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ORIGINAL PAPER

Ferric chloride as an efficient and reusable catalyst for methanolysis of poly(lactic acid) waste

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Abstract Ferric chloride ($FeCl_3$) was used to catalyze the methanolysis of poly(lactic acid) (PLA) to recover methyl lactate. The effects of experimental parameters such as reaction temperature, reaction time, amount of $FeCl_3$ and dosage of methanol on results were studied in detail. The results showed that under the optimized reaction conditions of n(methanol):n(PLA)=5:1, n($FeCl_3$):n(PLA)=0.01:1, 130 °C and 4.0 h, the conversion of PLA reached 96.0 % and the yield of methyl lactate was up to 87.2 %. $FeCl_3$ could be repeatedly used at least 6 times without significant decrease in the conversion of PLA and yield of methyl lactate under the given conditions. The kinetics of the reaction was also investigated. The results indicated that the methanolysis of PLA catalyzed by $FeCl_3$ was a first-order kinetic reaction with activation energy of 32.41 kJ/mol.

Keywords Poly(lactic acid) · Methanolysis · $FeCl_3$ · Methyl lactate

Introduction

Currently, both climate warming and depletion of fossil fuels are critical problems in our word, which has emphasized the need for new complementary resources. In order to solve this problem, several types of bio-based materials have been developed. Among them, poly(lactic acid) (PLA), as a biodegradable and biocompatible polymer, has become the focus of attention as one alternative to conventional undegradable polymers. In recent year, PLA has been used in medical devices, industries, textiles, food packages, etc. [1–5]. With the widespread use and increasing consumption of PLA, the amount of waste PLA generated is growing rapidly. In most cases PLA is biodegradable, but it takes a long time for PLA to be degraded completely [6–8]. Therefore, an effective degradation process is required for chemical recycling of PLA waste, which is a meaningful subject [9–12].

Although some methods for chemical recycling of PLA have been extensively studied in various environments or by various media such as pyrolysis [13–17], hydrolysis [18–22], and alcoholysis [23–26], etc., which are very difficult to recover corresponding monomers or other small molecule materials. As for thermal pyrolysis, the high temperature is not inevitable, which may cause many side reactions [17]. In contrast with thermal pyrolysis, the hydrolysis reaction does not require severe operating conditions or catalysts, therefore, it is very difficult to obtain the hydrolysis product. Although, it is relatively easy to obtain alkyl lactate by alcololysis, the PLA does not dissolve in alcohol [24], a higher temperature and a larger quantity of catalysts are required in reported alcoholysis methods, which are accompanied with some shortcomings, such as laborious and complex workup for purification, significant amounts of waste materials and pollution problems, hence its application is limited.

Recently, our group demonstrated the effectiveness of conversion of some polymers into monomers, such as polycarbonate (PC), poly(ethylene terephthalate) (PET) and PLA under ionic liquid conditions [27–30]. Some good results have been obtained for PLA methanolysis in the presence of ionic liquid [29], but the ionic liquids are quite complex to synthesize and their production costs are very high. Therefore, there are some difficulties for them to be used industrially. In this paper, $FeCl_3$ is cheap and industrially available, which was

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used as a catalyst in the methanolysis of PLA. The effects of reaction conditions on methanolysis results of PLA were studied. The results showed that $FeCl_3$ exhibited an excellent catalytic activity, and a high conversion of PLA and yield of methyl lactate were obtained under optimum conditions. Moreover, the reusability of $FeCl_3$ and kinetics of this reaction were also investigated. To our knowledge, this is the first report on the methanolysis of PLA to recover methyl lactate using $FeCl_3$ as a active catalyst.

Experimental

Materials

Pure PLA pellets (3.0 mm length and 2.5 mm diameter) were obtained from Shenzhen ESUN Industrial Co., Ltd., China. The weight-average and number-average molecular weights were 225,000 and 102,000 respectively, which were determined by GPC (Waters-515) in tetrahydrofuran (THF) solution at 25 °C. $FeCl_3$ was purchased from Shanghai Shanpu Chemical Co., Ltd. Other materials such as the methyl lactate standard sample (99.5 %) were purchased from Sigma-Aldrich China Inc. All other materials (AR) were used without any further purification.

Instruments

The purity of methyl lactate was analyzed by Varian CP-3800 gas chromatography (GC) equipped with an AC-10 column, 30 m×0.32 mm×0.5 μm (oven temperature 250 °C, FID detector temperature 250 °C, vaporizer temperature 250 °C). Methanol was as the solvent, toluene was used as internal standard. FTIR spectra were determined using a Nicolet 510P FTIR spectrometer using KBr or liquid film in the range of 4000–400 cm^{-1}.

Methanolysis of PLA catalyzed by $FeCl_3$

Certain amounts of PLA (w_0), methanol, and $FeCl_3$ were charged into a 75 mL autoclave with a stirrer and a thermometer. The mixture was heated up to the given temperature and reacted for the prescribed time at autogenous pressure. When the methanolysis reaction finished, the mixture was cooled to room temperature. Then the undepolymerized PLA was removed by filtration, the residual PLA was collected, dried, and weighed (w_1). The conversion of PLA is defined by Eq. (1):

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

Simultaneously, the filtrate was distilled to recover unreacted methanol at atmospheric pressure and main product (methyl lactate) at reduced pressure. The residue after distillation was mainly $FeCl_3$, which was reused directly as a catalyst without any treatment. The yield of methyl lactate was calculated by Eq. (2):

$$\text{Yield of methyl lactate} = \frac{w_3}{w_0} \times \frac{M(PLA)}{M(methyllactate)} \times 100\% \quad (2)$$

Where w_3 represents the weight of obtained methyl lactate, M(PLA)and M(methyl lactate) are the molar masses of the repeating unit of PLA and methyl lactate respectively.

Characterization of the main product

In order to confirm the structure of main product of methanolysis, the FTIR spectra of methyl lactate standard sample and the main product were recorded (Fig. 1). It can be clearly seen the spectrum contains a -OH band at 3435 cm^{-1}, a C=O stretching at 1750 cm^{-1}, an alkyl C-H at 2990 cm^{-1} and 2953 cm^{-1},and C-O of ester at 1223 cm^{-1} and 1132 cm^{-1}. The IR spectrum of the obtained product is almost the same as that of the methyl lactate standard sample. From GC analysis, it indicated that the product had the same retention time as the standard sample, and the product purity is 99.3 %.

Results and discussions

Selection of catalysts

To examine the catalytic performances of different catalysts in PLA methanolysis, the methanolysis tests were carried out using different catalysts under the same conditions of n(CH_3OH):n(PLA)=5:1, n(catalyst):n(PLA)=0.01:1, temperature130 °C and reaction time 4.0 h. The results are

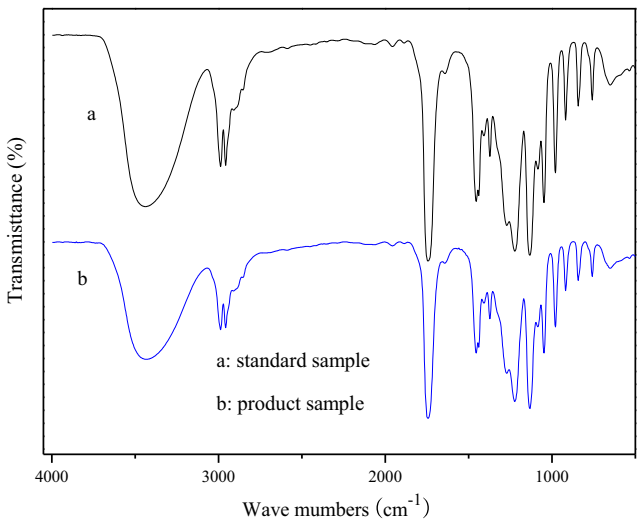

Fig. 1 IR spectra of obtained product and standard methyl lactate sample

summarized in Table 1. From Table 1, it indicated that the methanolysis of PLA could not take place without a catalyst (Entry 1), and both acidic and basic catalysts could catalyze PLA methanolysis (Entries 2–12). It is well-known that the methanolysis of PLA is a transesterification reaction, acidic or alkaline catalysts are beneficial to the reaction. However, when the strong acidic catalyst such as H_2SO_4 was used, a relatively higher temperature was required and the reaction rate was usually very slow, accompanying with many side reactions. To our surprise, some Lewis acids have good catalytic activities in PLA methanolysis (Entries 2 and 5); especially $FeCl_3$ exhibits an outstanding performance in PLA methanolysis. When $FeCl_3$ was used as a catalyst, the conversion of PLA and yield of product were much better than using other Lewis acids such as $ZnCl_2$, $AlCl_3$ and $SnCl_4$ as catalysts. The conversion of PLA could reach 96.0 % and the yield of methyl lactate was 87.2 %. Thus, $FeCl_3$ was chosen as an excellent catalyst for further investigation.

Effects of reaction conditions on methanolysis of PLA

Effect of reaction temperature

Figure 2 showed the effects of reaction temperature on conversion of PLA and yield of methyl lactate. From Fig. 2, it could be seen that the reaction temperature had a significant effect on the results. When the temperature was raised from 100 to 130 °C, the conversion of PLA increased apparently from 69.1 to 96.0 %, at the same time the yield of methyl lactate increased from 61.3 to 87.2 %. However, the increasing tendency was retarded when the temperature was higher than 130 °C. Because the methanolysis of PLA was reversible,

Table 1 Effect of catalysts on methanolysis reaction of PLA

Entry	Catalysts	PLA Conversion /%	methyl lactate yield /%
1	None	0	0
2	$ZnCl_2$	92.9	85.9
3	$AlCl_3$	84.7	78.8
4	$SnCl_4 \cdot 5H_2O$	43.1	37.6
5	$FeCl_3$	96.0	87.2
6	ZnAc	89.7	76.3
7	NaAc	88.2	74.2
8	NaOH	91.0	70.8
9	CH_3ONa	90.5	84.6
10	Zinc Octoate	90.3	84.8
11	HCl	50.6	42.7
12	H_2SO_4	73.8	68.4

Reaction conditions: n(CH_3OH):n(PLA)=5:1, n(cat):n(PLA)=0.01:1, T=130 °C and t=4.0 h

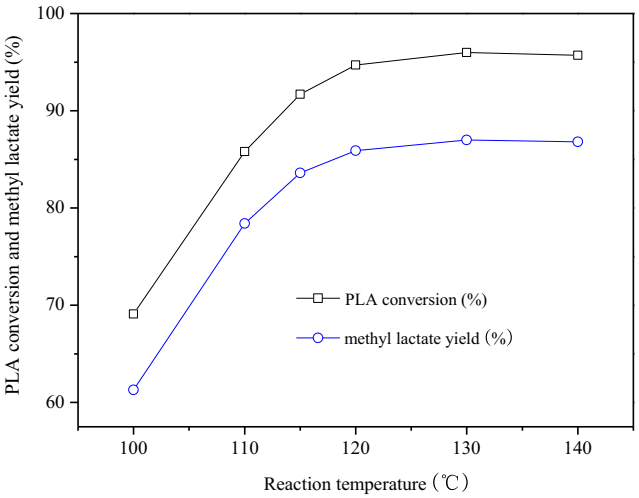

Fig. 2 Effect of reaction temperature on methanolysis of PLA

the equilibrium was reached at 130 °C. Thus, reaction temperature was a critical factor in the methanolysis of PLA, and 130 °C was the right choice for the methanolysis of PLA.

Effect of methaolysis time

The effects of methanolysis time on PLA conversion and methyl lactate yield were examined in Fig. 3. It indicated that with the prolonging of methanolysis time, the PLA conversion was increased distinctly, the yield of methyl lactate increased correspondingly. When reaction time was prolonged to 4.0 h, PLA conversion could reach 96.0 % and methyl lactate yield was 87.2 %. However, both PLA conversion and methyl lactate yield were stable when methanolysis time was further prolonged. It is maybe that the reaction equilibrium was reached at 4.0 h.

Effect of catalyst dosage

The effects of catalyst dosage on conversion of PLA and yield of methyl lactate were presented in Fig. 4. It showed that PLA could not be depolymerized by methanol in the absence of catalyst. The PLA conversion was increased with the increasing of $FeCl_3$ dosage, and 96 % conversion of PLA was obtained when n($FeCl_3$):n(PLA) was 0.01:1. The yield of methyl lactate was also increased with the increasing of catalyst dosage. When n($FeCl_3$):n(PLA) was 0.01:1, a maximum yield of 87.2 % was obtained. With the further increasing of catalyst dosage, both PLA conversion and methyl lactate yield were almost stable.

Effect of methanol dosage

The effect of methanol dosage on methanolysis results was shown in Fig. 5. From Fig. 5, it could be seen that methanol dosage could also affect the methanolysis results of PLA. The

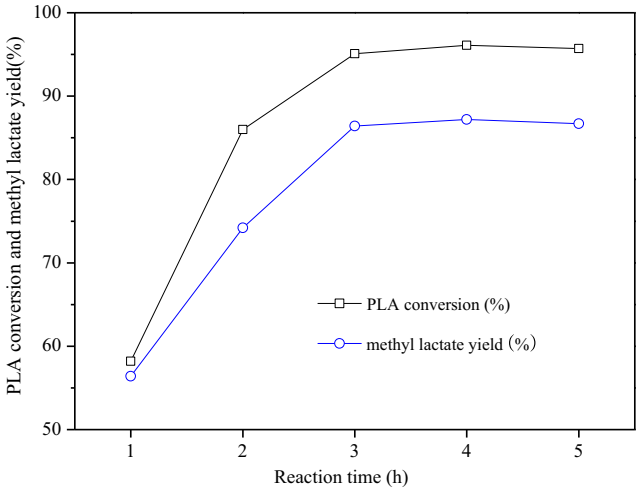

Fig. 3 Effect of reaction time on methanolysis of PLA

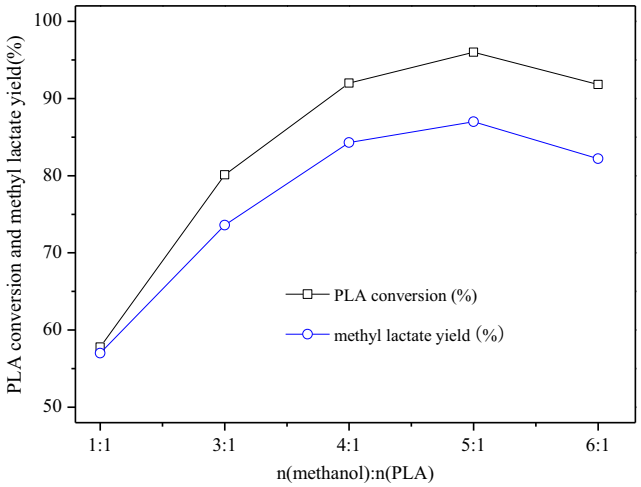

Fig. 5 Effect of methanol dosage on methanolysis of PLA

optimum mole ratio of methanol to PLA was 5:1. Under the reaction conditions of n(methanol):n(PLA)=5:1, $n(FeCl_3)$:n(PLA)=0.01:1, temperature 130 °C and time 4 h, the PLA conversion and methyl lactate yield were 96 and 87.2 % respectively. However, both PLA conversion and methyl lactate yield decreased with methanol dosage further increasing. It is maybe that the concentration of catalyst in reaction mixture decreases with the increasing of methanol dosage, which results in the decreasing of reaction rate.

Reusability of the catalyst

Reusability of the catalyst is absolutely required after PLA methanolysis, from the standpoint of environmental conservation. In the reusability tests, after methyl lactate was distilled from the mixture, the residue which is mainly $FeCl_3$ was reused directly as catalyst without any treatment. The results were shown in Fig. 6. From Fig. 6, $FeCl_3$ could be reused for six times without significant change in PLA conversion and methyl lactate yield. It is well known that the main factor which affects the reusability of catalyst is its stability under the temperature and reaction fluid surroundings. Because $FeCl_3$ itself has a good thermal stability and reaction temperature is only 130 °C, it is reasonable that the catalyst has a good reusability. Therefore, $FeCl_3$ is an effective and reusable catalyst for methanolysis of PLA.

Mechanism of PLA methanolysis

In order to further understand the mechanism of PLA methanolysis, the IR spectra of residual PLA obtained at different conversions were recorded and shown in Fig. 7. It could be seen that with the increasing of PLA conversion, the peak at 3500 cm^{-1} which belongs to the hydroxyl group of lactate structure became stronger. This means that C-O bond in PLA molecule breaks during the methanolysis reaction, some oligomers exist in the PLA residue. A possible mechanism for PLA methanolysis catalyzed by $FeCl_3$ was shown in Fig. 8.

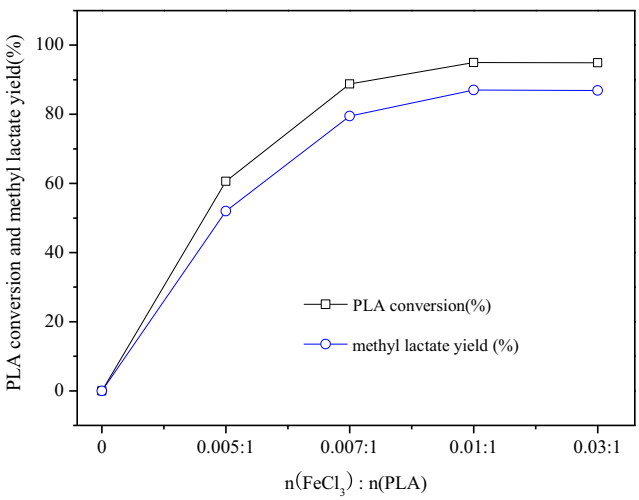

Fig. 4 Effect of $FeCl_3$ dosage on methanolysis of PLA

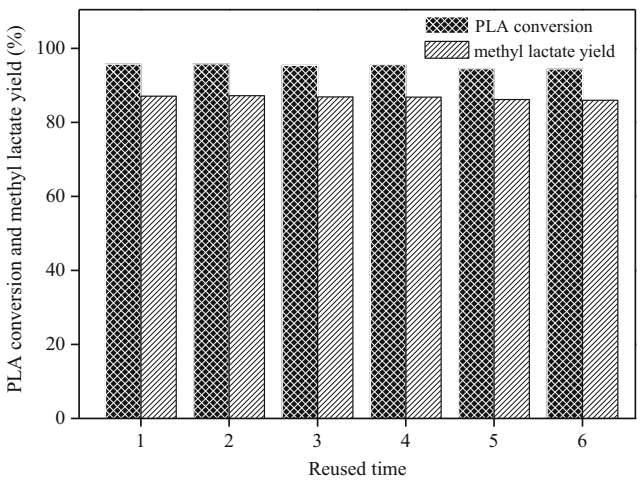

Fig. 6 Recycling use of $FeCl_3$

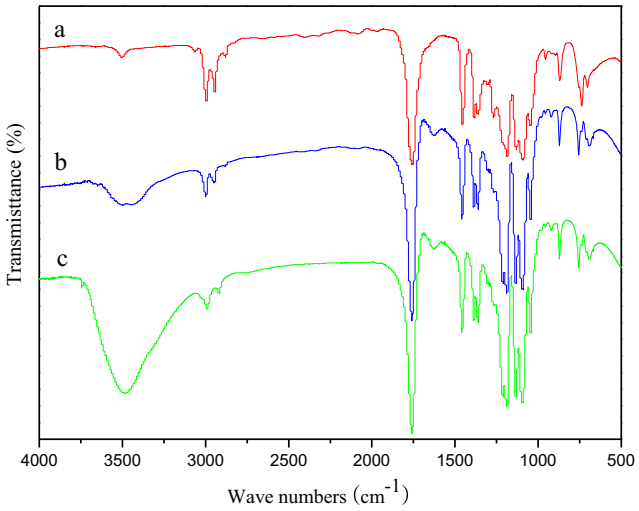

Fig. 7 IR spectra of the residues obtained at different conversions of PLA (a, 0 %; b, 33.7 %; c, 71.3 %)

After PLA is dissolved or swelled in the reaction system, the Lewis acid $FeCl_3$ interacts with the O=C group in PLA molecule, which increases the positive electricity of the carbonyl carbon. Meantime, the oxygen atom in CH_3OH attacks the carbonyl carbon to result in the breakage of the C-O bond, and some oligomers are obtained. Then the oligomers react further with methanol to generate the product, methyl lactate.

Kinetics of PLA methanolysis

In studies of the degradation kinetics of polymers, the reaction order was usually considered to be first-order in some papers [20]. Therefore, the methanolysis of PLA

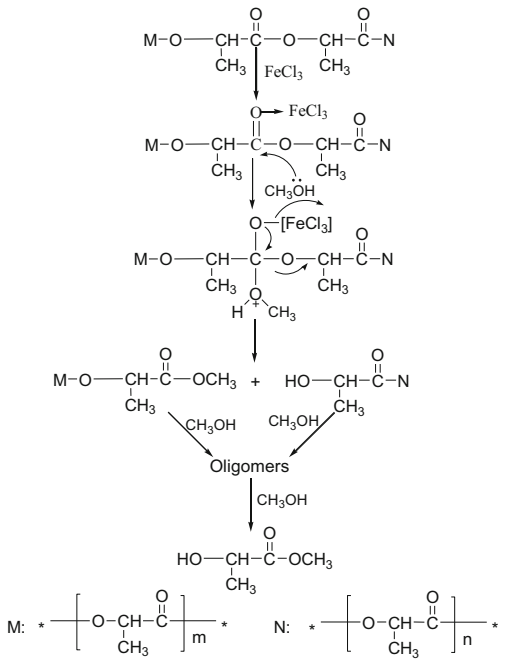

Fig. 8 Possible mechanism of PLA methanolysis catalyzed by $FeCl_3$

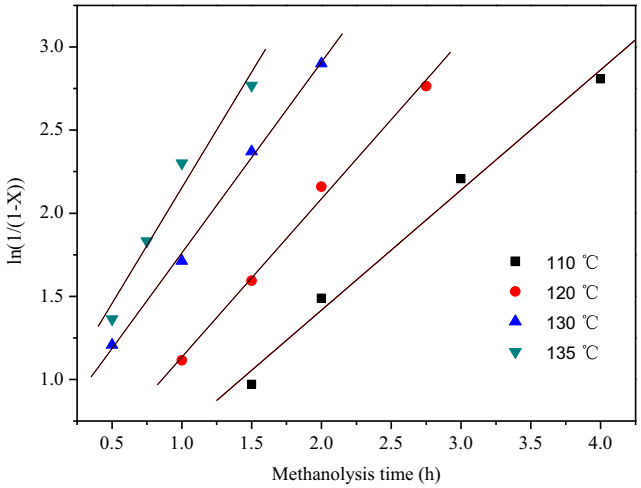

Fig. 9 Effect of reaction temperature on methanolysis rate of PLA

catalyzed by $FeCl_3$ was initially assumed to be controlled by first-order kinetic Eq. (3).

$$\frac{d(C_{PLA})}{dt} = -kC_{PLA} \tag{3}$$

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

$$C_{PLA} = C_{PLA0}(1-X) \tag{4}$$

where X represents the PLA conversion, so Eq. (3) could be written as follows:

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

Equation (5) was integrated against time to give Eq. (6).

$$\ln\frac{1}{1-X} = kt \tag{6}$$

As a catalyst, $FeCl_3$ is used in the PLA methanolysis, the influences of reaction temperature on the rate are presented in Fig. 9, and the linear regression results of the data in Fig. 9 are shown in Table 2. From Table 2, it is clear that all of the linear correlative coefficients are higher than 0.98, which indicates that ln1/(1-X) is proportional to the reaction time at different

Table 2 Linear regression results of the data in Fig. 9

Reaction temperature/ °C	Regressive equation	Linear correlative coefficient
110	y=−0.02986+ 0.72319x	0.99485
120	y=0.18137+0.9529x	0.99760
130	y=0.6135+ 1.1474x	0.99876
135	y=0.76243+ 1.39074x	0.98258

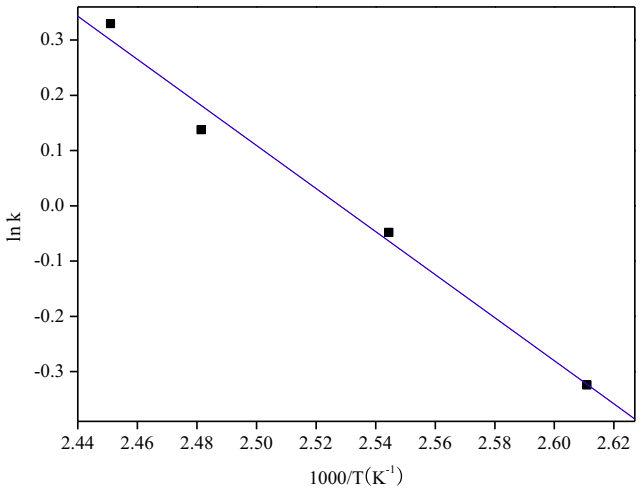

Fig. 10 Arrhenius plot of rate constant of PLA methanolysis

temperatures, and this process is a first-order kinetic reaction, that is to say, the methanolysis rate of PLA catalyzed by $FeCl_3$ is proportional to the PLA concentration. The slope values of the straight lines are 0.72319 h^{-1},0.9529 h^{-1}, 1.1474 h^{-1} and 1.39074 h^{-1} from Fig. 9, which represent the rate constants of the methanolysis reaction at 110 °C, 120 °C, 130 °C and 135 °C, respectively.

Using above rate constants, the activation energy (E_a) could be obtained by Eq. (7).

$$\ln k = \ln A - \frac{E_a}{RT} \tag{7}$$

where A is the Arrhenius constant, R is the gas constant (8.31 J/k mol) and T is the temperature in Kelvin. According to the relationship of rate constant with reaction temperature, the Arrhenius plot of the rate constant of the methanolysis of PLA catalyzed by $FeCl_3$ is shown in Fig. 10. The E_a of this reaction calculated from the slope was 32.41 kJ/mol. The E_a value is close to that of methanolysis of PLA in ionic liquid [HSO_3-pmim][HSO_4] [30].

Conclusion

Poly(lactic acid) can be effectively depolymerized by methanolysis to obtain methyl lactate using $FeCl_3$ as catalyst. Under the conditions of reaction temperature 130 °C, reaction time 4.0 h, n($FeCl_3$):n(PLA)=0.01:1 and n(CH_3OH):n(PLA)= 5:1, the methanolysis conversion of PLA was over 96 % and the yield of methyl lactate was 87.2 %, respectively. Especially, the catalyst can be reused for six times without any decrease in its catalytic activity and selectivity. This method can overcome the shortcomings associated with conventional methods, such as unfeasible recycle of catalyst, equipment corrosion, tedious workup processes. Moreover, the kinetics of this reaction was investigated. Results indicated that the methanolysis of PLA catalyzed by $FeCl_3$ was a first-order kinetic reaction and the activation energy was 32.41 kJ/mol.

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