



# Chemical Recycling of Bio-based Poly(3-hydroxybutyrate) Wastes Under Methanolysis Condition Catalyzed by Fe-Containing Magnetic Ionic Liquid

Xiuyan Song<sup>1,2</sup> · Hui Wang<sup>3</sup> · Chan Wang<sup>1</sup> · Fusheng Liu<sup>1</sup> · Shitao Yu<sup>1</sup> · Shiwei Liu<sup>1</sup> · Ziyang Song<sup>2</sup>

Published online: 18 February 2019

© Springer Science+Business Media, LLC, part of Springer Nature 2019

## Abstract

An efficient method for chemical recycling of bio-based polymers Poly(3-hydroxybutyrate) (PHB) wastes was established from the perspective of biorefinery. This methanolysis reaction archived successfully transformation PHB into corresponding monomer catalyzed by imidazolium-based Fe-containing ionic liquid, 1-butyl-3-methylimidazolium tetrachloroferrate ([Bmim]FeCl<sub>4</sub>). Compared with FeCl<sub>3</sub> or ionic liquid [Bmim]Cl, this ionic liquid showed excellent catalytic performance. The obtained product methyl 3-hydroxybutyrate (M3HB) with high purity, as a chemical raw material, can be used in various fields. Investigation also indicated that the thermal stability of catalyst played an important role in this reaction, this ionic liquid could be reused for six times without apparent decrease in the conversion of PHB or yield of M3HB. Furthermore, the effects of experimental factors, such as temperature, time, catalyst dosage and methanol dosage on the methanolysis results of PHB were examined. Kinetic study indicated that this reaction was first-order kinetic reaction with activation energy of 27.44 kJ/mol. Additionally, a possible mechanism of PHB methanolysis was proposed.

**Keywords** Chemical recycling · Fe-containing magnetic ionic liquid · Catalysis · Methanolysis

## Introduction

With the development of economy and technology, plastic products have been widely used in all aspects, which makes our lives convenient, and at the same time leads to the serious social and environmental problems [1]. Poly(3-hydroxybutyrate) (PHB) or poly( $\beta$ -hydroxybutyrate) as a kind of biodegradable and biocompatible materials [2], can

be used in food packages, biomedical, tissue engineering and many other fields [3–6]. In the near future, PHB will have great potential to replace the traditional plastics. With the rapid growth of PHB materials production and consumption, PHB wastes will become more and more. Although PHB can be degraded naturally in the environment, its degradation period is much longer. Therefore, the technology of chemical recycling PHB has attracted much more attention by researchers [7, 8].

Recently, various methods for recycling PHB, such as pyrolysis [8–10], hydrolysis [11–14] and alcoholysis [15–18], have been reported in many previous references. However, it was very difficult to recover the corresponding monomers or high value-added products in those reported methods. Such as thermal pyrolysis [8], the reaction temperature was carried out from 170 to 300 °C, the obtained products were mixtures, including crotonic acid (CA) and well-defined oligomers and cyclic oligomers. The hydrolysis of PHB does not need high temperature and high pressure, but a large amount of inorganic acid or alkali was used as catalyst. They need to be neutralized, washed and other operations, which led to process cumbersome, equipment corrosion, environmental pollution and other issues [13]. Moreover, these catalysts cannot be reused for the

**Electronic supplementary material** The online version of this article (<https://doi.org/10.1007/s10924-018-1347-8>) contains supplementary material, which is available to authorized users.

✉ Fusheng Liu  
liufusheng63@sina.com

<sup>1</sup> College of Chemical Engineering, Qingdao University of Science and Technology, Qingdao 266042, China

<sup>2</sup> State Key Laboratory Base of Eco-chemical Engineering, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, China

<sup>3</sup> College of Chemistry and Pharmaceutical Sciences, Qingdao Agricultural University, Qingdao 266109, China

next time [14]. Enzyme was used as catalyst in degradation of PHB had been reported [19, 20], but the final products containing a large of enzyme, which was very difficult to separate. Compared with the above mentioned methods, photocatalytic degradation of PHB could overcome those shortcomings [21, 22], but its degradation period was too long and the composition of the obtained product was also complex.

Ionic liquids (ILs) as a new kind of medium and soft functional materials, they are developed under the framework of “green chemistry”. Due to their unique properties [23–25], such as non-volatile, low flammability, excellent thermal stability, good solubility, adjustable physical and chemical properties, they have been widely used in many chemical reactions, for instance organic synthesis [26, 27], catalysis [28], extraction [29, 30], electrochemistry [31, 32] and other fields. Recently, ILs have been used to catalyze the degradation of polymers, such as polyethylene (PE) [33], polyamide (PA) [34], poly(ethylene terephthalate) (PET) [35–37], polycarbonate (PC) [38, 39] and poly(lactic acid) (PLA) [40, 41]. Science 2010, metal-containing ILs have attracted much more attention by some researchers. Wang et al. [35] and Yue et al. [36] used Fe or Zn-containing ILs, Al-Sabagh et al. [37] reported Cu- and Zn-acetate containing ILs in the PET glycolysis, which also showed higher catalytic activity. In this study, a series of imidazolium-based Fe-containing magnetic ILs with different molar fraction were synthesized, and used as catalysts in the methanolysis of PHB, a higher conversion of PHB and yield of M3HB were obtained. Compared with the Brønsted acidic IL 1-methyl-3-(3-sulfopropyl)-imidazolium hydrogen sulfate ([HSO<sub>3</sub>-pmim][HSO<sub>4</sub>]) [42], 1-butyl-3-methylimidazolium tetrachloroferrate ([Bmim]FeCl<sub>4</sub>) showed better catalytic activity in the methanolysis of PHB. The influences of reaction parameters on the conversion of PHB and the yield of M3HB were discussed in detail. Additional, the mechanism of methanolysis was proposed, and the reaction kinetics was also investigated.

## Experimental

### Materials and Instruments

Pure PHB pellets (3.0 mm × 2.8 mm × 3.0 mm) were obtained from Ningbo Tianan biological material Co. Ltd., China. The weight-average molecular weight, number-average molecular weight and PDI of PHB were 430,000 g/mol, 204,000 g/mol and 2.11 respectively, which were measured by GPC (Waters-515) in chloroform solution at 25 °C. *N*-Methyl imidazole (MIM), and anhydrous ferric chloride (FeCl<sub>3</sub>) were

purchased from Shanghai McLean Biochemical Science and Technology Co. Ltd., China. Methanol was purchased from Chinese Medicine Group Chemical Reagent Co. Ltd. All other materials (AR) were used without any further purification.

Varian CP-3800 gas chromatography (GC) with an ENX5 capillary chromatography column (30 × 0.32 mm, 0.25 μm) and a FID hydrogen detector was used for GC analysis. All infrared spectroscopy measurements were performed on a Bruker Tensor-27 Fourier transforms infrared spectroscopy (FT-IR) spectrometer in the range of 4000–400 cm<sup>-1</sup> using KBr optics and liquid film. Raman spectra were recorded using a Thermo Scientific DXR Raman Microscope. Mass spectrum was measured by Bruker Maxis Quadruple Ultra-high Resolution Time-of-Flight mass instrument (Q-TOF MS). <sup>1</sup>H NMR was recorded on a Bruker AV 500 Digital NMR Spectrometer using D<sub>2</sub>O as solvent. Thermogravimetric analysis (TGA) curves were recorded by Mettler-Toledo STAR System TGA/DSC 1SF thermogravimetric analyzer in an atmosphere of nitrogen over a temperature range from 20 to 600 °C at a heating rate of 10 °C/min.

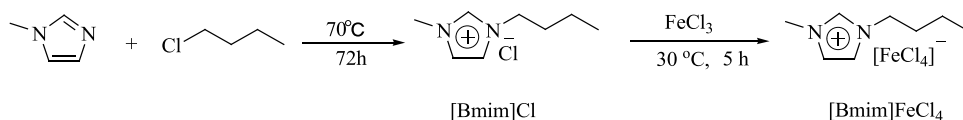
### Synthesis of the Fe-Containing Magnetic Ionic Liquid

The different molar fraction of Fe-containing magnetic ionic liquid [Bmim]FeCl<sub>4</sub> was synthesized according to the methods described in the previous literatures [36, 41] (Scheme 1). Firstly, the ionic liquid [Bmim]Cl was synthesized according to the following procedures:

In a three-necked flask equipped with a thermometer and a reflux condenser, a certain amount of *N*-methylimidazole (mim) was added, which was put into an ice-water bath. Under vigorous stirring, the equimolar 1-chlorobutane was slowly added to this flask in the nitrogen atmosphere. After the dropwise was over, the mixture was still stirred for 1.0 h at room temperature, then rapidly heated to 70 °C and refluxed for 72.0 h. When the reaction was completed, the colorless viscous liquid was obtained, using ethyl acetate washed to remove the unreacted 1-chlorobutane. and then dried under vacuum conditions (40 °C, 10 mmHg) for 6 h, the white solid [Bmim]Cl was produced with a yield of 92.4%. The structure of [Bmim]Cl was verified by <sup>1</sup>H NMR and FT-IR spectroscopy, and the data were as following:

<sup>1</sup>H NMR (Fig. S1, 500 MHz, D<sub>2</sub>O, ppm): 0.89(m, CH<sub>3</sub>CH<sub>2</sub>), 1.29(m, CH<sub>3</sub>CH<sub>2</sub>), 1.83(m, NCH<sub>2</sub>CH<sub>2</sub>), 3.98(s, NCH<sub>3</sub>), 4.18(m, NCH<sub>2</sub>CH<sub>2</sub>), 7.42(s, 1H), 7.47(s, 1H), 8.71(s, 1H). IR (Fig. S2, KBr film): 3050 (ν, C–H of imidazole ring), 2970, 2870 (ν, –CH<sub>2</sub>\*–CH<sub>3</sub>\*), 3390 (ν, H–OH\*), 1570 (ν,

**Scheme 1** Synthesis of ionic liquid [Bmim]FeCl<sub>4</sub>



–C=N and –C=C of imidazole ring), 1480, 1150 ( $\beta$ , C–H), 1230–1172 ( $\nu_{\text{as}}$ , –SOH<sub>3</sub><sup>\*</sup>), 853 ( $\gamma$ , –CH<sub>2</sub><sup>\*</sup>–CH<sub>3</sub><sup>\*</sup>), 748 ( $\gamma$ , C–H of imidazole ring).

Under N<sub>2</sub> atmosphere, different molar fraction of [Bmim]Cl and anhydrous FeCl<sub>3</sub> were mixed at 30 °C and stirred constantly until FeCl<sub>3</sub> solid particles disappear. A dark brown liquid was obtained, which was extracted with dichloromethane. The dichloromethane was removed by rotating evaporation and the dark brown liquid was gotten. After drying in a vacuum oven 60 °C (10 mmHg) for 6 h to obtain the different molar fraction of ionic liquid [Bmim]FeCl<sub>4</sub>.

### General Procedure for the Methanolysis of PHB

A 50 mL autoclave with a thermometer was loaded with PHB ( $w_1$ ), catalyst ( $w_2$ ) and a certain amount of methanol. Under the magnetic stirring, the methanolysis of PHB was heated up to the reaction temperature from 110 to 140 °C for the prescribed of 1.0–3.0 h under autogenous pressure. When the reaction was finished, the mixture was cooled to room temperature rapidly. Then the mixture was distilled to recover the unreacted methanol at atmospheric pressure, and obtained the main product M3HB ( $w_3$ ) by vacuum distillation. The residue ( $w_4$ ) after distillation was mainly undepolymerized PHB and catalyst, which was reused directly as a catalyst for the next cycle reaction without any treatment. The conversion of PHB and yield of main product were calculated by Eqs. (1, 2) as follows.

$$\text{Conversion of PHB} = \frac{w_1 - (w_4 - w_2)}{w_1} \times 100\% \quad (1)$$

$$\text{Yield of M3HB} = \frac{w_3}{w_1} \times \frac{M_1}{M_2} \times 100\% \quad (2)$$

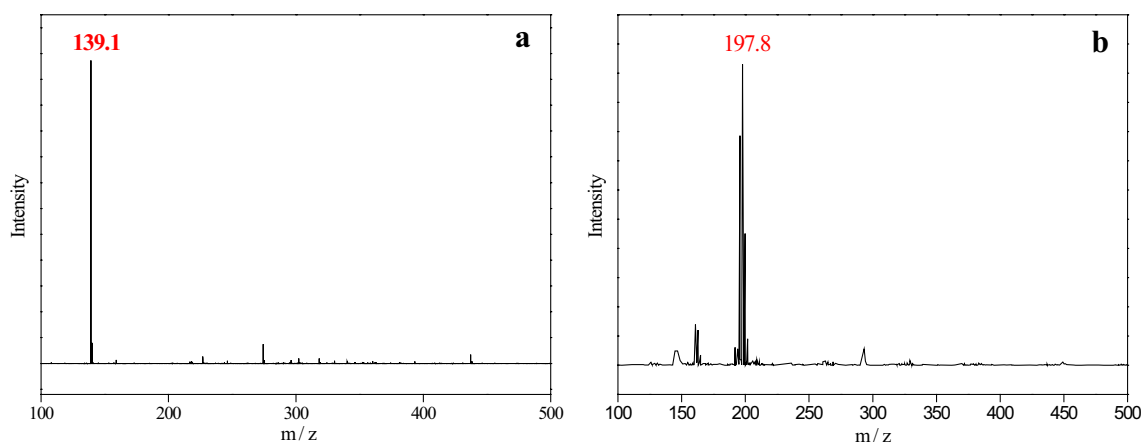
$M_1$  and  $M_2$  are the molar masses of the repeating unit of PHB and the M3HB, respectively.

## Results and Discussion

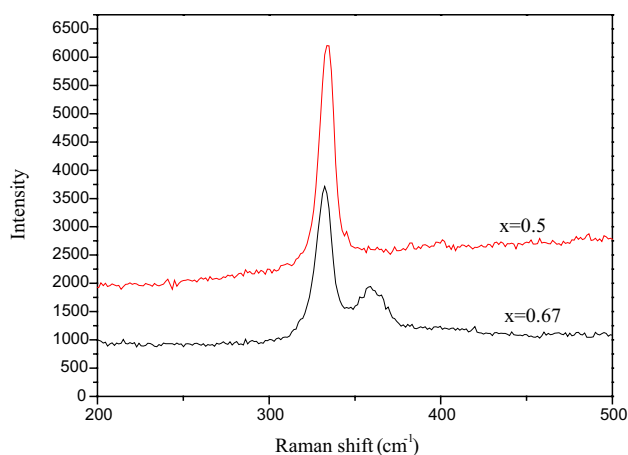
### Characterizations of ILs

The synthesized ionic liquid was characterized by MS and Raman spectroscopy. From Fig. 1, it was seen that the peaks up to  $m/z$  139 and 197.8 were ascribed to the positive ion [Bmim]<sup>+</sup> and negative ion [FeCl<sub>4</sub>]<sup>−</sup> in the ionic liquid. The Raman spectra of different molar fraction ionic liquids were shown in Fig. 2, it was clear from the spectra that there was a strong absorption peak at 330 cm<sup>−1</sup> in the each curve, which was belong to the totally symmetric Fe–Cl stretch vibration of [FeCl<sub>4</sub>]<sup>−</sup> [35, 42]. The medium absorption peak at 370 cm<sup>−1</sup> in the ionic liquid ( $x = 0.67$ ), which was related to the presence of [Fe<sub>2</sub>Cl<sub>7</sub>]<sup>−</sup>. Other parts of absorption peaks were almost exactly the same in the two spectra, which were assigned to the vibrations of the cation [Bmim]<sup>+</sup>. Then, results of MS and Raman spectra confirmed the structures of the synthesized ionic liquid.

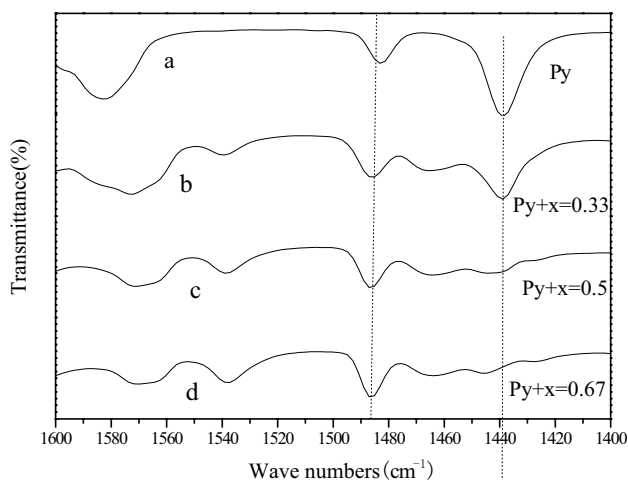
The acidity determination of ionic liquid by pyridine IR probe method was shown in Fig. 3. As we all known, pyridine has been extensively used as a molecular probe for determination the Lewis acid sites by monitoring the bands in the range of 1700–1400 cm<sup>−1</sup> arising from its ring vibration modes [43]. It can coordinate with Lewis acidic substances to form Py-L, their absorption peaks near 1445–1460 cm<sup>−1</sup> and 1600–1640 cm<sup>−1</sup>. In Fig. 3b–d, the presence of a band near 1558 cm<sup>−1</sup>, 1636 cm<sup>−1</sup> showed that Py-L acid sites. When FeCl<sub>3</sub>  $x = 0.33$ , these absorption peaks were quite weak. With increasing the molar fraction of FeCl<sub>3</sub>, the peaks at these acid sites became more and more strong.



**Fig. 1** Q-TOF mass spectra of [Bmim]FeCl<sub>4</sub> **a** positive ion [Bmim]<sup>+</sup>, **b** negative ion [FeCl<sub>4</sub>]<sup>−</sup>



**Fig. 2** Raman spectra of ionic liquid [Bmim]FeCl<sub>4</sub> (x: molar fraction of FeCl<sub>3</sub>)



**Fig. 3** IR spectra of [Bmim]FeCl<sub>4</sub> using pyridine as molecular probe (a: pure pyridine; b: py/[Bmim]FeCl<sub>4</sub>, x=0.33; c: py/[Bmim]FeCl<sub>4</sub>, x=0.5; d: py/[Bmim]FeCl<sub>4</sub>, x=0.67)

### Analysis of the Main Product

The purity and structure of the obtained product were characterized by GC, IR and <sup>1</sup>H NMR and the results were shown in Fig. S3 and Fig. 4. From Fig. S3, the only peak was ascribed as the main product, at the retention time is about 1.48 min. From the peak area, the product purity is over 98%. From Fig. 4A, the spectra of the obtained products at different conversion are almost identical, indicating that they were the same compound. The spectra contained a –OH band at 3435 cm<sup>-1</sup>, a C=O stretching at 1740 cm<sup>-1</sup>, and C–O bending at 1132 cm<sup>-1</sup>, which indicated the existence of an ester group. And alkyl bonds of C–H at 2990 cm<sup>-1</sup> and 2953 cm<sup>-1</sup>, a –CH<sub>3</sub> bending at 1380 cm<sup>-1</sup>. In Fig. 4B, the double signal at δ 1.00–1.19 ppm was belonged to the

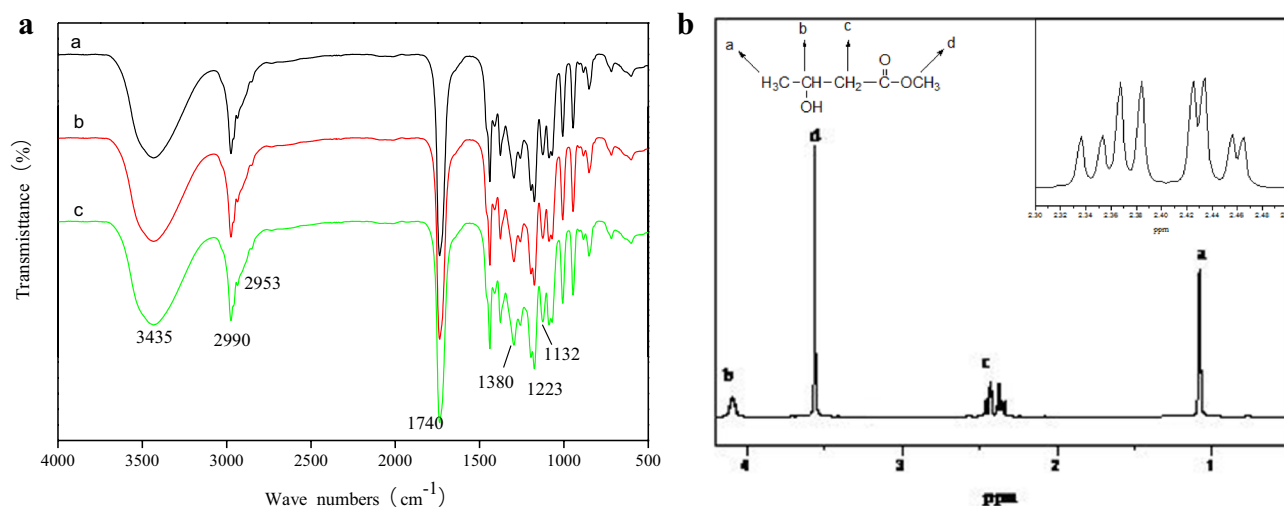
methyl protons of –CH<sub>3</sub>, the multiple at δ 2.32–2.48 ppm represented the methylene protons of –CH<sub>2</sub>–, the single signal at δ 3.595 ppm indicated the methyl protons of –OCH<sub>3</sub>, the multiple at δ 4.15 ppm was ascribed to the methenyl proton of –CH–. Therefore, from these characterizations data of IR and <sup>1</sup>H NMR, it can confirm that the structure of the product is M3HB.

### Selection of the Catalysts

The catalytic properties of different molar fraction of FeCl<sub>3</sub> ionic liquids were shown in Table 1. From Table 1, the PHB methanolysis cannot have happened, when [Bmim]Cl was used as the catalyst (Entry 1). It was maybe that the PHB methanolysis is a transesterification, acidic or alkaline catalyst is beneficial to it, however [Bmim]Cl is a neutral catalyst. With increasing of FeCl<sub>3</sub> molar fraction, the conversion of PHB and yield of M3HB were exhibited a significant upward trend. When temperature 140 °C, time 3.0 h and x=0.67, the conversion of PHB and yield of M3HB reached the maximum values were 94.1% and 85.0%, respectively (Entry 5). But when x > 0.67, there was no apparent increasing in the conversion of PHB and yield of M3HB. The reason was maybe that increasing the molar fraction of FeCl<sub>3</sub>, the Lewis acidity was enhanced, which was consistent with those results in pyridine IR. So the molar fraction of FeCl<sub>3</sub> was 0.67 in the ionic liquid [Bmim]FeCl<sub>4</sub> was chosen as a catalyst in the subsequent study.

### Effects of Reaction Condition

Table 2 showed the effects of reaction conditions on PHB methanolysis results. From Table 2, we could see that reaction temperature had a great influence on the methanolysis of PHB. When the temperature increased from 110 to 140 °C, the conversion of PHB increased from 68.1 to 94.1%, and the yield of M3HB was added from 63.3 to 85.0%, respectively (Entries 1–4). With prolonging the reaction time, both the PHB conversion and the M3HB yield increased gradually (Entries 4–7). When reaction time was 3.0 h, the PHB conversion and the M3HB yield were 94.1% and 85.0%, respectively (Entry 3). PHB conversion and M3HB yield did not increase significantly, even if the reaction time was extended to 4.0 h (Entry 5). The reason was maybe that this transesterification was a reversible reaction, the equilibrium had been reached at 3.0 h. With adding the methanol amount, the conversion of PHB and the yield of M3HB increased slightly. And at the same condition, their maximum values were 94.1% and 85.0%, when n(CH<sub>3</sub>OH):n(PHB) = 5.0:1 (Entry 4). However, when n(CH<sub>3</sub>OH):n(PHB) was increased to 6.0:1 (Entry 9), there was an obvious decrease in the conversion of PHB and the yield of M3HB. The reason was that the



**Fig. 4** **A** IR spectra of M3HB at different conversion of PHB (a: 39.6%; b: 73.0%; c: 94.1%); **B**  $^1\text{H}$  NMR of M3HB

**Table 1** Selection of the catalysts<sup>a</sup>

| Entry | Time (h) | Temperature (°C) | x, molar fraction of $\text{FeCl}_3$ | C (%) | Y (%) |
|-------|----------|------------------|--------------------------------------|-------|-------|
| 1     | 3        | 140              | 0                                    | 0     | 0     |
| 2     | 3        | 140              | 0.33                                 | 78.0  | 72.5  |
| 3     | 3        | 140              | 0.50                                 | 91.6  | 78.4  |
| 4     | 3        | 140              | 0.63                                 | 92.5  | 80.5  |
| 5     | 3        | 140              | 0.67                                 | 94.1  | 85.0  |
| 6     | 3        | 140              | 0.75                                 | 93.8  | 82.5  |
| 7     | 1        | 110              | 0.67                                 | 10.3  | 7.4   |
| 8     | 2        | 110              | 0.67                                 | 48.9  | 36.4  |
| 9     | 3        | 110              | 0.67                                 | 68.1  | 63.3  |
| 10    | 4        | 110              | 0.67                                 | 78.6  | 72.8  |
| 11    | 5        | 110              | 0.67                                 | 86.3  | 81.9  |
| 12    | 1        | 110              | 1                                    | 6.5   | 0     |
| 13    | 2        | 110              | 1                                    | 41.8  | 36.2  |
| 14    | 3        | 110              | 1                                    | 62.6  | 59.7  |
| 15    | 4        | 110              | 1                                    | 72.9  | 70.1  |
| 16    | 5        | 110              | 1                                    | 83.4  | 79.6  |

C: conversion of PHB, Y: yield of methyl 3-hydroxybutyrate

<sup>a</sup> $n(\text{CH}_3\text{OH}):n(\text{PHB})=5:1$ ,  $n(\text{cat}):n(\text{PHB})=0.05:1$

concentration of catalyst decreased in the mixture, due to an increase in the mixture. Which led to an obvious decrease in its catalytic activity. The influences of catalyst dosage on PHB conversion and M3HB were also investigated (Entries 4, 10–11). It was indicated that the methanolysis conversion increased with the amount of catalyst. With the increase in the amount of catalyst, more cations and anions in ionic liquid would interact with the active sites in the substrates (shown in Scheme 2).

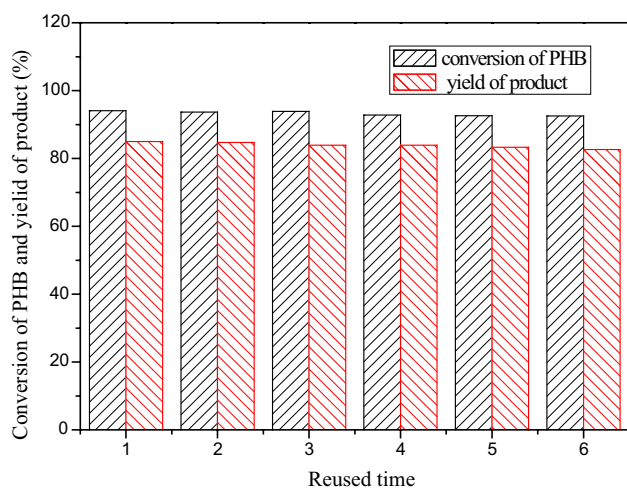
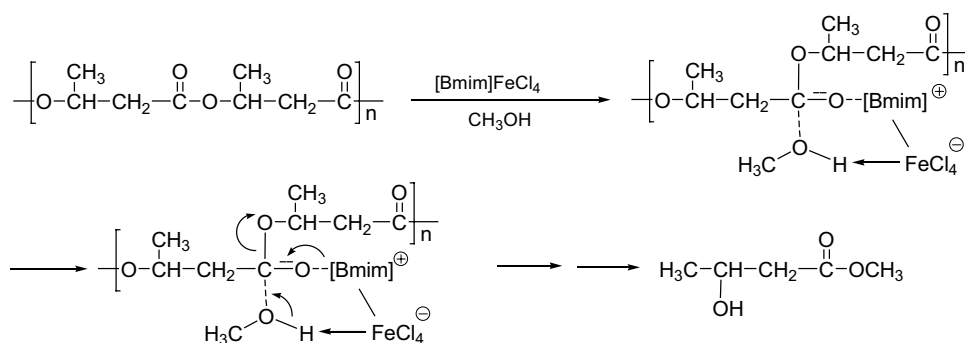
## Reusability of ILs

Figure 5 shown the reusability performance of IL  $[\text{Bmim}]\text{FeCl}_4$  ( $x=0.67$ ), under the conditions: temperature 140 °C, time 3.0 h,  $n(\text{CH}_3\text{OH}):n(\text{PHB})=5.0:1$  and  $n(\text{cat}):n(\text{PHB})=0.05:1$ . As showed in Fig. 5, there was no significantly decrease in the conversion of PHB and yield of the product were decreased slightly, when the catalyst was reused up to six cycles. That is to say, the catalyst exhibited an excellent activity. The IL was characterized by IR and the results were presented in Fig. 6. Comparing the spectrum of the reused IL with that of fresh one, their structures were almost exactly the same. It can be clearly seen that a ring stretching vibration at 1164  $\text{cm}^{-1}$ , a C=N stretching vibration at 1566  $\text{cm}^{-1}$ , a C=C ring double bond stretching vibration at 1616  $\text{cm}^{-1}$ , an alkyl C–H at 2962  $\text{cm}^{-1}$ , 2935  $\text{cm}^{-1}$  and a aromatic heterocycle C–H stretching vibration at 3149  $\text{cm}^{-1}$ . Figure 7 showed that the TGA curves of the reused IL and that of the fresh one. After six times reused, the thermal stability of ILs had virtually no change. When the temperature was over 100 °C, there was a small mass loss due to a bit of water. At the temperature 425 °C, the weight loss was very obviously, the decomposition temperature of ionic liquid was reached. When the temperature reached 520 °C, the ionic liquid had decomposed completely. However, this methanolysis temperature was only 140 °C, the catalyst could be exist stably. From the two IR spectra and the two TGA curves, there was no change in chemical structure after the ionic liquid was reused for six times. Therefore,  $[\text{Bmim}]\text{FeCl}_4$  ( $x=0.67$ ) was an excellent and reusable catalyst for the methanolysis of PHB.

**Table 2** Effects of reaction conditions on methanolysis results

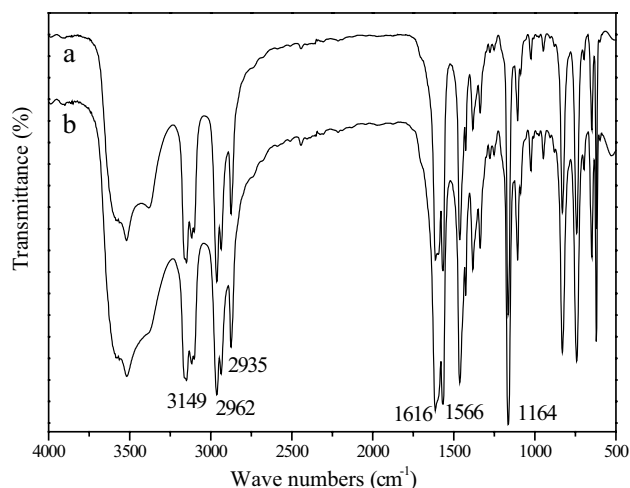
| Entry | Time (h) | Temperature (°C) | n(CH <sub>3</sub> OH):n(PHB) | n([Bmim]FeCl <sub>4</sub> ):n(PHB) | C (%) | Y (%) |
|-------|----------|------------------|------------------------------|------------------------------------|-------|-------|
| 1     | 3        | 120              | 5:1                          | 0.05:1                             | 74.3  | 70.4  |
| 2     | 3        | 130              | 5:1                          | 0.05:1                             | 82.0  | 75.8  |
| 3     | 3        | 140              | 5:1                          | 0.05:1                             | 94.1  | 85.0  |
| 4     | 1        | 140              | 5:1                          | 0.05:1                             | 76.2  | 70.4  |
| 5     | 2        | 140              | 5:1                          | 0.05:1                             | 89.5  | 83.6  |
| 6     | 3        | 140              | 4:1                          | 0.05:1                             | 87.4  | 81.6  |
| 7     | 3        | 140              | 6:1                          | 0.05:1                             | 76.4  | 70.1  |
| 8     | 3        | 140              | 5:1                          | 0.04:1                             | 90.8  | 82.8  |
| 9     | 3        | 140              | 5:1                          | 0.03:1                             | 86.6  | 81.1  |

C: conversion of PHB, Y: yield of methyl 3-hydroxybutyrate

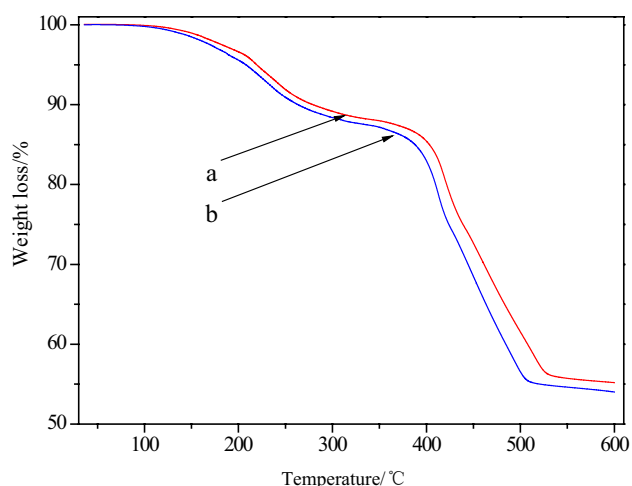
**Scheme 2** Possible mechanism of the PHB methanolysis catalyzed by [Bmim]FeCl<sub>4</sub>**Fig. 5** Reusability results of [Bmim]FeCl<sub>4</sub> ( $x=0.67$ ) ( $T=140\text{ }^{\circ}\text{C}$ ,  $t=3.0\text{ h}$ ,  $n(\text{[Bmim]Cl-FeCl}_3):n(\text{PHB})=0.05:1$ ,  $n(\text{methanol}):n(\text{PHB})=5:1$ )

### Mechanism of PHB Methanolysis

In order to study the reaction mechanism of PHB methanolysis catalyzed by Fe-containing magnetic ionic liquid [Bmim]FeCl<sub>4</sub> ( $x=0.67$ ), the residues of PHB (which were mainly composed of some oligomers) at different conversion were

**Fig. 6** IR spectra of [Bmim]FeCl<sub>4</sub> ( $x=0.67$ ) used in methanolysis of PHB (a: fresh; b: reused for six times)

characterized by IR. From Fig. S4, it could be seen that the peak at about  $3500\text{ cm}^{-1}$  was ascribed to the hydroxyl ( $-\text{OH}$ ) group got stronger, when the conversion of PHB was added from 0 to 39.6–73.0%. The peak at  $1750\text{ cm}^{-1}$  was belonged to the carbonyl ( $-\text{C}=\text{O}$ ) group also had the same change. This might be due to the cleavage of the  $\text{C}-\text{O}$  bond in the ester group of the substrate, the  $-\text{OH}$  and  $-\text{C}=\text{O}$  groups were



**Fig. 7** TGA curves of fresh and reused [Bmim]FeCl<sub>4</sub> (a: before reused; b: after reused)

exposed. With increasing the conversion of PHB, some oligomers containing –OH and –C=O groups became stronger increasingly. The main products obtained at different conversions were characterized by IR, and the results were shown in Fig. 4A. It was obviously seen that these three IR curves were almost exactly the same, regardless of the conversion was 39.6% and 73.0%, or 94.1%.

In our previous work, PHB pellets could dissolve or swell in the methanol without any solvent under the same conditions. From Fig. S5, we can see there is not any difference in the IR. So based on the above results, the possible mechanism was proposed and was shown in Scheme 2. After the rigid PHB was dissolved or swelled in the methanol, it was beneficial to react with some small molecule. When Fe-containing magnetic ionic liquid [Bmim]FeCl<sub>4</sub> ( $x=0.67$ ) was used as catalyst, the synergic effect was presumed to exist between the cation and anion [35]. The cation [Bmim]<sup>+</sup> reacted with –C=O in the ester of PHB, which improved the positivity of the carbonyl carbon. At the same time the anion [FeCl<sub>4</sub>]<sup>–</sup> reacted with the –H atom in the –OH of methanol, forming a transition state of six-membered ring. These caused the oxygen in the hydroxyl group of methanol to be more electronegative, and attack the carbonyl carbon of the ester easily. Afterwards, the hydrogen atom leaved the methanol and the [Bmim]<sup>+</sup> also leaved the six-membered ring, the electrons on the oxygen atom transferred to form C=O. The acyl-oxygen cleaved and the alkoxy group leaved. This transformation was repeated, and the monomer M3HB was obtained.

### Kinetics of PHB Methanolysis

The kinetics of PHB methanolysis was also investigated under the optimum conditions. This methanolysis reaction

could take place only when the rigid PHB was dissolved or swelled in this mixture, because it is a reaction between a solid polymer macromolecule and a small liquid molecule. And the concentration of PHB would be very low because the PHB cannot dissolve completely in this system, whereas the molar ratio of CH<sub>3</sub>OH to PHB was 5:1, so the concentration of CH<sub>3</sub>OH was a greatly excessive. Furthermore, In many literatures of chemical depolymerization polymers [44, 45], the reaction order was usually assumed to be first-order. Therefore, the methanolysis of PHB catalyzed by [Bmim]FeCl<sub>4</sub> ( $x=0.67$ ) was initially assumed to be controlled by first-order kinetic Eq. (3).

$$\frac{d(C_{PHB})}{dt} = -kC_{PHB} \quad (3)$$

where  $k$  represents the rate constant of the reaction, and  $C_{PHB}$  represents the concentration of PHB at time  $t$ .

$$C_{PHB} = C_{PHB0}(1 - X) \quad (4)$$

where  $X$  represents the conversion of PHB, Eq. (3) could be written as follows.

$$\frac{dX}{dt} = k(1 - X) \quad (5)$$

Equation (5) was integrated for time to obtain Eq. (6).

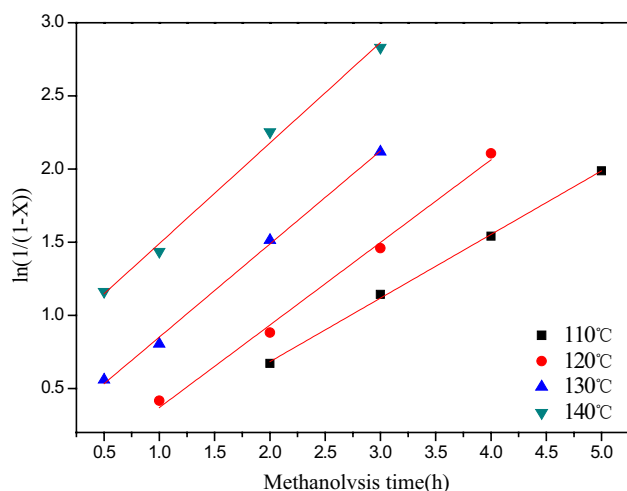
$$\ln \frac{1}{1 - X} = kt \quad (6)$$

In order to study the kinetics of the PHB methanolysis catalyzed by Fe-containing magnetic IL [Bmim]FeCl<sub>4</sub> ( $x=0.67$ ), the influences of reaction time on PHB methanolysis from 110 to 140 °C were investigated, under the following conditions of  $n(\text{CH}_3\text{OH}):n(\text{PHB})=5.0:1$  and  $n(\text{cat}):n(\text{PHB})=0.05:1$ . The results were shown in Fig. 8, and the linear regression data were shown in Table 3. It could be clearly seen from Table 3 that the linear correlation coefficients were over 0.98, indicating that  $\ln 1/(1 - X)$  was proportional to time, that is to say, this methanolysis process is first-order kinetics reaction and methanolysis rate constant was proportional to the concentration of PHB in reaction mixture. The four straight lines slopes values were 0.43484 h<sup>–1</sup>, 0.56463 h<sup>–1</sup>, 0.63629 h<sup>–1</sup>, 0.68684 h<sup>–1</sup>, which were the rate constants of the methanolysis reaction at temperatures of 110 °C, 120 °C, 130 °C and 140 °C, respectively.

Based on these above methanolysis rate constants, the reaction activation energy ( $E_a$ ) could be calculated from Arrhenius equation Eq. (7).

$$\ln k = \ln A - \frac{E_a}{RT} \quad (7)$$

where  $A$  is the pre-exponential factor,  $R$  is the gas molar constant (8.31 J/mol K) and  $T$  is the thermodynamics



**Fig. 8** Effects of reaction temperature on methanolysis rate of PHB catalyzed by [Bmim]FeCl<sub>4</sub>

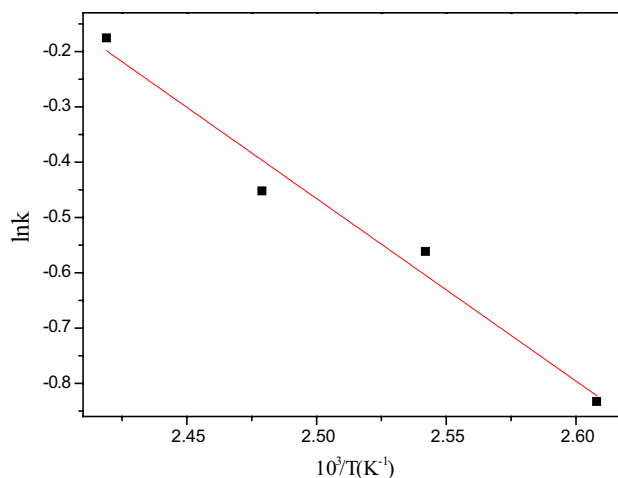
**Table 3** Linear regression results of the data in Fig. 8

| Reaction temperature (°C) | Regressive equation       | Linear correlation coefficient |
|---------------------------|---------------------------|--------------------------------|
| 110                       | $y = -0.18605 + 0.43484x$ | 0.99863                        |
| 120                       | $y = -0.19507 + 0.56463x$ | 0.99214                        |
| 130                       | $y = 0.21543 + 0.63629x$  | 0.99639                        |
| 140                       | $y = 0.80411 + 0.68684x$  | 0.99123                        |

temperature in Kelvin. The Arrhenius plot was achieved in Fig. 9, and the activation energy ( $E_a$ ) of this reaction calculated from the slope was 27.44 kJ/mol.

## Conclusions

In summary, the Fe-containing magnetic ionic liquid [Bmim]FeCl<sub>4</sub> ( $x = 0.67$ ) can be used as an efficient and eco-friendly catalyst in the methanolysis of PHB. It was indicated that temperature was an important factor in this reaction. Under the optimum conditions:  $T = 140\text{ }^\circ\text{C}$ ,  $t = 3.0\text{ h}$ ,  $n(\text{cat}):n(\text{PHB}) = 0.05:1$  and  $n(\text{CH}_3\text{OH}):n(\text{PHB}) = 5:1$ , the PHB conversion and the M3HB yield were 94.1% and 85.0%, respectively. Meanwhile, the catalyst exhibited an excellent reusability, its catalytic activity was not significantly reduced after being reused for six times. The kinetics study indicated that this methanolysis was a first-order kinetic reaction, with an activation energy of 27.44 kJ/mol. Moreover, a possible mechanism indicated that the synergic effect between the cation and anion in the ionic liquid made this nucleophilic substitution occur much easier.



**Fig. 9** Arrhenius plot of rate constant of PHB methanolysis catalyzed by [Bmim]FeCl<sub>4</sub>

**Acknowledgements** This research was supported financially by the National Natural Science Foundation of China (No. 51673106), Shandong Province Natural Science Foundation (No. ZR2015BL027) and the Taishan Scholars Projects of Shandong (ts 201511033).

## References

- Al-Salem SM, Lettieri P, Baeyens J (2010) Prog Energy Combust Sci 36:103–129
- Kikkawa Y, Fukuda M, Ichikawa N, Kashiwada A, Matsuda K, Kanesatoa M, Hiraishic T (2013) J Mater Chem A 1:4667–4670
- Fakhouri FM, Carvalho M, Barreto PLM, Jesus RCD, Martelli SM (2015) Green Chem 2015:208–226
- Lu X, Wang L, Yang Z, Lu H (2013) Adv Biosci Biotechnol 4:731–740
- Xavier FL, Olyveira GM, Basmaji P, Costa LM (2013) J Nanosci Nanotechnol 13:4715–4719
- Danis O, Ogan A, Tatlican P, Attar A, Cakmakci E, Mertoglu B, Birbir M (2015) Extremophiles 19:515–524
- Soroudi A, Jakubowicz I (2013) Eur Polym J 49:2839–2858
- Ariffin H, Nishida H, Hassan MA, Shirai Y (2010) Biotechnol J 5:484–492
- Ariffin H, Nishida H, Shirai Y, Hassan MA (2009) J Appl Polym Sci 111:323–328
- Mamat MRZ, Ariffin H, Hassan MA, Zahari MAK (2014) J Clean Prod 83:463–472
- Bonartsev AP, Boskhomodgiev AP, Iordanskii AL, Bonartseva GA, Rebrov AV, Makhina TK, Myshkina VL, Yakovlev SA, Filatova EA (2012) Mol Cryst Liq Cryst 556:288–300
- Cui Y, Barford J, Renneberg R (2007) Anal Lett 40:2915–2924
- Yu J, Plackett D, Chen LXL (2005) Polym Degrad Stab 89:289–299
- Saeki T, Tsukegi T, Tsuji H, Daimon H, Fujie K (2005) Polymers (Basel) 46:2157–2162
- Lee Y, Park SH, Lim IT, Han K, Lee SY (2000) Enzyme Microb Technol 27:33–36
- Spekreijse J, Nôtre JL, Sanders JPM, Scott EL (2015) J Appl Polym Sci 132:42462
- Dacosta CF, Posada JA, Ramirez A (2016) J Clean Prod 137:942–952



18. Spekreijse J, Ortega JH, Sanders JPM, Bitter JH, Scott EL (2016) *Bioresour Technol* 211:267–272
19. Rodríguez-Contreras A, Calafell-Monfort M, Marqués-Calvo MS (2012) *Polym Degrad Stab* 97:597–604
20. Ju D, Han L, Bian J, Guo Z, Li F, Chen S, Dong L (2015) *RSC Adv* 5:5474–5483
21. Lim J, Kim J (2016) *Macromol Res* 24:9–13
22. Pagnan CS, Mottin AC, Oréfice RL, Ayres E, Câmara JJD (2018) *J Polym Environ* 26:1169–1178
23. Welton T (1999) *Chem Rev* 99:2071–2084
24. Earle MJ, Seddon KR (2000) *Pure Appl Chem* 72:1391–1398
25. Welton T, Hallett JP (2011) *Chem Rev* 111:3508–3576
26. Xiao Y, Malhotra SV (2005) *J Mol Catal A* 230:129–133
27. Vidiš A, Ohlin C, Laurenczy G, Küsters E, Sedelmeier G, Dyson PJ (2005) *Adv Synth Catal* 347:266–274
28. Vafaezadeh M, Alinezhad H (2016) *J Mol Liq* 218:95–105
29. Xun S, Zhu W, Zheng D, Zhang L, Liu H, Yin S, Zhang M, Li H (2014) *Fuel* 136:358–365
30. Wang H, Xie C, Yu S, Liu F (2014) *Chem Eng J* 237:286–290
31. Sun X, Liao C, Shao N, Bell JR, Guo B, Luo H, Jiang A (2013) *J Power Sources* 237:5–12
32. Yin K, Zhang Z, Yang L, Hirano S (2014) *J Power Sources* 258:150–154
33. Adams CJ, Earle MJ, Seddon KR (2000) *Green Chem* 2:21–24
34. Kamimura A, Yamamoto S (2007) *Org Lett* 9:2533–2535
35. Wang H, Yan R, Li Z, Zhang X, Zhang S (2010) *Catal Commun* 11:763–767
36. Yue Q, Xiao L, Zhang M, Bai X (2013) *Polymers (Basel)* 5:1258–1271
37. Al-Sabagh AM, Yehia FZ, Eissa AMF, Moustafa ME, Eshaq G, Rabie AM, ElMetwally AE (2014) *Polym Degrad Stab* 110:364–377
38. Iannone F, Casiello M, Monopoli A, Cotugno P, Sportelli MC, Picca RA, Cioff N, Dell’Annac MM, Nacci A (2017) *J Mol Catal A* 426:107–116
39. Song X, Liu F, Li L, Yang X, Yu S, Ge X (2013) *J Hazard Mater* 244:204–208
40. Liu H, Song X, Liu F, Liu S, Yu S (2015) *J Polym Res* 22:135
41. Liu H, Zhao R, Song X, Liu F, Yu S, Liu S, Ge X (2017) *Catal Lett* 147:2298–2305
42. Yue Q, Yang H, Zhang M, Bai X (2014) *Adv Mater Sci Eng* 2014:1–6
43. Zhao H, Yu N, Ding Y, Tan R, Liu C, Yin D, Qiu H, Yin D (2010) *Microporous Mesoporous Mater* 136:10–17
44. Nostrum CFV, Veldhuis TFJ, Bos GW, Hennink WE (2004) *Polymers (Basel)* 45:6779–6787
45. Codari F, Lazzari S, Soos M, Storti G, Morbidelli M, Moscatelli D (2012) *Polym Degrad Stab* 97:2460–2466