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# Degradation of polycarbonate waste to recover bisphenol A and dimethyl carbonate using urea as a cheap green catalyst†

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Various excellent catalysts have been explored for the methanolysis of polycarbonate (PC), but it is still challenging to develop green and economical catalysts for solvent-free PC methanolysis to recover both bisphenol A (BPA) and dimethyl carbonate (DMC). Herein, green, efficient and solvent-free degradation of PC to BPA and DMC was achieved using urea as a cheap green catalyst. At 140 °C for 3 h, PC was completely degraded to BPA and DMC with yields of 93.4% and 74.7%, respectively. A possible catalytic degradation mechanism of PC was proposed by kinetic experiments and NMR, where urea, methanol and carbonate formed a six-membered ring in the reaction. It was found that the increase of urea concentration significantly reduced the activation energy, which was attributed to the fact that the increase of urea concentration made the six-membered ring easier to form and activated the carbonate bond. The degradation system can be reused directly up to 10 times and 100% degradation rate can be maintained. This work provides a simple, green and economical method for industrial PC recycling.



## Introduction

Polycarbonate (PC) is an important thermoplastic with excellent mechanical properties, biocompatibility and thermal stability, widely used in aircraft, automotive, electronics, construction, medical, and other fields.[1] Its global annual production has increased to 5 million tons and is still growing fast.[2] Meanwhile, under the severe situation of resource depletion and environmental pollution, the recycling of PC wastes has become an urgent problem. Therefore, it is significant to develop eco-friendly and efficient PC recycling methods.

At present, chemical recycling is an economical and promising recycling method. Chemical recycling aims to regenerate monomer raw materials and synthesize value-added chemicals,[3] so it can truly realize the high-value recycling of plastics and establish a plastic circular economy.[2] Currently, the chemical recycling methods of PC mainly include hydrolysis,[4,5] alcoholysis,[3,6–11] ammonolysis,[12,13] and reduction.[14,15] Among them, alcoholysis is particularly appealing because through a transesterification reaction, it can not only recover the monomer bisphenol A (BPA), but also use PC waste as a green carbonyl feedstock to synthesize valuable organic carbonates. Specifically, the methanolysis of PC is an efficient method to degrade PC to recover BPA and dimethyl carbonate (DMC).[3,6,7,10,16,17] DMC is an important chemical raw material with low toxicity, biodegradability and wide applications. For example, DMC can replace phosgene as a green carbonylation reagent and can also be used as a methylation reagent, green solvent, fuel additive, *etc.*[18,19] Therefore, the methanolysis of PC has attracted wide attention and great progress has been achieved.

Various excellent catalysts have been developed for the methanolysis of PC, such as $CeO_2$-CaO-$ZrO_2$,[20] Mg/Al-LDOs,[21] [HDBU][LAc][22], [Ch][Im],[23] *etc.*[24,25] However, they only focused on the recovery of BPA, while the study on the recovery of DMC was lacking. Other catalysts, such as NaOH,[7,10,26–28] TBD (1,5,7-triazabicyclo[4.4.0]-dec-5-ene),[6] ZnO-NPs/$NBu_4Cl$[16] and $Zn^{II}$-complexes,[9] recovered both BPA and DMC with high

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yields under mild conditions, but all of them require additional organic solvents. For instance, since NaOH easily converts the carbonate bond of PC into $Na_2CO_3$, toxic organic solvents such as toluene, 1,4-dioxane, and tetrahydrofuran are often needed to obtain organic carbonates.[7,26,27] To avoid using auxiliary solvents, DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) was applied to catalyze solvent-free alcoholysis of PC, with both BPA and DMC reaching high yields.[3] However, strong base DBU is corrosive and irritating, and it forms a salt with BPA that complicates the separation. Besides, although high-yield BPA and DMC were also obtained in ionic liquid (IL) [Bmim][Cl],[17] the preparation of ILs is cumbersome and costly, and the toxicity of their raw materials remains a concern. Therefore, it is necessary to explore greener and more economical catalysts for solvent-free PC methanolysis to recover both BPA and DMC.

Herein, we provide a green, economical and solvent-free PC methanolysis method to recover BPA and DMC using urea as a catalyst. Compared to the catalysts reported above, urea has the remarkable advantages of being green, mild and cheap. Specifically, urea itself is an extensively used neutral fertilizer and has little adverse effects on the human body and the environment. Moreover, urea is mass produced, readily available and cheap. These advantages make it a greener and more economical reagent with great potential for industrial applications than reported catalysts. More importantly, using green and economical urea as a catalyst instead of toxic and expensive solvents and catalysts while recovering both BPA and DMC has not been reported so far. Under the catalysis of urea, PC was completely degraded, and both BPA and DMC were obtained. The kinetics of the model compound showed that the increase of urea concentration significantly reduced the activation energy. Combining kinetic and NMR studies, a possible catalytic degradation mechanism of PC was proposed, where urea, methanol and carbonate formed a six-membered ring in the reaction. NMR studies further clarified that the increase of urea concentration changed the interaction between urea, methanol and carbonate, which made the six-membered ring easier to form and activated the carbonate bond, thus contributing to the significant reduction in activation energy. In addition, the degradation system can be reused directly up to 10 times and 100% degradation rate can be maintained. Moreover, environmental impact factors (E-factors) and process mass intensity (PMI) analysis suggested that the cyclic degradation mode produced less waste and demonstrated the greenness and economy of this method. This method has the advantages of a cheap and green catalyst, simultaneous recovery of BPA and DMC and no additional solvents. It offers a green and practical process for industrial PC recycling.

# Experimental

### Materials

The used drinking bucket from Taiyuan Shangshan Drinking Water Co., Ltd was cut into small pieces of about 2 × 2 × 1 mm for use. Methanol (MeOH), sodium hydroxide (NaOH) and cyclohexane were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. Ethanol (EtOH) and urea were obtained from Tianjin Beichen Fangzheng Reagent Factory. Dimethyl carbonate (DMC) was obtained from Tianjin Guangfu Fine Chemical Research Institute. Diethyl carbonate (DEC) and *n*-hexane were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Ethyl methyl carbonate (EMC) and pyrazine were supplied by Aladdin Industrial Corporation, China. The water in all experiments was distilled water. All the reagents were analytical purity grade and used as received.

### General procedure for the catalytic degradation of PC

The degradation of PC was performed in a 10 mL Teflon-lined stainless autoclave. Typically, 0.2 g of PC pieces ($W_1$), 4.0 g of methanol and 0.2 g of urea (5 wt% urea to methanol, $mol_{urea}/mol_{CO_3} = 4.2$) were added into the autoclave. Then it was transferred to a homogeneous reactor (an oven with a rotating shaft that can rotate the autoclave to enhance mass and heat transfer), heated to the set temperature ranging from 130 °C to 150 °C and kept for 1–6 h at 30 r $min^{-1}$. After that, the autoclave was cooled naturally to room temperature. The undegraded PC residual was filtered and washed with methanol, dried at 80 °C for 4 h and then weighed ($W_2$) to calculate the degradation rate. The degradation solution was distilled. The distillate containing methanol and DMC was collected and analyzed by GC to determine DMC yield. The separation of an azeotropic mixture of DMC/MeOH can refer to the industrial method.[29,30] The distillation residue, a pale yellow viscous liquid containing BPA and urea, was dissolved in DMSO-$d_6$ for $^1$H NMR and $^{13}$C NMR analyses. BPA yield was calculated by quantitative $^1$H NMR with pyrazine as the internal standard. To separate BPA and urea, ethyl acetate was added to the residue of distillation. The insoluble urea was filtered, washed, dried at 80 °C, weighed, and analyzed by NMR. The filtrate was evaporated, and the remaining solid was washed with water and dried to obtain BPA, which was analyzed by IR, EA and NMR. The PC degradation rate ($R_d$), DMC yield ($Y_{DMC}$) and BPA yield ($Y_{BPA}$) were calculated using the following eqn (1)–(3), respectively:

$$\text{Degradation rate}(R_d) = \frac{W_1 - W_2}{W_1} \times 100\% \quad (1)$$

$$\text{DMC yield}(Y_{DMC}) = \frac{m_{DMC}}{m^0_{DMC}} = \frac{m_{DMC}}{\frac{W_1}{M_{PC}} \times M_{DMC}} \times 100\% \quad (2)$$

$$\text{BPA yield}(Y_{BPA}) = \frac{m_{BPA}}{m^0_{BPA}} = \frac{m_{BPA}}{\frac{W_1}{M_{PC}} \times M_{BPA}} \times 100\% \quad (3)$$

where $W_1$ represents the initial weight of PC and $W_2$ represents the weight of undegraded PC residual. $M_{PC}$, $M_{DMC}$ and $M_{BPA}$ are the molar masses of the PC repeating unit (254 g $mol^{-1}$), DMC (90 g $mol^{-1}$) and BPA (228 g $mol^{-1}$), respectively; $m^0_{DMC}$ and $m^0_{BPA}$ are the theoretical masses of generated DMC and BPA, respectively; $m_{DMC}$ and $m_{BPA}$ are the actual masses of generated DMC and BPA determined by GC

and $^1$H NMR, respectively. $m_{BPA}$ was calculated using the following formula (4):[31]

$$m_{(x)} = P_{(std)} \times \frac{MW_{(x)}}{MW_{(std)}} \times \frac{nH_{(std)}}{nH_{(x)}} \times \frac{m_{(std)}}{P_{(x)}} \times \frac{I_{(x)}}{I_{(std)}} \quad (4)$$

in which $m_{(x)}$ and $m_{(std)}$ are the masses in g, $MW_{(x)}$ and $MW_{(std)}$ are the molecular weights in g mol$^{-1}$, $P_{(x)}$ and $P_{(std)}$ are the purities, $nH_{(x)}$ and $nH_{(std)}$ are the numbers of protons generating the selected signals for integration, and $I_{(x)}$ and $I_{(std)}$ are the integrals for the selected peaks of the analyte ($x$) and the internal standard (std), respectively.

### Kinetic study of transesterification between DEC and MeOH

The kinetic experiments of the transesterification reaction between DEC and MeOH were conducted in a 10 mL Teflon-lined stainless autoclave at different temperatures and times at urea concentrations of 10 wt% and 30 wt% separately. Generally, 0.46 g DEC, 2.52 g MeOH (molar ratio is 1 : 20) and a certain concentration of urea (10 wt% or 30 wt% urea to methanol) were added into the autoclave. Then it was put in a homogeneous reactor, heated to the set temperature ranging from 120 °C to 180 °C and kept for 0.67–10 h at 30 r min$^{-1}$. After that, the autoclave was immediately put into cold water to quench the reaction. After cooling to room temperature, the reaction solution was analyzed by GC. The conversion of DEC ($x$), EMC yield and DMC yield were defined using the following eqn (5)–(7), respectively:

$$\text{Conversion of DEC}(x) = (\text{the converted mass of DEC})/(\text{the initial mass of DEC}) \times 100\% \quad (5)$$

$$\text{EMC yield} = (\text{the actual mass of generated EMC})/(\text{the theoretical mass of generated EMC}) \times 100\% \quad (6)$$

$$\text{DMC yield} = (\text{the actual mass of generated DMC})/(\text{the theoretical mass of generated DMC}) \times 100\% \quad (7)$$

Reaction rate constants ($k$) at different reaction temperatures were calculated using the linear regression of ($t$,ln[1/(1 − $x$)]) according to eqn (8), where $k$ (h$^{-1}$) is the rate constant and $x$ is the conversion of DEC at reaction time $t$.

$$\ln[1/(1-x)] = kt \quad (8)$$

The reaction activation energy ($E_a$) at different urea concentrations was calculated according to the Arrhenius equation (9), where $k$ (h$^{-1}$) is the rate constant, $E_a$ (J mol$^{-1}$) is the activation energy, $A$ (h$^{-1}$) is the pre-exponential factor, $R$ (8.314 J mol$^{-1}$ K$^{-1}$) is the molar gas constant, and $T$ (K) is the reaction temperature.

$$\ln\ k = -\frac{E_a}{RT} + \ln A. \quad (9)$$

### Analysis and characterization

Gas chromatography (GC) analysis was performed on a 2010-Plus AFAPC Shimadzu GC (capillary column: Rtx®-1 PONA, 100 m × 0.25 mm) with a flame ionization detector (FID). The inlet and detector temperatures were both set at 300 °C. In PC methanolysis experiments, cyclohexane was chosen as the internal standard of DMC, and the oven-heat procedure was set as follows: the temperature was kept at 40 °C for 16 min, and then ramped from 40 °C to 70 °C at a rate of 10 °C min$^{-1}$, and then held at 70 °C for 2 min. In the kinetic study of transesterification between DEC and MeOH, $n$-hexane was used as the internal standard for DMC, and cyclohexane was chosen as the internal standard of DEC and EMC. The oven-heat procedure was carried out as follows: the temperature was kept at 40 °C for 16 min, and then ramped from 40 °C to 140 °C at a rate of 10 °C min$^{-1}$, and then held at 140 °C for 2 min. Nuclear magnetic resonance (NMR) analysis was carried out on a Bruker AVANCE-III 400 MHz spectrometer. Fourier transform infrared (FT-IR) spectroscopy characterization was performed using an EQUINOX-55 spectrometer. Elemental analysis (EA) was carried out using a Vario EL CUBE elemental analyser made in Germany.

## Results and discussion

### Methanolysis of PC catalyzed by urea

Initially, we investigated the degradation of PC in $H_2O$, MeOH, EtOH, and MeOH-50 wt% $H_2O$, respectively, and NaOH and urea were used separately as the catalyst for comparison (Table 1). Without a catalyst, PC hardly degraded in any of the four reagents, indicating the necessity of catalysts for PC degradation (entries 1–4, Table 1). With NaOH or urea as a catalyst, the hydrolysis of PC was difficult due to the hydrophobicity of PC (entries 5 and 9, Table 1).[2,10,27] When NaOH was used as the catalyst, in line with previous studies,[7,26] although a high PC degradation rate and BPA yield were obtained, the carbonate bonds of PC turned into $Na_2CO_3$ white precipitates, and the degradation solutions required acidification to obtain BPA (entries 6–8, Table 1). Besides, the darker color of the

**Table 1** Catalytic degradation of PC in different degradation systems[a]

| Entry | Catalyst | Depolymerizing reagent | $R_d$[b]/% | Yield/% BPA | $(RO)_2CO$[c] |
|---|---|---|---|---|---|
| 1 | — | $H_2O$ | 0 | n.d.[d] | — |
| 2 | — | MeOH | 2.6 | n.d. | n.d. |
| 3 | — | EtOH | 0.4 | n.d. | n.d. |
| 4 | — | MeOH–50 wt% $H_2O$ | 0 | n.d. | n.d. |
| 5 | NaOH | $H_2O$ | 6.3 | 6.3 | — |
| 6 | NaOH | MeOH | 99.4 | 88.8 | n.d. |
| 7 | NaOH | EtOH | 100 | 91.4 | n.d. |
| 8 | NaOH | MeOH–50 wt% $H_2O$ | 94.0 | 87.7 | n.d. |
| 9 | Urea | $H_2O$ | 3.6 | 2.1 | — |
| 10 | Urea | MeOH | 97.6 | 92.3 | 52.1 |
| 11 | Urea | EtOH | 41.7 | 22.1 | n.d. |
| 12 | Urea | MeOH–50 wt% $H_2O$ | 49.1 | 48.9 | 10.4 |

[a] 10 mL Teflon-lined stainless autoclave, PC: 0.2 g, depolymerizing reagent: 4 g, catalyst: 0.2 g, $T$: 140 °C, $t$: 3 h. [b] $R_d$: the PC degradation rate. [c] $R$ = methyl or ethyl, and $(RO)_2CO$ corresponds to dimethyl carbonate (DMC) or diethyl carbonate (DEC), respectively. [d] Not detected.

degradation solutions indicated the oxidation of BPA (Fig. S1A–D†).

Excitingly, when urea was used as the catalyst, not only the degradation rate and BPA yield reached high levels (both more than 92%), but also DMC with a yield of 52.1% was obtained in methanol (entry 10, Table 1). Moreover, DMC with a yield of 10.4% was retained in MeOH-50 wt% $H_2O$ (entry 12, Table 1). The weaker degradation effect of PC in MeOH-50 wt% $H_2O$ than that in methanol may be due to the poor solubility and reactivity of water to PC (entries 10 and 12, Table 1).[10] In these cases, BPA yield was greater than DMC yield, which could be attributed to the partial hydrolysis of PC caused by the presence of water in methanol and urea[9,10] (entries 10 and 12, Table 1). Ethanol was found to be less reactive than methanol (entries 10 and 11, Table 1). The reason may relate to the increase in steric hindrance caused by the alkyl chain growth of alcohols.[3,6,23]

Additionally, considering the large amount of urea, we tried to reduce the amount of urea to 1/10 $m_{PC}$ (42 mol% to PC) for the methanolysis of PC. As shown in Fig. S2,† after reducing the amount of urea, the degradation reaction slowed down, requiring 6 h at 140 °C to reach a degradation rate of more than 90%. Despite this, urea at this concentration can still greatly accelerate the degradation of PC compared with no catalyst, which again demonstrates the catalytic effect of urea.

Therefore, the above results strongly prove the ability of urea to catalyze PC methanolysis while recovering both BPA and DMC. Thus, we choose the urea/methanol degradation system for further research.

Since the presence of water is usually unavoidable in industrial processes, the effect of water content on PC methanolysis was studied. As shown in Fig. 1a, when the water content increased from 0 to 25 wt%, the PC degradation rate and DMC yield gradually decreased from 97.6% and 52.1% to 62% and 22.8%, respectively. This agreed with the previous reports,[10] indicating that water inhibited the degradation of PC and the generation of DMC, which may result from the poor solubility and reactivity of water to PC. The stability of DMC in the urea/methanol system was also investigated. As shown in Fig. 1b, after heating at 140 °C for 2 h, the content of DMC remained at 99.7%. Then, with the extension of time, DMC content decreased gradually. When the temperature rose to 150 °C, DMC content dropped further. The loss of DMC may be due to the hydrolysis of DMC caused by the water in methanol and urea. Hence, lower temperature and shorter time are more favorable for the preservation of DMC.

The effects of reaction conditions on PC methanolysis were investigated. The effects of urea concentration on the PC degradation rate and BPA yield are shown in Fig. 1c and d. When the urea concentration increased, both the PC degradation rate and BPA yield increased, and the reaction rate increased, indicating that increasing the catalytic active sites can accelerate PC degradation. At 3 h, the degradation of PC was nearly complete, and the PC degradation rate, BPA yield

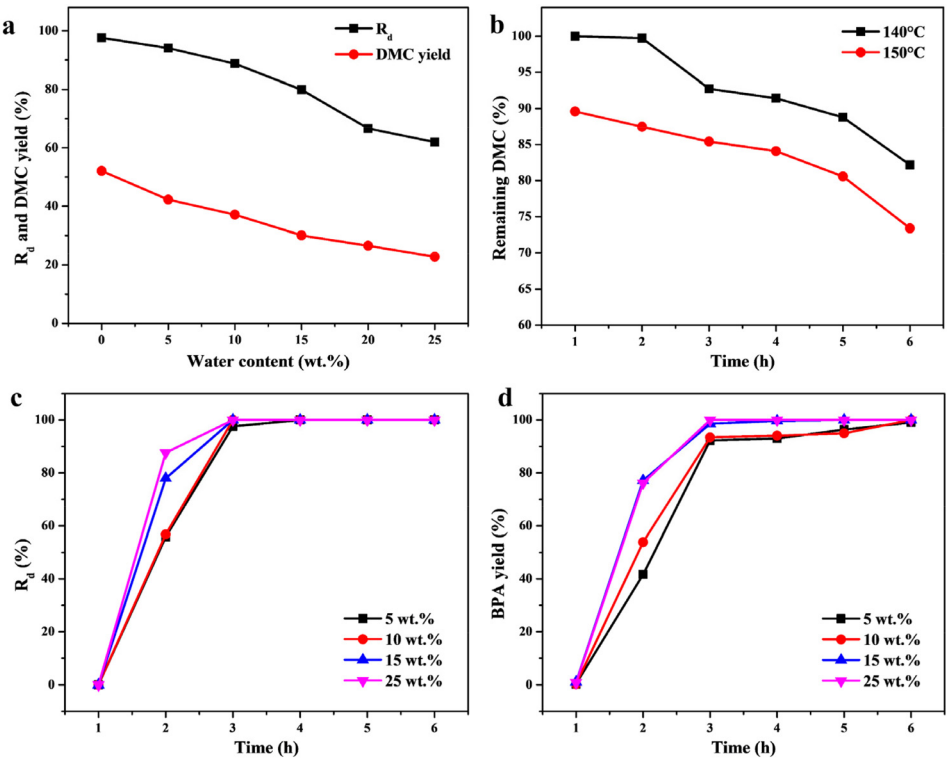
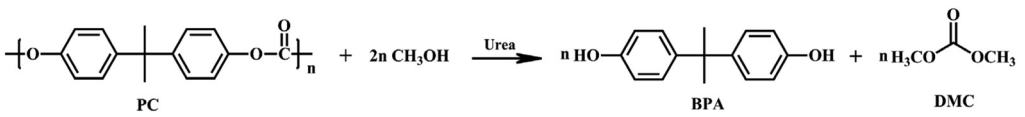



**Fig. 1** (a) Effect of water content on the $R_d$ (PC degradation rate) and DMC yield (0.2 g PC, 4 g MeOH–$H_2O$, 0.2 g urea, *T*: 140 °C, *t*: 3 h). (b) Stability of DMC in the urea/methanol system at different temperatures and times (0.2 g DMC, 4 g MeOH, 0.2 g urea). Effects of urea concentration on the (c) $R_d$ and (d) BPA yield (0.2 g PC, 4 g MeOH, *T*: 140 °C).

Table 2 Effects of the reaction conditions on PC methanolysis[a]




| Entry | $m_{PC}$/g | Urea concentration[b]/wt.% | Temp./°C | Time/h | $R_d$/% | $Y_{BPA}$[c]/% | $Y_{DMC}$[d]/% |
|---|---|---|---|---|---|---|---|
| 1 | 0.2 | 5 | 140 | 3 | 97.6 | 92.3 | 52.1 |
| 2 | 0.2 | 10 | 140 | 3 | 100 | 93.4 | 74.7 |
| 3 | 0.2 | 15 | 140 | 3 | 100 | 98.6 | 61.1 |
| 4 | 0.2 | 25 | 140 | 3 | 100 | 100 | 50.6 |
| 5 | 0.2 | 10 | 130 | 3 | 63.2 | 57.4 | 35.3 |
| 6 | 0.2 | 10 | 150 | 3 | 100 | 93.7 | 49.6 |
| 7 | 0.2 | 10 | 140 | 1 | Swollen | 0.3 | 8.3 |
| 8 | 0.2 | 10 | 140 | 2 | 56.8 | 53.9 | 39.3 |
| 9 | 0.2 | 10 | 140 | 4 | 100 | 94.1 | 65.6 |
| 10 | 0.3 | 10 | 140 | 3 | 96.8 | 87.1 | 49.4 |
| 11[e] | 0.2 | 12 | 140 | 2 | 76 | — | — |
| 12[f] | 0.2 | 12 | 140 | 2 | 77.5 | — | — |

[a] 10 mL Teflon-lined stainless autoclave, MeOH: 4 g. [b] $g_{urea}/g_{MeOH}$. [c] $Y_{BPA}$: BPA yield. [d] $Y_{DMC}$: DMC yield. [e] MeOH: 3.36 g. [f] MeOH: 3.36 g, DMC: 1 g.

and DMC yield are shown in Table 2. However, with the increase of urea concentration, the DMC yield first increased and then decreased, reaching a maximum of 74.7% at 10 wt% urea (entries 1–4, Table 2). The reason for the decrease in DMC yield may be that excessive urea exacerbated the hydrolysis of PC and DMC. Thus, the optimal urea concentration is 10 wt%.

The effects of reaction temperature, reaction time and PC dosage were also studied. When the reaction temperature increased, the PC degradation rate and BPA yield increased, suggesting that raising the temperature can promote PC degradation. While the DMC yield increased first and then decreased, reaching a maximum at 140 °C (entries 2, 5 and 6, Table 2), probably because high temperature aggravates the hydrolysis of PC and DMC. Hence, the optimum temperature is 140 °C. Similarly, the ideal reaction time is 3 h (entries 2 and 7–9, Table 2). When the PC dosage increased from 0.2 g to 0.3 g, the DMC yield decreased largely (entries 2 and 10, Table 2). Thus, the optimum PC dosage is 0.2 g. In these cases, the BPA yield was almost always greater than the DMC yield, which could be attributed to the partial hydrolysis of PC and DMC caused by the water in methanol and urea. Besides, since DMC itself is a good solvent and was reported to promote the degradation of PC,[6] we examined whether the product DMC can promote the degradation, but found that DMC had no obvious promoting effect on the degradation of PC (entries 11 and 12, Table 2). Additionally, it should be noted that as the reaction was conducted above the boiling point of methanol, some pressure could be generated within the autoclave, and that the pressure is generated spontaneously by the reaction without any external gas, so the pressure within the autoclave is certain at a certain temperature. The actual pressures of the urea/methanol solutions at reaction concentrations and temperatures were measured and are listed in Table S1.† Accordingly, the optimal conditions for PC methanolysis are: 0.2 g PC, 4 g methanol, 10 wt% urea (to methanol), reaction temperature 140 °C, and reaction time 3 h (autogenous pressure: *ca.* 0.88 MPa). Under the optimal conditions, PC is completely degraded, and the yields of BPA and DMC reach 93.4% and 74.7%, respectively.

After the reaction, the degradation products were separated according to the process shown in Scheme S1.† The degradation solution was distilled. DMC can be separated from the azeotropic mixture of DMC–MeOH by the industrial process,[29,30] while the distillation residue was analyzed by NMR. As shown in Fig. S3a and c,† except for the signals of urea and BPA, there were some unknown signals in the distillation residue. The blank experiment confirmed that these signals mainly correspond to methyl carbamate (MC) formed by urea and methanol (Fig. S3b and d†), and MC showed no catalytic activity on PC methanolysis (Table S2†). Given that DMC can also be synthesized from urea and methanol,[32,33] where urea and methanol first form MC, and then MC and methanol form DMC, we tested whether this would happen in our system. After raising the temperature or prolonging the reaction time, no DMC was detected in the reaction solution of methanol and urea. This indicated that in the PC degradation reaction, DMC was not generated from urea and methanol but from the methanolysis of PC.

To separate BPA and urea, ethyl acetate was added to the residue of distillation to dissolve BPA. After filtration, insoluble urea can be obtained with 99.4% purity (Fig. S4†). The filtrate was evaporated, and the remaining solid was washed with water and dried to obtain BPA white powder. IR spectra displayed that the structure of the product was basically the same as that of the standard BPA (Fig. S5†). EA showed that the value of each element in the product was very close to those in the standard BPA. The product contained a small amount of N, possibly owing to the presence of impurities such as urea (Table S3†). NMR analysis further determined that the purity of the product BPA was 99.2% and that the impurities in it were mainly MC (Fig. S6†), which confirmed the EA results.

The reusability of the urea/methanol degradation system was investigated. To reduce the energy consumption and urea loss during the separation, the degradation solution was reused directly for the next reaction. As shown in Table S4,† the degradation system maintained high efficiency even after 10 cycles, with a PC degradation rate of 100% and cumulative yields of BPA and DMC of 97.7% and 33%, respectively. As mentioned before, the low DMC yield may be attributed to the hydrolysis of PC and DMC over a long period of time.

To further evaluate the sustainability of the PC recycling process, we conducted the green metrics analysis[34–36] for the recycling of PC in two modes: (1) a single degradation and (2) 10 cycles of degradation, the details of which are provided in Tables S5 and S6.† Environmental impact factors (E-factors) and process mass intensity (PMI) were calculated. As shown in Table S6, a comparison of the simple E-factor (sEF), complete E-factor (cEF) and E-factor (EF) for different modes suggested that the main contributor to waste is solvent losses. It showed that all the values of the cyclic mode declined nearly 90% compared with those of the single mode. In the single mode, the E-factor, waste amount and PMI were 3.41 kg $kg^{-1}$, 3.76 kg $kg^{-1}$ PC and 20.17 kg $kg^{-1}$, respectively, while in the cyclic mode, they were 0.38 kg $kg^{-1}$, 0.38 kg $kg^{-1}$ PC and 3.04 kg $kg^{-1}$, respectively. The larger waste amount and PMI in a single degradation are due to the excess methanol and large urea dosage. This suggested that the cyclic degradation mode produced less waste and showed greater efficiency for industrial PC recycling, which demonstrated the greenness and economy of this method. Furthermore, the above data were obtained in a small-scale 10 ml reactor in the laboratory. It can be reasonably speculated that after process optimization and scale-up tests, the amount of waste in the process could be significantly reduced.

To sum up, the above results demonstrate that urea can be used as a green economical catalyst for PC methanolysis while recovering both BPA and DMC. The whole recycling process is simple, green and economical. The comparison of our system with previous representative catalytic systems for PC methanolysis is shown in Table S7.† It can be clearly seen that we have the distinct advantage of using green and economical urea as a catalyst instead of toxic and expensive solvents and catalysts while recovering both BPA and DMC, which has not been reported so far.

### Kinetics of transesterification between DEC and MeOH

Due to the complex structure of the polymer, it is difficult to accurately quantify PC during the reaction. To explore the reaction kinetics and mechanism, we chose diethyl carbonate (DEC) as a model compound and studied the kinetics of transesterification between DEC and MeOH. Under the experimental conditions used, the transesterification reaction between DEC and MeOH is a two-step process (Scheme 1). The intermediate ethyl methyl carbonate (EMC) is produced in the first step and further converted to DMC by reacting with methanol in the second step.

The kinetic reaction curves are shown in Fig. S7.† When urea concentration was 10 wt%, the reaction was quite slow at

(a) $(C_2H_5O)_2CO$ (DEC) $\underset{CO(NH_2)_2}{\overset{+CH_3OH}{\rightleftharpoons}}$ $CH_3OCOOC_2H_5$ (EMC) $\underset{CO(NH_2)_2}{\overset{+CH_3OH}{\rightleftharpoons}}$ $(CH_3O)_2CO$ (DMC)

(b) $(C_2H_5O)_2CO + 2CH_3OH \overset{CO(NH_2)_2}{\rightleftharpoons} (CH_3O)_2CO + 2C_2H_5OH$

**Scheme 1** (a) The two-step process and (b) the overall reaction equation of the transesterification reaction between DEC and MeOH catalyzed by urea.

**Table 3** Kinetic parameters of the transesterification reaction between DEC and MeOH

| Urea concentration[a] (wt.%) | Temp. (°C) | $k$[b] ($h^{-1}$) | $E_a$[c] (kJ $mol^{-1}$) |
|---|---|---|---|
| 10 | 140 | 0.0442 | 97.59 |
| | 160 | 0.1215 | |
| | 180 | 0.5479 | |
| 30 | 120 | 0.0902 | 60.21 |
| | 140 | 0.1910 | |
| | 160 | 0.4965 | |

[a] $g_{urea}/g_{MeOH}$. [b] $k$: rate constant. [c] $E_a$: activation energy.

140 °C, and the DMC yield was only 3.1% at 6 h (Fig. S7a†). After increasing the temperature (Fig. S7a–c†) or urea concentration (Fig. S7a, e, b and f†), the conversion of DEC increased markedly, while the yields of EMC and DMC increased slightly. In the reaction, the conversion of DEC was the fastest, the generation of EMC was the second, and the generation of DMC was the slowest. At a higher temperature, the reaction rate was faster and the EMC yield increased first and then decreased, indicating that EMC is an intermediate product (Fig. S7b, c and f†). It showed that the DMC yield also had a peak value at a higher temperature (Fig. S7c and f†). The decrease in DMC yield may be due to the hydrolysis of DMC exacerbated by the high temperature.

Since methanol is in large excess relative to DEC, the concentration of methanol can be regarded as a constant, so the experimental data in Fig. S7† were fitted by the first-order reaction[9,25] and the kinetic parameters were further calculated (Fig. S8, 9† and Table 3). As shown in Table 3, when the temperature or urea concentration increased, the reaction rate constant increased, indicating that raising the temperature and increasing the catalytic active sites can accelerate the reaction. Surprisingly, the increase of urea concentration significantly reduced the reaction activation energy. When the urea concentration increased from 10 wt% to 30 wt%, the activation energy decreased markedly from 97.59 kJ $mol^{-1}$ to 60.21 kJ $mol^{-1}$. This indicated that the promoting effect of the increase of urea concentration may not only be caused by the increase in catalytic active sites, but also more likely by the change in the interaction between the catalyst and reactants.

### Catalytic degradation mechanism of PC

Based on the above conjecture, we chose DMC as a model compound for the carbonate and explored the interaction

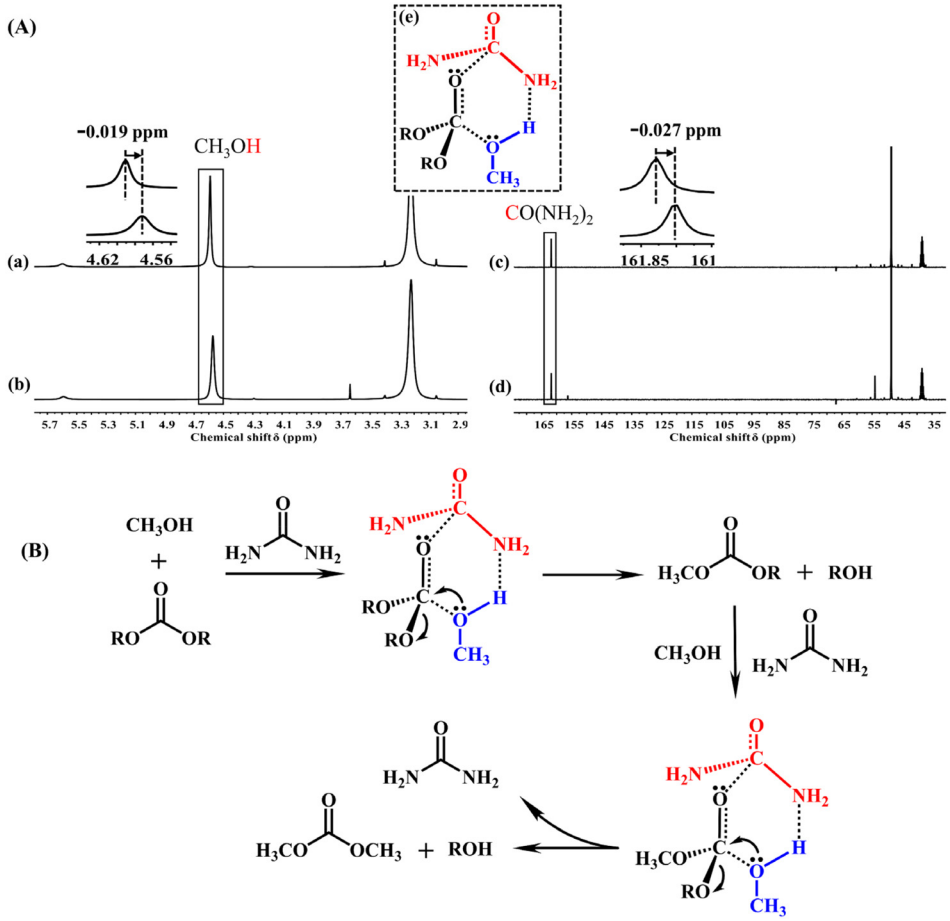



Fig. 2 (A) $^{1}$H NMR and $^{13}$C NMR spectra of the mixture of urea and methanol (a and c) before and (b and d) after the addition of DMC; (e) the six-membered ring formed by urea, methanol and carbonate. (B) The mechanism of PC degradation catalyzed by urea.

between urea, methanol and DMC by $^{1}$H NMR and $^{13}$C NMR (Fig. 2A). After adding DMC to the mixture of urea and methanol, the hydrogen of the hydroxyl of methanol and the carbon of urea moved to the high field by 0.019 ppm and 0.027 ppm, respectively (Fig. 2Aa and b, c and d). It is well known that in the transesterification reaction, the alkoxy group of the nucleophile alcohol will attack the ester carbonyl, so the oxygen of methanol should interact with the carbonyl carbon of carbonate. Besides, it has been reported that the hydroxyl hydrogen of the alcohol and the nitrogen of urea can form hydrogen bonds, which enhances the nucleophilicity of the alcohol and thus promotes the degradation reaction.[25,37] Therefore, we speculated that urea, methanol and carbonate formed a six-membered ring, as depicted in Fig. 2Ae. In the ring, the hydroxy hydrogens of methanol form hydrogen bonds with the nitrogen of urea. For methanol, compared with the hydrogen bonds formed by the methanol molecules themselves, because the electronegativity of the nitrogen atom is weaker than that of the oxygen atom, the electron cloud density of the hydroxy hydrogen of methanol relatively increased, as indicated by the upfield shift of the hydroxy hydrogen of methanol (Fig. 2Aa and b). For urea, in the ring, the carbonyl oxygen with lone pair electrons of the carbonate can give electrons to the relatively electron-deficient carbon of urea (Fig. 2Ae), so the electron cloud density of the carbon of urea also increased, as suggested by the upfield shift of the carbon of urea (Fig. 2Ac and d).

Based on the above experimental results, a possible catalytic degradation mechanism of PC was proposed (Fig. 2B). Firstly, methanol, the carbonate $(RO)_2CO$ and urea interact to form a six-membered ring. Then in the ring, electrons move from the oxygen of methanol through the carbonyl carbon of the carbonate to the alkoxy group –OR. Then the old carbonate bond breaks and new bonds form to give $CH_3O(CO)OR$ and ROH. Finally, $CH_3O(CO)OR$, methanol and urea undergo ring formation and electron transfer again to give DMC and ROH.

## The origin of the effect of urea concentration

Based on our understanding of the catalytic reaction mechanism, we further explored the origin of the effect of urea concentration. The interactions between urea, methanol and carbonate were studied at different urea concentrations by NMR. First, we studied the interaction between urea and methanol at high (30 wt%) and low (5 wt%) urea concentrations. In the mixture of urea and methanol, it was shown that as the urea concentration increased, the chemical shifts of the hydroxyl

hydrogen and the carbon of methanol, and the hydrogen and carbon of urea all moved to the lower field (Fig. 3A). Based on this, we constructed the interaction models of methanol and urea at low and high urea concentrations separately (Fig. 3B). As shown in Fig. 3Ba, at low urea concentrations, there are many methanol molecules around a urea molecule. The oxygen with lone pair electrons of methanol can donate electrons to the relatively electron-deficient carbon of urea. When the urea concentration increases, the number of methanol molecules around a urea molecule decreases (Fig. 3Bb), and the average opportunity for each urea molecule to get electrons from methanol decreases correspondingly, so the electron cloud density of hydrogen and carbon in urea decreases, as suggested by the downfield shift of the hydrogen and carbon of urea (Fig. 3A). For methanol, the increase of urea concentration makes more methanol molecules donate electrons to urea, and thus the average electron cloud density of each methanol molecule decreases, thus decreasing the electron cloud density of the carbon and hydroxyl hydrogen of methanol, as indicated by the downfield shift of the carbon and hydroxyl hydrogen of methanol (Fig. 3A).

Combining the interaction and the catalytic reaction mechanism, it is clear that at low urea concentrations (Fig. 3Ba), since a urea molecule is surrounded by many methanol molecules, the carbonate, urea and methanol have a large steric hindrance to form the six-membered ring. When the urea concentration increases, the number of methanol molecules around urea decreases (Fig. 3Bb), so the steric hindrance of ring formation decreases, and thus the energy required for ring formation decreases. Therefore, the increase of urea concentration makes it easier for carbonate, methanol and urea to form the six-membered ring.

Then we studied the interaction between urea, methanol and DMC (a model compound for carbonate) at high (30 wt%) and low (5 wt%) urea concentrations by NMR. In the mixture of urea, methanol and DMC, it was shown that as the urea concentration increased, the chemical shifts of the hydroxyl hydrogen and the carbon of methanol, the hydrogen and carbon of

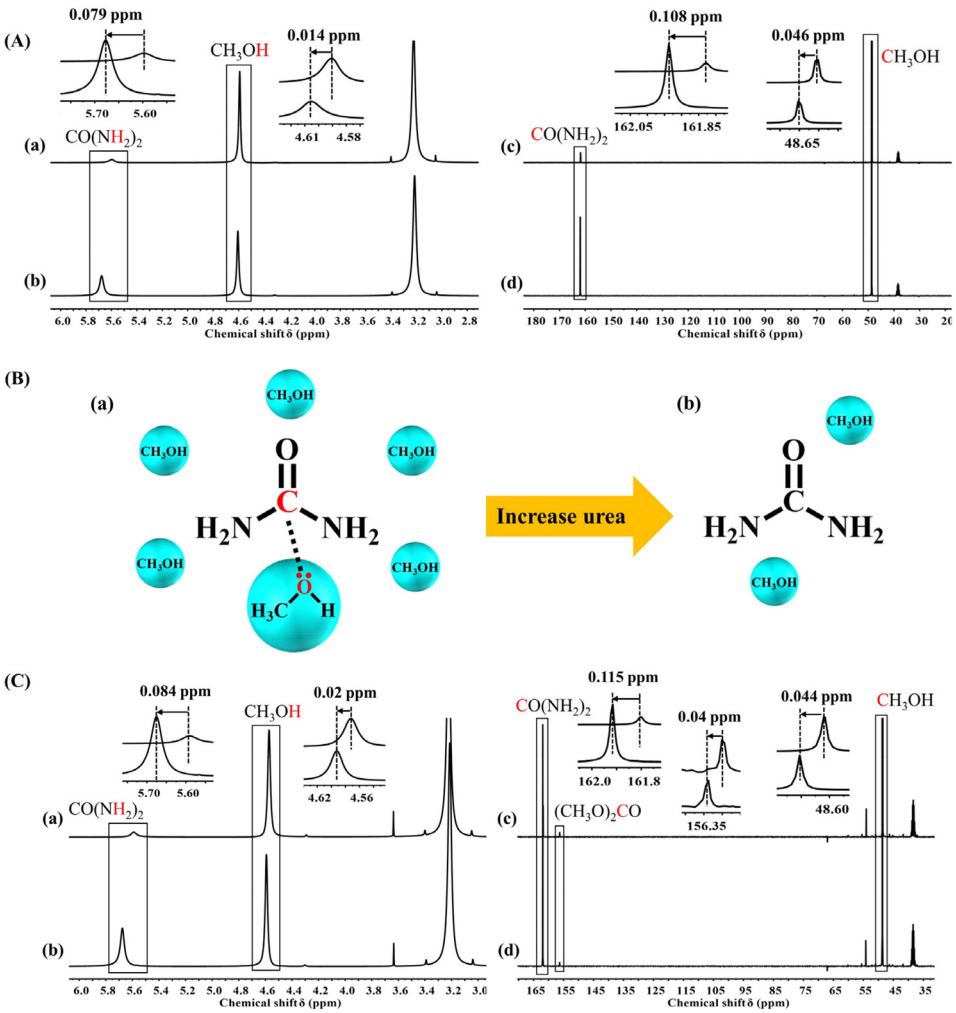



Fig. 3 (A) $^{1}$H NMR and $^{13}$C NMR spectra of the mixture of urea and methanol at 5 wt% (a and c) and 30 wt% (b and d) urea concentrations. (B) The interaction models of methanol and urea at low (a) and high (b) urea concentrations. (C) $^{1}$H NMR and $^{13}$C NMR spectra of the mixture of urea, methanol and DMC at 5 wt% (a and c) and 30 wt% (b and d) urea concentrations.

urea, and the carbonyl carbon of DMC all moved to the lower field (Fig. 3C), which agrees with the trend in urea and methanol mixtures (Fig. 3A). In particular, the increase of the electropositivity of the carbonyl carbon in DMC indicated that the carbonate bond was activated, which facilitates the nucleophilic attack of methanol and the transfer of electrons.[25,38]

Therefore, the increase of urea concentration changed the interaction between urea, methanol and carbonate, which made the six-membered ring easier to form and activated the carbonate bond. The two aspects contributed to the significant reduction in activation energy, thus accelerating the reaction.

## Conclusions

In summary, green efficient and solvent-free methanolysis of PC to BPA and DMC was achieved with urea as a cheap green catalyst. In 10 wt% urea/methanol at 140 °C for 3 h, PC was completely degraded to BPA and DMC with yields of 93.4% and 74.7%, respectively. Through kinetic and NMR studies, a possible catalytic degradation mechanism of PC was proposed, where urea, methanol and carbonate formed a six-membered ring in the reaction. The kinetics of the model compound showed that the increase of urea concentration significantly reduced the activation energy. NMR studies further revealed that the increase of urea concentration changed the interaction between urea, methanol and carbonate, which made the six-membered ring easier to form and activated the carbonate bond, thus contributing to the significant reduction in activation energy and promoting the reaction. The degradation system can be reused directly up to 10 times and 100% degradation rate can be maintained. Moreover, environmental impact factor and process mass intensity analysis suggested that the cyclic degradation mode produced less waste and showed great potential for industrial PC recycling, which demonstrated the greenness and economy of this method. This method has the advantage of using green and economical urea as a catalyst instead of toxic and expensive solvents and catalysts while recovering both BPA and DMC. This work offers a simple, green and economical method for the degradation of PC and also demonstrates the great potential of urea in the catalytic degradation of polymers.

## Author contributions

Nan Hu: data curation, investigation, and writing – original draft. Lijuan Su: methodology and software. Hongyan Li: methodology. Ning Zhang: methodology. Yongqin Qi: resources and software. Hongliang Wang: writing – review & editing. Xiaojing Cui: writing – review & editing. Xianglin Hou: resources, funding acquisition, investigation, and project administration. Tiansheng Deng: conceptualization, resources, methodology, supervision, validation, project administration, and writing – review & editing.

## Data availability

The data supporting the findings of this study are available from the corresponding author upon reasonable request.

## Conflicts of interest

There are no conflicts to declare.

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