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Degradation of polycarbonate to produce bisphenol A catalyzed by imidazolium-based DESs under metal- and solvent-free conditions†

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Bisphenol A (BPA) is an important chemical raw material, but the traditional preparation process of BPA is costly and complicated, so it is necessary to find an efficient and environmentally friendly method for the production of BPA. Deep eutectic solvents (DESs) have attracted widespread attention due to their low cost, low toxicity, low melting point, non-volatilization, easy preparation, recyclability and biodegradability. In this work, a series of imidazolium-based DESs were synthesized and used for the degradation of polycarbonate (PC), and BPA was obtained from the methanolysis of PC catalyzed by DESs under metal- and solvent-free conditions. It was found that imidazolium-based DES [EmimOH]Cl-2Urea showed excellent catalytic activity and reusability. Under the optimized reaction conditions (the mass ratio of DES to PC is 0.1 : 1, the molar ratio of CH₃OH to PC is 5 : 1, 120 °C, reaction time 2 h), the PC conversion and BPA yield were almost 100% and 98%, respectively. Moreover, the kinetics of methanolysis catalyzed by [EmimOH]Cl-2Urea was investigated in the temperature range 100–120 °C, and the results indicated that it is a pseudo-first order reaction with an activation energy of 133.59 kJ mol⁻¹. In addition, a possible catalytic mechanism of PC methanolysis is proposed.

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1. Introduction

Polycarbonate (PC), as a high-performance engineering plastic, has been widely used in compact disk manufacturing, glass assembly industry, automotive industry, medical equipment, food packaging, *etc.*¹ With the rapid growth of PC production and sales, more and more PC waste has been generated. Although this PC waste is non-toxic and harmless, it is bulky and difficult to degrade naturally, which may cause serious environmental pollution and waste resources. From the perspective of resource conservation and sustainable development, chemical recycling of this discarded PC is still an important issue and has attracted widespread attention.^{2,3}

Several chemical methods, including thermal pyrolysis,^{4–6} glycolysis,^{7,8} hydrolysis^{9–11} and aminolysis^{12,13} have been studied by many researchers. Some good results with high conversion and high yield have been obtained, but there are still many disadvantages, such as low purity of BPA, slow reaction rate,

unrecyclable catalyst and harsh reaction conditions, resulting in high cost and high energy consumption. Compared with these methods, alcoholysis, especially methanolysis, is a more important approach for PC recycling due to its mild reaction conditions and relatively easy recovery of raw material monomers. Various catalysts, including concentrated base or superbases (NaOH,^{14,15} DBU¹⁶ and TBD¹⁷), ZnO-NPs/NBu₄Cl nanoparticles,¹⁸ mesoporous molecular sieves (CaO, SrO, BaO)/SBA-15 (ref. 19) and CaO-CeO₂/SBA-15 (ref. 20) and some ionic liquids ([Bmim]Cl,²¹ [Bmim]OAc,²² [Bmim]Cl-2.0FeCl₃,²³ [HDBU][Lac]²⁴ and [HDBU][Im]²⁵) have been used to catalyze the PC methanolysis (Table S1†) and have several advantages, such as high PC conversion and yield of BPA,^{14,21–25} easy to separate solid catalyst,^{18,20} low temperature (60, 70 °C)^{14,22,25} and short reaction time.²⁴ However, there are also some disadvantages, such as equipment corrosion,^{14,15} cumbersome operation, waste water generation,^{14,15} large amount of solvent (toluene,¹⁴ or THF^{18,20}) or catalyst,^{21,22} and the synthesis process of ionic liquids are very complicated, costly, metal ions contaminate the product²³ and cannot be biodegraded. As a result, finding a new simple, environmentally benign and low-cost synthetic process is still an unsolved issue in this field as the methods mentioned above are not green.

To develop a cost-effective and environmentally friendly method, we focus on exploring a new and affordable catalyst for the methanolysis of PC under “green” conditions. Deep eutectic solvents (DESs) were first described by Abbott²⁶ *et al.* in 2003,

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and are usually synthesized by simply mixing hydrogen bond acceptors (HBAs) and hydrogen bond donors (HBDs). As an alternative, DESs not only have similar properties to ionic liquids, but also have many other advantages, including simple preparation, cheap raw materials, low toxicity, biodegradability and no further purification.²⁷ Because of these properties, DESs have gradually become a new type of green solvents and catalysts, and have been widely used in biocatalysis,^{28,29} extraction,^{30,31} carbon dioxide capture,^{32–34} biomedical applications,³⁵ material synthesis^{36–38} and other fields. In recent decades, DESs as a reaction medium have attracted widespread attention, making them have broad application prospects in industrial production.³⁹

Although their application as catalysts in PC degradation has not been reported, DESs such as urea/metal salt, $\text{ChCl}/\text{Zn}(\text{Ac})_2$ and 1,3-dimethylurea/ $\text{Zn}(\text{OAc})_2$ have been successfully used for the alcoholysis of polyethylene terephthalate (PET),^{40–42} and achieved some good results. At present, DESs are mainly made of choline chloride (ChCl) and urea or certain metal salts, but almost no other types of DESs have been reported. In our previous work, $\text{ChCl}\text{-}2\text{Urea}$ ⁴³ was successfully used to catalyze the PC methanolysis, with 100% C_{PC} and 99% Y_{BPA} at 130 °C for 2.5 h. Compared with $\text{ChCl}\text{-}2\text{Urea}$, imidazolium-based DES has lower viscosity, lower melting point, wider liquid phase range, higher electrical conductivity and better thermal stability. Therefore, this kind of DESs will have a broader application fields in the future.

In order to obtain an efficient and green catalyst for PC methanolysis, a series of $[\text{EmimOH}]\text{Cl}/\text{urea}$ DESs (molar ratio from 4 : 1 to 1 : 5) was synthesized by using $[\text{EmimOH}]\text{Cl}$ and urea as HBA and HBD in this work. The effects of reaction conditions, such as reaction temperature, reaction time, PC/methanol molar ratio, and DESs/PC mass ratio were further examined in detail. In addition, the recycling of $[\text{EmimOH}]\text{Cl}/\text{urea}$, the mechanism of PC methanolysis and the kinetics of this reaction were also investigated.

2. Experimental

2.1 Material and instruments

Pure PC pellets (3 mm length and 2.5 mm diameter) were used as model plastics and purchased from Idemitsu Kosan Co., Ltd. of Japan. The weight average molecular weight (M_w) and number average molecular weight (M_n) were 23 563 g mol^{-1} and 8993 g mol^{-1} , respectively. *N*-Methylimidazole, 2-chloroethanol and urea were obtained from Shanghai McLean Biochemical Technology Co., Ltd., China. Methanol, oxalic acid (OA), succinic acid (SA), benzoic acid (BA), *p*-toluenesulfonic acid (PTSA), aniline (AN), acetamide (AA), glycerol (Gly), glucose (Glc), anhydrous manganese chloride (MnCl_2) and anhydrous cupric chloride (CuCl_2) were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd., China. All chemicals (AR) were utilized directly without any further treatment.

Infrared (IR) spectra of the main degradation product and DES were recorded on a BRUKER FT-IR VERTEX 70 spectrometer in the range of 4000–400 cm^{-1} by liquid film or KBr discs. ¹H and ¹³C Nuclear magnetic resonance (NMR) spectra were

measured on a BRUKER AV 500 Digital NMR spectrometer in d_6 -DMSO solution. The TGA curves were recorded with a NETZSCH STA 409 PC/PG thermogravimetric analyzer in a nitrogen atmosphere at a flow rate of 100 mL min^{-1} over a temperature range from room temperature to 600 °C at a heating rate of 20 °C min^{-1} . The M_w and M_n of fresh PC and residues were checked by Gel permeation chromatography (GPC) (TOSOH-8320) under the condition of room temperature, solvent tetrahydrofuran (THF) as the mobile phase at a flow rate of 1.0 mL min^{-1} . The GPC is equipped with a differential refraction detector and TSK gel Super Mutipore HZ-M*2 columns. Calibration of GPC was performed with standard polystyrene samples.

2.2 Synthesis of imidazolium-based DESs

2.2.1 Preparation of precursor $[\text{EmimOH}]\text{Cl}$. In a 250 mL three-necked flask equipped with a reflux condenser, a thermometer and a magnetic stirrer, adding (32.843 g, 0.4 mol) *N*-methylimidazole, (32.330 g, 0.4 mol) 2-chloride ethanol and 150 mL ethyl acetate. Under nitrogen atmosphere, the mixture was heated to reflux and stirred for 48 h, then cooled to room temperature, and a large amount of white precipitate appeared at the bottom of the flask. The precipitate was collected by filtration, washed three times with ethyl acetate, and dried for 8 h under vacuum at 80 °C to obtain a white solid powder, 1-hydroxyethyl-3-methylimidazolium chloride $[\text{EmimOH}]\text{Cl}$. The product weighed 50.54 g with the yield of 77.5%. ¹³C NMR (126 MHz, d_6 -DMSO), $\delta = 136.8$ (s), 123.2 (s), 122.6 (s), 59.2 (s), 51.5 (s), 35.6 (s) (see Fig. S1†).

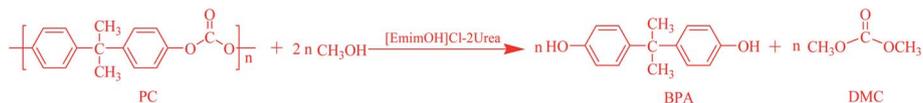
2.2.2 Preparation of $[\text{EmimOH}]\text{Cl}\text{-}2\text{Urea}$. Take (8.187 g, 0.05 mol) precursor $[\text{EmimOH}]\text{Cl}$ and (6.004 g, 0.1 mol) urea, and put into a 100 mL round bottom flask equipped with a reflux condenser and a thermometer. Under a nitrogen atmosphere, the reaction was heated and stirred at 80 °C for 2.0 h, until a colorless, transparent and homogeneous liquid was completed, the reaction was over and the product $[\text{EmimOH}]\text{Cl}\text{-}2\text{Urea}$ (13.8 g) was collected with the yield of 97.5%. $[\text{EmimOH}]\text{Cl}\text{-}2\text{Urea}$ ¹³C NMR (126 MHz, d_6 -DMSO), $\delta = 159.7$ (s), 136.8 (s), 123.3 (s), 122.6 (s), 59.3 (s), 51.5 (s), 35.6 (s) (see Fig. S2†).

According to the above method, DES of $[\text{EmimOH}]\text{Cl}$ and urea with a molar ratio of 4 : 1 to 1 : 5 were synthesized, and other DESs were synthesized by mixing $[\text{EmimOH}]\text{Cl}$ with different HBAs, such as $[\text{EmimOH}]\text{Cl}\text{-}2\text{OA}$, $[\text{EmimOH}]\text{Cl}\text{-}2\text{SA}$, $[\text{EmimOH}]\text{Cl}\text{-}2\text{BA}$, $[\text{EmimOH}]\text{Cl}\text{-}2\text{PTSA}$, $[\text{EmimOH}]\text{Cl}\text{-}2\text{CuCl}_2$, $[\text{EmimOH}]\text{Cl}\text{-}2\text{MnCl}_2$, $[\text{EmimOH}]\text{Cl}\text{-}2\text{AN}$, $[\text{EmimOH}]\text{Cl}\text{-}2\text{AA}$, $[\text{EmimOH}]\text{Cl}\text{-}2\text{Gly}$ and $[\text{EmimOH}]\text{Cl}\text{-}2\text{Glc}$.

2.3 General procedure for catalytic methanolysis of PC

In each experiment, (4.0 g, 15.7 mmol) PC (w_1) was degraded, using methanol catalyzed by urea or one kind of synthesized DESs. The mass ratio of catalyst to PC ranges from 0.05 : 1 to 0.1 : 1, and the amount of methanol ranges from 0.047 mol to 0.11 mol. A 50 mL autoclave equipped with a thermometer and a stirrer was put into an oil bath for all the methanolysis experiments. The reaction was carried out under autogenous





Scheme 1 Reaction formula of PC methanolysis catalyzed by [EmimOH]Cl-2Urea.

pressure at reaction temperatures ranging from 110–125 °C for reaction time of 1.0–2.5 h. After the methanolysis reaction was completed, the autoclave was cooled to room temperature. The unreacted PC residue (w_2) was collected by filtration and dried at 100 °C for 4 h, weighed (w_2) to calculate the conversion of PC (C_{PC}), which is determined by eqn (1):

$$C_{PC} = \frac{w_1 - w_2}{w_1} \times 100\% \quad (1)$$

where w_1 refers to the initial weight of PC, w_2 refers to the weight of unreacted PC. Additionally, a light yellow viscous liquid was obtained by removing methanol and dimethyl carbonate (DMC) from the distilled filtrate under atmospheric pressure, which was then dissolved in an equal volume of ethyl acetate and distilled water till the mixture separated into two phases. The upper liquid was removed ethyl acetate by rotary evaporation to obtain a white solid, which was dried for 8 h under vacuum to obtain the product BPA (w_3). The lower liquid was mainly DES and water, which was treated by vacuum distillation to remove water. The residue was mainly DES, can be reused for the next experiment without any further treatment. Yield of BPA (Y_{BPA}) is defined by eqn (2):

$$Y_{BPA} = \frac{w_3}{w_1} \times \frac{M(PC)}{M(BPA)} \times 100\% \quad (2)$$

where w_3 represents the weight of the obtained BPA, $M(PC)$ and $M(BPA)$ are the molar mass of the repeating unit of PC and molecular weight of BPA, which are 254 g mol⁻¹ and 228 g mol⁻¹, respectively.

The reaction formula is shown in Scheme 1.

3. Results and discussion

3.1 Selection of catalyst for PC methanolysis

The effect of different molar ratio of DESs on the methanolysis of PC was investigated, and the results are shown in Fig. 1. When $n([\text{EmimOH}]\text{Cl}) : n(\text{urea})$ was added from 4 : 1 to 1 : 2, the C_{PC} increased from 62% to 100%, and the Y_{BPA} increased from 62% to 99%, respectively. In other words, when the molar ratio of [EmimOH]Cl/urea is 1 : 2, PC is completely degraded into products. The reason may be due to the formation of hydrogen bonds between HBD and HBA, when $n([\text{EmimOH}]\text{Cl}) : n(\text{urea}) = 1 : 2$, the synergistic effect between them is better, improving the catalytic performance of DES. Continue to increase the molar ratio to 1 : 5, the C_{PC} and Y_{BPA} decreased slightly, the reason may be caused by the operation process.

In addition, the catalytic performance of synthesized DESs in the PC methanolysis was evaluated and the results were presented in Table 1. It was indicated that this reaction cannot occur without any catalyst (entry 1). Some acidic DESs like

[EmimOH]Cl-OA, [EmimOH]Cl-SA, [EmimOH]Cl-BA, [EmimOH]Cl-PTSA (entries 2–5), and some neutral DESs like [EmimOH]Cl-2Gly, [EmimOH]Cl-2Glc (entries 8 and 9) had no catalytic effect on the PC methanolysis. The Lewis acidic DESs like [EmimOH]Cl-2MnCl₂ and [EmimOH]Cl-2CuCl₂ (entries 6 and 7), although they can catalyze this reaction, the C_{PC} is very low and no BPA is obtained. However, basic DESs like [EmimOH]Cl-2Urea, [EmimOH]Cl-2AN and [EmimOH]Cl-2AA (entries 10–12) can catalyze the methanolysis of PC. The reason may be that PC methanolysis is a transesterification reaction, basic catalysts are beneficial to this reaction. It was also found that when [EmimOH]Cl and urea were used as catalyst alone (entries 13 and 14), the methanolysis cannot take place. However, when adding the DES formed by the same quality of [EmimOH]Cl and urea (molar ratio is 1 : 2), [EmimOH]Cl-2Urea exhibited very good catalytic activity with 100% C_{PC} and 99% Y_{BPA} (entry 12). This high catalytic performance may be caused by the synergistic effect between [EmimOH]Cl and urea. Compare with ChCl-2Urea,⁴³ the catalyst not only decreased the reaction temperature but also shortened reaction time.

3.2 Characterization of [EmimOH]Cl-2Urea

The structure of [EmimOH]Cl-2Urea was characterized by FT-IR and ¹H NMR, and the results are shown in Fig. 2. The [EmimOH]Cl characteristic absorption peaks at 3285, 3093, 1642, 1572, 1167, 1072 cm⁻¹, and peaks of urea at 3443, 3346, 1642, 1572, 1167 and 1072 cm⁻¹. As can be seen that the IR spectrum of DES contains almost all the functional groups of [EmimOH]Cl and urea, such as the peaks of -NH₂, -C=O and C-Cl. But the

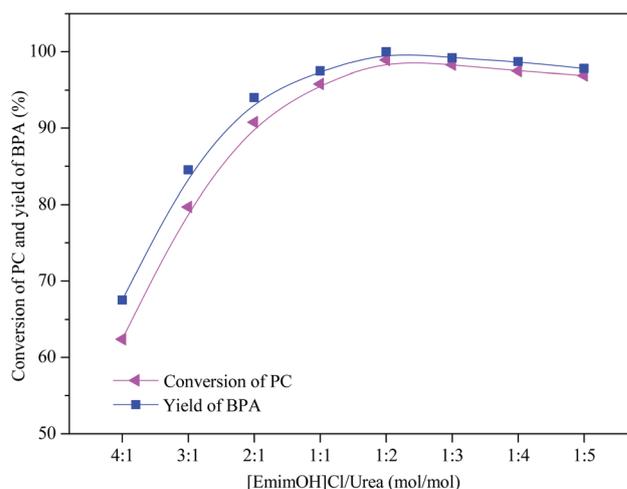


Fig. 1 Catalytic performance of DESs with different molar ratio of [EmimOH]Cl and urea (reaction conditions: PC (4.0 g), DES (0.4 g), $n(PC) : n(\text{CH}_3\text{OH}) = 1 : 5$, 120 °C and 2.0 h).



Table 1 Catalytic activities of different catalysts in the methanolysis of PC^a

Entry	Catalyst	$Y_{BPA}/\%$	$C_{PC}/\%$
1	Blank	0	0
2	[EmimOH]Cl-OA	0	0
3	[EmimOH]Cl-SA	0	0
4	[EmimOH]Cl-BA	0	0
5	[EmimOH]Cl-PTSA	0	0
6	[EmimOH]Cl-2MnCl ₂	0	4
7	[EmimOH]Cl-2CuCl ₂	0	2
8	[EmimOH]Cl-2Gly	0	0
9	[EmimOH]Cl-2Glc	0	0
10	[EmimOH]Cl-2AN	95	99
11	[EmimOH]Cl-2AA	0	6
12	[EmimOH]Cl-2Urea	99	100
13	[EmimOH]Cl ^b	0	0
14	Urea ^c	0	0

^a Experimental conditions: PC (4.0 g), catalyst (0.4 g), $n(\text{PC}) : n(\text{CH}_3\text{OH}) = 1 : 5$, $T = 120\text{ }^\circ\text{C}$, $t = 2\text{ h}$. ^b $m([\text{EmimOH}]\text{Cl}) = 0.234\text{ g}$. ^c $m(\text{Urea}) = 0.166\text{ g}$.

peak at 3336 cm^{-1} belongs to the N–H stretching vibration, is wider than that of [EmimOH]Cl and urea, and moved to a low wave number, showing a significant red shift. In addition, the peaks of C=O and N–H also have obvious red shifts.

In the ¹H NMR of [EmimOH]Cl, the peaks at $\delta = 9.3\text{--}9.5$, 7.84 and 7.81 ppm are assigned to the H of the imidazole ring. The multiple peaks at $\delta = 5.5\text{--}5.6$ ppm attributed to the H of –OH. The triplet peak appeared at $\delta = 4.2\text{--}4.3$ ppm belongs to 2H of –CH₂CH₂OH, another triplet peak at $\delta = 3.6\text{--}3.7$ ppm is ascribed to 2H of –CH₂CH₂OH. The singlet peak at $\delta = 3.8\text{--}3.9$ ppm belongs to 3H of N–CH₃ in the imidazole ring. Compared with the ¹H NMR peaks of [EmimOH]Cl, DES shows a single peak at $\delta = 5.6\text{--}5.7$ ppm, which is attributed to –NH₂ in urea. From ¹H NMR, DES basically contains all the peaks of the raw material.

From the above results, it can be seen that due to the interaction between HBD and HBA, a hydrogen bond is formed between [EmimOH]Cl and urea, resulting in obvious red shifts shown at the peaks of N–H and C=O in the IR spectrum. In the ¹H NMR of DES, some characteristic peaks, C–H for instance move toward high field, and the chemical shift values decrease.

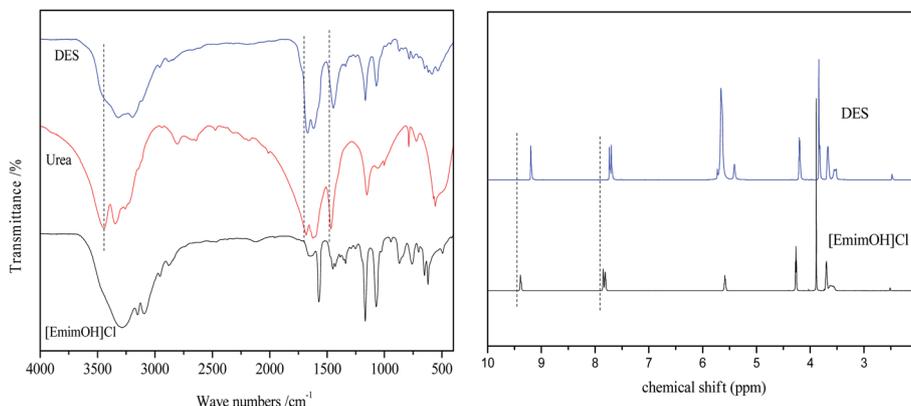


Fig. 2 FT-IR and ¹H NMR spectra of DES, [EmimOH]Cl and urea.

3.3 Qualitative analysis of methanolysis product

When the methanolysis was over, an equal volume of ethyl acetate and distilled water was put into the mixture. After removing the ethyl acetate in the upper phase by rotary evaporation, the product was mainly BPA. The FT-IR and ¹H NMR of the obtained product and standard BPA were shown in Fig. 3. In the FT-IR of the obtained product, the peak at 3335 cm^{-1} corresponds to the O–H stretching vibration of phenolic hydroxy group, the peak at 2964 cm^{-1} corresponds to the C–H stretching vibration of methyl, the peaks at $1446\text{--}1612\text{ cm}^{-1}$ corresponds to the C=C stretching vibration of the benzene ring, and the peaks at $1177\text{--}1237\text{ cm}^{-1}$ corresponds to the C–O stretching vibration. The peak at 827 cm^{-1} corresponds to C–H out-of-plane bending vibration of benzene ring, indicating it was *para*-substituted benzene.

From the ¹H NMR of the obtained product, it can be seen that the peak at $\delta = 1.50$ ppm (s, 6H) belongs to the hydrogen of –CH₃, The symmetrical peaks appears at $\delta = 6.61$ ppm (d, 4H), 6.95 ppm (d, 4H) attribute to the hydrogen of benzene ring, indicating a *para*-substitution. The peak at $\delta 9.14$ ppm (s, 2H) represents the hydrogen of –OH. Regardless of IR or ¹H NMR, the spectrum of obtained product is almost consistent with that of standard BPA, which proves that the obtained product is BPA.

3.4 Effect of experimental conditions on PC methanolysis

The influences of reaction conditions on PC methanolysis were investigated and the results are shown in Table 2. Obviously, reaction temperature is the main influencing factor on the PC methanolysis. When the temperature increased from 110 to 120 °C, the C_{PC} and Y_{BPA} increased from 14%, 8% to 100%, 99%, respectively (entries 1–3). However, when the reaction temperature was raised to 125 °C (entry 4), the C_{PC} and Y_{BPA} did not increase significantly. The reason may be that the methanolysis of PC is a transesterification reaction, and it reached equilibrium at 125 °C. When the reaction time was extended from 1.25 h to 2.0 h (entries 3 and 5–6), the C_{PC} increased from 24% to 100%, meanwhile, the Y_{BPA} reached the maximum 99% at 2.0 h. When $m(\text{DES}) : m(\text{PC})$ was added from 0.05 : 1 to 0.1 : 1, both C_{PC} and Y_{BPA} increased clearly, the C_{PC} from 56% to 100% and the Y_{BPA} from 53% to 99%, respectively. Moreover, as the



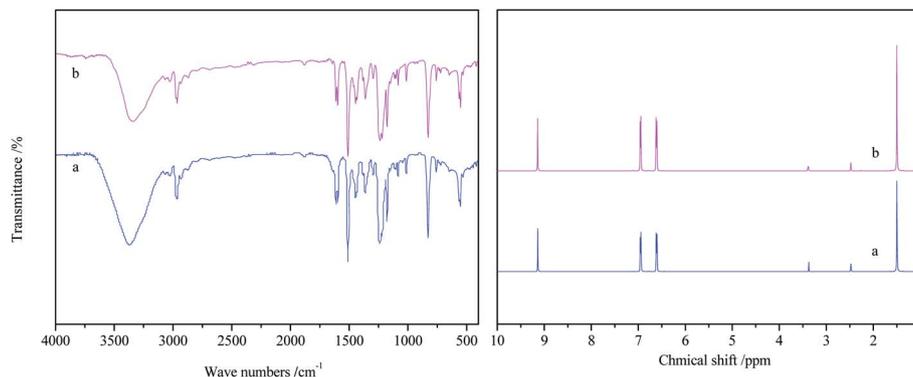


Fig. 3 FT-IR and ^1H NMR spectra of obtained product and standard BPA ((a) standard BPA; (b) obtained product) (reaction conditions: 4.0 g PC, 0.4 g DES, $n(\text{PC}) : n(\text{CH}_3\text{OH}) = 1 : 5$, 120°C and 2.0 h).

Table 2 Effects of reaction conditions on methanolysis of PC^a

Entry	Temperature/ $^\circ\text{C}$	Time/h	$m(\text{DES}) : m(\text{PC})$	$n(\text{CH}_3\text{OH}) : n(\text{PC})$	$C_{\text{PC}}/\%$	$Y_{\text{BPA}}/\%$
1	110	2.0	0.1 : 1	5 : 1	14	8
2	115	2.0	0.1 : 1	5 : 1	55	48
3	120	2.0	0.1 : 1	5 : 1	100	99
4	125	2.0	0.1 : 1	5 : 1	100	98
5	120	1.25	0.1 : 1	5 : 1	24	19
6	120	1.5	0.1 : 1	5 : 1	73	66
7	120	2.0	0.05 : 1	5 : 1	56	53
8	120	2.0	0.075 : 1	5 : 1	86	81
9	120	2.0	0.1 : 1	3 : 1	98	97
10	120	2.0	0.1 : 1	7 : 1	99	97

^a Experimental conditions: PC (4.0 g).

molar ratio of methanol to PC changed from 3 : 1 to 7 : 1 (entries 3 and 9–10), the C_{PC} and Y_{BPA} increased slightly. When the molar ratio of methanol to PC was 5 : 1, the C_{PC} and Y_{BPA} reached the maximum values, which were 100% and 99%, respectively. When $n(\text{CH}_3\text{OH}) : n(\text{PC})$ increased from 5 : 1 to 7 : 1 (entries 3 and 10), the C_{PC} and Y_{BPA} had a slight decrease, which may be due to excessive methanol addition, resulting in a decrease in the reactant concentration.

3.5 Reusability of [EmimOH]Cl-2Urea

From the perspective of environmental protection and sustainable development, it is necessary to study the reusability of DES in PC methanolysis. Under the following conditions: PC (4.0 g), DES (0.4 g), $n(\text{PC}) : n(\text{CH}_3\text{OH}) = 1 : 5$, 120°C and 2.0 h, the reusability of DES was investigated and the results were shown in Fig. 4. It can be clearly seen that even if the DES is reused for 4 times, the C_{PC} and Y_{BPA} are not apparently reduced, indicating that [EmimOH]Cl-2Urea has good reusability performance. After reused for 4 times, the C_{PC} and Y_{BPA} will decrease slightly due to the loss of catalyst during operation.

The fresh and reused [EmimOH]Cl-2Urea were characterized by FT-IR and TGA, and results were shown in Fig. 5. Comparing with the IR spectrum of fresh [EmimOH]Cl-2Urea, the reused one basically contained all the characteristic absorption peaks, indicating that there was no change in chemical structure of

[EmimOH]Cl-2Urea after reused for 4 times. In addition, the TGA curve of fresh DES is almost the same as that of reused one, demonstrating that the [EmimOH]Cl-2Urea has an excellent thermal stability. Moreover, the TGA curves also shows that the decomposition process of DES is mainly divided into two stages. The weight loss was nearly 38% in the range of $175\text{--}252^\circ\text{C}$, another weight loss is about 58% in the scope of $252\text{--}320^\circ\text{C}$.

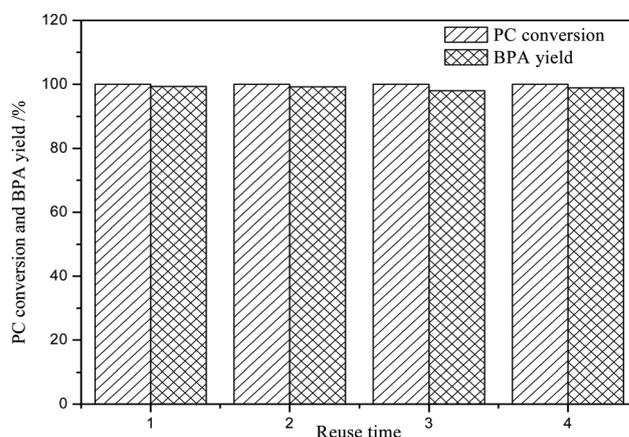


Fig. 4 Reusability results of [EmimOH]Cl-2Urea (reaction conditions: PC (4.0 g), DES (0.4 g), $n(\text{PC}) : n(\text{CH}_3\text{OH}) = 1 : 5$, 120°C and 2.0 h).



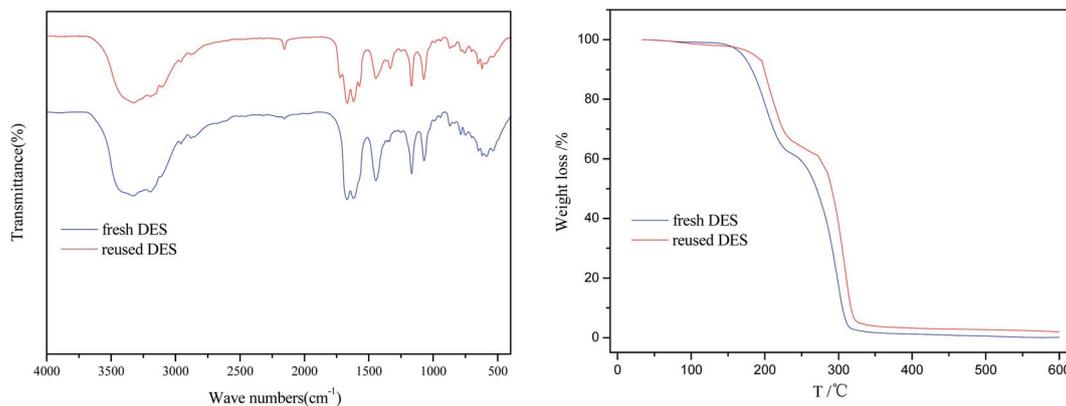


Fig. 5 FT-IR spectra and TGA curves of fresh and reused [EmimOH]Cl-2Urea.

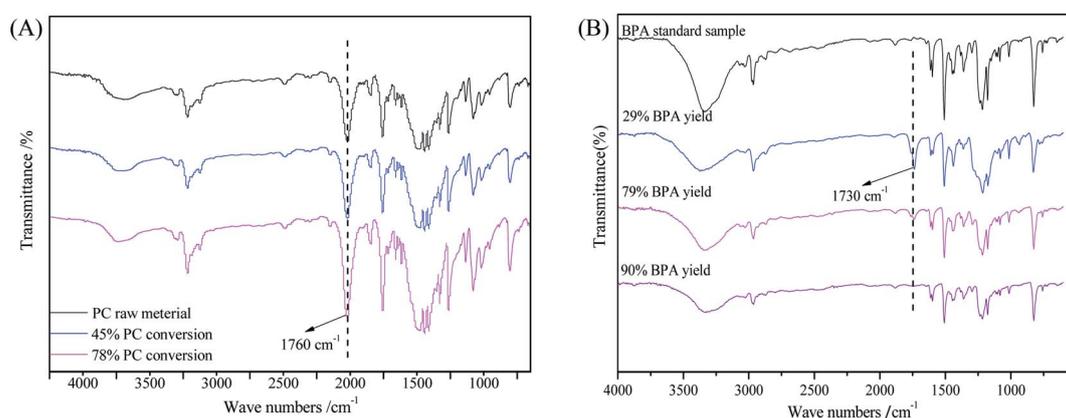


Fig. 6 FT-IR spectra of PC residues (A) and BPA (B) obtained at different conversions.

When the temperature exceeds 320 °C, the mass of the sample gradually approaches zero, meaning the sample is completely decomposed. However, the methanolysis temperature is only 120 °C, lower than the decomposition temperature of [EmimOH]Cl-2Urea, which shows that DES can stably exist and hard to decompose under the above conditions.

3.6 Mechanism of PC methanolysis catalyzed by [EmimOH]Cl-2Urea

To study the mechanism of PC methanolysis, FT-IR was used to characterize the PC residues and BPA products at different conversions. As shown in Fig. 6(A), the PC residue at low conversion of 46% showed characteristic peaks similar to that of PC raw material. With increasing PC conversion, the -OH peak at about 3500 cm^{-1} increases slightly, and the -C=O peak at about 1760 cm^{-1} becomes stronger. This might be due to the breakage of long chains into short chains during the reaction, resulting in more -OH and -C=O being exposed. The BPA product obtained at low yield of 29% showed an obvious difference in the carbonyl group at about 1730 cm^{-1} , indicating there are some oligomers in BPA product. As the Y_{BPA} increased to 78% and 90%, the carbonyl peak gradually weakened until completely disappeared. The structure of BPA obtained at

a yield of 90% is almost identical with that of the BPA standard sample (Fig. 6(B)).

The PC residues were also determined by GPC and the results are shown in Table 3. When the C_{PC} increased from 0 to 46% and 78%, the M_n of PC residue decreased from 8993 to 5589, 5423 g mol^{-1} , and the M_w of PC residue reduced from 23 563 to 14 130, 13 933 g mol^{-1} . The results indicate that with the increase of PC, the long-chain PC decomposed into some short-chain oligomers, which reduced the degree of polymerization and this was more favorable for further degradation.

To further investigate this mechanism, ^1H NMR spectroscopy analysis was performed in d_6 -DMSO. As shown in Fig. 7, in the absence of DES, the chemical shift of hydroxyl proton in methanol is 4.08 ppm. As the amount of DES increases (from curve 1 to 4), the signals of hydrogens in -OH move towards the

Table 3 Molecular weights of PC residues obtained at different conversions (a 0%; b 46%; c 78%)

Entry	M_n	M_w	M_w/M_n
a	8993	23 563	2.620
b	5589	14 130	2.528
c	5423	13 933	2.569



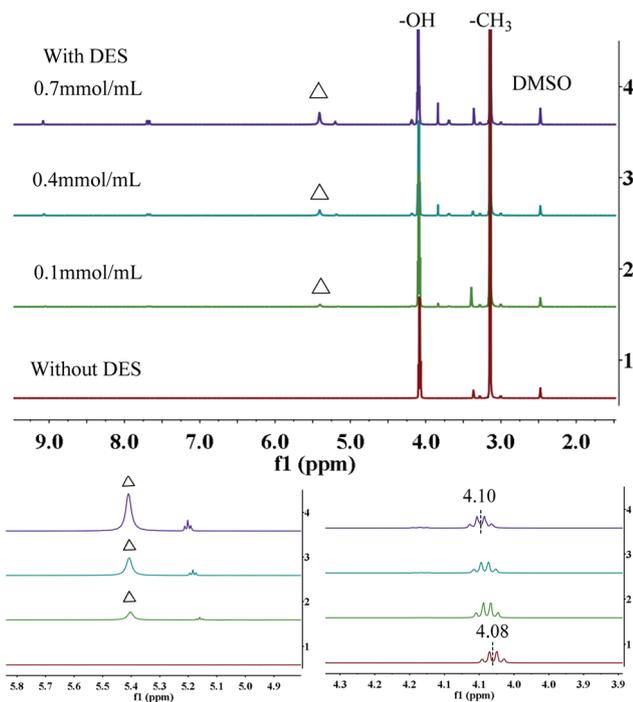


Fig. 7 ^1H NMR spectra of [EmimOH]Cl-2Urea and CH_3OH mixture with different molar ratio; the symbols in the ^1H NMR spectra identify the N-H (triangle) of urea.

lower field. When the amount of DES is 0.7 mmol mL^{-1} , the chemical shift of hydrogen in -OH reached 4.10 ppm ($\Delta\delta = +0.02 \text{ ppm}$). In addition, as the concentration of methanol increased (from curve 4 to 1), the N-H signal shifted from 5.43 to 5.42 ppm. However, as the concentration of DES increased from 0.1 to 0.4, 0.7 mmol mL^{-1} , the signals of - CH_3 ($\delta = 3.14 \text{ ppm}$) do not change obviously. Therefore, it can be reasonably speculated that the change of chemical shift is due to the strong hydrogen bond interaction between the hydroxyl group in methanol and the amino group in DES, which is similar to what reported by Zhang's group.^{40–42}

Based on the above experimental results, a probable mechanism of PC methanolysis catalyzed by [EmimOH]Cl-2Urea is proposed in Scheme 2. First, the H-bond is formed between the

amino group of urea and the hydroxyl group of methanol, improving the electronegativity of the oxygen atom in CH_3OH , which is conducive to $-\text{OCH}_3$ attacking the carbon atom in the ester group of PC, resulting in the breaking of the ester bond. PC gradually decomposes into different molecular weight oligomers. These oligomers then reacted with methanol repeatedly to form smaller oligomers and dimers until BPA and dimethyl carbonate were produced.

3.7 Kinetics of PC methanolysis

The methanolysis of PC previously reported in our group^{20–25,43} and the glycolysis of PET^{40–42} reported by Zhang groups. Kinetic studies of chemical degrading polymers were generally considered to be a pseudo-first order reaction. Therefore, the methanolysis of PC catalyzed by the DES [EmimOH]Cl-2Urea is also assumed to be a pseudo-first order, and the kinetic equation is as follows:

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

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

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

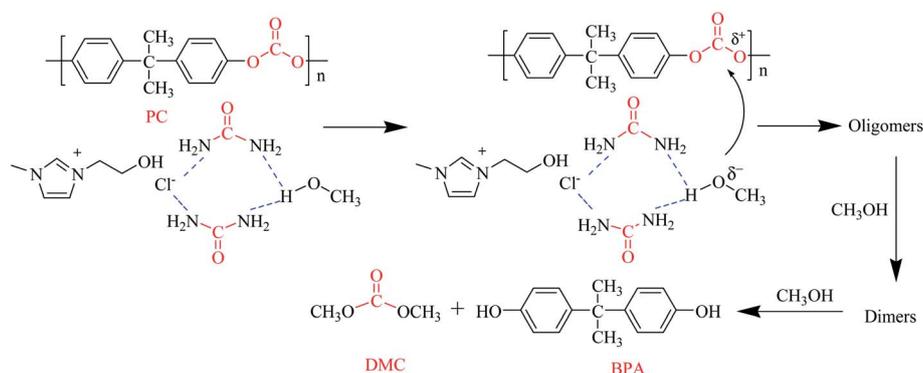
where X represents the conversion of PC, so eqn (3) can be converted to eqn (5):

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

Eqn (5) is integrated against time to get eqn (6).

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

Under the conditions of PC (4.0 g), $m(\text{DES}) : m(\text{PC}) = 0.1 : 1$, and $n(\text{CH}_3\text{OH}) : n(\text{PC}) = 5 : 1$, the effects of reaction temperature on the rate of PC methanolysis were shown in Fig. 8(A), and the corresponding linear regression results were shown in Table 4. It can be seen from Table 4 that all of the linear correlation coefficients were almost 0.98, indicating that $\ln 1/(1 - X)$ was



Scheme 2 Proposed mechanism of PC methanolysis catalyzed by [EmimOH]Cl-2Urea.



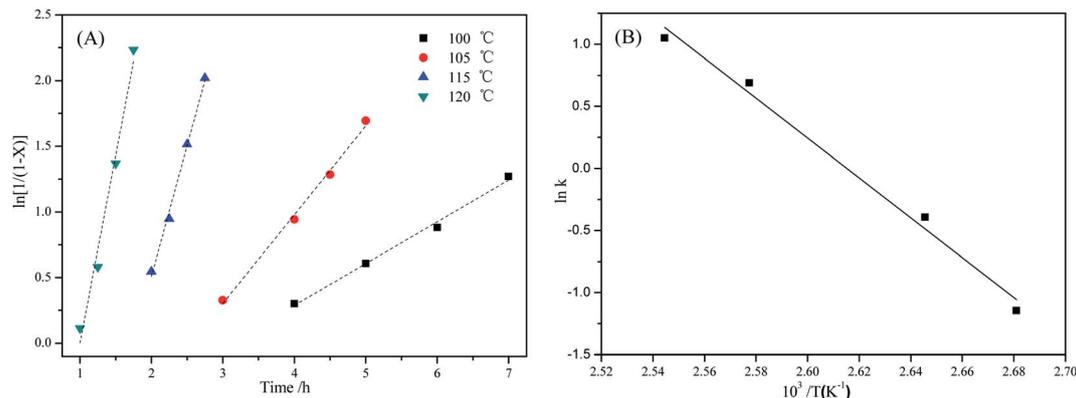


Fig. 8 (A) Effect of reaction temperature on methanolysis rate of PC catalyzed by [EmimOH]Cl-2Urea; (B) Arrhenius plot of rate constant of PC methanolysis (reaction conditions: PC (4.0 g), $m(\text{DES}) : m(\text{PC}) = 0.1 : 1$, $n(\text{CH}_3\text{OH}) : n(\text{PC}) = 5 : 1$).

Table 4 Linear regression results of the data in Fig. 8A

Reaction temperature/°C	Regressive equation	Rate constant	Linear correlation coefficient
120	$y = -2.857 + 2.859x$	2.859	0.976
115	$y = -3.478 + 1.994x$	1.994	0.993
105	$y = -1.725 + 0.676x$	0.676	0.993
100	$y = -0.984 + 0.318x$	0.318	0.992

proportional to time (t) at different reaction temperatures. In other words, the rate of PC methanolysis was proportional to PC concentration. So it can prove that the methanolysis of PC is also a pseudo-first order reaction. This reaction rate constants can be calculated from the slope values of straight line in Fig. 8(A), and they were 2.859 h^{-1} , 1.994 h^{-1} , 0.676 h^{-1} and 0.318 h^{-1} , respectively, which represented the rate constants of PC methanolysis reaction at $120 \text{ }^\circ\text{C}$, $115 \text{ }^\circ\text{C}$, $105 \text{ }^\circ\text{C}$ and $100 \text{ }^\circ\text{C}$.

Moreover, the rate constant increases rapidly with the reaction temperature, showing that the PC methanolysis is significantly influenced by reaction temperature, which is consistent with the previous experimental results (Table 2, entries 1–4).

Using the above rate constant, the reaction activation energy (E_a) can be calculated by the Arrhenius eqn (7).

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

where A is pre-exponential factor, R is molar gas constant ($8.314 \text{ J k}^{-1} \text{ mol}^{-1}$) and T is the Kelvin temperature. The Arrhenius plot of the rate constant was shown in Fig. 8(B), and E_a of PC methanolysis calculated from the slope of the Arrhenius plot is $133.59 \text{ kJ mol}^{-1}$, which is lower than that of methanolysis of PC catalyzed by ChCl-2Urea⁴³ ($141.47 \text{ kJ mol}^{-1}$).

4. Conclusions

Under metal- and solvent-free conditions, imidazolium-based DES [EmimOH]Cl-2Urea can effectively catalyze the PC methanolysis to obtain BPA, without using any traditional acid or base catalyst. Under the optimal reaction of [EmimOH]Cl-2Urea

(0.4 g), PC (4.0 g) and $n(\text{CH}_3\text{OH}) : n(\text{PC}) = 5 : 1$ for 2.0 h at $120 \text{ }^\circ\text{C}$, the C_{PC} and Y_{BPA} reached 100% and 99%, respectively. Moreover, [EmimOH]Cl-2Urea had good thermal stability and can be reused for 5 times without any apparent decrease in the C_{PC} and Y_{BPA} . The kinetics results suggest that the methanolysis of PC catalyzed by [EmimOH]Cl-2Urea is a pseudo-first order reaction with E_a of $133.59 \text{ kJ mol}^{-1}$. This study can provide important guidance for the design of effective DESs used to promote the degradation reaction of polymer wastes and other transesterification.

Conflicts of interest

There are no conflicts to declare.

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