Supporting Information

Quaternary Ammonium Hydroxide Catalyzed Methanolysis of Bisphenol-A Polycarbonate: Performance, Mechanism, and Scale-Up

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Content

Catalyst selection and characterization

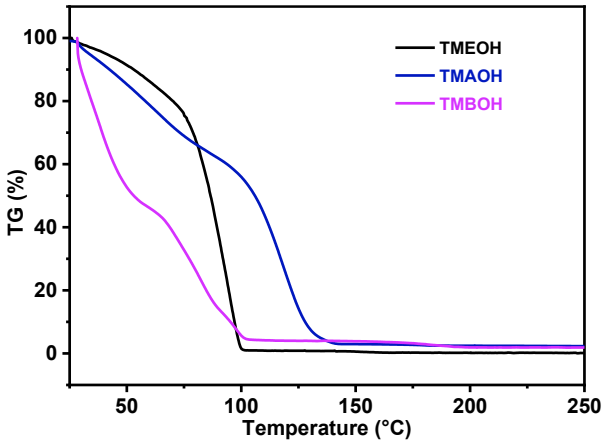


Figure S1. Thermal decomposition behavior of catalysts with varying compositions. All three catalysts exhibited complete decomposition at elevated temperatures.

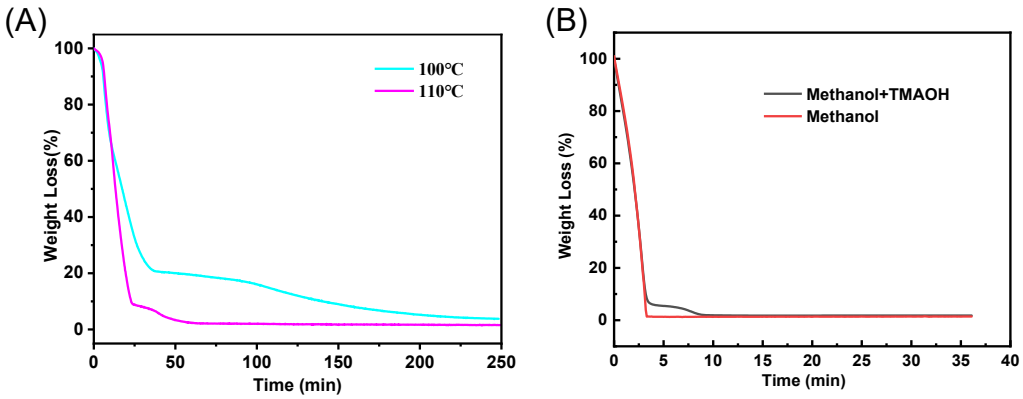


Figure S2. (A) Isothermal thermal decomposition curves of TMAOH at different temperatures**.** at 100 °C: After 120 min, the residual mass was 12.7% and after 240 min, the residual mass further decreased to 3.93%; whereas, the residual mass dropped significantly to only 1.87% at 110°C after 120 min. (B) Isothermal thermal decomposition curves of TMAOH in MeOH (the same concentration as the catalytic process) and MeOH. No detectable residual mass was observed.

Additionally, to further quantify the catalyst-derived residues in the depolymerization system, elemental analysis (EA) was performed on the liquid samples at 48 min and 120 min using an Elementar UNICUBE organic elemental analyzer. The measured nitrogen content was 0.09% and 0.00%, respectively. The self-eliminating mechanism of TMAOH primarily involves its decomposition to trimethylamine (boiling point 2.9 °C) and methanol. During sample handling, trimethylamine readily

volatilizes, resulting in minimal residual nitrogen in the reaction mixture. Consequently, catalyst residues are negligible and do not interfere with the purity of the final products.

Figure S3. Color comparison of BPA products (depolymerization liquid, crude product, and once-recrystallized product) obtained from TMAOH and NaOH catalyzed processes. BPA obtained from TMAOH-catalyzed depolymerization formed snow-white crystals after one recrystallization, whereas BPA from NaOH-catalyzed depolymerization remained visibly yellow. Even after recrystallization, the yellow coloration in the NaOH system was difficult to remove, which would negatively affect the color of the final polycarbonate product. BPA obtained from these colored depolymerization systems generally requires recrystallization multiple times to meet industrial color specifications, resulting in increased purification steps, higher energy consumption, and greater production cost, which are undesirable in industrial practice.

Depolymerization efficiency

The PC degradation rate was used to characterize the extent of the depolymerization reaction:

$$\text{PC degradation rate (\%)} = \frac{\text{PC addition-PC surplus}}{\text{PC addition}} \times 100\% \quad (1)$$

The recovery of BPA is the BPA obtained from the separation, denoted as m_1, and the theoretical mass of BPA is m_0.

$$\text{BPA yield (\%)} = \frac{m_1}{m_0} \times 100\% \quad (2)$$

$$m_0 = M_{BPA} \times n_{BPA_{theory}} \quad (3)$$

According to the PC methanol depolymerization reaction equation: $n_{BPA_{theory}}=n_{PC_{theory}}$, $n_{PC_{theory}}=\frac{m_{PC}}{M_{PC}}$, M_{PC}=254 g·mol^{-1}, M_{BPA}=228 g·mol^{-1};

$$m_0=M_{BPA}\times\frac{m_{PC}}{M_{PC}}=228\times\frac{m_{PC}}{254}$$

$$\text{BPA yield (\%)}=\frac{m_1}{m_0}\times100\%=\frac{254_{m1}}{228m_{PC}}\times100\% \quad (4)$$

Screening reaction conditions

Table S1. Conversion rate of PC and BPA yield under different reaction conditions with TMAOH catalysis.

Entry	Reaction temperature/℃	$C_{catalyst}$ /mol%	n_{MeOH} : n_{PC}	Reaction time/h	PC degradation rate/%	BPA crude yield/%
1	80	2.0	4:1	2	55	53.5
2	90	2.0	4:1	2	99.6	98.5
3	100	2.0	4:1	2	100	99.2
4	100	2.0	4:1	0.25	27.2	23.4
5	100	2.0	4:1	0.41	43.8	49.02
6	100	2.0	4:1	0.58	81.1	75.9
7	100	2.0	4:1	0.75	91.9	89.6
8	100	2.0	4:1	3	100	98.5
9	100	2.0	4:1	4	100	99.8
10	110	2.0	4:1	2	100	99.4
11	120	2.0	4:1	2	100	99.8
12	100	0.5	4:1	2	54.2	44.8
13	100	1.0	4:1	2	100	94.9
14	100	4.0	4:1	2	100	99.4
15	100	5.0	4:1	2	100	98.5
16	100	2.0	2:1	2	100	99.2
17	100	2.0	3:1	2	100	99.8
18	100	2.0	6:1	2	100	99.4
19	100	2.0	8:1	2	100	99.6

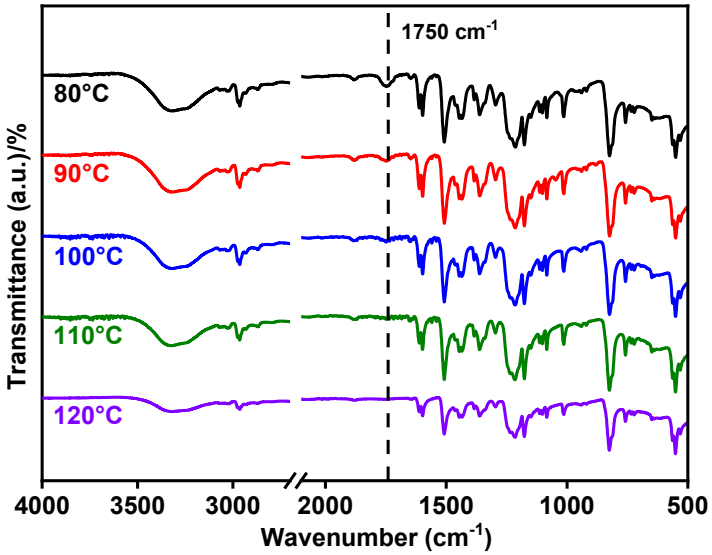


Figure S4. FT-IR spectra of depolymerization-derived BPA at varying temperatures. The carbon-related spectral signals completely disappear after 2 h of reaction with 2 mol% catalyst loading, requiring a reaction temperature ≥110 °C

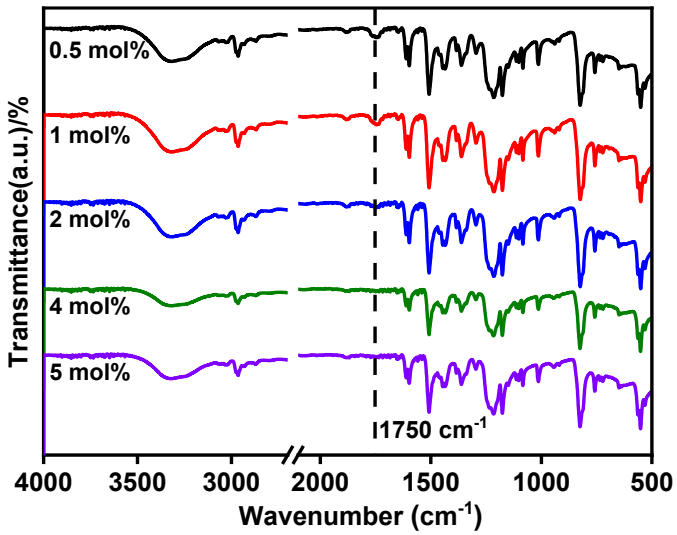


Figure S5. FT-IR spectra of depolymerization-derived BPA at different catalyst concentrations. The complete disappearance of the carbon-based signal peak within 2 h at 100°C requires a catalyst loading of ≥4 mol%.

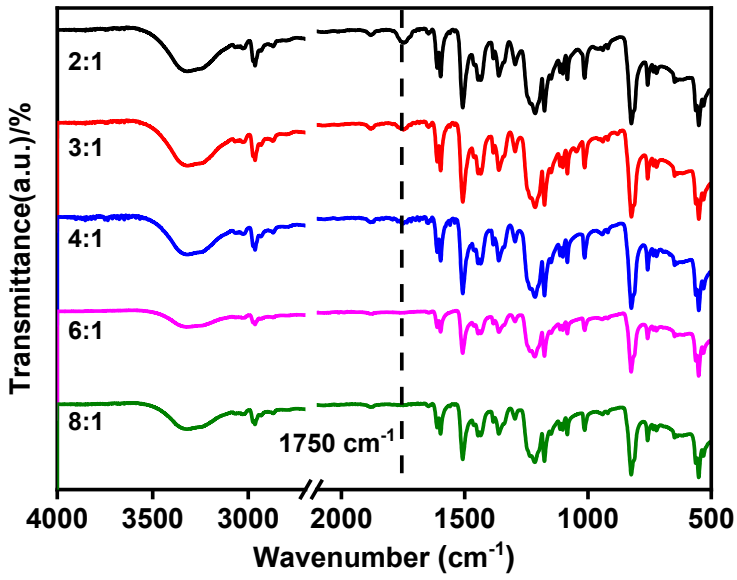


Figure S6. FT-IR spectra of depolymerization-derived BPA at different molar ratios of methanol to PC. 100°C for 2 h, complete elimination of oligomers required a minimum methanol-to-PC molar ratio of $n_{MeOH} : n_{PC} = 6 : 1$.

Based on these reactions, the optimal reaction conditions were determined to be: reaction temperature 110 °C, reaction duration 2 h, n_{MeOH}:n_{PC} = 4:1, with 2 mol% catalyst loading.

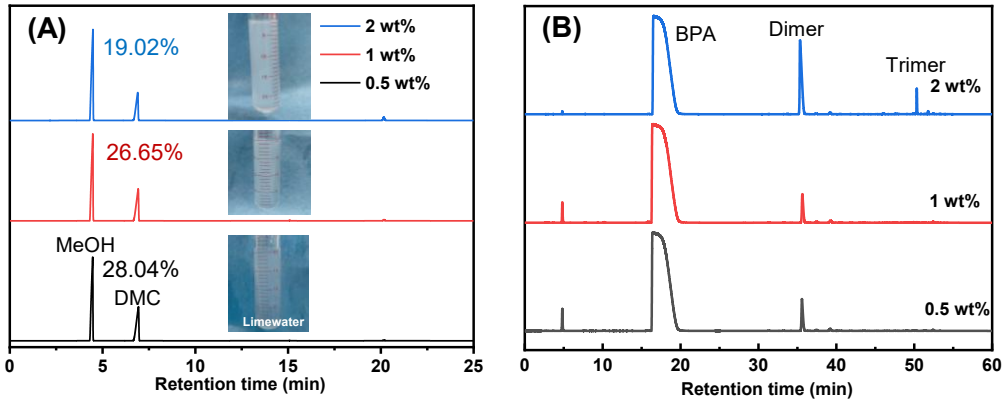


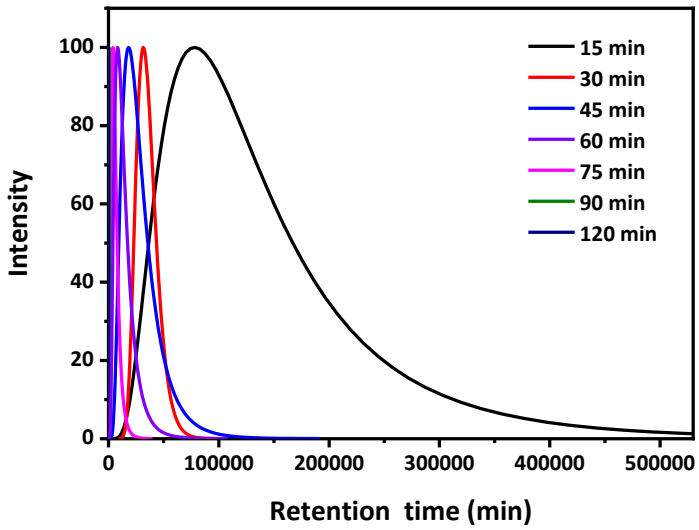
Fig. S7. Influence of water content on DMC selectivity, CO_2 evolution, and oligomer residue during PC methanolysis. With increasing water content, DMC yield decreased while CO_2 evolution increased. As detail, DMC yield decreased systematically with increasing water content, measured as 28.04%, 26.65%, and 19.02% for 0.5, 1.0, and 2.0 wt% water, respectively. And the CO_2 evolution also increased, as indicated qualitatively by the turbidity of limewater. These results can be attributed to the

additional water favors Path 1 (Figure 4d) and promotes hydrolysis of DMC, thereby reducing selectivity for the target product. Prolonged depolymerization time and increased oligomer residues. Although the disappearance time of PC particles at 0.5% and 1.0% water content remained comparable to that observed in the absence of added water (48 min), increasing the water content to 2.0% prolonged the depolymerization time to 51 min. HPLC analysis further revealed that the relative amounts of dimeric and trimeric species increased with increasing water content, indicating that extended reaction times are required to achieve complete depolymerization. This behavior is likely attributable to the suppression of contributions from Path 2, which is presumed to be a more efficient depolymerization pathway. The color of the final depolymerization mixtures remained similar across all conditions. Notably, the water content in 25 wt% TMAOH in methanol was measured to be 7.11% by Karl Fischer titration. The moisture content in MeOH was reported as ≤ 150 ppm, and its actual water residue was measured to be 0.013 wt% by Karl Fischer titration. The total water in depolymerization system is about 0.5 wt% of MeOH.

Study of the degradation process catalyzed by TMAOH

Table S2. Molecular weights and distributions of residual PC during depolymerization

Depolymerization time/min	M_w/Da	M_n/Da	PDI
0	26100	16800	1.55
15	25800	16500	1.56
25	25100	15300	1.64
35	23700	13900	1.71
45	23400	11200	2.09



Time/min	15	30	45	60	75	90	120
Particle size	7.8 μm	32 μm	18 μm	8.4 μm	4.1 μm	280 nm	~1 nm

Figure S8. Particle size distributions at different reaction times obtained by dynamic light scattering. The sample collected at 60 min appeared free of visible polymer particles even though the size was ~8 μm, might due to the combined effects of refractive index matching and the medium viscosity of the reaction system. This also indicates that visual inspection of depolymerization may overestimate the degree of degradation, although it remains a commonly used qualitative method, because the residual polymer is present at very low levels (even NMR may fail to observe it) and would require more sensitive techniques (such as HPLC, IR, and DLS for this system) to be reliably detected if necessary.

Table S3. The ratios of BPA, dimer, and trimers at different reaction time determined by HPLC.

Depolymerization time/min	Phenol/%	Oligomer/%	Multimer/%	BPA/%
15	10.79	1.57	0.39	87.25
25	8.77	2.74	0.86	87.62
35	2.80	2.18	0.44	94.58
45	0.64	2.86	0.76	95.75
48	0.60	1.82	0.21	97.37
120	0.57	0.00	0.00	99.43
240	0.56	0.00	0.00	99.44

Depolymerization mechanism

Table S4. Kinetics of catalytic depolymerization reaction of PC by TMAOH at different time points.

Temperature T/(°C)	Kinetic equation	Correlation coefficient R	Rate constant k/(h^{-1})	1000/T(K^{-1})	lnk
80	y=0.5629x-0.9402	0.9708	0.5629	2.8329	-0.5747
90	y=0.9613x-0.1523	0.9968	0.9613	2.7548	-0.0394
100	y=4.2600x-0.8582	0.9851	3.0148	2.6810	1.4493
110	y=7.7870x-1.6300	0.9808	7.7870	2.6110	2.0525

Based on previous literature reports, we assume that the kinetic model for the methanolysis of PC follows first-order kinetics, with the kinetic equation as shown in Equation (5):[1]

$$-\frac{dC_{PC}}{dt} = kC_{PC} \tag{5}$$

In the equation, k represents the reaction rate constant, and C_{PC} denotes the concentration of PC at time t.

$$C_{PC} = C_0(1-x) \tag{6}$$

In the formula, "degradation rate of PC at time t" is represented, and C_0 denotes the initial concentration of PC. Consequently, the equation can be transformed as follows:

$$\frac{dx}{dt} = k(1-x) \tag{7}$$

The integration of the equation concerning time yields:

$$\ln\left(\frac{1}{1-x}\right) = kt \tag{8}$$

To calculate the activation energy E_a using the Arrhenius equation, you can follow these steps:

$$k = Ae^{-\frac{E_a}{RT}} \tag{9}$$

$$\ln k = \ln A - \frac{E_a}{RT} \tag{10}$$

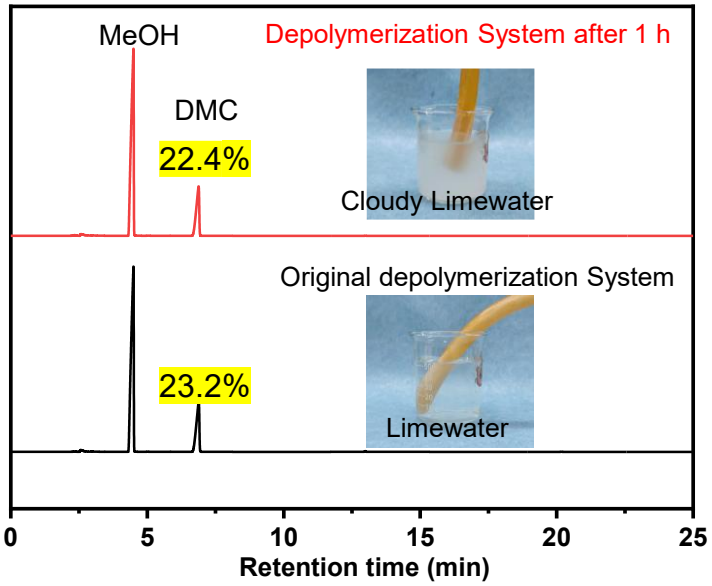


Figure S9. HPLC analysis and limewater test for DMC decomposition under catalytic conditions. DMC was heated in the presence of TMAOH under the same reaction conditions (2 mol% TMAOH, 110 °C, and the same volume of MeOH). After 1 h of reaction, the DMC content decreased from 23.2% to 22.4%, and bubbling the reaction gases through clear limewater led to turbidity, confirming that the decomposition of DMC under the catalytic conditions can indeed serve as a contributing pathway for CO_2 extrusion.

Depolymerization of Waste PC Materials and Mixed Plastics

Table S5. The yields and purity of BPA obtained from methanolysis of various PC products.

	Eyeglass frame	Lampshade	Water bottle	Molding specimen	Car headlight	Cup
m_{PC}, g	5.0021	5.0019	5.0062	5.0017	5.0049	5.0028
m_{BPA}, g	4.4191	4.3653	4.4617	4.4110	4.4703	4.4286
BPA productivity, %	98.42	97.23	99.28	98.25	99.50	98.62

Scale-Up Depolymerization and Repolymerization

Pilot-Scale Experimental Setup Design Concept. The pilot-scale PC methanolysis process adopts a modular coupled design, divided into depolymerization, methanol separation, and product separation units for efficient integration with existing industrial facilities. The depolymerization unit employs a batch reactor (110°C, 2 h), with products temporarily stored in a buffer tank before achieving continuous separation via a four-reactor linkage strategy. A primary evaporation tower (16-22 kPa) separates the methanol-DMC azeotrope (methanol: DMC ≈ 70:30 wt%), which is directly transferred to the existing DMC unit for co-distillation. Bottoms from the primary tower are further processed in a secondary evaporation tower (at -0.1 MPa gauge, 130-150°C) to remove residual DMC, with phenol (30-36 wt%) injected to suppress BPA crystallization, forming a pumpable BPA-phenol adduct (BPA : phenol ≈ 65 : 35 wt%) for transfer to the existing BPA facility, where standard recrystallization is applied.

This design enables seamless integration of pilot-scale products into industrial operations without modification through precise matching of material compositions (both the azeotrope and BPA adduct meet industrial feedstock specifications) and coupled process parameters. The dual functional use of phenol (as co-solvent and crystallization inhibitor) reduces auxiliary consumption. The system validates the industrial feasibility of PC chemical recycling and provides critical engineering data for scaling up to a 10,000-ton plant.

Table S6. Pilot-scale raw material specifications.

Material Type	Parameter	Unit	Specification
PC	Mw	g/mol	20000-33000
	PDI	-	1.7-2.5
	value-b	-	3.2
Methanol	Purity	wt%	≥ 99.95
	Moisture Content	ppm	≤ 150[a]
Phenol	Purity	wt%	≥ 99.9
	Chroma	Hazen	< 5
	Organic impurities	wt ppm	≤ 80
	Fe^{3+}	wt ppm	≤ 0.2
	Moisture Content	wt ppm	≤ 300

[a] The actual water residue was measured to be 0.013 wt% by Karl Fischer titration.

Figure S10. Pilot-scale depolymerization setup.

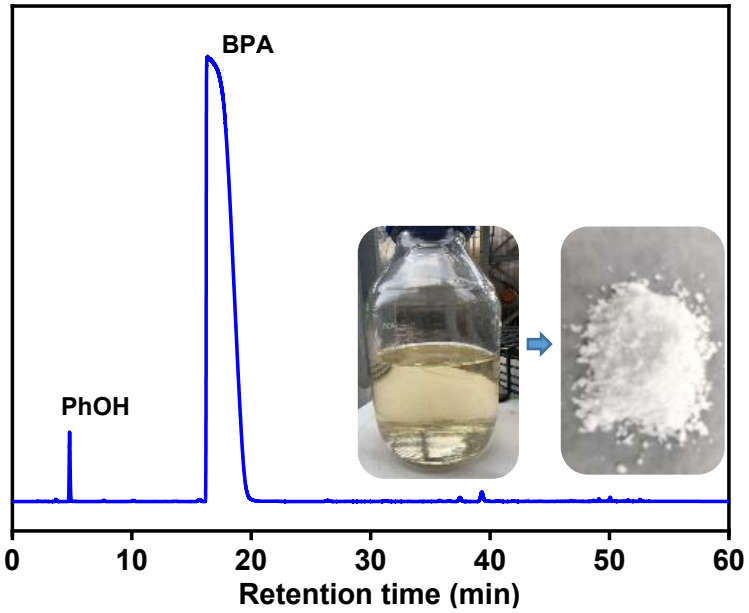


Figure S11. HPLC chromatogram of dried crude BPA from rotary-evaporated depolymerization liquor of pilot-scale unit. Excluding PhOH, total impurities of BPA is 1224 $mg \cdot kg^{-1}$.

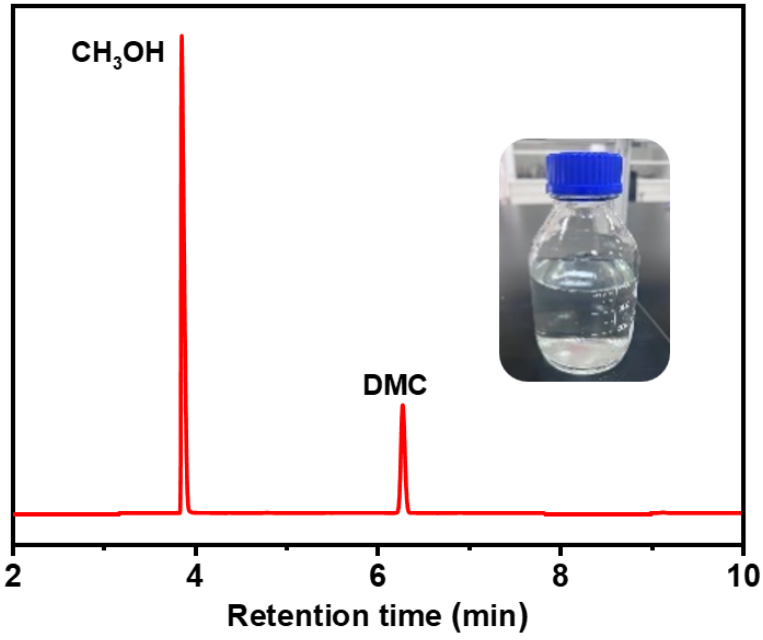


Figure S12. GC chromatogram of the distillate from rotary evaporation of depolymerization liquor in pilot-scale unit. Content of DMC 27.45%.

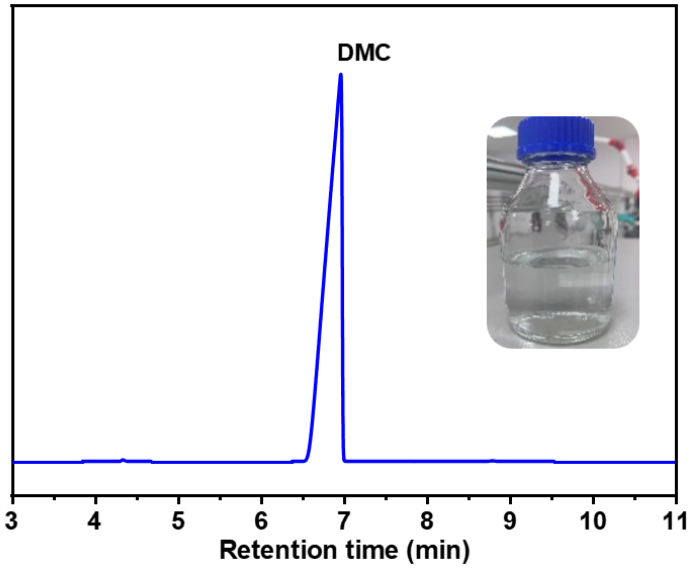


Figure S13. GC chromatogram of DMC sample from sampling port of pilot-scale depolymerization unit. Purity of DMC is 99.83%.

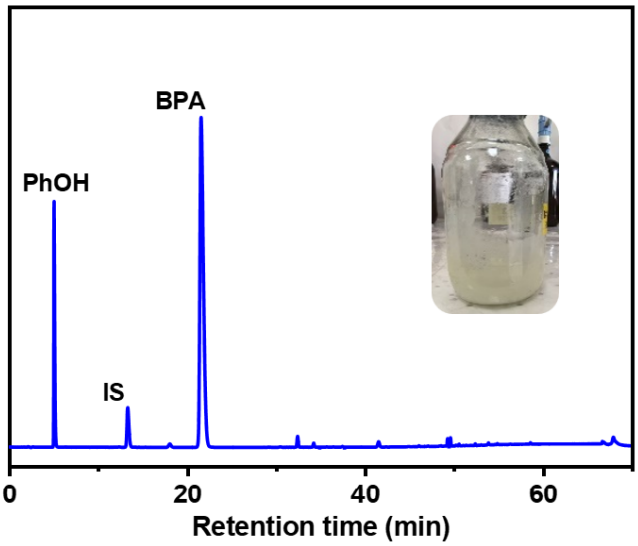


Figure S14. HPLC chromatogram of phenol-BPA adduct. Total impurity of BPA is 1532 $mg \cdot kg^{-1}$.

Figure S15. Repolymerization of recycled BPA to produce PC.

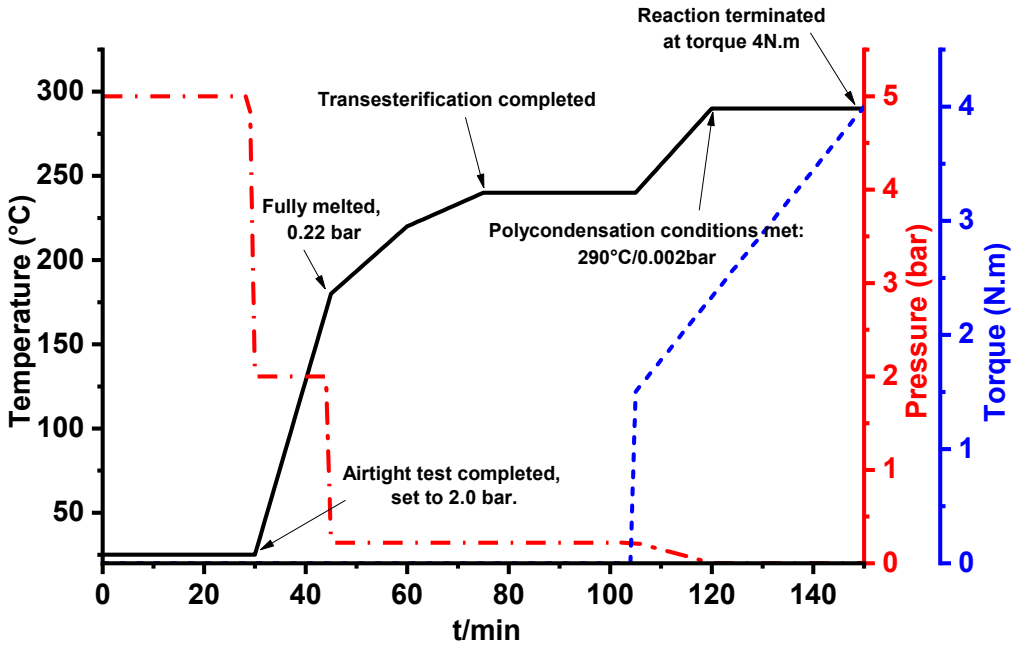


Figure S16. Time-dependent temperature and pressure profiles in the repolymerization of pilot-scale crude BPA.

Table S7. Molecular weight data of PC synthesized from different BPA sources versus commercial PC.

Sample	Mw	Mn	PDI
PC from crude BPA	26.8	14.6	1.84
Commercial PC	26.1	14.8	1.76
PC from crystalized BPA	26.9	15.9	1.69

Supplementary Note: Life-cycle assessment (LCA)

The system boundary of LCA was set as "cradle to gate" (the collection and transportation of waste plastic, the whole processes of depolymerization of waste plastic, the production of chemical raw materials) because the subsequent use and disposal of various products vary widely. The data on the collection and transportation of waste plastics refer to the database of existing process data, i.e. PC production, mechanical recycling of PC, etc. For analysis, our material balance and energy balance were derived from process data of PC production in the company. Other process data were derived from the actual experimental results of commodity polymers methanolysis. The LCA analysis followed the ISO standard series 14040 and 14067. Data used to build the life-cycle inventory were collected from scale-up experimental and the commercial database Ecoinvent 3.9.1. The mass allocation method was used to distribute the carbon emissions among the chemicals produced within the system. The average carbon footprint factor of electricity used in LCA is 0.6205 kg CO_2/kWh. This data is sourced from the *Announcement on Electricity Carbon Footprint Factor Data 2023*.

Table S8. Material and energy input-output of chemical recycling of waste PC into BPA and DMC.

Item	Quantity	Unit
Input: PC→BPA+DMC		
Waste plastic	1	t
Tetramethylammonium hydroxide	0.009	t
methanol	0.166	t
electricity, low voltage	2571.5	kWh
Output:		
dimethyl carbonate	0.346	t
Carbon dioxide, fossil	0.156	t
wastewater, average	0.000435	M^3
Bisphenol A	0.890	t

Table S9. Life-cycle environmental impact results for chemical recycle of 1-ton waste PC, which produces 0.89-ton BPA and 0.346-ton DMC.

Impact category	Recycle path	Unit
Climate change-global warming potential (GWP100)	2.0035	t
Human toxicity: carcinogenic - comparative toxic unit for human (CTUh)	0.0565	t
particulate matter formation - impact on human health	0.125	t

Table S10. Material and energy input-output of DMC using fossil fuel.

Item	Quantity	Unit
Input: PO+CO_2→DMC		
methanol	2.711	t
electricity, low voltage	1.301×10^3	kWh
propylene oxide, liquid	0.645	t
carbon dioxide, liquid	0.480	t
Output:		
propylene glycol, liquid	0.844	t
Dimethyl carbonate	1	t

Table S11. Life-cycle environmental impact results to 1-ton DMC using fossil fuel.

Impact category	Path1	Unit
Climate change-global warming potential (GWP100)	4.9841	t
Human toxicity: carcinogenic - comparative toxic unit for human (CTUh)	0.1876	t
particulate matter formation - impact on human health	0.2301	t

Table S12. Material and energy input-output of BPA using fossil fuel.

Item	Quantity	Unit
Input: phenol＋Propanone→BPA		
phenol	0.820	t
acetone, liquid	0.253	t
electricity, low voltage	1.592×10^3	kWh
Output:		
water, ultrapure	0.078	t
Bisphenol A	1	t

Table S13. Life-cycle environmental impact results to 1-ton BPA using fossil fuel.

Impact category	Path1	Unit
Climate change-global warming potential (GWP100)	4.1573	t
Human toxicity: carcinogenic - comparative toxic unit for human (CTUh)	0.0703	t
particulate matter formation - impact on human health	0.2140	t

Note: For chemical recycle of 1-ton waste PC, which produces 0.89-ton BPA and 0.346-ton DMC with a process GWP of 2004 kg $CO_{2\text{-eq}}\cdot t^{-1}$. In fossil fuel route, the production of the same quantity of BPA and DMC, require 5024 kg $CO_{2\text{-eq}}\cdot t^{-1}$ (GWP=4984×0.346+4157×0.890 ($CO_{2\text{-eq}}\cdot t^{-1}$)).

Table S14. Assumptions and parameters for the economic evaluation

Input	Unit cost [$/ton]	Quantity [ton]	Total cost [$]
Waste plastic	479	1.0	479.0
methanol	315	0.1775	55.9
TMAOH	6000	0.009	54.0
Output:			
BPA	1370	0.89	1219.3
DMC	821	0.3415	280.4

Economic benefit =1370×0.89+821×0.3415-479×1-315×0.1775-6000×0.009=910.8($)

Note: The unit price of each chemical was based on the market price at the time of calculation. Material quantities were evaluated based on actual yields during the experiment.

1. Guo, J.; Liu, M.; Gu, Y.; Wang, Y.; Gao, J.; Liu, F., Efficient Alcoholysis of Polycarbonate Catalyzed by Recyclable Lewis Acidic Ionic Liquids. *Ind. Eng. Chem. Res.* **2018,** *57*, 10915-10921.