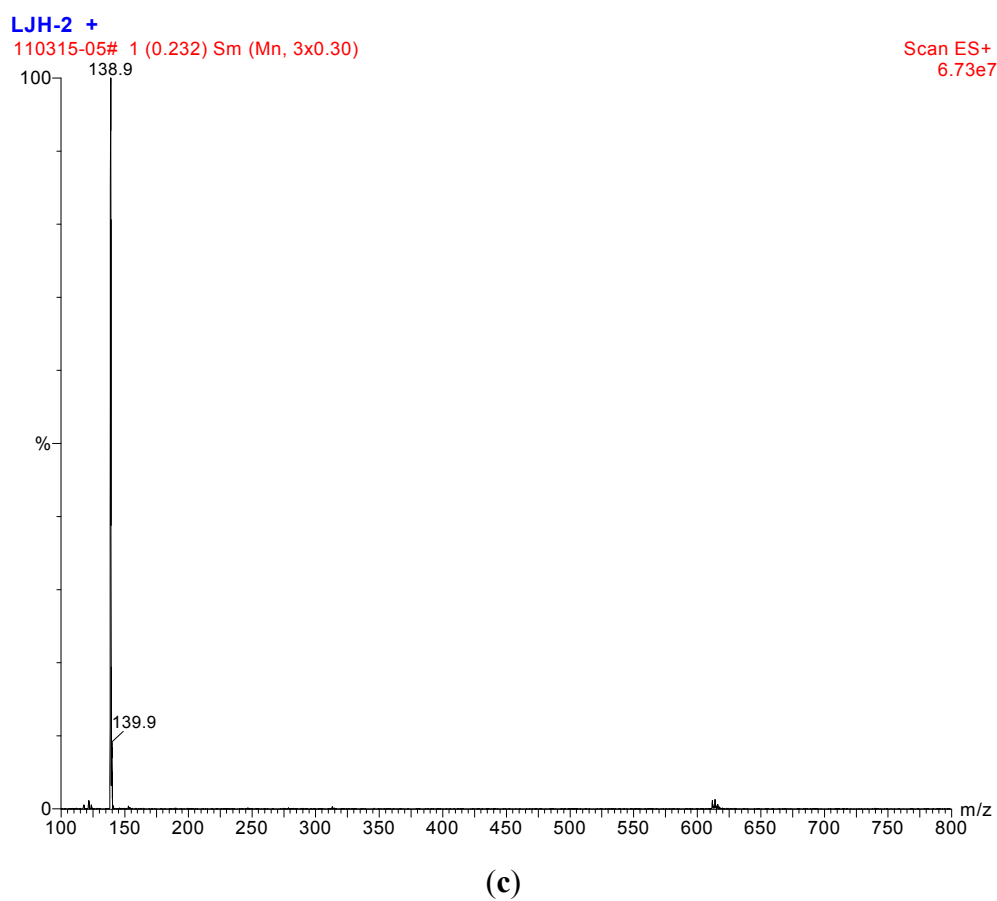
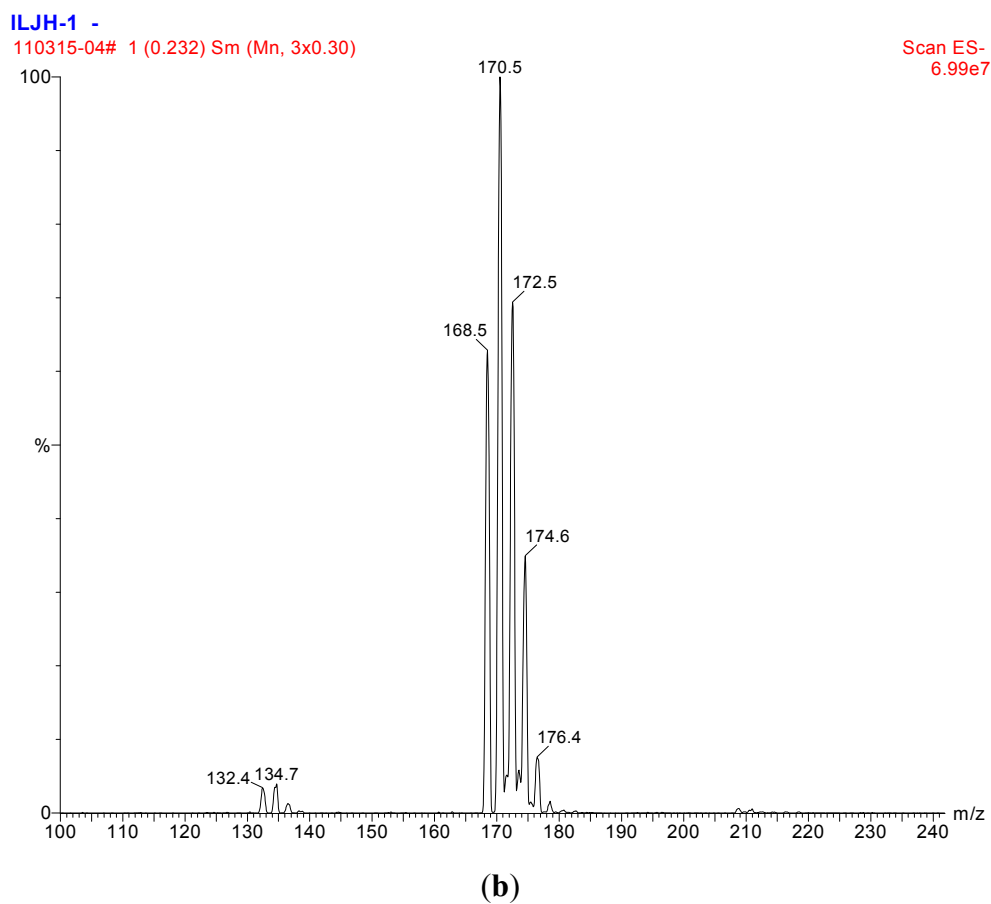
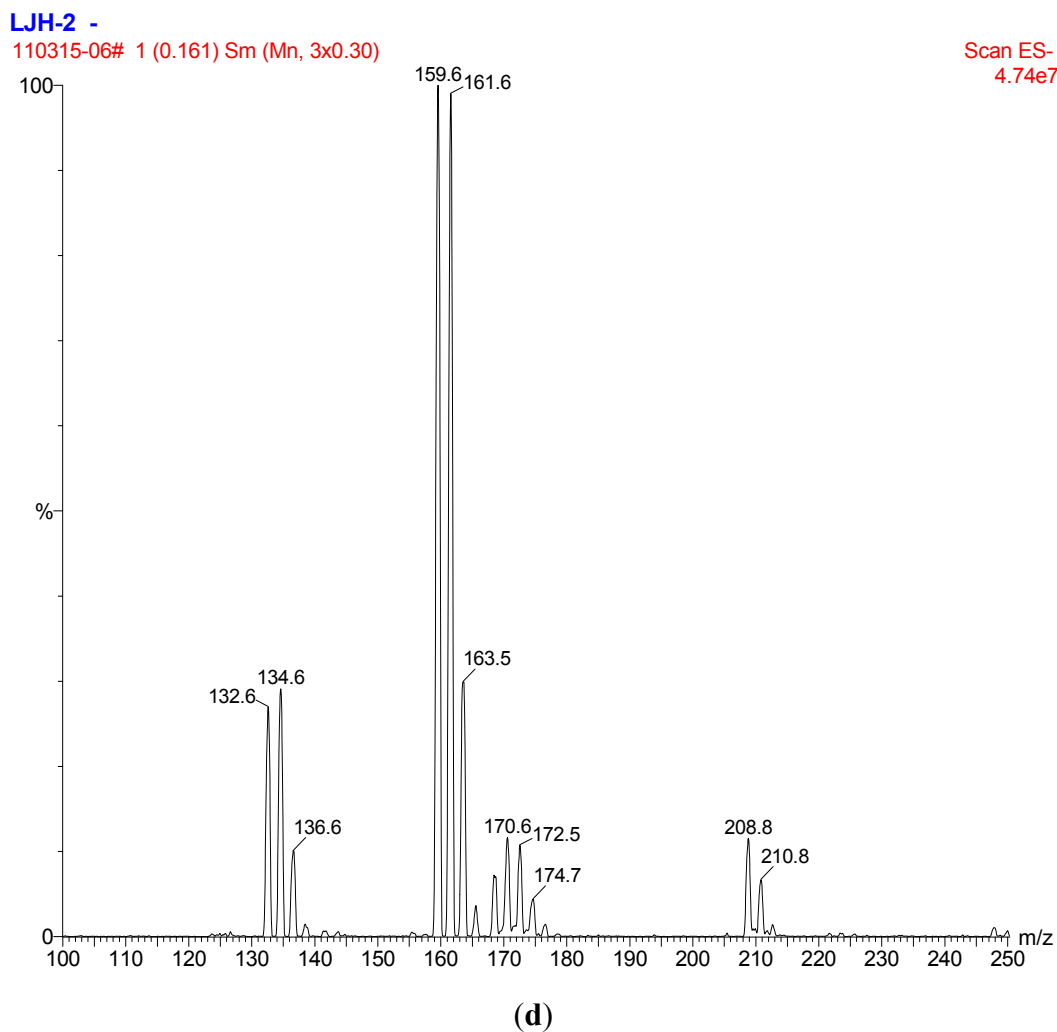
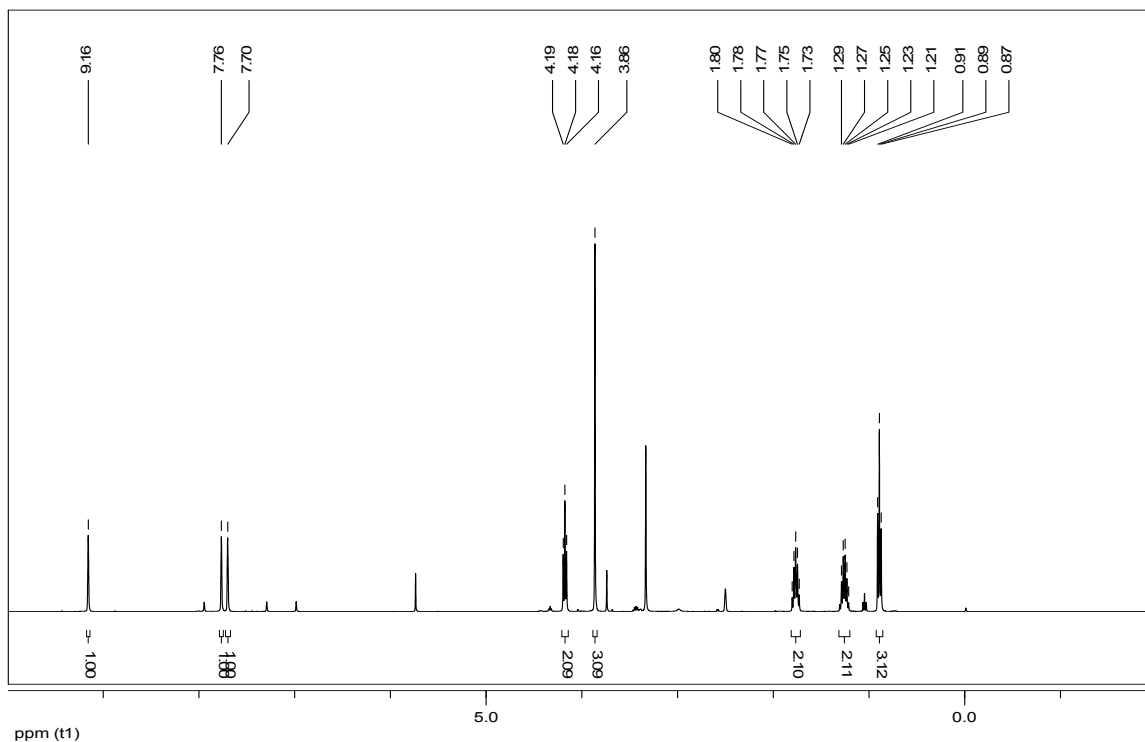


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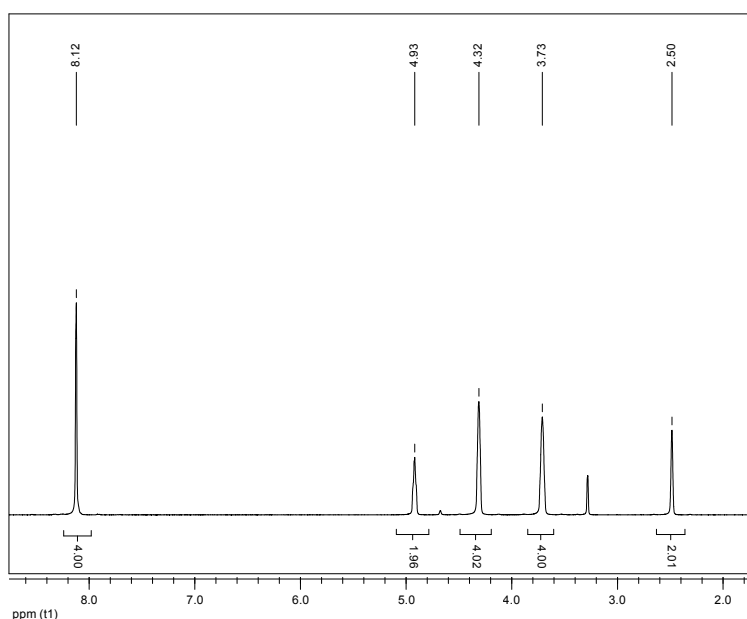


In order to determine the purity, [Bmim]ZnCl₃ was characterized by ¹H-NMR spectra (Figure 2). All the peaks were assigned: δ (ppm) 9.16 (s, N-CH-N), 7.77 (s, CH₃-N-CH-CH), 7.70 (s, CH₃-N-CH-CH) 4.18 (t, N-CH₂), 3.86 (s, N-CH₃), 1.75 (m, N-CH₂-CH₂), 1.25 (m, CH₂-CH₃), 0.89 (t, CH₂-CH₃). This result showed that the purity of [Bmim]ZnCl₃ was prepared successfully.

Figure 2. ^1H -NMR spectrum of $[\text{Bmim}]\text{ZnCl}_3$.

3.1.2. Qualitative Analysis of Glycolysis Product

^1H -NMR spectra of this fraction are reproduced in Figure 3 for illustration using $\text{DMSO-}d_6$ as a solvent. The signal at δ 8.12 ppm indicated the four aromatic protons of the benzene ring and the peak of the protons in the hydroxyl was shown at δ 4.93 ppm. The signals at δ 4.32 and 3.73 ppm were assigned to the methylene protons of COO-CH_2 and $\text{CH}_2\text{-OH}$. The triplet of DMSO appeared at δ 2.50 ppm [18], and the ^1H -NMR spectra also accord very well with those reported in the literature [19]. The result of ^1H -NMR indicated that the main product was BHET in the glycolysis of PET.

Figure 3. ^1H -NMR spectrum of main glycolysis product.

3.2. The Effects of Catalysts on the Glycolysis of PET

The catalytic performances of different catalysts were investigated and the results were shown in Table 1.

Table 1. Effect of catalysts on the glycolysis reaction of PET ^a.

Entry	Catalyst	Dosage of catalyst (wt %)	Time (h)	PET conversion (%)	BHET yield ^b (%)
1	[Bmim]Cl	5.00	2	3.3	—
2	[Bmim]Cl	5.00	4	35.4	8.8
3	[Bmim]Cl	5.00	6	57.2	14.0
4	[Bmim]Cl	5.00	8	100	57.1
5	[Bmim]ZnCl ₃	5.00	2	100	82.6
6	[Bmim]ZnCl ₃	2.50	2	100	83.0
7	[Bmim]ZnCl ₃	1.25	2	100	84.9
8	[Bmim]ZnCl ₃	0.63	2	100	83.4
9	[Bmim]ZnCl ₃	0.31	2	100	79.5
10	[Bmim]ZnCl ₃	0.16	2	52.2	36.0
11	ZnCl ₂	2.18 ^c	2	100	78.6
12	[Bmim]MnCl ₃	5.00	2	100	83.3
13	[Bmim]MnCl ₃	0.31	2	64.5	38.2

Notes: ^a reaction conditions: PET (2.0 g), EG (22.0 g), reaction temperature 190 °C; ^b The isolated yield;

^c The content of catalyst ZnCl₂ in the same amount of [Bmim]ZnCl₃ (Entry 5 tagged).

Firstly, [Bmim]Cl was used as a catalyst in the glycolysis of PET (Table 1, entries 1–4). The conversion of PET was achieved 3.3% in the presence of 5 wt % [Bmim]Cl, but no BHET was founded within 2 h (Table 1, entry 1). When the reaction time was prolonged, the conversion of PET was increased and the 8.8% BHET was given when the reaction was prolonged to 4 h (Table 1, entry 2). When the reaction time was prolonged to 8 h, the 100% conversion of PET and 57.1% yield of BHET were obtained in the presence of [Bmim]Cl (Table 1, entries 2–4).

Compared with [Bmim]Cl, the rate of depolymerization and the yield of BHET significantly increased in the presence of metal-containing ionic liquids. When the reaction time was shorted to 2 h, the conversion of PET in the glycolysis arrived at 100% in the presence of 5 wt % [Bmim]ZnCl₃, and the BHET yield rose to 82.6% (Table 1, entry 5), respectively. In the literature, ZnCl₂ showed better catalytic activity [20], but when using ZnCl₂ as a catalyst, the PET was glycolized completely, and the yield of BHET was decreased to 78.6% (Table 1, entry 11).

When [Bmim]ZnCl₃ was alternated by [Bmim]MnCl₃, the similar results were given under the same reaction conditions (Table 1, entry 12). These results indicated that the catalytic activity of metal-containing ionic liquids was higher than that of [Bmim]Cl. So, the Lewis acidic metal salt additive was necessary for increasing the catalytic activity of ionic liquids in the glycolysis of PET.

3.3. Effects of Reaction Parameters on the Glycolysis Reaction of PET

3.3.1. Effect of Catalyst Concentration

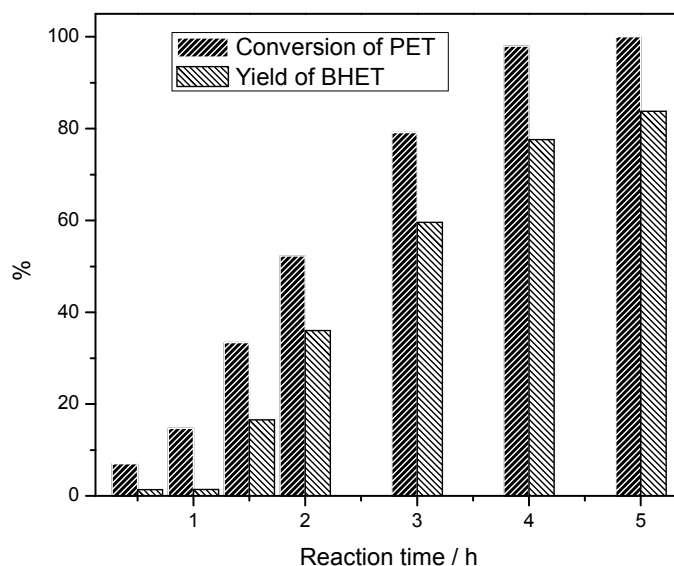
In our experiment, the effects of the catalyst loading were investigated and the results were shown in Table 1. It can be seen that similar catalytic performance was observed when the 5.00 wt % [Bmim]ZnCl₃ or [Bmim]MnCl₃ was used as a catalyst (Table 1, entries 5 and 12). However, by decreasing the catalytic dosage to 0.31 wt %, the catalytic activity of [Bmim]ZnCl₃ was higher than that of [Bmim]MnCl₃ (Table 1, entries 9 and 13). This was probably due to the different Lewis acidic ionic liquids that were formed by using the different Lewis acid ZnCl₂ and MnCl₂.

From Table 1, it also can be seen that the conversion of PET was 100% for 8.0 h at 190 °C in the presence of [Bmim]ZnCl₃ when the catalytic loading was more than 0.31 wt %, but the yield of BHET decreased by decreasing the catalyst loading to 0.31 wt %. The 52.2% conversion of PET and 36.0% yield of BHET were obtained when the catalyst concentration was decreased to 0.16 wt % (Table 1, entry 10).

3.3.2. Effect of Reaction Time

In order to decrease the loading of the catalyst, the glycolysis of PET was carried out with using the 0.16 wt % [Bmim]ZnCl₃ as a catalyst, and the results were shown in Figure 4. From Figure 4, it can be seen that the conversion of PET and the yield of BHET were increased by prolonging the reaction time. In the presence of 0.16 wt % [Bmim]ZnCl₃, the conversion of PET was 7.04% within 0.5 h and the BHET yield rose to 1.33%. When the reaction time was prolonged to 5.0 h, PET was glycolized completely and the yield of BHET was 83.8%. It was noticeable that the selectivity of BHET increased with prolonged reaction times. So, the using Lewis acidic ionic liquid as a catalyst was beneficial to increasing the yield and the selectivity for BHET in the glycolysis of PET.

Figure 4. The effects of reaction time on the PET glycolysis with 0.16 wt % catalysts.

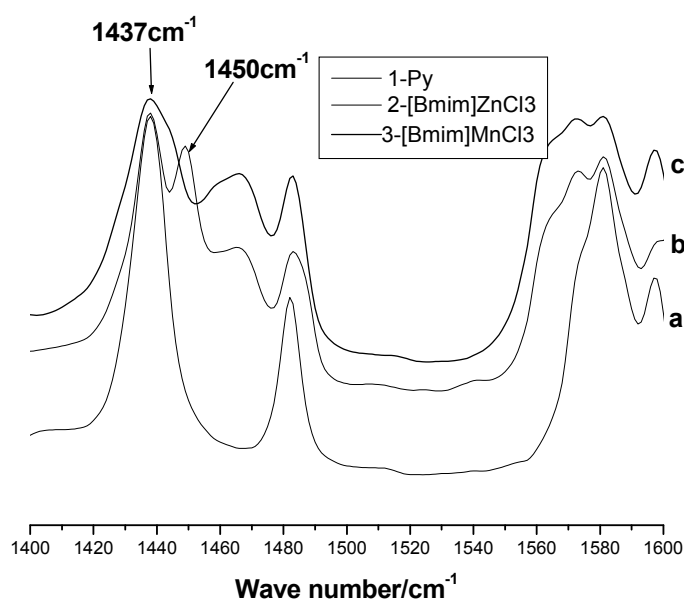


3.3.3. Effects of Lewis Acidity of Ionic Liquids

Previous research [21] showed that the acidity of ionic liquids could usually improve catalytic performance, accelerate reaction rate and provide higher yield for esterification reactions. So, the acidity of ionic liquids was determined and the results were showed in Figure 5.

The acidity of ionic liquid was characterized by FT-IR with using pyridine as a probe molecule by monitoring the bands in the range of $1400\text{--}1700\text{ cm}^{-1}$ arising from its ring vibration modes [22]. Neat pyridine [Figure 5(a)] shows a well resolved single band at 1437 cm^{-1} and the presence of a band near 1450 cm^{-1} is indicative of pyridine coordinated to Lewis acid sites. In the present work, pyridine was added to ionic liquids and the change of the bands was monitored by FT-IR. From the Figure 5(b), it can be seen that the band was shifted to 1450 cm^{-1} in the presence $[\text{Bmim}]\text{ZnCl}_3$ which consistent with the coordination of pyridine at Lewis acid sites, and it indicated that Lewis acidity was existent in the ionic liquid $[\text{Bmim}]\text{ZnCl}_3$. When pyridine was added into the $[\text{Bmim}]\text{MnCl}_3$ [Figure 5(c)], the neat pyridine showed a well resolved single band at 1437 cm^{-1} which was essentially unchanged. This result indicated that $[\text{Bmim}]\text{MnCl}_3$ was no Lewis acidity. From this experiment, it was confirmed that the catalytic activity of ionic liquid was strongly affected by its Lewis acid in the glycolysis of PET.

Figure 5. FTIR spectra of: (a) pure pyridine; (b) pyridine and $[\text{Bmim}]\text{ZnCl}_3$; and (c) pyridine and $[\text{Bmim}]\text{MnCl}_3$.



3.3.4. Reusability Test of Lewis Acidic Ionic Liquid

In order to develop the green and inexpensive catalytic system, the recyclability of $[\text{Bmim}]\text{ZnCl}_3$ was studied in the glycolysis of PET (Figure 6). In every run, the catalyst was separated from the reaction mixture by distillation, and directly reused for subsequent reaction under the optimized reaction conditions. From Figure 6, it can be clearly seen that the catalyst could be reused at least five times and no significant drop in the conversion of PET and the yield of BHET was observed.

Moreover, we characterized the recovered catalyst by NMR (Figure 7). It was found that the recovered catalyst showed results similar to those of the fresh one. It can be deduced that this catalyst was stable in the glycolysis of PET.

Figure 6. Recycling of [Bmim]ZnCl₃ in the glycolysis of PET.

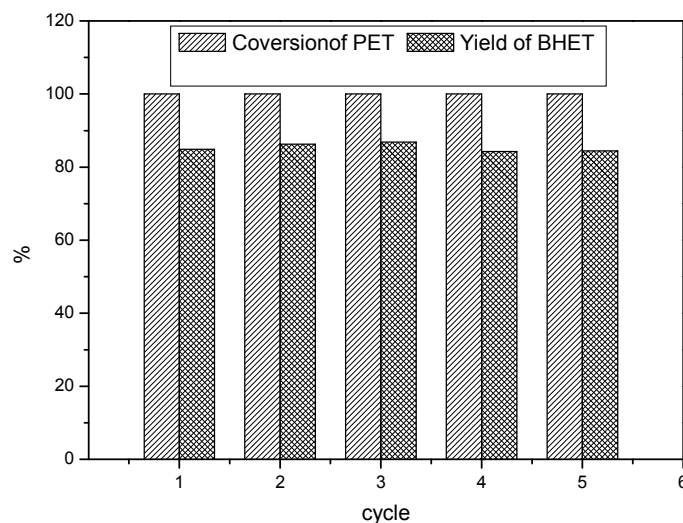
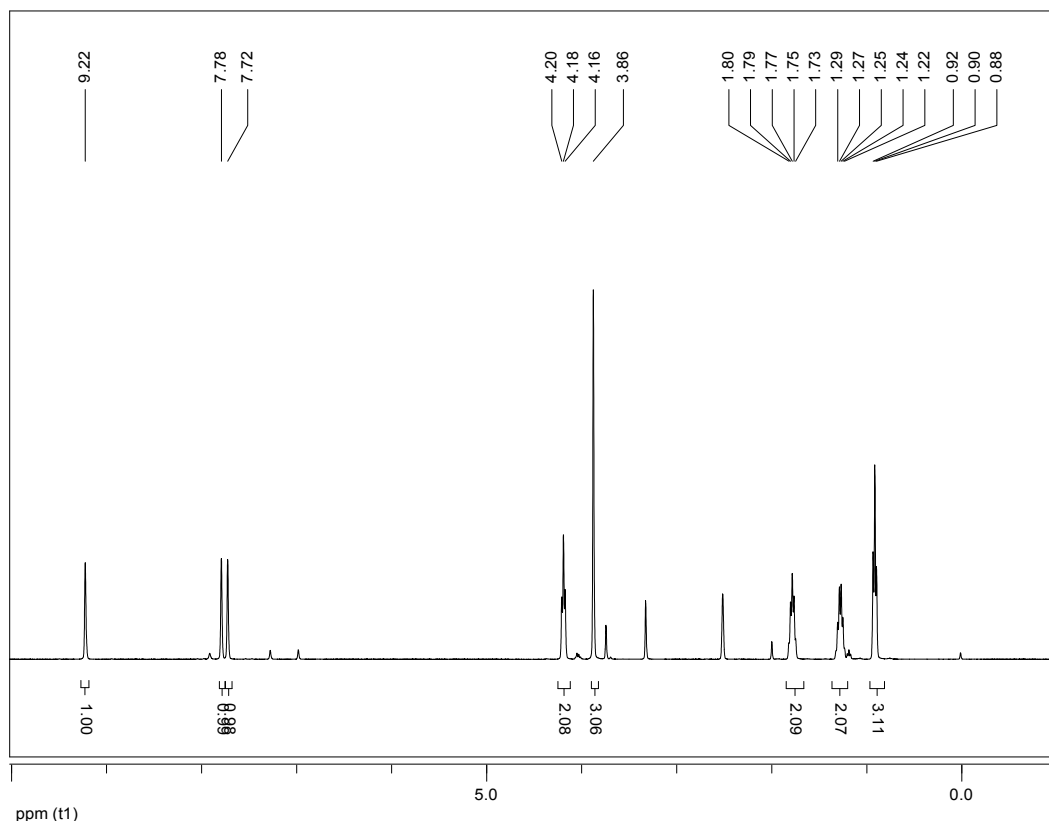
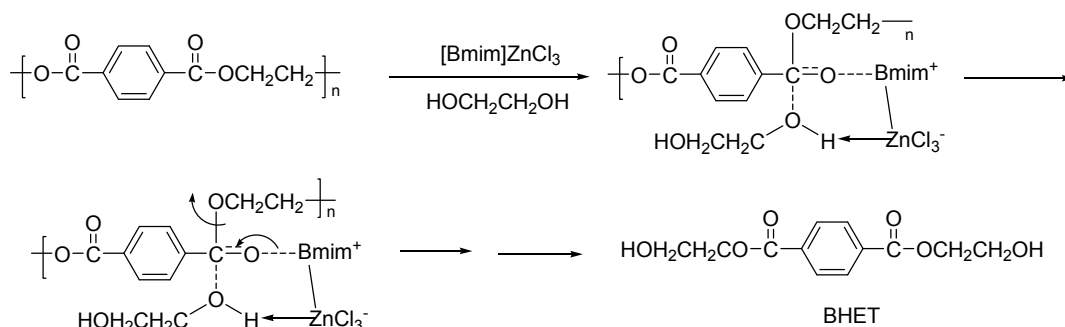


Figure 7. NMR spectra of recovered [Bmim]ZnCl₃.



3.3.5. Possible Mechanism for the Glycolysis of PET in the Presence of [Bmim]ZnCl₃

Based on previous literatures [9] and the results of this study, a reasonable catalytic cycle was proposed for the glycolysis over the [Bmim]ZnCl₃ catalyst (Scheme 1).

Scheme 1. Mechanism of the glycolysis of PET catalyzed by [Bmim]ZnCl₃.

The cation in the catalyst interacts with the carbonyl oxygen (C=O) in the ester, and then the oxygen in the hydroxyl of ethylene glycol attacks the carbon cation of the ester group, forming a tetrahedral intermediate. Afterwards, the hydrogen leaves the ethylene glycol. Then, the electrons on the oxygen in –OM transfer form C=O. The acyl-oxygen cleaves, and the –OCH₂CH₂– group leaves, combining with H⁺ to form HOCH₂CH₂–. These transfer processes repeat, and BHET monomer is formed.

4. Conclusions

In summary, the ionic liquids [Bmim]ZnCl₃ and [Bmim]MnCl₃ were synthesized by the reaction of [Bmim]Cl and ZnCl₂ or MnCl₂, and were characterized by the NMR, ESI-MS and FT-IR. When they were used as catalysts for glycolysis of PET, an excellent conversion of PET and yield of BHET were obtained. Meanwhile, the structure of the main reaction product, BHET, was determined by ¹H-NMR spectroscopy. As a catalyst, [Bmim]ZnCl₃ showed the highest catalytic activity for glycolysis of PET under the optimal reaction conditions. Furthermore, the loading of Lewis acidic ionic liquids catalyst was much lower than [Bmim]Cl with 100% conversion of PET. By analyzing of the FT-IR with using pyridine as a probe molecule, Lewis acidity of ionic liquid affected its catalytic activity in the PET glycolysis. Fresh and recovered [Bmim]ZnCl₃ was characterized and ¹H-NMR results showed that the catalyst is stable and reusable in the glycolysis of PET.

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Conflicts of Interest

The authors declare no conflict of interest.

References

1. Hayden, K.W.; Jaimys, A.; Russell, J.C.; Elena, P.I. Plastic degradation and its environmental implications with special reference to poly(ethylene terephthalate). *Polymers* **2013**, *5*, 1–18.
2. Hideki, K.; Masa-aki, O.; Kazuo, S.; Miura, H. Methanolysis of polyethylene terephthalate (PET) in the presence of aluminium triisopropoxide catalyst to form dimethyl terephthalate and ethylene glycol. *Polym. Degrad. Stab.* **2003**, *79*, 529–533.
3. Chen, J.W.; Chen, L.W. The glycolysis of poly(ethylene terephthalate). *J. Appl. Polym. Sci.* **1999**, *73*, 35–40.
4. Xi, G.X.; Lu, M.X.; Sun, C. Study on depolymerization of waste polyethylene terephthalate into monomer of bis(2-hydroxyethyl terephthalate). *Polym. Degrad. Stab.* **2005**, *87*, 117–120.
5. Firas, A.; Dumitru, P. Recycling of PET. *Eur. Polym. J.* **2005**, *41*, 1453–1477.
6. Ghaemy, M.; Mossaddegh, K. Depolymerisation of poly(ethylene terephthalate) fibre wastes using ethylene glycol. *Polym. Degrad. Stab.* **2005**, *90*, 570–576.
7. Baliga, S.; Wong, W.T. Depolymerization of poly(ethylene terephthalate) recycled from post-consumer soft-drink bottles. *J. Polym. Sci. A Polym. Chem.* **1989**, *27*, 2071–2082.
8. Troev, K.; Granchrov, G.; Tsevi, R.; Gitsov, I. A novel catalyst for the glycolysis of poly(ethylene terephthalate). *J. Appl. Polym. Sci.* **2003**, *90*, 1148–1152.
9. Wang, H.; Yan, R.Y.; Li, Z.X.; Zhang, X.P.; Zhang, S.J. Fe-containing magnetic ionic liquid as an effective catalyst for the glycolysis of poly(ethylene terephthalate). *Catal. Commun.* **2010**, *11*, 763–767.
10. Yoshioka, T.; Handa, T.; Grause, G.; Lei, Z.G.; Inomata, H.; Mizoguchi, T. Effects of metal oxides on the pyrolysis of poly(ethylene terephthalate). *J. Anal. Appl. Pyrolysis* **2005**, *73*, 139–144.
11. Liu, F.S.; Cui, X.; Yu, S.T.; Li, Z.; Ge, X.P. Hydrolysis reaction of poly(ethylene terephthalate) using ionic liquids as solvent and catalyst. *J. Appl. Polym. Sci.* **2009**, *114*, 3561–3565.
12. Wang, H.; Li, Z.X.; Liu, Y.Q.; Zhang, X.; Zhang, S.J. Degradation of poly(ethylene terephthalate) using ionic liquids. *Green Chem.* **2009**, *11*, 1568–1575.
13. Wang, H.; Liu, Y.Q.; Li, Z.X.; Zhang, Z.P.; Zhang, S.J.; Zhang, Y.Q. Glycolysis of poly(ethylene terephthalate) catalyzed by ionic liquids. *Eur. Polym. J.* **2009**, *45*, 1535–1544.
14. Yue, Q.F.; Wang, C.X.; Zhang, L.N.; Ni, Y.; Jin, Y.X. Glycolysis of poly(ethylene terephthalate) (PET) using basic ionic liquids as catalysts. *Polym. Degrad. Stab.* **2011**, *96*, 399–403.
15. Li, F.W.; Xiao, L.F.; Xia, C.G.; Hu, B. Chemical fixation of CO₂ with highly efficient ZnCl₂/[BMIm]Br catalyst system. *Tetrahedron Lett.* **2004**, *45*, 8307–8310.
16. Qiu, R.H.; Qiu, Y.M.; Yin, S.F.; Xu, X.H.; Luo, S.L.; Au, C.T.; Wong, W.Y.; Shimada, S. Highly efficient and selective synthesis of (*E*)- β -unsaturated ketones by crossed condensation of ketones and aldehydes catalyzed by an air-stable cationic organobismuth perfluorooctanesulfonate. *Adv. Synth. Catal.* **2010**, *352*, 153–162.
17. Pierre, B.; Ana-Paula, D.; Nicholas, P.; Kuppuswamy, K.; Michael, G. Hydrophobic highly conductive ambient-temperature molten salts. *Inorg. Chem.* **1996**, *35*, 1168–1178.
18. Gottlieb, H.E.; Kotlyar, V.; Nudelman, A. NMR chemical shifts of common laboratory solvents as trace impurities. *J. Org. Chem.* **1997**, *62*, 7512–7515.

19. Sharma, R.K.; Rawat, D.; Pant, P. Synthesis, characterization and catalytic behaviour of silica supported zinc salicylaldehyde complex. *J. Macromol. Sci. A Pure Appl. Chem.* **2008**, *45*, 394–399.
20. Pingale, N.D.; Palekar, V.S.; Shukla, S.R. Glycolysis of postconsumer polyethylene terephthalate waste. *J. Appl. Polym. Sci.* **2010**, *115*, 249–254.
21. Bao, Q.; Qiao, K.; Tomida, D.; Yokoyama, C. 1-Methylimidazolium chlorosulfate ([HMIm]SO₃Cl): A novel ionic liquid with dual Brønsted-Lewis acidity. *Chem. Lett.* **2010**, *39*, 728–729.
22. Yang, Y.L.; Kou, Y. Determination of the Lewis acidity of ionic liquids by means of an IR spectroscopic probe. *Chem. Commun.* **2004**, 226–227.

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