

Alcoholysis of waste polycarbonate plastic by methanol into bisphenol A under mild conditions

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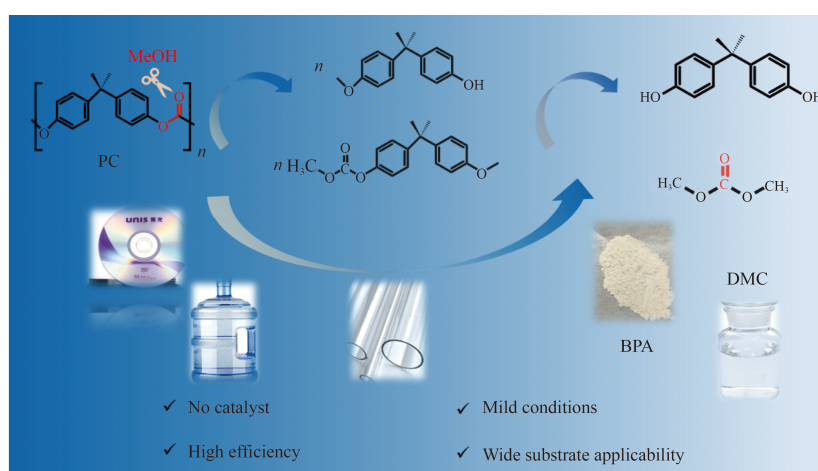
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Abstract: Polycarbonate (PC) is a widely utilized polymer in the chemical industry. Because toxic bisphenol A (BPA) leaches into the environment, the accumulation of waste PC poses a detrimental effect on both human health and the environment. To meet the demand for sustainable resource utilization and address environmental concerns, it is necessary to recover BPA from waste PC. In this work, methanol was used as the

solvent to depolymerize PC *via* alcoholysis under the catalyst-free and mild condition. Experimental results demonstrated that PC could be depolymerized into BPA monomer at moderate temperature (120–160 °C). 100.0% degradation of PC plastic could be achieved with high BPA yield of 95.0% at 160 °C without the addition of catalysts or auxiliary solvents. In a scaled-up experiment of 10 g PC, a facile separation process of BPA was designed, and the recovery of BPA was more than 85.0%. Additionally, this method was also effective in depolymerizing actual plastic mixtures, such as ABS-PC and other polyesters such as polylactic acid, polyglycolic acid, and polyethylene terephthalate. Based on SEM and GPC results, a probable alcoholysis depolymerization mechanism for PC was proposed. These results indicated that methanol had a wide range of universality for the alcoholysis of various polyesters. This work presents a facile, green, and efficient approach for the alcoholysis recovery of polyesters plastics.

Key words: polycarbonate; methanolysis; bisphenol A; catalysts-free; chemical recycling



Due to their light weight, low cost and high performance, plastics have become a necessity in our daily life^[1]. However, most plastics are notoriously difficult to degrade, leading to severe environmental pollution. Moreover, plastics, especially polycarbonate (PC), are recognized as one of the most extensively utilized engineering plastics,

with applications across diverse industries. Their annual production has reached 5 million tons and is expected to rise to 8 million tons by 2026^[2–3]. Discarded PC has resulted in significant resource waste and environmental pollution due to the enormous increase in plastics production and consumption. Given the high organic carbon content of PC

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plastics, waste PC can be recycled through the design of advanced recycling routes. Consequently, developing green, economical, and efficient recycling methods for waste PC is crucial for solving the plastic pollution problem and recycling of the spent carbon resources. Current waste plastics recycling methods include landfill, incineration, mechanical recycling, and chemical recycling. While landfill, incineration, and mechanical recycling methods are simple and feasible, each of them has notable drawbacks. The landfilled plastics can be converted into microplastics, which are readily absorbed by animals and humans^[4], causing harm to health and ecosystems^[5]. Incineration releases greenhouse and harmful substances^[6]. Mechanical recycling, a physical degradation processes involving cutting, crushing, and melting, is primarily used for optical disc waste recycling. Furthermore, these methods are also unable to achieve the effective recovery of carbon resources from waste plastics. In contrast, chemical recycling can break down waste plastics into monomers or other high-value chemicals, enabling a more effective recovery of carbon-based resources from waste plastics.

As a promising alternative, chemical recycling improves the resource utilization efficiency and promotes environmental sustainability^[7]. It not only facilitates the production of value-added chemicals through bond recombination but also mitigates the environmental exposure by converting waste PC into valuable BPA or its derivatives, thereby enabling the efficient recycling of waste PC^[8–9]. A effectively approach is chemical depolymerization of discarded PC into valuable compounds. Significant progresses have been realized *via* various methods in recent years such as thermal degradation^[10–11], photocatalysis^[12–13], biodegradation^[14–15], electrochemistry^[16], hydrogenolysis^[17–18] and solvolysis^[19–21]. Thermal degradation decomposes plastics into various lower molecular weight compounds under high temperature^[22]. Similarly, photocatalytic degradation produces a mixture of by-products, complicating the separation process^[23]. Biodegradation requires suitable enzymes or strains, and the associated screening and the products separation increase the difficulty of industrialization. Electrochemical degradation method employs renewable energy such as solar energy, wind energy or geothermal energy to degrade waste plastics into small molecular compounds. Although hydrogenolysis can effectively depolymerize PC, the harsh reaction conditions limit practical industrial application. Solvolysis, the decomposition of waste plastics in certain functional solvents, can selectively cleave chemical bonds, primarily ester bonds, to recover high-value chemicals and monomers. Compared to pyrolysis, the solvolysis method operates at lower reaction temperature with less energy consumption. Compared to photodegradation, it shows the higher degradation efficiency and product selectivity. Unlike biodegradation, the solvents required for the solvolysis method are available, and the degradation process is highly efficient. Moreover, the solvolysis method

is more technologically mature than electrolytic depolymerization, and operates under mild reaction conditions than hydrogenolysis, which is conducive to practical industrial application.

Several solvolysis methods have been reported, such as ammonolysis, hydrolysis and alcoholysis^[24–26]. Ammonolysis, employing amine nucleophiles, breaks down of PC into valuable urea chemicals^[27–28]. Hydrolysis can degrade PC into BPA and dimethyl carbonate (DMC) in an environment ally friendly solvent, but exhibits low selectivity with the non-ideal by-product of CO₂^[29]. Besides, high temperatures and pressures are required to enable interaction between polymer and water due to the rigidity and hydrophobicity of PC chains. In this instance, the presence of the solvent can improve the depolymerization degree^[30–32]. Alcoholysis produces depolymerizes PC through the cleavage of ester linkages by alcohols such as methanol, ethanol and ethylene glycol, yielding high-value small molecules^[33–35]. Compared to hydrolysis, although product separation is still difficult, the alcoholysis method has the advantages of high yield, mild conditions, and short reaction time.

Alcoholysis of PC waste can yield alkyl carbonate compounds in addition to BPA. However, a significant amount of concentrated base or superbase, such as DTU^[33], TBD^[36] and NaOH^[37–38], was usually utilized in the reported alcoholysis methods, which can cause in equipment corrosion, laborious procedures, and more wastewater. While solid catalysts such as NaAlO₂^[39], ZnO-NPs/NBu₄Cl nanoparticles^[40], CaO-CeO₂/SBA-15^[41], CaO (SrO, BaO)/SBA-15^[42] can accelerate the alcoholysis process, they necessitate the additional solvent of THF, resulting to cumbersome post-processing. Moreover, although the solid catalysts enhance reaction rate at mild conditions, they also increase costs and decrease product purity. Methanol has the advantages of low boiling point, strong nucleophilicity and easy recovery, making it preferred for PC depolymerization compared to other alcohols. Therefore, the method of catalyst-free alcoholysis of PC is of great significance for the recovery of its monomer BPA.

This work describes an efficient, catalyst-free alcoholysis route for PC depolymerization in methanol to recover its monomer BPA. The effects of different alcoholic solvents and reaction parameters on depolymerization degree and BPA yield were studied. Complete depolymerization of PC and 95.0% yield of BPA were achieved at 160 °C for 8 h using methanol. The method proved effective for the alcoholysis of the real mixed plastics containing PC and other polyesters, achieving 100.0% depolymerization. A facile BPA separation process was developed, yielding a BPA recovery ratio over 85.0%. Besides, the route was successfully demonstrated in the scale-up experiment using 10 g PC as the substrate. The recovered BPA was characterized by GC-MS, FT-IR and NMR. Finally, a probable depolymerization mechanism was proposed. This work provides a simple and green recycling strategy for the valuable upgradation of waste PC.

1 Experimental

1.1 Materials

Bisphenol A polycarbonate (PC, with molecular weight of 45000 Da), bisphenol A and dimethyl carbonate (DMC), were purchased from Shanghai Macklin Biochemical Technology Co., Ltd. Methanol (CH_3OH , chromatographically pure, 99.9%), ethanol absolute ($\text{CH}_3\text{CH}_2\text{OH}$, chromatographically pure, 99.9%), glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$, chromatographically pure, 99.9%), propanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$, chromatographically pure, 99.9%), ethylene glycol ($\text{OHCH}_2\text{CH}_2\text{OH}$, chromatographically pure, 99.9%), and glycerol ($\text{HOCH}_2\text{CHOHCH}_2\text{OH}$, chromatographically pure, 99.9%) were purchased from Beijing Innochem Technology Co., Ltd. The other organic solvents used in the experiment are analytical grade. All the agents are used directly without further treatment. Real PC waste (optical discs, water bucket, PC basin, PC phone case, PC mask, PC tube, transparent plate, flame retardant shell) were purchased from the market.

1.2 Depolymerization reaction

Depolymerization of pure PC. The experimental procedure for PC degradation and product separation schedule is illustrated in Figure 1. The alcoholysis of PC was performed in a 15 mL Teflon lined stainless steel autoclave equipped with a magnetic stirrer. Typically, PC (0.1 g) and methanol (5 mL) were added to the reactor. Then, the internal air was replaced with nitrogen three times, and 0.3 MPa N_2 was filled. The reactor was heated in a constant temperature heating magnetic stirrer for the required reaction time. Then the reactor was cooled down in the ice water to quench the reaction. The depolymerization mixture was centrifuged at 9000 r/min. The remaining solid

PC residue was washed three times with distilled water and dried at 80 °C for 12 h to calculate the depolymerization degree of PC. The liquid products were analyzed and quantified by GC-MS.

Depolymerization of real PC waste. To test the generality of the catalyst-free alcoholysis, various actual PC waste, including waste optical disc, waste water bucket, PC basin, PC phone case, PC mask, PC tube, transparent plate, and fragments of flame-retardant shell, were tested. Firstly, the PC wastes were cut into 1 cm × 1 cm pieces, and cleaned with distilled water. To remove the printing layer from the optical disk's surface, the waste disc fragments were chemically eluted using a mixture of NaClO (3 g, 10.0% available chlorine), NaOH (2 g, AR), and deionized H_2O (28.3 g). After being cleaned with water, the discs were dried at 80 °C for 12 h. The depolymerization method of the real PC was the same as that of the above pure PC.

Scale-up depolymerization of real PC waste. A 200 mL reactor with a silex lining was used for the waste disc degrading reaction. 10 g of waste discs and 70 mL of methanol was added to the reactor, the reaction was quenched with ice water after 16 h of degradation at 160 °C. Liquid products were analyzed by GC-MS and GC.

1.3 Analysis of the depolymerized products

GC-MS (Agilent 7890A-5977) was used to qualitatively and quantitatively analyze the liquid-phase products. The chromatographic column (Agilent 19091S-433UI) was a 30 m (0.32 mm × 0.25 μm) quartz capillary column, the carrier gas was high-purity helium, the injection port temperature was 250 °C, the electron energy was 70 eV, the ion source temperature was 200 °C and the filament current was 80 μA . The temperature program was programmed as follows: a starting temperature of 40 °C was kept for 3 min, then it was heated with a rate of 10 °C/min to 310 °C, and hold for 5 min. After the operation, the GC was cooled by helium purging, and the total running time was 35 min.

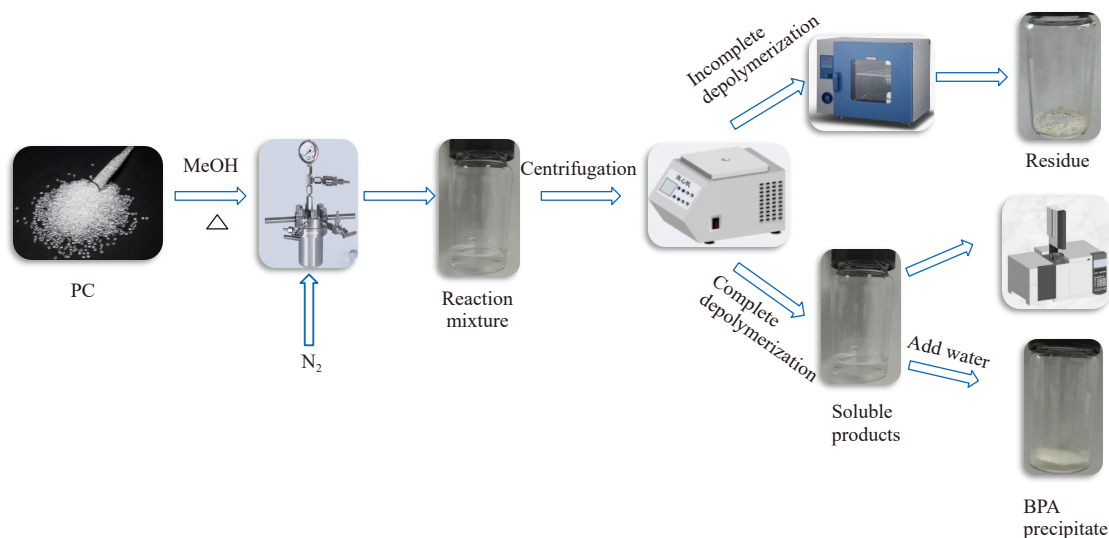


Fig. 1 Experimental process and product separation of PC degradation

The depolymerization degree of PC was calculated according to Equation 1, and the yield of various products was calculated according to Equation 2. The standard curves of different products by GC were shown in Figure S1.

$$\text{Depolymerization degree}(\%) = (m_0 - m_1) / m_0 \times 100\% \quad (1)$$

$$\text{Yield}(\%) = C_{\text{mol}_1} / C_{\text{mol}_0} \times 100\% \quad (2)$$

$$\text{Recovery ratio of BPA}(\%) = m_2 / m_3 \times 100\% \quad (3)$$

where m_0 : the initial weight of PC, g; m_1 : the weight of undegraded PC residual, g; m_2 : the quality of BPA actually obtained, g; m_3 : the quality of BPA obtained theoretically supposing PC fully converted to BPA, g; C_{mol_1} : the total amount of carbon atom (C) in product, mol; C_{mol_0} : the total amount of carbon atom (C) in PC, mol.

1.4 Separation and characterization of BPA product

The separation and purifying process of BPA were performed as follows: The reaction solution was first subjected to rotary evaporation to remove most of the methanol. To precipitate BPA, 30 mL of deionized water was added to the remaining solution, followed by centrifugation of the solid-liquid mixture. The obtained solid was dried in an oven at 105 °C for 12 h to remove the by-product DMC. Subsequently, the dried solid was completely dissolved in 10 mL of methanol, and then 30 mL of deionized water was added to completely precipitate BPA. The mixture was centrifuged, the obtained solid

product was dried at 105 °C for 12 h. To obtain high purity BPA, the above steps of methanol dissolution, water precipitation, and drying were repeated twice. The final mass of BPA was recorded, and the recovery ratio was calculated using Equation (3).

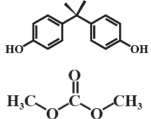
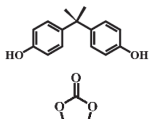
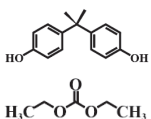
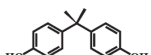
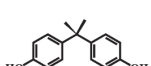
The recovered BPA was characterized by nuclear magnetic resonance (NMR) and Fourier-transform infrared spectroscopy (FT-IR). NMR analysis was carried out to confirm the chemical structure of the recycled BPA using the Agilent NMR spectrometer (500 MHz). CDCl_3 (0.01 mg/mL) was used as the solvent for sample preparation and tetramethylsilane was used as the internal standard for testing. For FT-IR analysis, the BPA sample and potassium bromide (KBr) were dried at 100 °C for 12 h to remove the moisture. The sample and KBr powder were then carefully milled into a fine powder and homogeneously mixed in a mass ratio of 1:200. FT-IR spectra were collected from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} .

2 Results and discussion

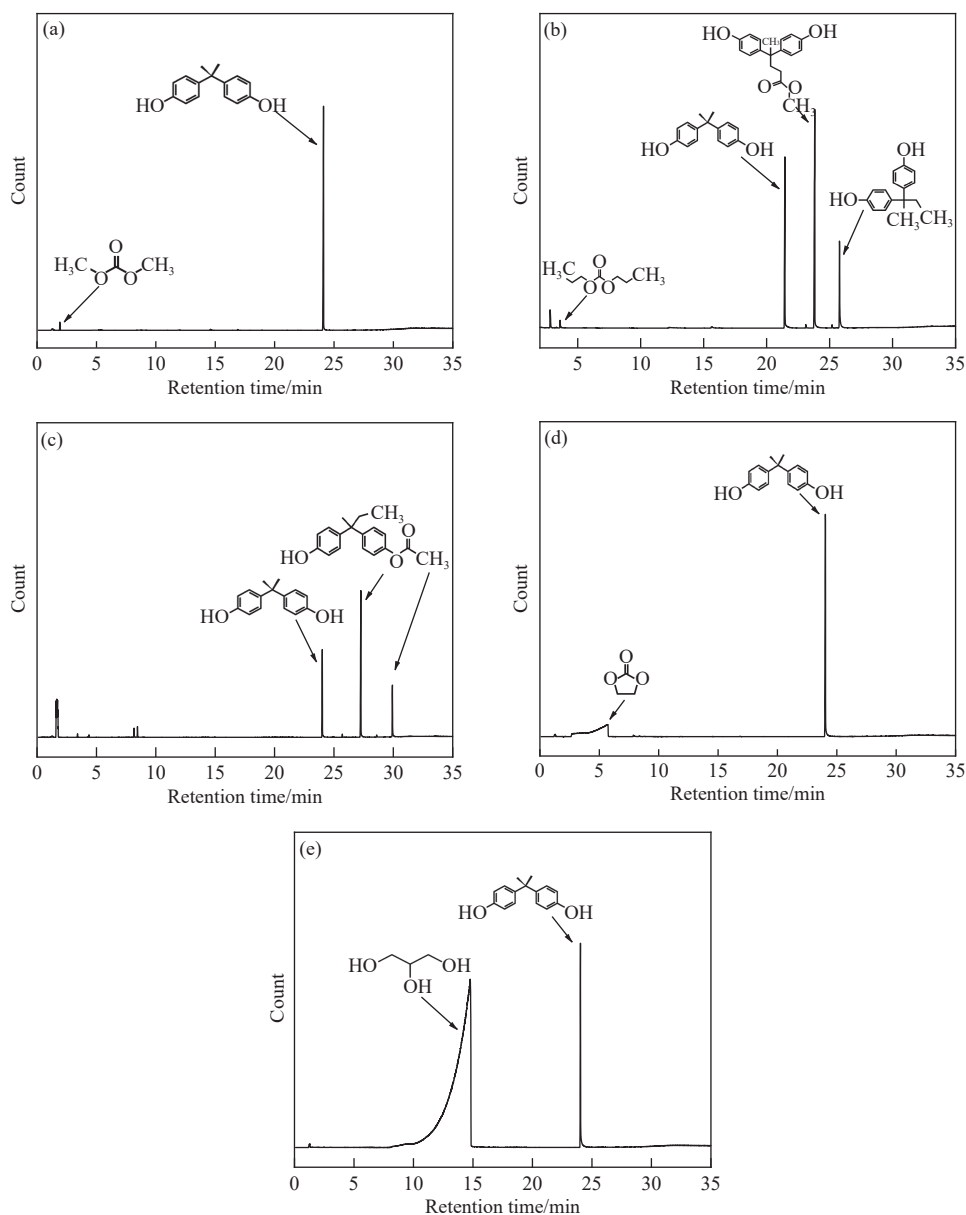
2.1 Effects of different alcohols on PC alcoholysis

The depolymerization degree and product composition of PC alcoholysis were investigated using various alcohol solvents, including methanol, ethanol, glycol, propanol and glycerol (Table 1, Figure 2). The results showed that all the alcohols yielded BPA as the main product with different PC depolymerization degree. When methanol was employed as the solvent, BPA and DMC were obtained with no other major by-products detected in the liquid products (Figure 2(a)).

Table 1 Comparison of PC alcoholysis in different alcohols^a

Entry	Solvent	Structure of main products	Depolymerization degree/%	BPA yield/%
1	methanol		100.0	95.0
2	glycol		100.0	96.0
3	ethanol absolute		74.0	67.0
4	propanol		47.2	35.0
5	glycerol		21.6	20.0

^a: Reaction conditions: PC (0.1 g), solvent (5 mL), 160 °C, 8 h, 0.3 MPa N_2 . DMC= Dimethyl carbonate, EC= Ethylene carbonate, DEC= Diethyl carbonate, DPC= Dipropyl carbonate.



(a): methanol; (b): ethanol; (c): propanol; (d): glycol; (e): glycerol.

Fig. 2 GC-MS analysis of depolymerization products in different alcohol solvents

Similarly, glycol achieved the same PC depolymerization degree and BPA selectivity, although the products contained EC instead of DMC (Figure 2(d)). Although a higher product selectivity was obtained by using glycerol, the depolymerization degree of PC and the yield of BPA was relatively low. Ethanol and propanol could also facilitate the depolymerization of PC, but the depolymerization degree was low and there were many by-products (Figure 2(b)–(e)). Given the high degree of depolymerization and product selectivity, methanol was chosen as the most suitable solvent and nucleophile for PC depolymerization.

2.2 Effect of reaction conditions

The effect of reaction temperature on PC alcoholysis was

investigated. As shown in Figure 3(a), the depolymerization degree of PC increased significantly from 15.4% to 89% when the reaction temperature was raised from 120 to 150 °C. The yield of BPA was approximately 94.2% and the depolymerization degree reached 100.0% when the temperature raised to 160 °C. With the increase of temperature, the yield of BPA gradually increased, whereas the yield of DMC was less affected. On one hand, due to the absence of a catalyst, the cleavage of carbonate bonds requires higher energy during PC was the methanol depolymerization of PC. The nucleophilic substitution reaction involving methanol attacking carbonyl carbon should overcome an energy barrier. Therefore, increasing the reaction temperature promotes the alcoholysis of PC. On the other hand, DMC was unstable at high temperature (160 °C) and decomposed into methanol and CO₂. As shown in Tables S1 and S2, CO₂ was generated during the

reaction, confirming the partial decomposition of DMC. At a lower temperature (120 °C), the reaction rate was slow, most of the PC remained undepolymerized, only a small amount of BPA was generated, and no DMC was detected. Under the investigated conditions, 160 °C was selected as the appropriate reaction temperature because it was high enough for PC depolymerization, while balancing energy input and depolymerization degree.

The effect of methanol dosage on product yield was examined. The depolymerization reaction was carried out at 160 °C for 8 h, and the results were shown in Figure 3(b). Methanol acted as both the reactant in the transesterification and the solvent. When the amount of methanol was very low (the ratio of PC to methanol is 1:10), the depolymerization degree could reach 100.0%, but the yields of BPA and DMC were low. As the methanol amount increased, the alcoholysis equilibrium shifted to BPA product formation, and the BPA yield increased

accordingly. Considering the BPA yield, the optimal ratio of PC to methanol under the present reaction conditions was determined to be 1:50.

Based on the above optimized reaction conditions, the depolymerization performance was studied over extended time, as shown in Figure 3(c). The absence of detectable low-molecular-weight products in the first 2 h suggested the slow swelling stage of PC. The degree of depolymerization and product yields grew as the reaction progressed. Meanwhile, no discernible solid residue remained because the PC particles were severely fragmented until complete depolymerization was achieved.

To investigate the evolution of the surface structure of PC during alcoholysis, the PC residues at different depolymerization degree were characterized by SEM. Figure 4 showed the surface of PC residues at different methanolysis reaction times.

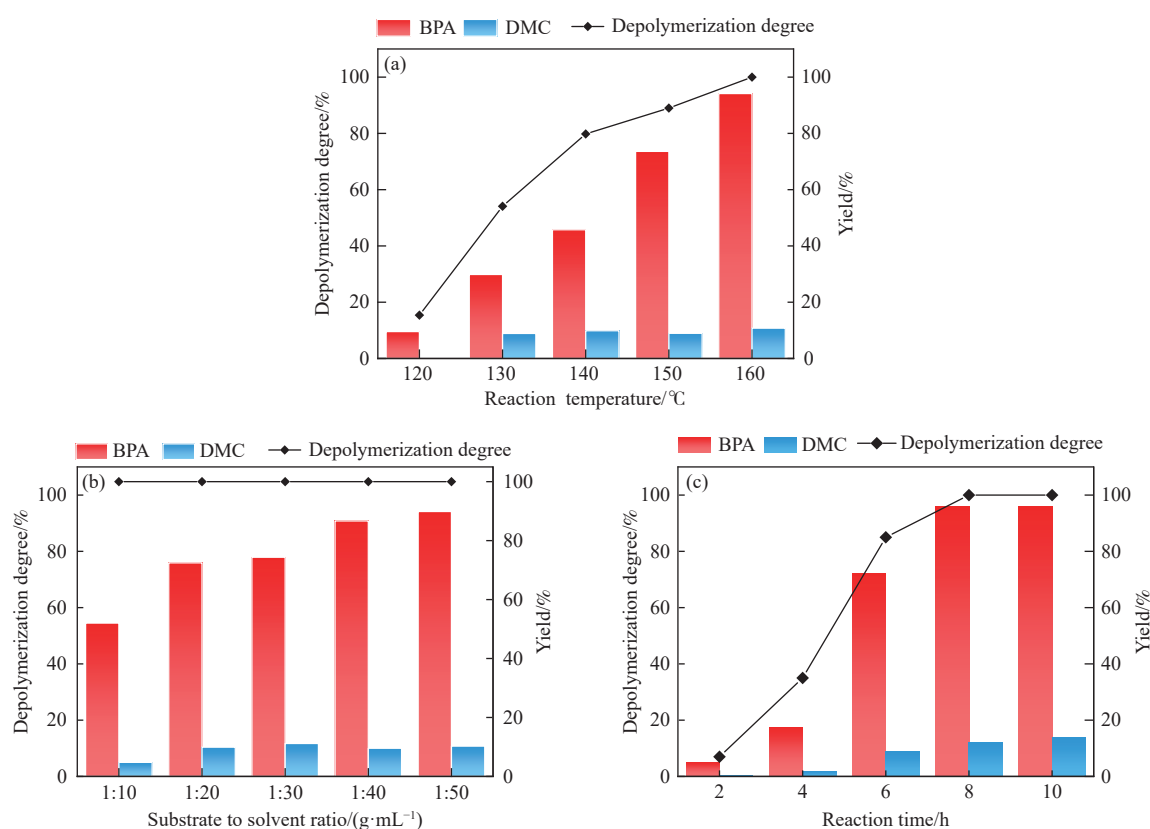
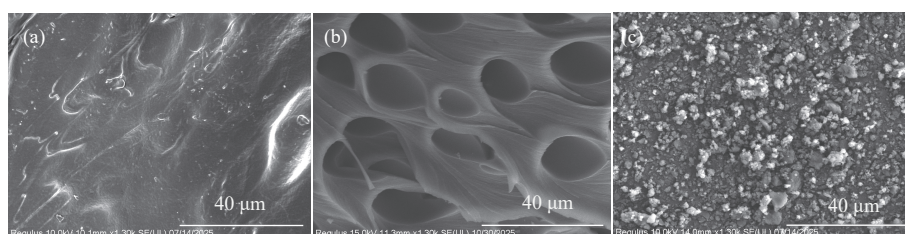


Fig. 3 Effects of different reaction conditions on PC alcoholysis reaction: (a) reaction temperature, (b) methanol dosage, (c) reaction time. Reaction conditions: PC (0.1 g), (a) methanol (5 mL), 8 h; (b) methanol (5 mL), 160 °C, 8 h; (c) methanol (5 mL), 160 °C.



(a): 0 min; (b): 30 min; (c): 360 min.

Fig. 4 SEM images of PC processed at different times. Reaction condition: 0.1 g PC, 160 °C, 5 mL MeOH.

As shown in Figure 4(a), the surface of the unreacted PC particles is dense and smooth. After 30 min of reaction, corresponding to a depolymerization degree of 1.2%, obvious protrusions and pore growth appeared on the surface of PC particles (Figure 4(b)). Compared with original PC particles, the appearance of protrusions and cavities was beneficial to the penetration of methanol into PC particles, thus promoting the random fracture of PC. Figure 4(c) showed that PC had broken down into fine grains or powders, namely oligomer-particles at the reaction time of 360 min with depolymerization degree of 75.6%. This rough surface structure enhanced the swelling and dissolution of PC, further accelerating the depolymerization process.

Under optimized reaction conditions, the methanol used in this work was compared with other commonly reported solvents (Table S3). While all the solvents can achieve complete conversion of PC to BPA, the methanol solvent in this study exhibited comparable performance of the high

yield of BPA at medium reaction temperature without the inclusion of catalysts or auxiliary solvents. Additionally, methanol has a lower boiling point compared to other alcohols, which facilitated the separation of product from the solvent.

2.3 Depolymerization of real PC waste

To confirm the universal applicability of methanol alcoholysis to actual PC-based waste, a substrate extension experiment was conducted using optical disks, buckets, masks, pipes, transparent plates, flame-retardant casings, phone cases and sinks (Figure 5(a)). Experimental results indicated that only the optical disk was completely depolymerized under the optimal reaction conditions. Considering the structural complexity of real PC waste, the reaction time was extended to 16 h, after which all the other real waste plastics were completely depolymerized.

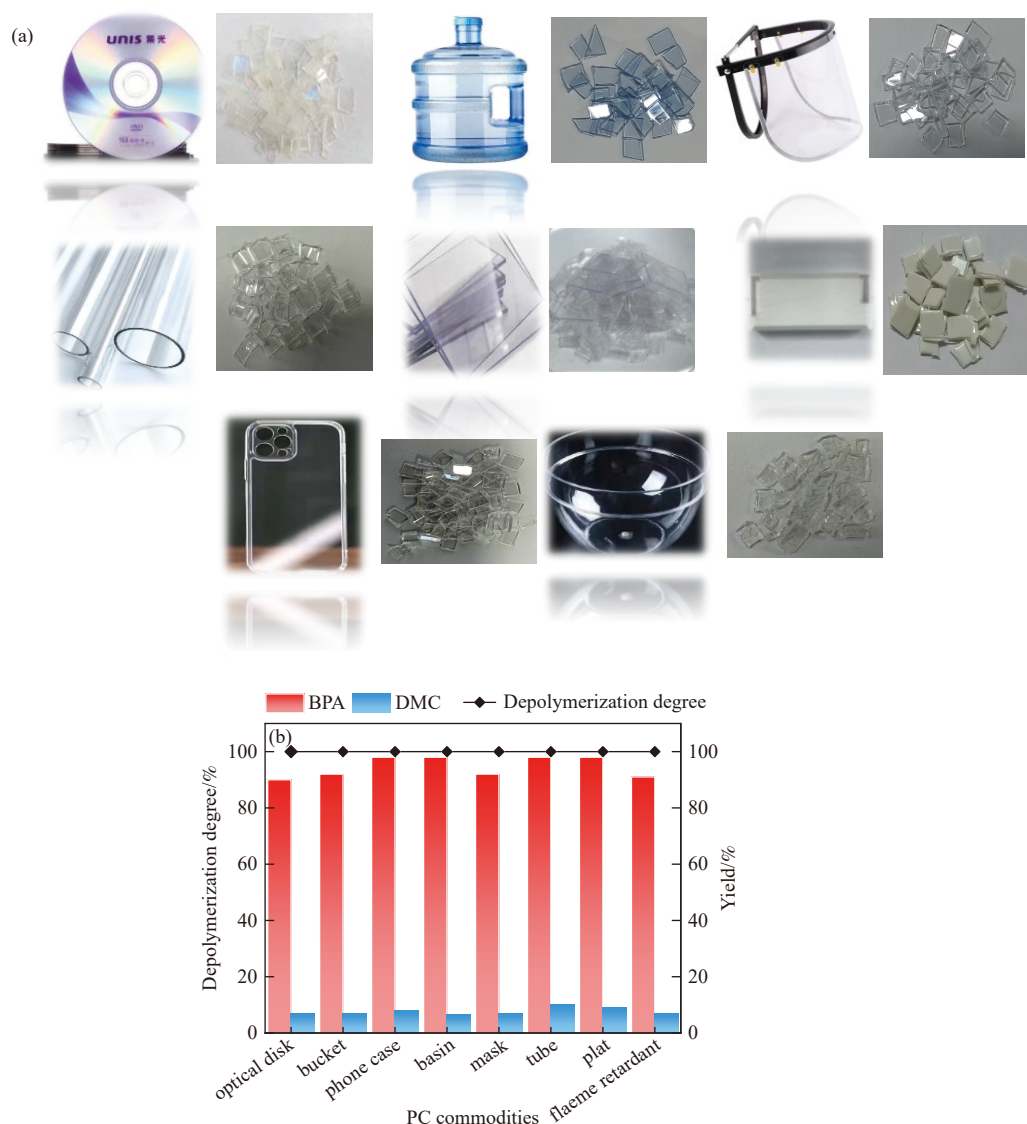


Fig. 5 (a) Photographs of real PC waste, (b) the degradation results of PC waste
Reaction condition: 0.1 g PC waste, 160 °C, reaction time: 8 h for optical disk, 16 h for other real PC waste.

For these PC wastes, the yields of BPA were between 90.0% and 99.0%, and the degradation products were identical to those obtained from pure PC (Figure 5(b)). These results showed that the methanol alcoholysis route was applicable for real PC based plastics.

In addition to the real PC wastes mentioned above, ABS-PC (a mixture of acrylonitrile-butadiene-styrene (ABS) copolymer resin and PC resin) was also used as the substrate to evaluate the feasibility of the methanol alcoholysis method. As shown in Table 2 and Figure S2, a depolymerization degree of ABS-PC was achieved to 90.0% under the above optimized conditions. The main products were BPA and DMC, similar to those obtained from pure PC. Furthermore, other polyester materials, including polylactic acid (PLA), polyglycolic acid (PGA), and polyethylene terephthalate (PET), were also depolymerized. Under the optimized condition, these polyesters (PLA, PGA and PET) could be effectively depolymerized with a higher degree than 88.0%. The results demonstrated that PLA, PGA and PET could be depolymerized into corresponding monomers and the derived esters. The depolymerization degree, product selectivity and product yield for these polyester plastics were influenced by reaction temperature and time. When the reaction temperature was low or the reaction time was short, the polymer could not be completely depolymerized, and the yield of the polymer monomer was low. Extending the reaction time significantly improved the monomer yield (Table 2). These results demonstrated the broad applicability of methanol alcoholysis for real PC-based wastes.

2.4 The results of amplification experiment

To evaluate the applicability of methanol alcoholysis, gram-scale experiments (10 g of PC) were performed. The feedstocks included pure PC, discarded broken optical disks and water bucket, processed under the optimized reaction conditions. 10 g of PC waste was degraded in 70 mL of methanol at 160 °C. During the reaction progress, large fragments gradually dissolved into the system, leaving only a small amount of unidentified solid, probably inert additives from the plastics. The depolymerization degree for both the optical disk and water bucket waste reached 100.0% with BPA yields up to 95.0%. These results confirmed that the developed methanol alcoholysis route provided an economical, practical, and green route for converting PC waste into its monomer.

2.5 Separation and characterization of BPA

The separation route for recovering BPA from the depolymerization solution was established (Figure 6). BPA separation was performed on a gram-scale using 10 g of optical disk as feedstock. After the depolymerization reaction, the solid residues were removed by centrifugation. Methanol was recovered by evaporation, and the crude BPA was obtained. Water was then added to dissolve and remove the soluble impurities, taking advantage of the insolubility of BPA in water. This process achieved a high BPA recovery ratio of >85.0%.

Table 2 The main depolymerization products and yields for different plastics

Substrate	Depolymerization degree/%	Reaction condition	Structure of main products	Yield/%
ABS-PC	90.0	180 °C, 0.3 MPa N ₂ , 24 h	<chem>Oc1ccc(cc1)C(C)(C)c2ccc(O)cc2</chem>	92.0
			<chem>COC(=O)OC</chem>	6.9
<chem>*O[C@H](C)C(=O)*</chem> (PLA)	88.7	160 °C, 0.3 MPa N ₂ , 24 h	<chem>C[C@H](OC(=O)C)OC(=O)C</chem>	72.7
			<chem>COC1=CC=C(C=C1)O</chem>	8.2
<chem>*O[C@H](C=O)O*</chem> (PGA)	100.0	160 °C, 0.3 MPa N ₂ , 24 h	<chem>OC(=O)CO</chem>	92.0
<chem>*OC(=O)c1ccc(cc1)C(=O)O*</chem> (PET)	100.0	180 °C, 0.3 MPa N ₂ , 36 h	<chem>COC(=O)c1ccc(OC)cc1</chem>	94.9
			<chem>OCCO</chem>	3.5

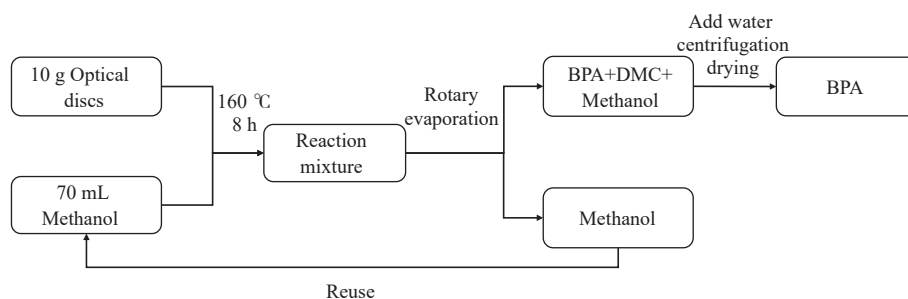


Fig. 6 Separation and recovery process of BPA

The structure of the recovered BPA was characterized and compared to BPA standard by GC-MS, FT-IR and NMR, respectively. The GC-MS results (Figure 7(a), (b)) showed a peak at approximately 24 min with an m/z of 228.1 ($[C_{15}H_{15}O_2]+H$)⁺ for the recovered BPA, matching that of the commercial BPA standard without other peaks observed. In the FT-IR spectrum (Figure 7(c)), the strong peak at 3361 cm^{-1} was attributed to the O–H stretching vibration of phenol groups, the peak at 2964 cm^{-1} was attributed to the C–H bond stretching vibration of methyl ($-CH_3$), and the peaks at 1618–1446 cm^{-1} were attributed to the C=C stretching vibration of aromatic rings. The peak at 825 cm^{-1} , corresponding to the C–H out-of-plane bending vibration of aromatic rings, confirmed the para-substituted benzene ring^[43–44].

¹H NMR and ¹³C NMR spectra of the recovered BPA were shown in Figure 8 and Figure S3. The methyl protons appeared as a singlet at $\delta = 1.62$, while the phenolic hydroxyl proton given another singlet at $\delta = 4.59$. The aromatic protons of the para-substituted aromatic rings were represented by symmetrical signals at $\delta = 6.73$ and 7.08. In the ¹³C NMR spectra (Figure 8(c), (d) and Figure S3(b)–(d)), aromatic carbons were associated with the peaks at 114.68 (C_3), 127.91 (C_4), 143.31 (C_5) and 153.21 (C_6). Furthermore, the methyl carbons C_1 and C_2 were observed at 31.05 and 41.68, respectively. The GC-MS, FT-IR and NMR results of the recovered BPA were exactly the same as the standard BPA, confirming that the obtained product was BPA^[24,43].

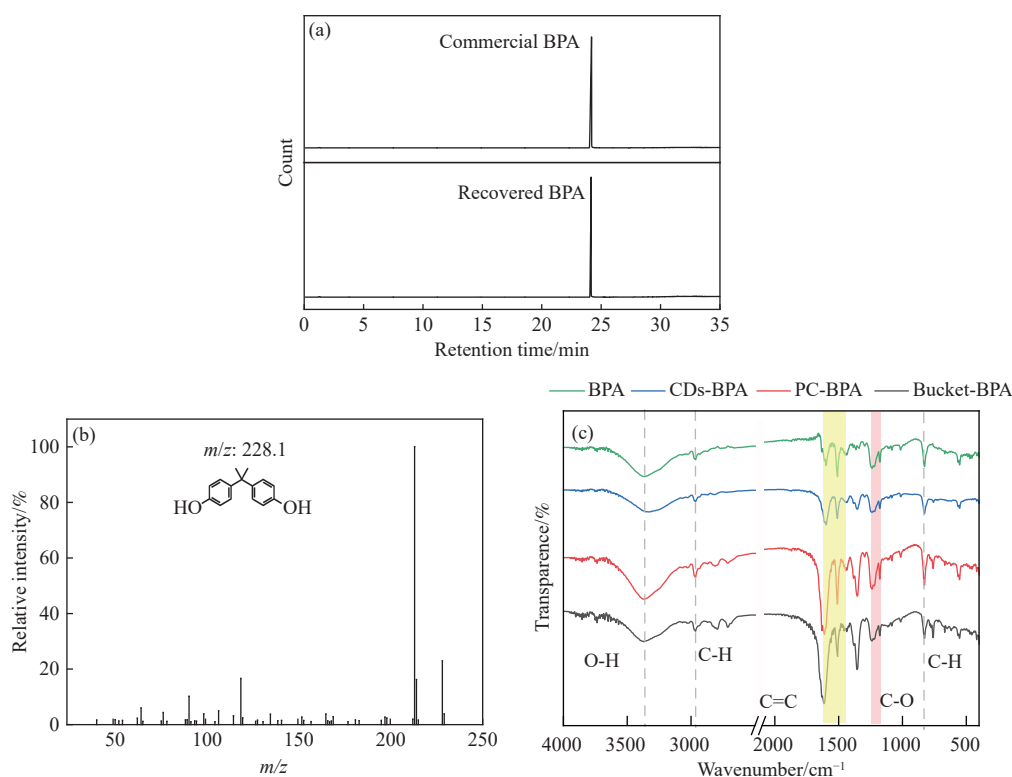


Fig. 7 (a) GC-MS chromatogram of commercial and recovered BPA; (b) Mass spectrum of the recovered BPA; (c) FT-IR spectra of the recovered BPA (BPA was obtained under the reaction conditions: Substrate (10 g); MeOH (70 mL); 160 °C; reaction time: 8 h for PC and optical disks, 16 h for water bucket)

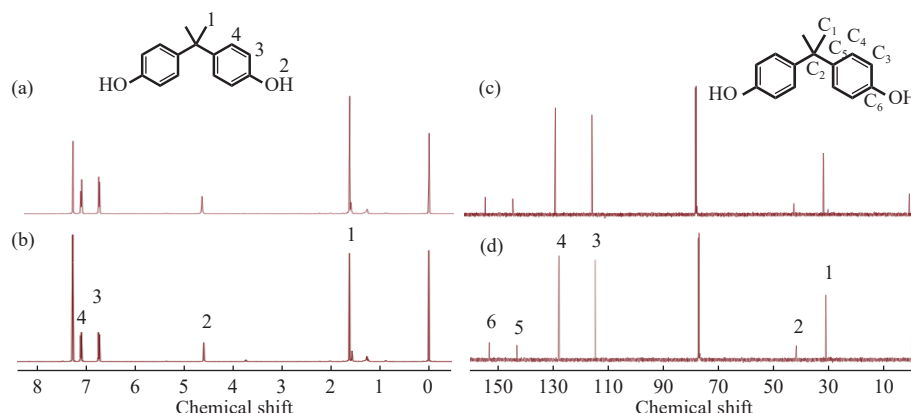


Fig. 8 ¹H NMR and ¹³C NMR spectra of the obtained product from optical disks (a) and (c), standard BPA (b) and (d)

BPA was obtained under the reaction conditions:

optical disks (10 g); MeOH (70 mL); 160 °C; reaction time: 8 h.

2.6 Analysis of PC depolymerization mechanism

The above results demonstrated that PC could be effectively depolymerized by methanol. To gain further insights towards the process of methanol depolymerization of PC, the evolution of the molecular weight of the soluble products was monitored and analyzed (Table 3, Figure S4(a)). The results showed that the number-average molar mass (M_n) decrease sharply in the initial stage, followed by a gradual decrease. During the initial stage of depolymerization, solid PC was swelled, as shown in SEM image (Figure 4). The swelling of PC enhanced the contact between methanol and PC, leading to the alcoholysis of PC into soluble macromolecules. These soluble macromolecules were further depolymerized into smaller products until the final product BPA was formed. The polymer dispersity index (PDI) initially increased and then decreased (Table 3, Figure S4(b)), indicating that the molecular weight distribution of the soluble products broadened initially and then narrowed as depolymerization proceeded. According to the literatures, PC initially undergoes random chain cleavage^[45]. Due to the randomness of fracture position, carbonate bonds at any position along the long PC chain could be broken, generating various chain segments. This resulted in a broad

molecular weight distribution and an increased PDI. As depolymerization continued, the high molecular weight components disappeared, yielding the low molecular weight fragments^[46]. In the later stage, the breakage of the polymer was dominated by chain-end depolymerization. When the hydroxyl group (OH–Ar–O–) at the chain end was adjacent to a carbonate bond^[47], nucleophilic attack by methanol was favored due to the proximity effect, triggering chain-end depolymerization and the gradual releasing of BPA.

Based on the SEM and GPC characterization of PC at different reaction times, along with the literature reports, a possible depolymerization mechanism was proposed (Figure 9). Under the reaction conditions, methanol molecules first penetrated into the PC polymer particles to swell the particle surfaces, then the methoxy group attacked the C–O bonds in the ester group of PC. Subsequently, the methoxy group connected with the C=O bond in the ester group, while the hydrogen atom from –OH of methanol connected with the C–O bond on the benzene ring of the PC, regenerating a phenolic hydroxyl group^[48–49]. As the reaction proceeded, the methoxy group combined with the C=O unit to form DMC, and the hydrogen atom connected with the other C–O bond on the benzene ring, yielding BPA.

Table 3 The average molecular weight at different stage of depolymerization

Reaction time/h	PC depolymerization degree/%	$M_n/(\text{g} \cdot \text{mol}^{-1})$	$M_w/(\text{g} \cdot \text{mol}^{-1})$	$\text{PDI}/(M_w \cdot M_n^{-1})$
0.5	1.2	39716	73606	1.8
1	7.6	23010	49426	2.1
2	18.3	14646	34936	2.4
4	37.5	5923	13406	2.3
6	75.6	3256	7039	2.2

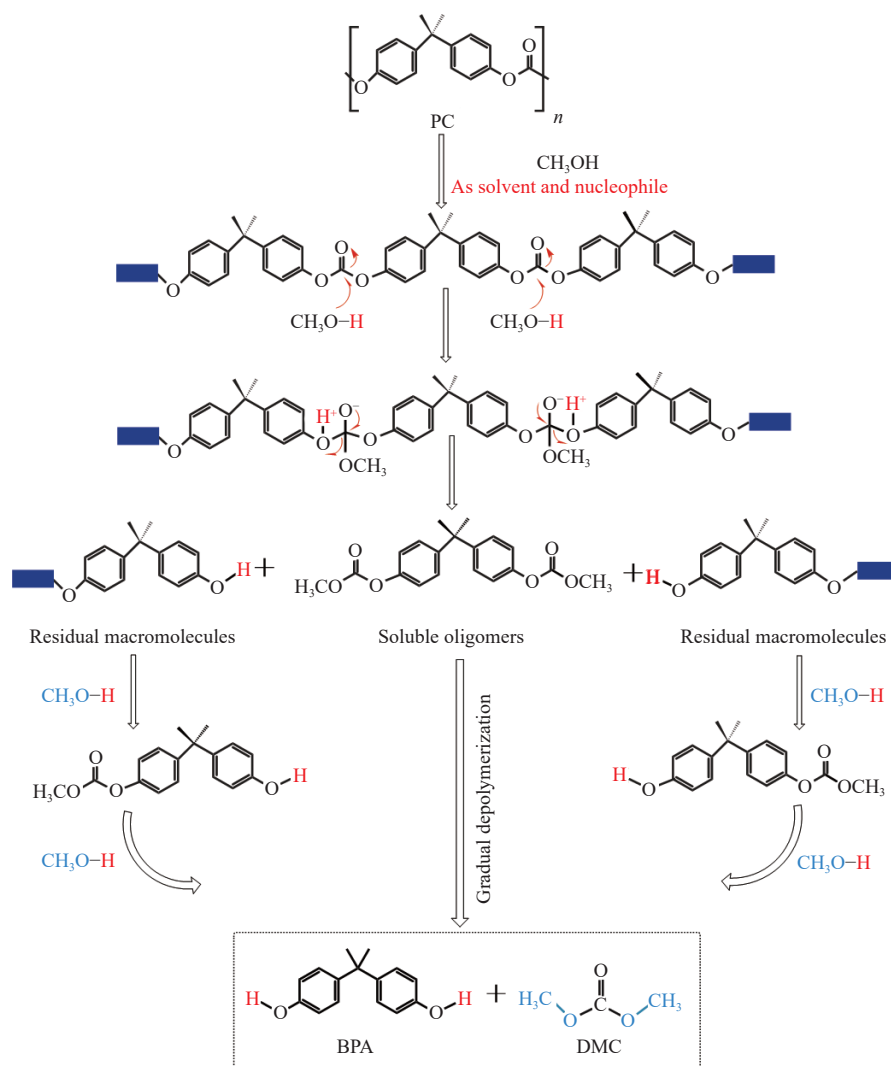


Fig. 9 Possible methanol alcoholysis mechanism of PC

3 Conclusion

In summary, an economical, practical and green route for the alcoholysis recycling of waste PC and polyester plastics has been developed. At 160 °C, the conversion of PC reached 100.0% with a BPA yield of 95.0%. It has been demonstrated that the route was suitable for various types of commercial PC. It was also effective for mixed plastics containing PC and other polyester plastics, showing excellent depolymerization performance. Furthermore, an efficient separation process for recovering BPA from the depolymerization solution has been developed, achieving high recovery ratio and high purity. The practical applicability of the route has been further confirmed. With prolonged reaction time, PC was swollen by methanol and depolymerized into soluble macromolecules with a broad molecular weight distribution. Then the macromolecules were gradually depolymerized into smaller molecules with a narrower molecular weight distribution, ultimately yielding the final product BPA. This work provides a facile, efficient, and green strategy for the valuable upgradation of PC waste under mild conditions.

Declaration of Competing Interest

The authors declare no conflict of interest.

Data availability

Data will be made available on request.

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废聚碳酸酯塑料在温和条件下甲醇解生成双酚 A

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摘 要: 聚碳酸酯(PC)是化学工业中广泛使用的聚合物材料。废弃 PC 在环境中的积累会释放出有毒物质双酚 A(BPA), 从而对环境和人类健康产生了负面影响。从 PC 废弃物中回收 BPA 是满足可持续资源利用需求和解决环境问题的先决条件。本研究采用甲醇作为溶剂, 在无催化剂和温和的条件下, 通过醇解作用来解聚 PC。研究表明, PC 可以在中等温度(120–160 °C)下解聚为其单体 BPA。在 160 °C 条件下, 无需添加催化剂或辅助溶剂, 可实现 PC 塑料的 100.0% 降解, BPA 的产率高达 95.0% 以上。在放大实验(10 g PC)中, 设计了简便的 BPA 分离流程, BPA 的回收率大于 85.0%。此外, 该方法还可以有效地解聚实际塑料混合物, 如 ABS 树脂、PC 和其他聚酯, 如聚乳酸、聚乙醇酸和聚对苯二甲酸乙二醇酯。结合 SEM 和 GPC 表征结果, 提出了 PC 可能的解聚机理。结果表明, 甲醇对不同聚酯塑料具有广泛的普适性。这项工作

为聚酯塑料的醇解回收提供了一种简便、绿色且高效的方法。

关键词: 聚碳酸酯; 甲醇解; 双酚 A; 无催化剂; 化学回收

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