Methanolysis of polycarbonate catalysed by ionic liquid [Bmim][Ac]

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ABSTRACT

The methanolysis of polycarbonate (PC) was studied using ionic liquid [Bmim][Ac] as a catalyst. The effects of temperature, time, methanol dosage and [Bmim][Ac] dosage on the methanolysis reaction were examined. It was shown that the conversion of PC was nearly 100%, and the yield of bisphenol A (BPA) was over 95% under the following conditions: m([Bmim][Ac]):m(PC) = 0.75:1; m(methanol):m(PC) = 0.75:1; a reaction temperature of 90 °C and a total time of 2.5 h. The ionic liquid could be reused up to 6 times with no apparent decrease in the conversion of PC and yield of BPA. The kinetics of the reaction was also investigated. The results indicated that the methanolysis of PC in [Bmim][Ac] was a first-order kinetic reaction with an activation energy of 167 kJ/mol.

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1. Introduction

Due to its excellent properties, polycarbonate (PC) is widely used in the manufacture of compact disks, bulletproof windows, food packaging and soft-drink bottles. With the rapid increase in the production and consumption of PC, the chemical recycling of waste PC to obtain valuable products has received greater attention in recent years. Waste PC can be depolymerised through a chemical treatment to produce monomers that can be used to reproduce virgin PC products. Various methods for the chemical recycling of waste PC to recover raw materials have been reported; these methods include thermal pyrolysis [1,2], alcoholysis [3,4] and hydrolysis [5,6]. It is difficult to recover pure bisphenol A (BPA) using thermal pyrolysis, and only BPA can be obtained using hydrolysis. Therefore, methanolysis has become the most important method used to recover pure monomers of BPA and dimethyl carbonate (DMC). However, due to the insolubility of PC in methanol, reported methanolysis methods require higher temperatures and pressures as well as the presence of large quantities of concentrated acids or bases. The acid or base catalysts used in traditional methods cannot be reused, and these methods are associated with other disadvantages, such as equipment corrosion, tedious workup procedures and environmental problems. Although the supercritical method could overcome some of the aforementioned shortcomings [7,8], it has disadvantages as well, such as severe conditions; its application has therefore been limited. In our previous

research, ionic liquid [Bmim][Cl] was found to exhibit excellent catalytic activity and reusability [9] when used as catalyst in the methanolysis of PC. In this study, ionic liquid [Bmim][Ac] was synthesised and used as catalyst in the methanolysis of PC. Compared with [Bmim][Cl], [Bmim][Ac] had much higher catalytic activity for the methanolysis of PC. In addition, the kinetics of the methanolysis of PC in the presence of [Bmim][Ac] was investigated and its activation energy obtained. To the best of our knowledge, no article concerning the methods outlined here has been published.

2. Experimental

2.1. Chemicals and instruments

Pure PC pellets (3 mm length and 2.5 mm diameter with MW about 20,000) were used as model plastics. The n-methylimidazole (MIM, 99%), n-butylchloride and other chemicals (AR) were commercially available and used without further purification.

Infrared (IR) spectra were recorded using a Nicolete 510P FT-IR spectrometer in the range of 4500–400 cm^{-1}. The NMR spectra were recorded on a BRUKER AV500 spectrometer and calibrated with tetramethylsilane (TMS) as an internal reference.

2.2. Synthesis of ionic liquids

2.2.1. Synthesis of 1-n-butyl-3-methylimidazolium chloride ([Bmim][Cl])

[Bmim][Cl] was synthesised according to the methods outlined in Ref. [9].

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2.2.2. Synthesis of 1-butyl-3-methylimidazolium acetate ([Bmim][Ac])

Charged into a round bottom flask equipped with a reflux condenser and a thermometer were 26.20 g (0.15 mol) [Bmim][Cl], 16.69 g (0.17 mol) potassium acetate and 65.00 g ethanol. The mixture was reacted, with stirring, at 40 °C for 6 h. The precipitate generated was removed using a filtration system, and the filtrate was distilled at 85 °C under reduced pressure (5 mmHg) to remove the ethanol. The resulting mixture was filtered again to remove precipitated potassium acetate and sodium chloride. The filtrate was cooled to −10 °C and maintained at that temperature for 24 h to further precipitate out potassium acetate and sodium chloride. The precipitate generated was removed by filtration; the liquid obtained was [Bmim][Ac] (yield 88%). The ^{1}H NMR (500 MHz, CDCl$_3$) included peaks at: δ = 10.80 (s, 1H, CH), δ 7.27 (s, 1H, CH), δ 7.18 (s, 1H, CH), δ 4.07 (t, 2H, NCH$_2$), δ 3.81 (s, 3H, NCH$_3$), δ 1.73 (s, 3H, CH$_3$CO), δ 1.66 (m, 2H, CH$_2$), δ 1.13 (m, 2H, CH$_2$), δ 0.71 (t, 3H, CH$_3$). ^{13}C NMR (500 MHz, CDCl$_3$): δ = 176.87, 138.26, 123.22, 121.57, 48.99, 35.64, 31.70, 25.00, 18.94, 12.94. The IR wave numbers were at: ν(cm^{-1}) = 3146, 3081, 2963, 2937, 2875, 1665, 1573, 1465, 1393, 1173, 881, 754, 644, 625.
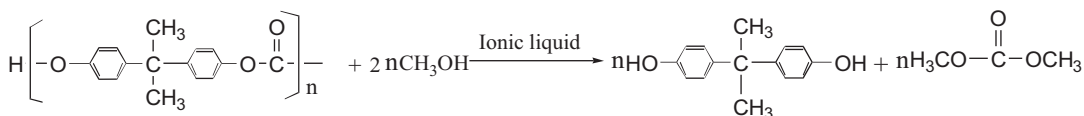
2.3. Methanolysis of PC

Weighed amounts of PC (w_1), methanol and ionic liquid were charged into an autoclave with a stirrer and a thermometer. The mixture was heated to the given temperature and reacted for the prescribed time at autogenous pressure. An equal volume of ethyl acetate was added to the resulting mixture. The unreacted PC (w_2) was removed by filtration and the filtrate separated into two phases. The upper phase, which was composed mainly of BPA, DMC, methanol and ethyl acetate, was analysed by a HP 5890 gas chromatograph equipped with a 50 m long DB-5 glass capillary column to obtain the weight of BPA (w_3); the lower phase, which was mainly ionic liquid, was reused directly as a catalyst. Conversion of PC and yield of BPA were calculated by the following formulae:

$$\text{Conversion of PC} = \frac{w_1 - w_2}{w_1} \times 100\% \qquad (1)$$

$$\text{Yield of BPA} = \frac{w_3}{w_1} \times \frac{M(PC)}{M(BPA)} \times 100\% \qquad (2)$$

where M(PC) and M (BPA) are the molar masses of the repeating unit of PC and BPA.

The reaction formula was as follows:

3. Results and discussion

3.1. Activities of [Bmim][Cl] and [Bmim][Ac] ionic liquids in methanolysis of PC

The activities of [Bmim][Cl] and [Bmim][Ac] in the methanolysis of PC were investigated (Table 1). As can be seen from Table 1, [Bmim][Ac] exhibited a much higher activity in the methanolysis of PC than [Bmim][Cl]. When the reaction temperature was 105 °C and no other solvent, such as tetrahydrofuran (THF), was used, the conversion of PC was almost 100% in the presence of [Bmim][Cl] or [Bmim][Ac] (Entries 1 and 2). However, when the temperature was 90 °C, almost no methanolysis of PC took place in the presence of [Bmim][Cl], whereas the conversion of PC was still 100% in the presence of [Bmim][Ac] (Entries 3 and 4). This may be attributed to the difference in solubility or swelling of PC in [Bmim][Cl] and

Table 1
Activities of [Bmim][Cl] and [Bmim][Ac] ionic liquids in methanolysis of PC.[a]

Entry	Ionic liquids	m(Ionic liquid): m(PC)	m(THF) :m(PC)	T (°C)	PC conversion (%)	BPA yield (%)
1	[Bmim][Cl]	0.5:1	0	105	100	95.6
2	[Bmim][Ac]	0.5:1	0	105	100	96.0
3	[Bmim][Ac]	0.5:1	0	90	100	95.5
4	[Bmim][Cl]	0.5:1	0	90	0	0
5	[Bmim][Ac]	0.05:1	1:1	105	100	95.4
6	[Bmim][Cl]	0.05:1	1:1	105	0	0

[a] m(methanol):m(PC) = 1.5:1, t = 2.5 h.

Table 2
Dissolubility of PC in [Bmim][Cl] and [Bmim][Ac].[a]

Entry	Ionic liquids	T (°C)	Dissolubility of PC(g)
1	[Bmim][Ac]	105	0.97
2	[Bmim][Ac]	90	0.46
3	[Bmim][Ac]	70	0.08
4	[Bmim][Cl]	105	Swelling significantly
5	[Bmim][Cl]	90	Swelling insignificantly
6	[Bmim][Cl]	70	No swelling

[a] A mixture of 5 g ionic liquid and 2 g PC was stirred at given temperature for 2.5 h. The resulting mixture was filtered under vacuum immediately and the PC residue was washed with 10 ml ethanol for three times and dried at 100 °C for 2 h, then weighted.

[Bmim][Ac] at different temperatures. It is well known that PC is a rigid polymer, and it is extremely difficult for PC to react with methanol if PC does not dissolve or swell in the reaction medium. Hence, the dissolubility or swelling of PC in the reaction mixture is the rate-determining step for the methanolysis of PC [9]. To explain the results, tests on the solubility of PC in [Bmim][Cl] and [Bmim][Ac] were carried out (Table 2). The solubility of PC in 5 g [Bmim][Ac] was as high as 0.97 g at 105 °C and 0.46 g at 90 °C. Although PC did not dissolve in [Bmim][Cl] at 105 °C, it swelled significantly. However, there was insignificant swelling of PC in [Bmim][Cl] at 90 °C, and it was expected that the swelling of PC would decrease even further in the reaction mixture at 90 °C because of the presence of methanol. Therefore, it is reasonable that no methanolysis of PC took place in the presence of [Bmim][Cl] at 90 °C.

As can be seen from Table 1, when tetrahydrofuran was used as a solvent and m(Ionic liquid):m(PC) was decreased from 0.5:1 to 0.05:1, [Bmim][Ac] still had excellent activity for the methanolysis of PC (Entry 5), whereas [Bmim][Cl] had almost no activity under the same conditions (Entry 6). This may have been due to the stronger basicity of [Bmim][Ac] compared to [Bmim][Cl]. It was determined that the pH values of [Bmim][Cl] and [Bmim][Ac] were 7.56 and 9.57, respectively. It is well-known that the methanolysis of PC is a nucleophilic substitution reaction; the stronger the basicity of the catalyst, the higher its activity. The catalytic mechanism of PC methanolysis in [Bmim][Ac] is suggested in Fig. 1.

3.2. Effects of reaction conditions on methanolysis results of PC

The effects of the reaction conditions on the methanolysis results are shown in Table 3. It can be seen that the temperature had a significant effect on the methanolysis results of PC.
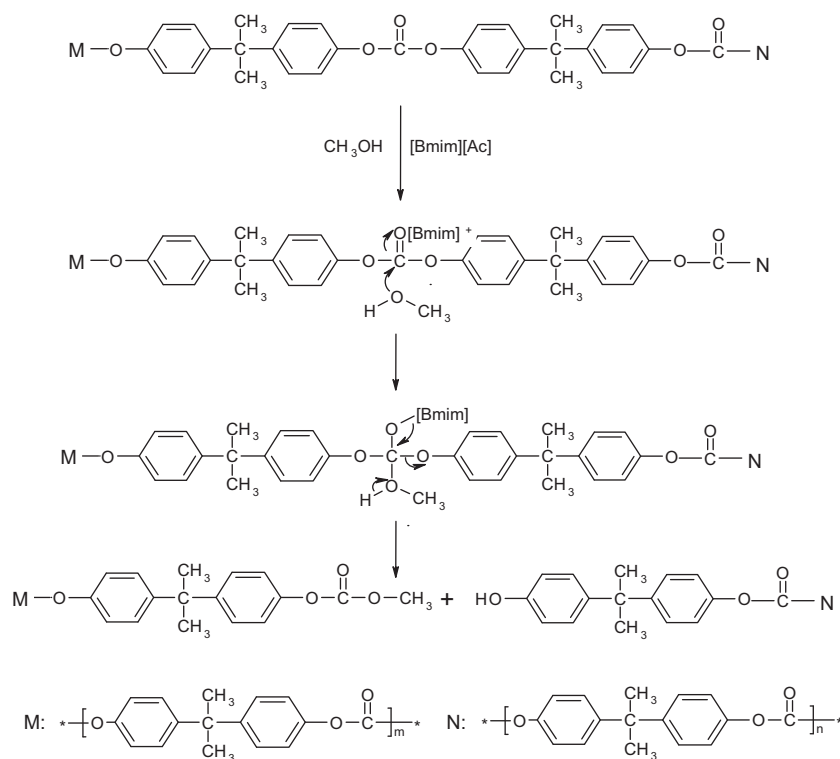
Fig. 1. Catalytic mechanism of PC mathanolysis in [Bmim][Ac].

Table 3
Effects of reaction conditions on methanolysis results.[a]

Entry	Temperature (°C)	m(methanol):m(PC)	m([Bmim][Ac]):m(PC)	PC conversion (%)	BPA yield (%)
1	70	0.75:1	1:1	10.5	5.2
2	80	0.75:1	1:1	50.8	42.3
3	90	0.75:1	1:1	100	95.6
4	90	0.75:1	0.5:1	100	95.4
5	90	0.75:1	0.3:1	95.5	91.1
6	90	0.75:1	0.1:1	79.3	72.7
7	90	0.5:1	0.5:1	95.8	90.4
8	90	1.5:1	0.5:1	100	95.2
9	90	2:1	0.5:1	95.0	90.5

[a] $t = 2.5$ h.

When the temperature was 70 °C, the conversion of PC was only 10.5% (Entry 1) under the given conditions. When the temperature was increased, the conversion of PC increased gradually. When the temperature was increased to 90 °C under the same conditions, the methanolysis reaction of PC was almost complete, and the yield of BPA was over 95% (Entry 3). When the [Bmim][Ac] dosage was increased, both the conversion of PC and the yield of BPA increased. When m([Bmim][Ac]):m(PC) increased from 0.1:1 to 0.5:1, the conversion of PC increased from 79.3% (Entry 6) to 100% (Entry 4). Moreover, when the methanol dosage was increased, the conversion of PC increased initially. However, when m(methanol):m(PC) increased further from 0.75:1 to 2:1, the conversion of PC decreased from 100% (Entry 4) to 95% (Entry 9). All these results could be explained by the difference in solubility or swelling of PC in the reaction mixture. The higher the temperature, the more rapidly PC could dissolve or swell in the reaction mixture (see Table 2). Moreover, either too little [Bmim][Ac] dosage or too much methanol dosage was unfavourable for improving the solubility or swelling of PC in the reaction mixture. It has previously been suggested that the solubility or swelling of PC in the reaction mixture is the rate-determining step for the methanolysis of PC [9].

3.3. Reusability of [Bmim][Ac]

One of the most attractive properties of ionic liquid is its reusability when used as either a catalyst or a reaction medium. The reusability of ionic liquid [Bmim][Ac] in the methanolysis of PC was investigated, and the results are shown in Table 4. The ionic liquid could be reused up to 6 times without an apparent decrease in the conversion of PC and yield of BPA under the given conditions. Therefore, the ionic liquid had a good reusability for methanolysis of PC. It is well-known that the main factor that affects the reusable performance of ionic liquid is its stability under the reaction temperature and in the reaction fluid. Because ionic liquid [Bmim][Ac] itself had a good thermal stability, the reaction mixture was almost neutral and the reaction temperature was only 90 °C, it is reason-

Table 4
Reusability results of [Bmim][Ac].[a]

Cycle	1	2	3	4	5	6
PC conversion (%)	100	99.5	98.9	98.3	97.5	97.2
BPA yield (%)	95.6	95.0	95.8	94.3	94.5	93.8

[a] m([Bmim][Ac]):m(PC) = 0.75:1, m(methanol):m(PC) = 0.75:1, $T = 90$ °C, $t = 2.5$ h.
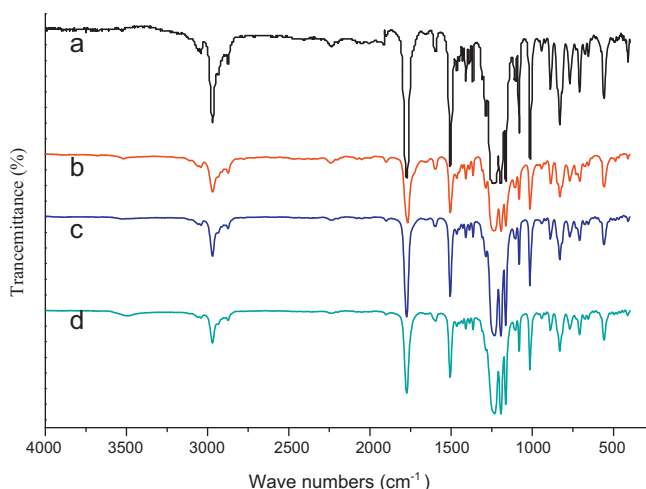
Fig. 2. The IR spectra of the residue obtained at different conversions (a, 0%; b, 50.8%; c, 79.3%; d, 95.5%).

able that [Bmim][Ac] had a good reusable performance. The loss of activity was perhaps due to the loss of [Bmim][Ac] during the workup. Therefore, the ionic liquid [Bmim][Ac] was an effective and reusable catalyst for the methanolysis of PC. Using the ionic liquid as a catalyst for other reactions has been part of ongoing work in our lab.

3.4. Methanolysis mechanism of PC

BPA and the PC residue were characterised by IR to further understand the methanolysis of PC. The IR spectra of the PC residue obtained at different conversion percentages are shown in Fig. 2. As can be seen from Fig. 2, when the conversion of PC was lower than 79.3%, the IR spectrum of the PC residue was almost the same as that of the pure PC starting material; there was no observed hydroxyl peak at 3400–3500 cm⁻¹. Although the conversion of PC was as high as 95.5%, the IR spectrum of PC residue had a very weak hydroxyl peak at 3500 cm⁻¹. The results showed that there was almost no oligomer in the residue. It was further demonstrated that the solubility or swelling of PC in the reaction mixture was the rate-determining step for the methanolysis of PC; PC rapidly depolymerised into final products or smaller oligomers as soon as it dissolved or swelled in the reaction mixture.

The IR spectra of the BPA products obtained at different levels of PC conversion are shown in Fig. 3. As can be seen from Fig. 3, with
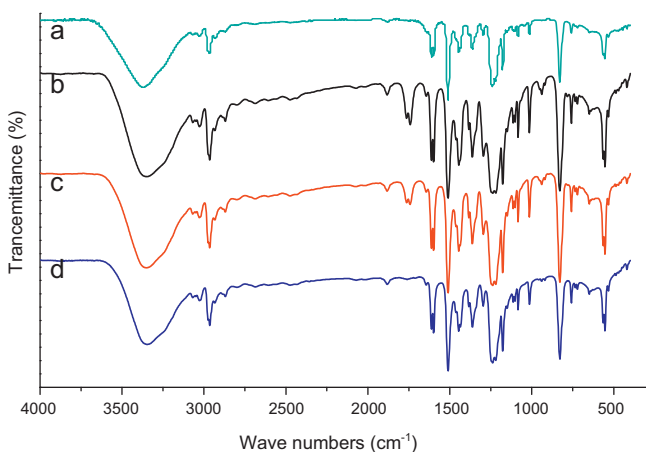
Fig. 3. The IR spectra of BPA obtained at different conversions (a, pure BPA; b, 50.8%; c, 79.3%; d, 100%).

an increase in PC conversion, the peak at about 1750 cm⁻¹ that belonged to the carbonyl group became weaker. When the conversion of PC was lower than 79.3%, there was an obvious carbonyl group peak at about 1750 cm⁻¹. It was demonstrated that some smaller oligomers existed in the BPA products obtained, such as compounds A and/or B (shown in Fig. 4). When the conversion of PC was 100%, the IR spectrum of the BPA obtained from methanolysis of PC was almost the same as that of pure BPA; no obvious carbonyl group peak (1750 cm⁻¹) was observed. It was demonstrated that PC was completely depolymerised into BPA and DMC monomers; no intermediates of oligomers existed in the product obtained.

A mechanism for the methanolysis of PC in the presence of ionic liquid [Bmim][Ac] is suggested in Fig. 4. After PC was dissolved or swelled in the ionic liquid, it reacted with methanol to form oligomers under ionic liquid catalysis. Then, the resulting oligomers reacted with methanol further to produce the final products, BPA and DMC.

Several tests were carried out to further understand the role of [Bmim][Ac] in the methanolysis of PC, and the results obtained are showed in Table 5. It could be seen that PC methanolysis did not take place in the absence of [Bmim][Ac] and THF (Entry 3). Even when THF, in which PC could significantly dissolve, was used as the reaction medium, no PC methanolysis took place in the absence of [Bmim][Ac] (Entry 4). However, when a catalytic amount of [Bmim][Ac] was added to the mixture, the PC conversion reached levels as high as 92.6% (Entry 5). It was demonstrated that [Bmim][Ac] has excellent catalytic activity for methanolysis of PC. Moreover, in the absence of THF, the PC conversion increased with an increased dosage of [Bmim][Ac] (Entries 1 and 2). It was demonstrated that [Bmim][Ac] played a role in dissolving or swelling PC in addition to the role of catalysis.

3.5. Kinetics of methanolysis of PC

In studies of depolymerisation kinetics of polymers, the reaction order is usually considered to be first-order [4,10–13]. Therefore, the methanolysis of PC in the presence of [Bmin][Ac] was initially assumed to be controlled by the first-order kinetic equation (3):

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

where k is the rate constant of the reaction, and C_{pc} is the concentration of polycarbonate at t.

$$C_{pc} = C_{pc0}(1 - X) \tag{4}$$

where X is the conversion of PC; Eq. (3) could then be written as follows:

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

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

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

The effect of the reaction temperature on the methanolysis rate of PC in the presence of [Bmim][Ac] is shown in Fig. 5 and the linear regression results of the data are shown in Table 6. All of the linear correlative coefficients in Table 6 were higher than 0.97 and higher than 0.99 at 85 °C and 75 °C, which indicated that $\ln 1/(1 - X)$ was proportional to the reaction time at different temperatures, and that this process was a first-order kinetic reaction. The rate of the methanolysis of PC in the ionic liquid was proportional to the PC concentration. The straight lines in Fig. 5 give slope values of 2.06192 h⁻¹, 1.23457 h⁻¹, 0.40622 h⁻¹, 0.18437 h⁻¹ and 0.09552 h⁻¹, which were the rate constants of the methanolysis reaction at 90 °C, 85 °C, 80 °C, 75 °C and 70 °C, respectively.
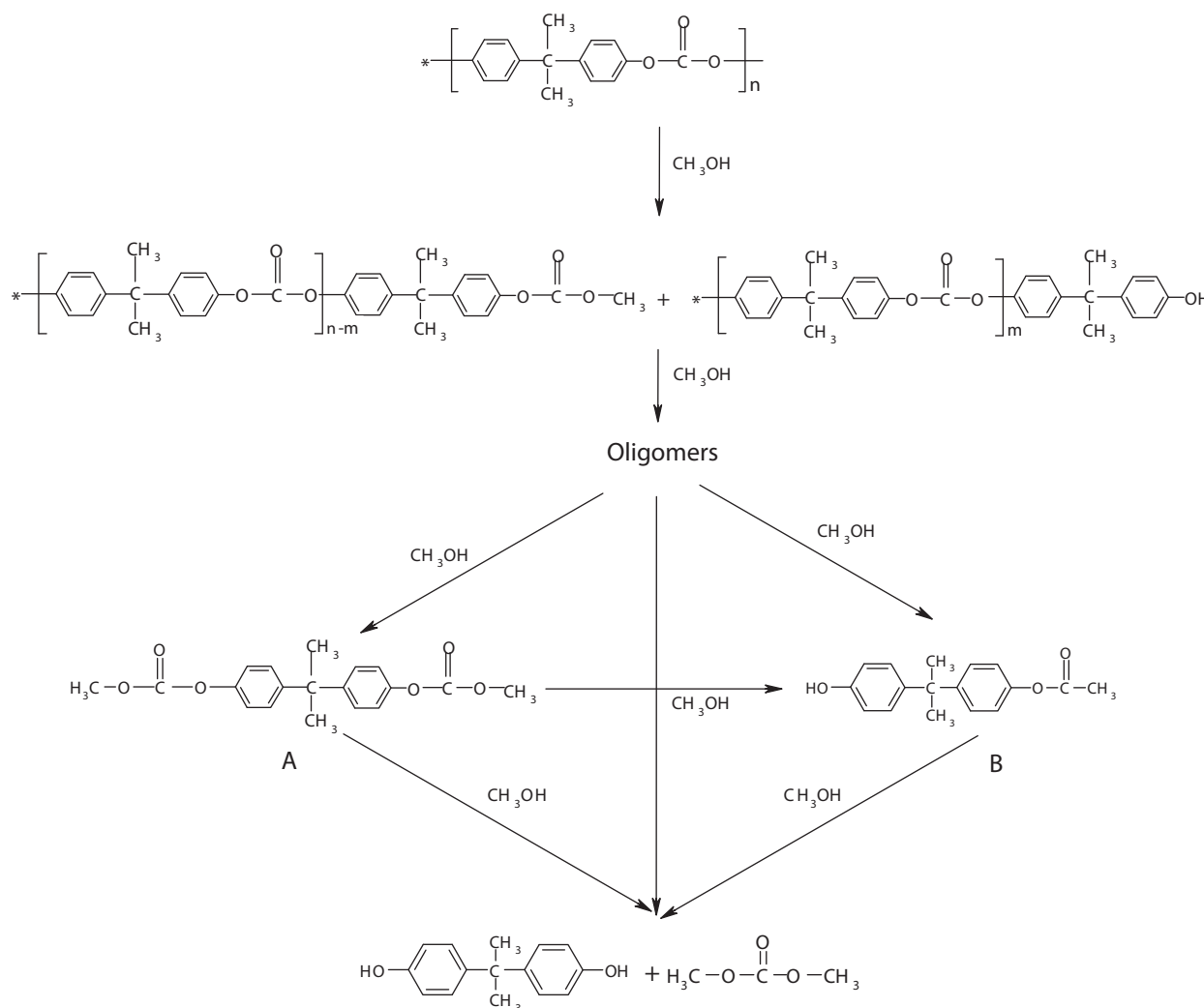
Fig. 4. Methanolysis mechanism for PC in the presence of ionic liquid [Bmim][Ac].

Using the rate constants above, the activation energy (E_a) could be obtained by Eq. (7).
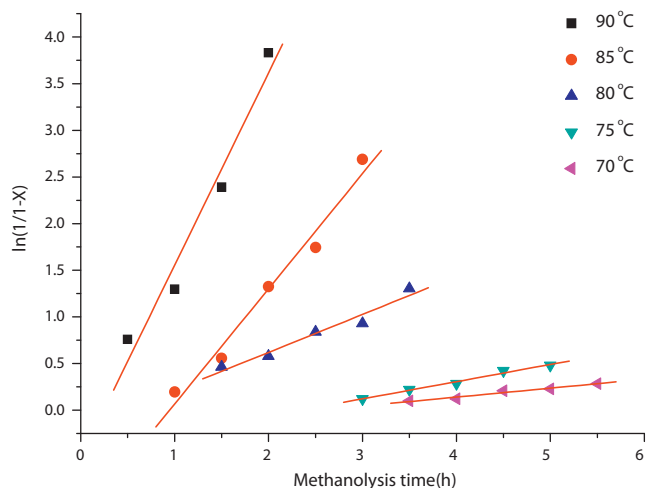
$$\ln k = \ln A - \frac{E_a}{RT} \tag{7}$$

Fig. 5. Effect of reaction tempreture on methanolysis rate of PC in [Bmim][Ac].

Table 5
Effect of reaction medium on methanolysis results of PC.[a]

Entry	m(THF):m(PC)	m([Bmim][Ac]):m(PC)	PC conversion (%)
1	0	0.1:1	79.3
2	0	0.5:1	100
3	0	0	0
4	1:1	0	0
5	1:1	0.05:1	92.6

[a] m(methanol):m(PC) = 0.75:1, T = 90 °C, t = 2.5 h.

where A is the pre-exponential factor, R is the gas constant (8.31 J/k mol) and T is the temperature in Kelvin. The activation energy for this reaction, calculated from the slope of the Arrhenius plot shown in Fig. 6, was 167 kJ/mol.

Table 6
Linear regression results of the data in Fig. 5.

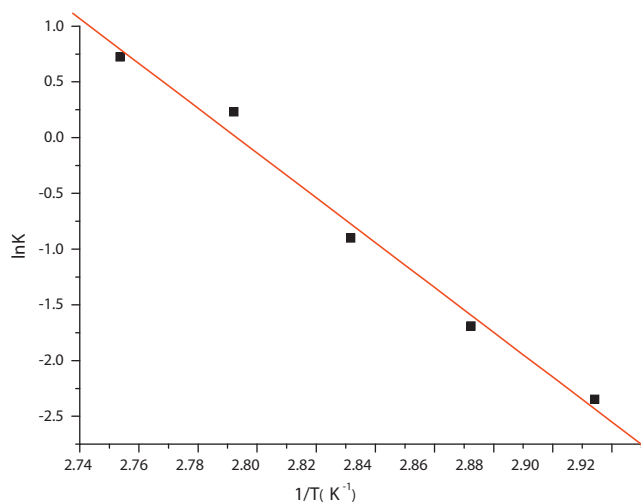| Reaction temperature/°C	Regressive equation	Linear correlative coefficient
90	$y = -0.50798 + 2.06192x$	0.98126
85	$y = -1.16794 + 1.23457x$	0.99031
80	$y = -0.19279 + 0.40622x$	0.97791
75	$y = -0.43199 + 0.18437x$	0.99328
70	$y = -0.2421 + 0.09552x$	0.98277

Fig. 6. Arrhenius plot of rate constant of methanolysis of PC in [Bmim][Ac].

4. Conclusion

The methanolysis of PC to obtain its starting monomers, BPA and DMC, could occur in the presence of ionic liquid [Bmim][Ac] under moderate conditions without an acid or base catalyst. The methanolysis conversion of PC was nearly 100% and the yield of BPA was over 95% under the following conditions: m([Bmim][Ac]):m(PC) = 0.75:1, m(methanol):m(PC) = 0.75:1, a reaction temperature of 90 °C and a total time of 2.5 h. The ionic liquid [Bmim][Ac] could be reused up to 6 times without an apparent decrease in the conversion of PC and yield of BPA. This strategy could overcome the shortcomings associated with the traditional methods, such as the infeasibility of reusing the catalyst, equipment corrosion, tedious workup procedures and environmental problems. Moreover, the investigation on kinetics indicated that the methanolysis of PC in [Bmim][Ac] was a first-order reaction and the activation energy was 167 kJ/mol.

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