

Methanolysis of Poly(lactic acid) Using Acidic Functionalized Ionic Liquids as Catalysts

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ABSTRACT: The methanolysis of poly(lactic acid) (PLA) was studied by using acidic ionic liquids (ILs) as catalyst in detail. The results showed that HSO₃-functionalized ILs exhibited higher catalytic activity than non-functionalized ILs and traditional acid catalyst such as H₂SO₄. The influences of experimental parameters, such as the amount of catalyst, reaction temperature, methanolysis time, and dosages of methanol on the conversion of PLA, yield of methyl lactate were investigated. Under the optimal conditions, using 1-methyl-3-(3-sulfopropyl)-imidazolium hydrogen sulfate ([HSO₃-pmim][HSO₄]) as catalyst, the IL could be reused up to six times without apparent decrease in the conversion of PLA and yield of methyl lactate. The kinetics of the reaction was also investigated. The results indicated that the methanolysis of PLA in [HSO₃-pmim][HSO₄] was a first-order kinetic reaction with activation energy of 47.01 kJ/mol and Arrhenius constant of $2.7 \times 10^7 \text{ min}^{-1}$. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40817.

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INTRODUCTION

Currently, climate warming and depletion of fossil fuels are serious problems. Fossil fuels, as energy resources and raw materials, are used in the production of various chemical materials, such as plastics. In contemporary society, plastic products have been widely used in industry and in our daily life, but their waste and environmental treatment remain a challenge. For example, plastic products are the main source of carbon dioxide emission, which is a greenhouse gas.¹ To solve this problem, several types of bio-based materials have been developed, because they can be used as alternative raw materials. Among of them, poly(lactic acid) (PLA), as a biodegradable and biocompatible polymer, has been attracting much attention due to its excellent material properties that permit a wide variety of potential applications in areas, such as medical devices, textiles, food packages.^{2,3} With the widespread use and increasing consumption, the amount of waste PLA is growing rapidly. Although this kind of polyester is biodegradable, it takes a long time to be decomposed in nature.⁴ Thus, from the perspectives of preservation of natural resources and protection of environment, the effective recycling of PLA waste is a significant subject for researchers. There are two principal methods for recycling waste PLA, which are physical and chemical ones. Chemical method is an advantageous method because it can improve the efficiency of PLA utilization.⁵

Several methods have been reported for the chemical recycling of PLA, such as thermal pyrolysis,^{6–8} hydrolysis,^{9–11} and alcoholysis.^{12–14} The thermal pyrolysis must be carried out at high temperature and under vacuum conditions, in the presence of suitable catalysts. The hydrolysis, unlike the thermal degradation, it does not require severe operating conditions or catalysts. The hydrolysis of PLA in an aqueous environment is essentially influenced by the pH, the temperature, and the crystallinity of the PLA. Alcoholysis is one of the techniques of chemical degradation of PLA, which has been reported way back in 1990s.^{15,16} However, due to the insolubility of PLA in alcohol, reported alcoholysis methods require higher temperature and large quantities of catalysts.¹⁴ The acid or base catalysts used in traditional methods cannot be reused, and these methods are associated with obvious drawbacks, such as laborious and complex workup and purification, significant amounts of waste materials and environmental problems. Although microwave irradiation could avoid using these catalysts,¹³ it has other shortcomings, such as severe conditions, hence its application has been limited.

Ionic liquids (ILs) being considered as environmentally friendly solvents and catalysts have received a lot of interest for their unusual properties such as a wide liquid range, high ionic conductivity, a wide voltage window, non-volatility, and non-flammability.^{17–21} Recently, ILs have been successfully used in the

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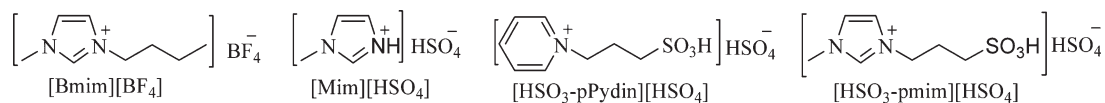


Figure 1. ILs prepared for use in the present study.

degradation of polymers such as polycarbonate,²² polyethylene,²³ polyamide,²⁴ and poly(ethylene terephthalate).^{25–28} In our previous study, we have found that basic IL [Bmim][Ac] could catalyze methanolysis of PLA and more than 97% conversion of PLA and more than 92% yield of methyl lactate were obtained.²⁹ In this article, methanolysis of PLA catalyzed by acidic ILs was investigated, and the results showed that using ([HSO₃-pmim][HSO₄]) as a catalyst for methanolysis of PLA, the high conversion of PLA and yield of methyl lactate were also obtained. The effects of experimental conditions on the methanolysis of PLA were also illustrated. Moreover, the reusability of the IL and kinetics of this reaction were investigated. To our knowledge, it is the first report on the use of acidic functionalized ILs as homogeneous catalysts for methanolysis of PLA into methyl lactate.

EXPERIMENTAL

Materials

PLA pellets (3.0 mm length and 2.5 mm diameter) were supplied by Shenzhen ESUN Industrial Co. Ltd., China, their average molecular weight, measured by GPC (Waters-515) in tetrahydrofuran (THF) solution at 25°C, was found to be 3.8×10^4 g mol⁻¹. 1-Methylimidazole (MIM, 99%) was purchased from Zhejiang Kaile Chemicals Co. Ltd. Other materials, such as 1,3-propane sultone (1,3-PS, 99%) and a standard sample of methyl lactate (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. Fourier transform infrared spectroscopy (FTIR) spectra, which were determined using a Nicolet 510P FTIR spectrometer using KBr or liquid film. Thermal gravimetric analysis (TGA) was used to measure the weight of the reused and the fresh ILs by a NETZSCH STA 409 PC/PG thermogravimetric analyzer in an atmosphere of nitrogen over a temperature range from room temperature to 500°C at a heating rate of 20°C/min.

Synthesis of Ionic Liquids

The ILs used in this article (Figure 1) are synthesized according to the procedures in the previous literatures.^{30–32}

Acid Detection

Prepared 0.01 mol/L standard solution by dissolving 0.001 mol IL into 100 mL deionized water. The pH value was measured by PHS-25 pH meter (Shanghai Precision & Scientific Instrument Co. Ltd.) (repeated three times).

Methanolysis of PLA in the Presence of Ionic Liquid

Weighed amounts of PLA (w_0), methanol, and IL were charged into an 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 each methanolysis reaction finished, the content of the reactor 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):

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

Meanwhile, the filtrate was distilled to recover the unreacted methanol at atmospheric pressure and obtained the main product by vacuum distillation. The residue after distillation was mainly IL, which was reused directly as a catalyst without any treatment. The yield of main product was calculated by eq. (2):

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

Qualitative Analysis of the Main Product

Qualitative analysis of the obtained product in the methanolysis of PLA was performed. The GC chromatograms are shown in Supporting Information Figure S1. It indicates that the main product in the presence of [HSO₃-pmim][HSO₄] has the same retention time as the standard methyl lactate under the same chromatogram conditions. This means that the obtained product in the methanolysis process is probably methyl lactate. Supporting Information Table S1 indicates that purity of the main product obtained in our research is 99.13%.

In order to confirm that the main product of methanolysis is methyl lactate, FTIR of main product and standard methyl lactate sample were performed. FTIR spectra are shown in Figure 2. It can be clearly seen the spectrum contains a -OH band at 3476 cm⁻¹ and 1145 cm⁻¹, a C=O stretching at 1742 cm⁻¹, an alkyl C-H at 2990 cm⁻¹ and 2953 cm⁻¹, and C-O of ester at

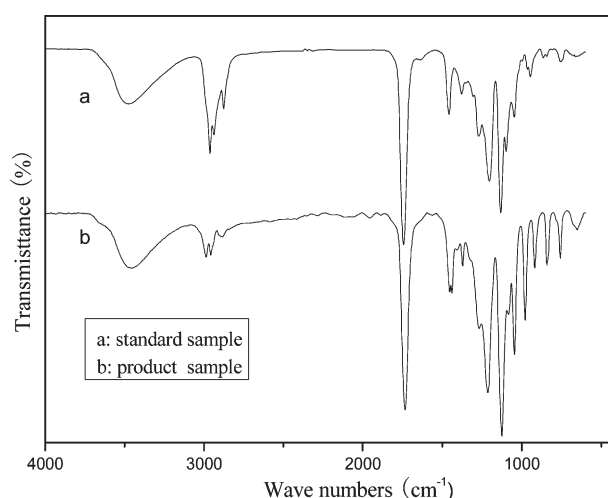


Figure 2. FTIR spectra of methanolysis main product and standard methyl lactate sample.

Table I. Effect of Catalysts on the Methanolysis of PLA^a

Entry	Catalyst	PLA conversion (%)	Methyl lactate yield ^b (%)	PH value
1	None	0	0	-
2	[Bmim][BF ₄]	0	0	6.88
3	H ₂ SO ₄	75.12	50.87	1.87
4	[Mim][HSO ₄]	28.2	12.3	2.02
5	[HSO ₃ -Pydin][HSO ₄]	82.1	69.9	1.80
6	[HSO ₃ -pmim][HSO ₄]	94.8	86.9	1.74

^aReaction conditions: PLA (2.0 g), $n(\text{CH}_3\text{OH}) : n(\text{PLA}) = 5 : 1$, ionic liquid (0.04 g), reaction temperature 115°C, reaction time 3.0 h.

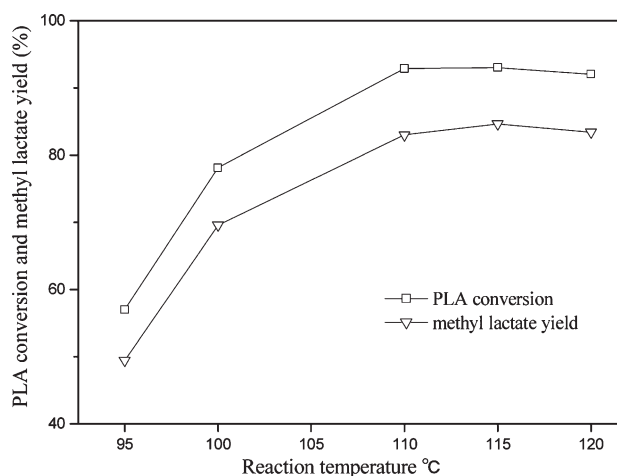
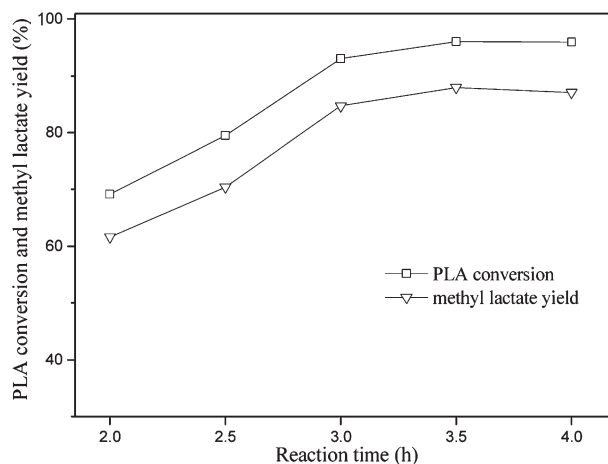
^bThe isolated yield.

1223 cm⁻¹ and 1132 cm⁻¹. The IR spectrum of the obtained product is almost the same as that of a standard sample.

RESULTS AND DISCUSSION

Selection of the Catalysts

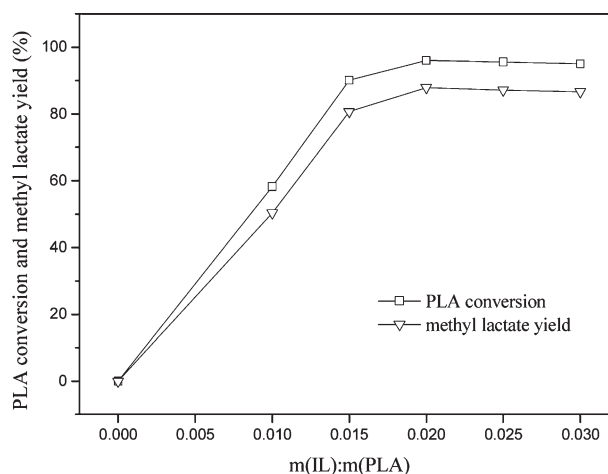
The catalytic performance of the synthesized ILs on the methanolysis of PLA was investigated, and the results are summarized in Table I. From Table I, it can be seen that the methanolysis of PLA could not take place without a catalyst (Entry 1), and neutral IL [Bmim][BF₄] (Entry 2) could not catalyze PLA methanolysis. Both H₂SO₄ and acid ILs (Entry 4–6) can accelerate the methanolysis process. It is well known that the methanolysis of PLA is a transesterification reaction, so acidic catalysts are beneficial to the reaction. When the acidic IL [Mim][HSO₄] was used as a catalyst, the conversion of PLA was arrived at 28.2%, however the yield of methyl lactate was only 12.3% (Entry 4). In order to increase the yield of product in the methanolysis of PLA, the strong acidic ILs were utilized, especially acidic functionalized ILs such as [HSO₃-pPydin][HSO₄] and [HSO₃-pmim][HSO₄]. The conversion of PLA catalyzed by [HSO₃-pPydin][HSO₄] and [HSO₃-pmim][HSO₄] could reach 82.1% and 94.8%, respectively (Entry 5 and 6). It was indicated that enhancing the acidity of the IL was advantageous to increase

**Figure 3.** Effect of reaction temperature on the methanolysis of PLA.**Figure 4.** Effect of reaction time on the methanolysis of PLA.

the conversion of PLA and the yield of methyl lactate. The results show that the acidic functionalized IL [HSO₃-pmim][HSO₄] was an excellent catalyst for the methanolysis of PLA.

Effects of Reaction Conditions on the Methanolysis Reaction of PLA

Effect of Reaction Temperature. The effect of reaction temperature on the conversion of PLA and the yield of methyl lactate was investigated and the results are shown in Figure 3. From Figure 3, it can be seen that a significant increase in PLA conversion and the methyl lactate yield increasing reaction temperature were observed. When temperature was 95°C, the PLA conversion was only 57%. Subsequently, with increasing methanolysis temperature, the conversion of PLA increased apparently and rapidly reached 93% when the temperature was set at 115°C. Furthermore, the yield of methyl lactate increased as the reaction temperature was raised. When the methanolysis temperature was 95°C, the yield of methyl lactate was only 0.46% after 3.0 h. Then it dramatically increased from 0.46% to 84.5% when the methanolysis temperature raised to 115°C. Thus, high temperature was beneficial to the formation of methyl lactate

**Figure 5.** Effect of catalyst concentration on the methanolysis of PLA.

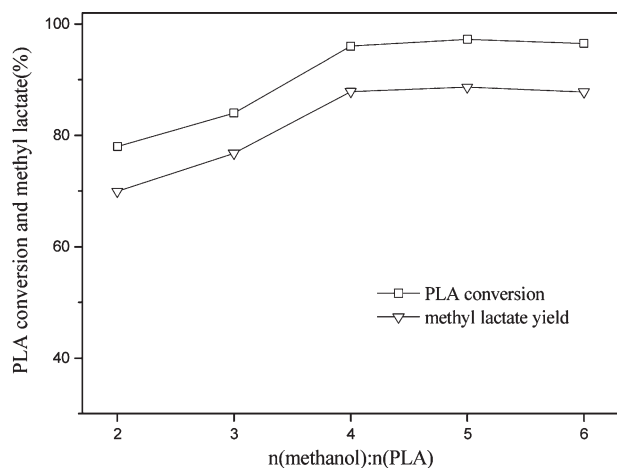


Figure 6. Effect of the mole ratio of methanol to PLA on the methanolysis of PLA.

from the methanolysis of PLA. So, the reaction temperature is a critical factor in the methanolysis of PLA.

Effect of Reaction Time. The effects of reaction time on the conversion of PLA and the yield of methyl lactate were examined and the results are presented in Figure 4. It indicated that the conversion of PLA increases distinctly with increasing methanolysis time. When the reaction time was extended to 3.5 h, the methanolysis conversion was achieved 96.3% and the yield of methyl lactate was over 87.9%. Moreover, the PLA conversion and the methyl lactate yield almost leveled off with prolonging reaction time, it maybe that the transesterification is a reversible reaction, the equilibrium is reached at 3.5 h, the maximum conversion of PLA is reached.

Effect of Catalyst Concentration. The influence of the dosage of the catalyst on the conversion of PLA and the yield of methyl lactate is shown in Figure 5. It showed that the conversion of PLA was increased with the amount of the acidic IL $[\text{HSO}_3\text{-pmim}][\text{HSO}_4]$ and over 96% conversion of PLA was obtained when the mass ratio $m(\text{IL}) : m(\text{PLA})$ was more than 0.02 : 1 under the given conditions. So the dosages of the catalyst $[\text{HSO}_3\text{-pmim}][\text{HSO}_4]$ were 0.02 : 1 (0.04 g), the methanolysis of PLA almost finished and the yield of methyl lactate was arrived at 87.9%.

Effect of Methanol Dosages. Methanol to PLA ratio is also a very important parameter for the methanolysis. The effect of methanol to PLA ratio on the depolymerization reaction is summarized in Figure 6. Under the optimum mole ratio of methanol : PLA of 5 : 1, reaction temperature 115°C, and time 3.5 h, the conversion of PLA and the yield of methyl lactate were over 97% and 88.7%, respectively. The PLA conversion

and methyl lactate yield all decreased with dosage of methanol growing, at $n(\text{methanol}) : n(\text{PLA})$ ratio is 6:1. It may be attributed to the decrease of catalytic consistence when we increase methanol dosages.

Reusability of $[\text{HSO}_3\text{-pmim}][\text{HSO}_4]$ for Methanolysis of PLA

From the viewpoint of environmental conservation and economics of the process, recycling use of the catalyst IL is absolutely required after the methanolysis of PLA. The reuse performances of the IL $[\text{HSO}_3\text{-pmim}][\text{HSO}_4]$ in the methanolysis of PLA are shown in Table II. $[\text{HSO}_3\text{-pmim}][\text{HSO}_4]$ could be reused for six times without significant change in the conversion of PLA and yield of methyl lactate under the given conditions. It is well known that the main factor which affects the reuse performance of IL is its stability under the reaction temperature and reaction fluid surroundings. Because the IL $[\text{HSO}_3\text{-pmim}][\text{HSO}_4]$ itself had a good thermal stability and the reaction temperature was only 115°C, it is reasonable that IL $[\text{HSO}_3\text{-pmim}][\text{HSO}_4]$ had a good reusability. The TGA curve in Supporting Information Figure S2 indicated that the IL $[\text{HSO}_3\text{-pmim}][\text{HSO}_4]$ was thermally stable when the temperature was below 330°C. Therefore, $[\text{HSO}_3\text{-pmim}][\text{HSO}_4]$ is an effective and reusable catalyst for methanolysis of PLA.

Kinetics of PLA Methanolysis

In studies of depolymerization kinetics of polymers, the reaction order was usually considered to be first-order in some literatures.³³ Therefore, the methanolysis of PLA in the presence of $[\text{HSO}_3\text{-pmim}][\text{HSO}_4]$ was initially assumed to be controlled by first-order kinetic [eq. (2)].

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

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

$$C_{\text{PLA}} = C_{\text{PLA}0}(1-X) \quad (4)$$

where X represents the conversion of PLA, so eq. (2) could be written as follows:

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

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

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

The effect of reaction temperature on the rate of methanolysis of PLA in the presence of $[\text{HSO}_3\text{-pmim}][\text{HSO}_4]$ is shown in Figure 7 and the linear regression results of the data in Figure 7 are shown in Table III. All of the linear correlative coefficients in Table III were higher than 0.99, which indicated that $\ln(1/(1-X))$ was proportional to the reaction time at different

Table II. Recycling Use of $[\text{HSO}_3\text{-pmim}][\text{HSO}_4]$ ^a

Reused times	1	2	3	4	5	6
PLA conversion (%)	97.54	96.55	96.02	95.5	95.03	94.58
Methyl lactate yield (%)	88.85	87.47	86.82	87.86	86.82	86.55

^a $m([\text{HSO}_3\text{-pmim}][\text{HSO}_4]) : m(\text{PLA}) = 0.02 : 1$, $n(\text{CH}_3\text{OH}) : n(\text{PLA}) = 5 : 1$, $T = 115^\circ\text{C}$, $t = 3.5$ h.)

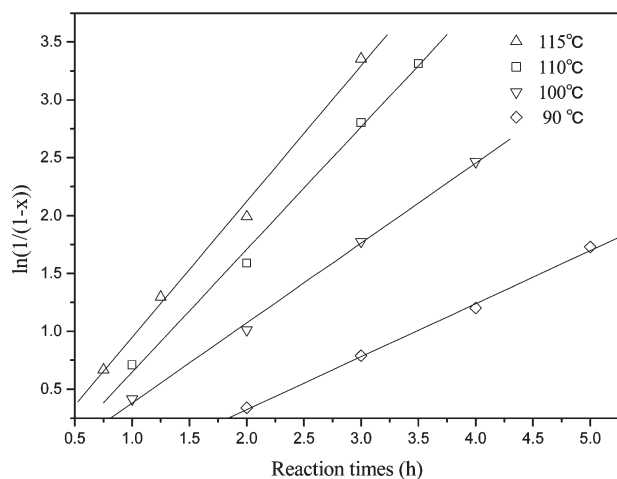


Figure 7. Effect of reaction temperature on methanolysis rate of PLA in $[\text{HSO}_3\text{-pmim}][\text{HSO}_4]$.

temperatures, and that this process was a first-order kinetic reaction. The methanolysis rate of PLA in $[\text{HSO}_3\text{-pmim}][\text{HSO}_4]$ was proportional to the PLA concentration. The straight lines in Figure 7 give the slope values of 0.45887 h^{-1} , 0.69126 h^{-1} , 1.06059 h^{-1} , and 1.17532 h^{-1} . Thus, the rate constants of 0.45887 h^{-1} , 0.69126 h^{-1} , 1.06059 h^{-1} , and 1.17532 h^{-1} , were recorded for this methanolysis reaction at temperatures of 90°C , 100°C , 110°C , and 115°C , respectively.

To calculate the energy of activation (E_a) and Arrhenius constant (A), the methanolysis reactions were undertaken at $90\text{--}115^\circ\text{C}$. Using the rate constants above, the activation energy (E_a) could be obtained from eq. (7). Various values of methanolysis rate constants as a function of temperature were used to construct an Arrhenius plot (Figure 8). The slope of this plot (Figure 8) was obtained and recorded that was used to calculate the value of energy of activation (E_a) by employing the well-known modified Arrhenius equation, $\ln k = -E_a/RT + \ln A$.

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

This equation shows the value of the slope of Arrhenius plot (Figure 8) equal to $-E_a/RT$. By substitution of the value of R , the value of E_a was calculated that was recorded as 47.01 kJ/mol . The intercept of an Arrhenius plot (Figure 8) is equal to $\ln A$, from which the value of an Arrhenius constant (A) was calculated that was recorded as $2.7 \times 10^7 \text{ min}^{-1}$. Our value of E_a is little higher than that of alcoholysis of PLA under microwave irradiation.¹³

Table III. Linear Regression Results of the Data in Figure 7

Reaction temperature($^\circ\text{C}$)	Regressive equation	Linear correlative coefficient
115	$y = -0.22803 + 1.17532x$	0.9923
110	$y = -0.41399 + 1.06059x$	0.9972
100	$y = -0.31063 + 0.69126x$	0.9981
90	$y = -0.59114 + 0.45887x$	0.9988

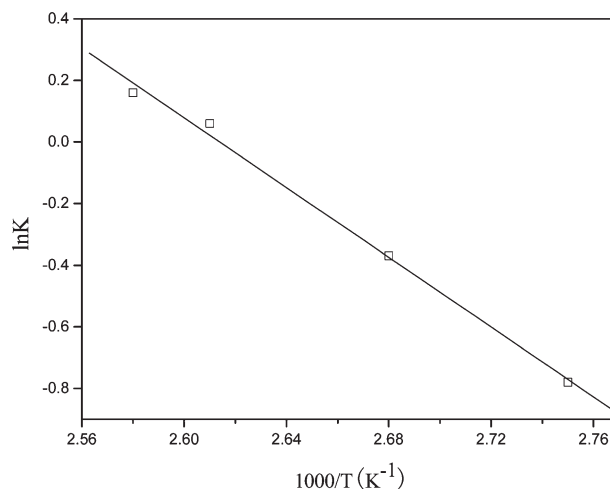


Figure 8. Arrhenius plot of rate constant of methanolysis of PLA in $[\text{HSO}_3\text{-pmim}][\text{HSO}_4]$.

CONCLUSIONS

In summary, it was demonstrated that $[\text{HSO}_3\text{-pmim}][\text{HSO}_4]$ could behave as the efficient catalyst for the depolymerization of PLA in methanol. A significant increase in PLA conversion and methyl lactate yield was observed when the reaction temperature increased from 95°C to 115°C . Results show that the reaction temperature is a critical factor in this reaction. Under the optimal conditions: reaction temperature 115°C , reaction time 3.5 h, weight ratio of PLA : IL is 1 : 0.02 and molar ratio of PLA : CH_3OH is 1 : 5, the conversion of PLA and methyl lactate yield was over 97% and 88.7%, respectively. Importantly, the catalyst is easily separated from the production mixture and can be reused a minimum of six times. Thus, the IL $[\text{HSO}_3\text{-pmim}][\text{HSO}_4]$ show a high catalytic activity and stability. In addition, the kinetics of this reaction was investigated. Results indicated that the methanolysis of PLA in $[\text{HSO}_3\text{-pmim}][\text{HSO}_4]$ was a first-order kinetic reaction and the activation energy was 47.01 kJ/mol .

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