

## Supplemental Information

### **Selectively self-recyclable, highly transparent and fire-safe polycarbonate plastic enabled by thermally responsive phosphonium-phosphate**

Pan Deng, Lin Chen\*, Yue Li, Bo-Wen Liu, Xiu-Li Wang\* and Yu-Zhong Wang

Collaborative Innovation Center for Eco-Friendly and Fire-Safety Polymeric Materials (MoE), National Engineering Laboratory of Eco-Friendly Polymeric Materials (Sichuan), State Key Laboratory of Polymer Materials Engineering, College of Chemistry, Sichuan University, Chengdu 610064, China

E-mail: [linchen410@scu.edu.cn](mailto:linchen410@scu.edu.cn), [xiuliwang1@163.com](mailto:xiuliwang1@163.com)

## **Materials.**

Polycarbonate (PC, 2600) was purchased from Bayer (Germany). Polyethylene terephthalate (PET) and high-density polyethylene (HDPE) were collected from commercially available beverage bottles. Polyvinyl chloride (PVC) sheets were purchased from Alibaba (China) Co., Ltd. Polypropylene (PP) flakes were taken from a centrifuge tube in the laboratory. Bisphenol A (BPA), antioxidant 1010 (A1010), triphenylphosphine (TPP) and diphenyl hydrogen phosphate (DPPA) were purchased from Shanghai Adamas Reagent Co., Ltd. Trimethyl orthoformate, ethylene carbonate (EC), Diphenyl carbonate (DPC) and triphenylphosphine oxide (TPPO) were supplied by Aladdin Reagent (Shanghai) Co., Ltd. Toluene, ethylene glycol (EG), dichloromethane (DCM) and ethyl acetate (EA) were obtained from Chengdu Kelong Chemical Reagent Co., Ltd. 1,3,5-trimethoxybenzene was purchased from Beijing Innochem Reagent Co., Ltd. Anti-dripping agent polytetrafluoroethylene (PTFE) was obtained from Guangdong Dingxin Polymerization Technology Co., Ltd. All the reagents and solvents were used directly without further purified.

## **Synthesis of aromatic methyltriphenylphosphonium diphenylphosphate (DP).**

DP was synthesized by TPP and DPPA with trimethyl orthoformate as the alkyl donor, as shown in Fig. 2A. 10.49 g TPP (40 mmol), 26.52 g trimethyl orthoformate (250 mmol) and 10.01 g DPPA (40 mmol) were reacted at 115 °C for 12 h. After the reaction mixture was cooled, the excess trimethyl orthoformate was removed by rotary evaporation at 90 °C. Then the solid mixture was completely dissolved with 80 mL dichloromethane, and 250 mL ethyl acetate was added subsequently. After standing, a large amount of white precipitate is gradually generated in the solution. The precipitate was filtered and washed with ethyl acetate. Subsequently, the product was dried in a vacuum oven at 70 °C for 12 h. Finally, the white solid powder DP was obtained with a yield of 66%.

## **Density functional theory computational details.**

Geometric structure optimization was performed individually on the TPP, DPPA, and DP molecules using the Gaussian 09 software. Given the relatively large molecular weights of these structures, a standard computational level was chosen to ensure better convergence of the calculations. The B3LYP functional and the 6-31G(d) basis set were used for the calculations. Additionally, a calculation temperature of 513.15 K was set to match the experimental processing temperature of PC. Ultimately, the minimum energy structures of the three molecules were obtained, allowing for a comparison of their energies.

## **Preparation of PC/DP.**

PC/DP was prepared by melt blending method. Firstly, in the vacuum oven, PC, DP and A1010 were dried for 12 h at 80 °C. Then they were blended through a torque rheometer (RM-200C, provided by Harbin Hapu Electrical Technology Co., LTD.) at

240 °C under 100 rpm. The total melt blending time was 6 minutes. The ratios of PC, DP, and A1010 were listed in Table S1.

### **Preparation of PC/(TPPO+DPPA).**

Firstly, 6.96 g triphenylphosphine oxide (TPPO, 25 mmol) and 6.25 g diphenylphosphoric acid (DPPA, 25 mmol) were dissolved in 100 mL dichloromethane. Then stir the mixture at 25 °C for 1 hour. After that, the solvent dichloromethane was removed by vacuum distillation at 25 °C. The residual was dried in a vacuum oven at 80 °C for 12 hours, which is named TPPO+DPPA. PC/(TPPO+DPPA) was prepared by melt blending method through torque rheometer at 240 °C under 100 rpm. The total melt blending time was 6 minutes. The ratios of PC, TPPO+DPPA, and A1010 were listed in Table S1.

### **Chemical recycling experiment.**

1.0 g PC/DP2.0 pieces and 5.0 g EG were mixed in a 25 mL single-neck flask. Then the mixture was immersed in an oil bath and stirred at 180 °C for different reaction time. Subsequently, after the reaction was stopped and cooled to room temperature, excess deionized water was added. A large amount of white precipitate precipitated, and then it was filtered to obtain bisphenol A (BPA) recycled product. The remaining solution was rotary evaporated at 80°C to remove water. Then an appropriate amount of toluene was added, and the solution separated into two layers. The separated upper layer was distilled to remove toluene to obtain ethylene carbonate (EC) product. The separated lower layer was distilled to remove ethylene glycol to obtain the catalyst DP.

### **Repolymerization of chemical recycling product.**

Recycled bisphenol A (BPA, 22.8 g, 0.1 mol), diphenyl carbonate (DPC, 21.4 g, 0.1 mol) and NaOH (catalyst, 600 ppm) were used as raw materials for repolymerization synthesis of virgin PC. Firstly, the mixtures were reacted at 170 °C for 2 h under N<sub>2</sub> atmosphere to carry out the transesterification reaction. Then, the reaction was performed at 220 °C for 2 h, and the vacuum was kept below 100 Pa. Finally, the polycondensation temperature was kept at 270 °C for 2 h.

### **Characterization.**

The nuclear magnetic resonance (NMR) was obtained by a Bruker AV II NMR spectrometer (400 MHz) at 298 K. Fourier transform infrared spectroscopy (FT-IR) was tested by a Nicolet 6700 infrared spectrophotometer, and all samples were prepared in KBr powder. High resolution mass spectrum (HRMS) was obtained by a mass spectrometry (AB X500R, Singapore).

Thermostability of samples were measured on a Thermal Analyzer (TGA 5500, TA, America). Samples were heated under N<sub>2</sub> atmosphere and a 10 °C/min heating rate, the temperature range is 40~700 °C. In another case, a heating process at 240 °C for 45 min

was conducted under N<sub>2</sub> atmosphere. The specimen mass is 3~5 mg.

The melt point of samples was tested on a TA Q200 DSC instrument in a 50 mL/min N<sub>2</sub> flow. The weight of sample is approximately 5 mg. The heating temperature range is 40~180 °C, and the heating rate is 10 °C/min.

PC and PC/DP films used for the ultraviolet and visible light transmittance test were prepared by a flat vulcanizer (Qingdao Yadong Rubber Machinery Co., Ltd.) at 240 °C and 10 MPa. The thickness of the film was 0.05 mm. The transmittance was characterized by the Cary50 ultraviolet and visible spectrophotometer. The wavelength scanning range is 800-200 nm.

The specimens used for observing quenched section were immersed in liquid nitrogen for 12 hours, then taken out and rapidly fractured. After drying in a vacuum oven (80 °C for 10 h), the surface of specimens was coated with a thin layer of gold. The morphology and phosphorus contents of samples were analyzed using a scanning electron microscope (Phenom ProX, Netherlands) which was coupled with an energy-dispersive x-ray spectrometer (EDX) at an acceleration voltage of 10 kV.

The UL-94 vertical combustion test was conducted on a KB-RS instrument (Kebao Test Equipment Co., Ltd., Guangdong, China) according to ASTM D3801 standard (sample size: 130 × 13 × 3.2 mm<sup>3</sup>). The limiting oxygen index (LOI) test was performed on a JF-6 instrument (Tianhui Testing Machinery Co., Ltd., Jiangsu, China) according to ASTM D2863-97 (sample size: 130 × 6.5 × 3.2 mm<sup>3</sup>). The specimens used for LOI and UL-94 tests were prepared using a micro injection molding machine (Haake MiniJet Pro, Thermo Scientific, Germany). The chamber temperature was maintained at 240 °C, while the mold temperature was set at 25 °C. The injection pressure was established at 750 bar, with an injection duration of 10 s. The holding pressure was maintained at 700 bar, accompanied by a holding duration of 5 s.

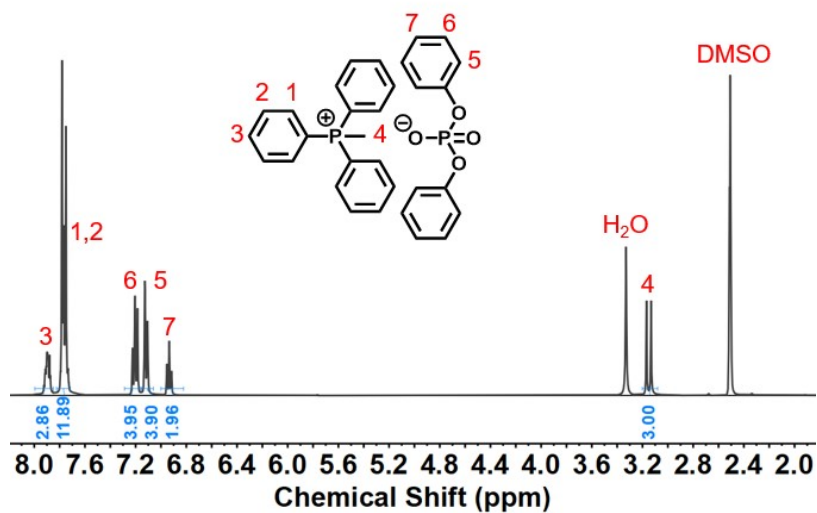
The rheological behaviors of PC and PC/DP was investigated by a Discovery Hybrid Rheometer (DHR-2, TA) at 240 °C and a fixed 1% strain. The sample size was 25 mm in diameter and 1 mm in thickness, which was prepared by flat vulcanizer.

Pyrolysis-gas chromatography/mass spectrometry (Py-GC-MS) was conducted by a CDS 5200 pyrolyzer, which is equipped with a Perkin-Elmer Clarus680-SQ8 gas chromatography-mass spectrometer. The samples (0.6 mg) were mixed with helium or air as the carrier gas. All samples were heated to a certain temperature for 15 s at a 20 °C/ms heating rate. The pyrolysis temperatures for DP, PC and PC/DP2.0 are 500 °C, 550 °C and 550 °C, respectively. The results were analyzed according to the NIST library. Gas chromatograph-mass coupling test (GC-MS) was evaluated in a GCMS-QP2010 Plus spectrometer. The injection temperature was 290 °C, the purge flow rate was 5.0 mL min<sup>-1</sup>, the shunt ratio was 10. The outflow time range for MS detection was 2-40 min. The m/z detection range was 33-500.

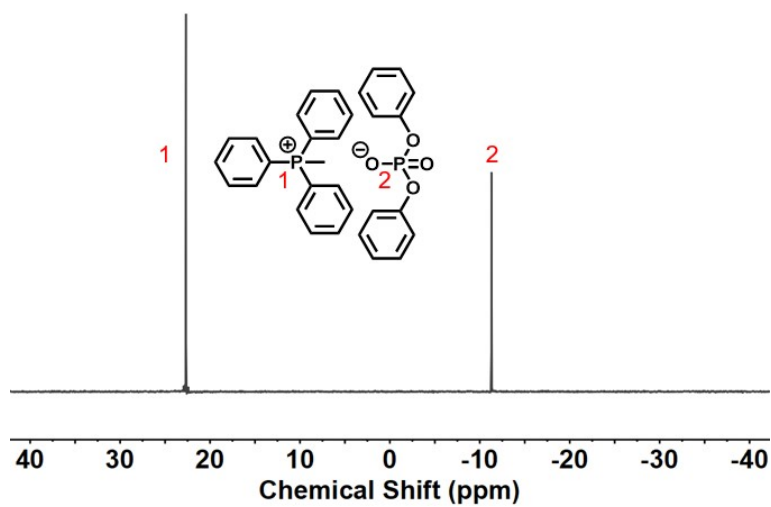
According to ISO 5660, cone calorimetry test (sample size: 100 × 100 × 3.2 mm<sup>3</sup>)

was conducted by FTT cone calorimeter device, the heat flux was 50 kW/m<sup>2</sup>. The specimens used for cone calorimeter test were prepared by a flat vulcanizer (Qingdao Yadong Rubber Machinery Co., Ltd.). The molding temperature was set at 240 °C. The plasticizing duration was 8 minutes, followed by a hot-pressing period of 3 minutes at 10 MPa. Finally, a cold-pressing procedure was conducted for 2 minutes at 10 MPa.

The UV-Vis absorption spectrum of BPA in methanol solution were characterized by the Cary50 ultraviolet and visible spectrophotometer. The wavelength scanning range is 800-200 nm. The molecular weights were measured on a gel permeation chromatograph (Agilent 1260). The solvent was CHCl<sub>3</sub> (concentration: 4 mg mL<sup>-1</sup>), the injection volume was 100 μL, the flow rate was 1.0 mL/min, the test temperature was 35 °C and polystyrene (PS) was used as standard sample.



**Fig. S1.**  $^1\text{H}$  NMR spectrum of DP (400 MHz,  $\text{DMSO-d}_6$ , 298 K).



**Fig. S2.**  $^{31}\text{P}$  NMR spectrum of DP (400 MHz,  $\text{DMSO-d}_6$ , 298 K).

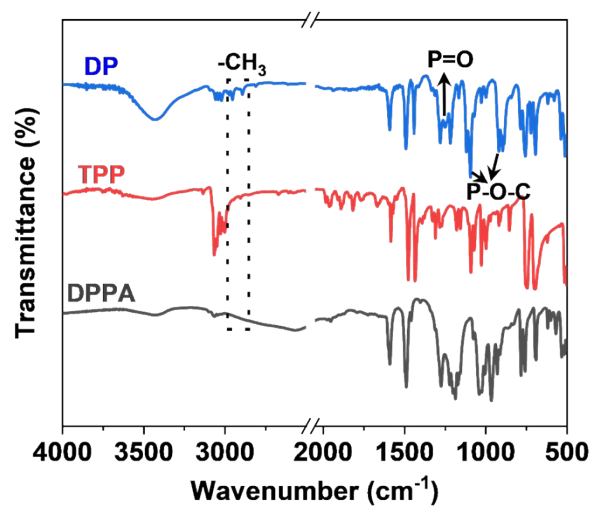


Fig. S3. FT-IR spectra of DP.

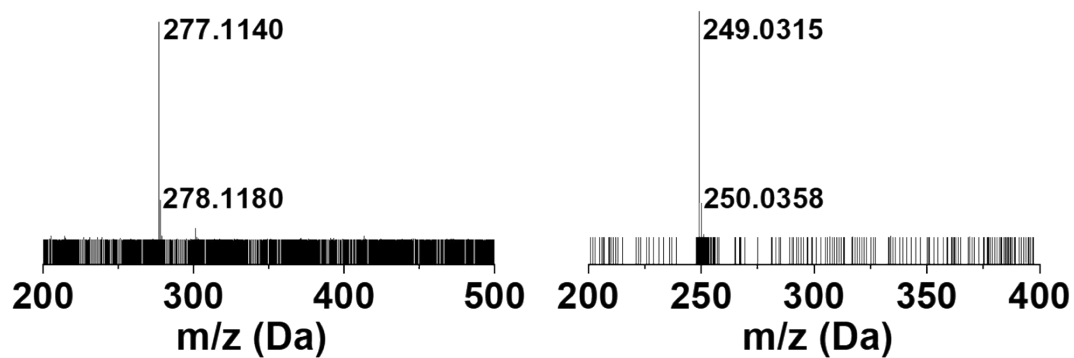


Fig. S4. Mass spectra of DP.

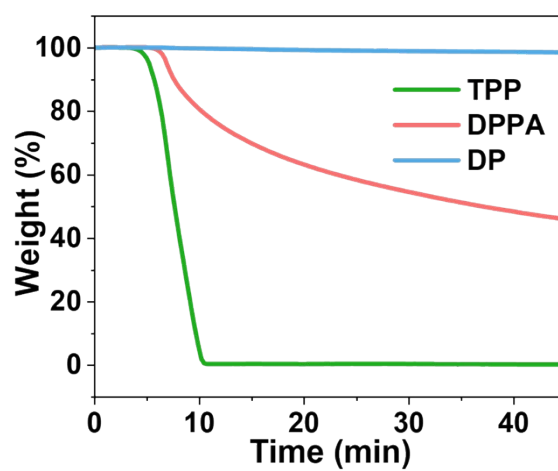
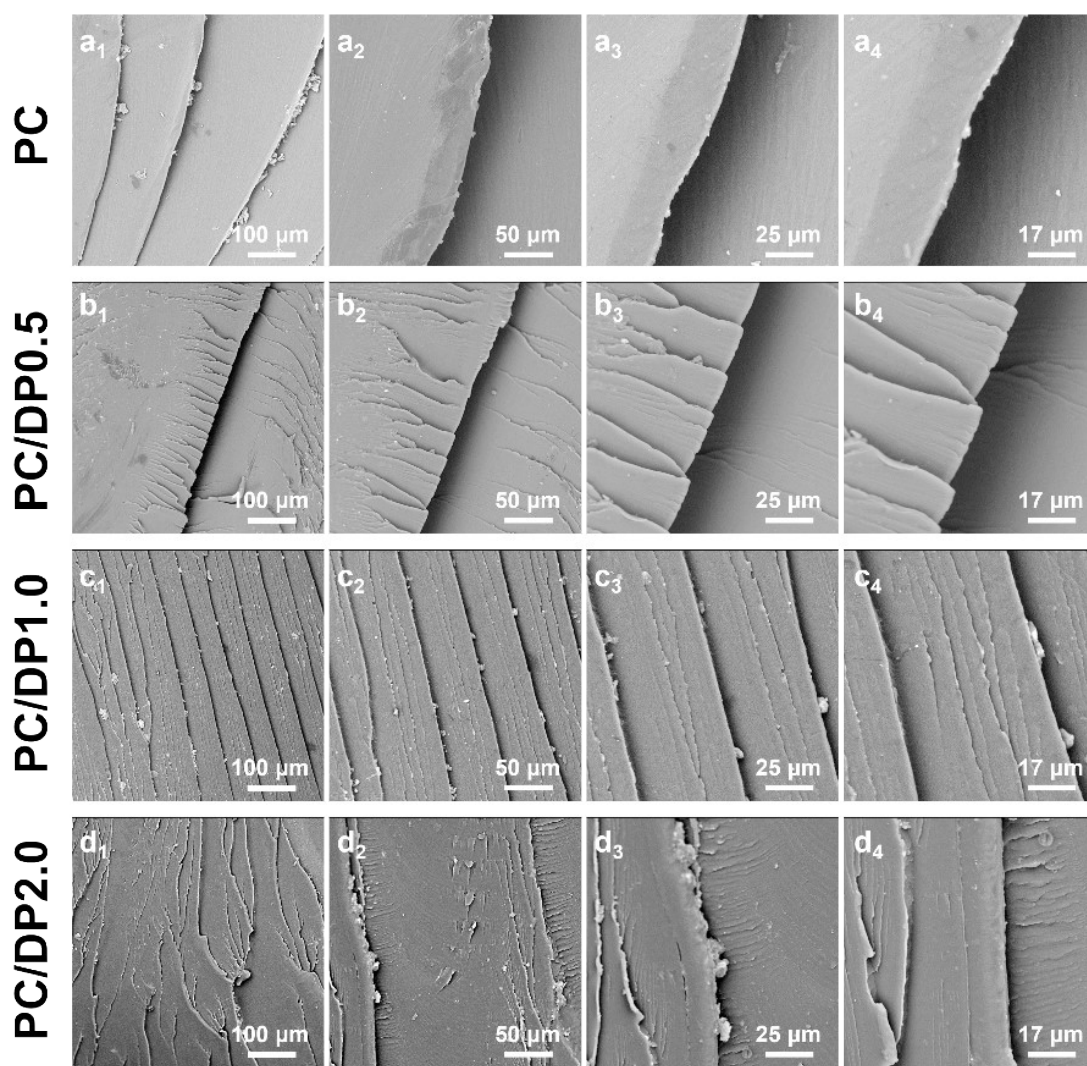


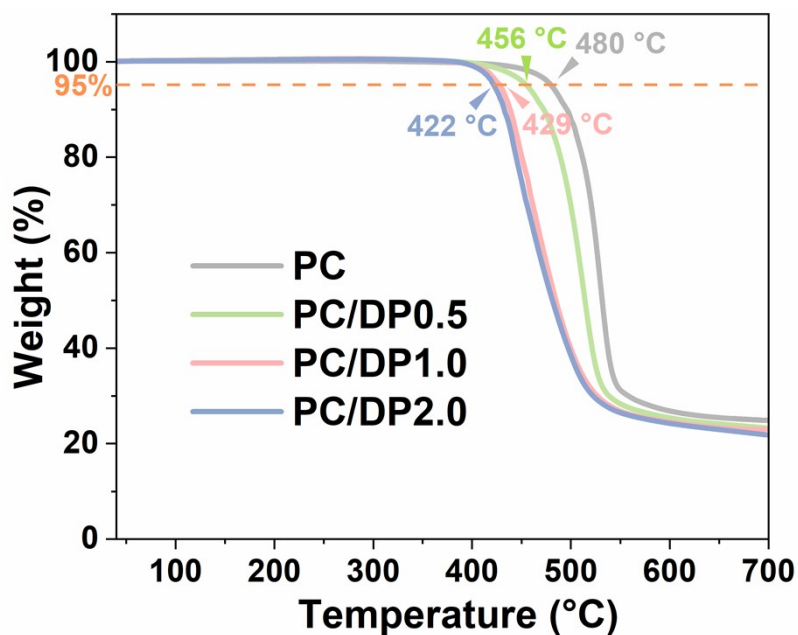
Fig. S5. Isothermal thermogravimetric curves of DPPA, TPP and DP at 240 °C.



**Fig. S6.** SEM images of quenched section of PC and PC/DP.

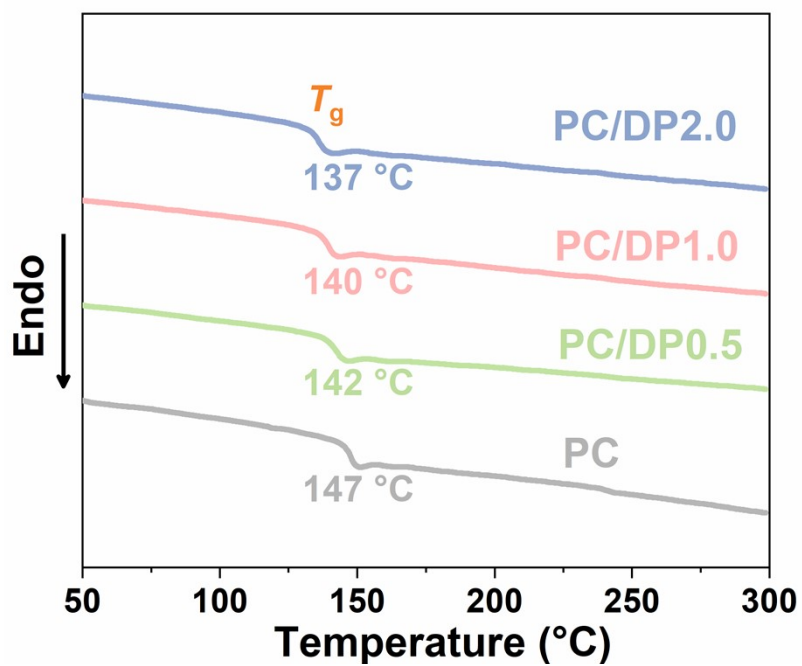
All PC/DP samples show a homogeneous phase without phase separation. This shows that the additive DP has good compatibility with the PC matrix.





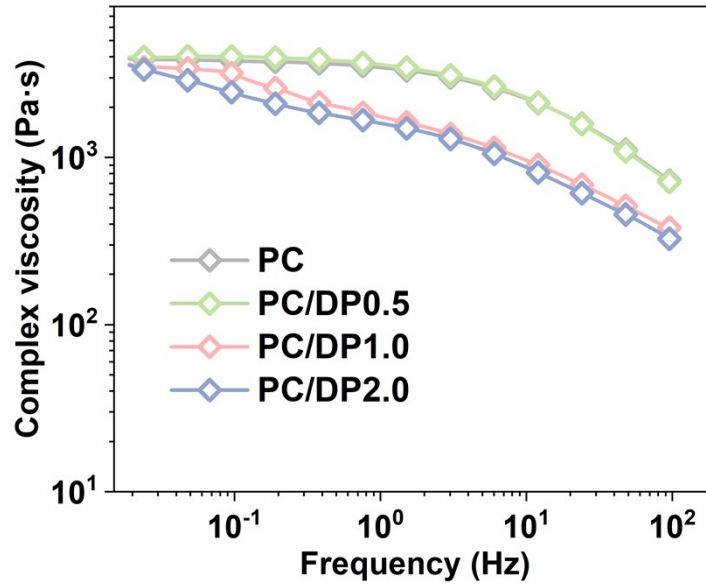
**Fig. S7.** Thermogravimetry curves of PC and PC/DP in N<sub>2</sub> atmosphere

The addition of DP reduces the thermal stability of polycarbonate. The initial decomposition temperature ( $T_{5\%}$ ) of PC is 480 °C, and the  $T_{5\%}$  values of PC/DP0.5, PC/DP1.0 and PC/DP2.0 are 456 °C, 429 °C and 422 °C, respectively. This is because the  $T_{5\%}$  of DP (351 °C, Fig. 2b in Manuscript) is much lower than that of polycarbonate (480 °C). During combustion, DP decomposes in advance before PC to release triphenylphosphine and phosphorus-containing radicals, which play a key role in gas phase flame retardance. But overall, PC/DP still maintains good thermal stability ( $T_{5\%} > 420$  °C).



**Fig. S8.** DSC heating curves of PC and PC/DP in N<sub>2</sub> atmosphere

The  $T_g$  of PC/DP decreases slightly as the DP content increases. This is due to the plasticizing effect of DP small molecules on PC macromolecular chains. In brief, PC/DP also maintains high glass transition temperature.



**Fig. S9.** Melt complex viscosity of PC and PC/DP at different frequency

At 240 °C, the complex viscosities of PC/DP are slightly lower than that of PC. This is also due to the plasticizing effect of small molecule DP flame retardant on PC macromolecular chain. In addition, the complex viscosity of all samples decreases with increasing shear frequency, showing the typical characteristic of pseudoplastic fluids. Combined with the experimental phenomena in the injection molding process, PC and PC/DP can be stably processed at this temperature (240 °C).

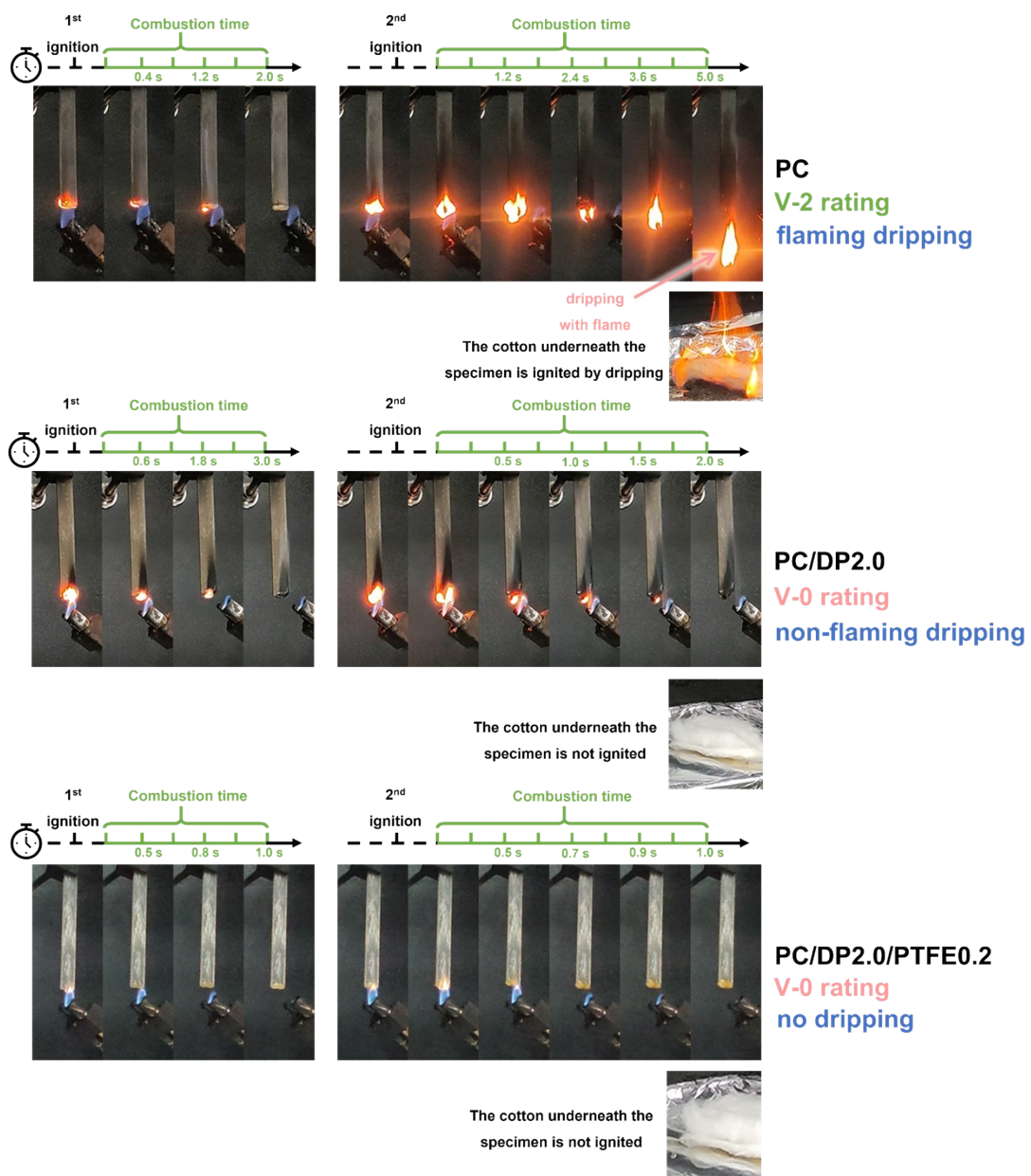
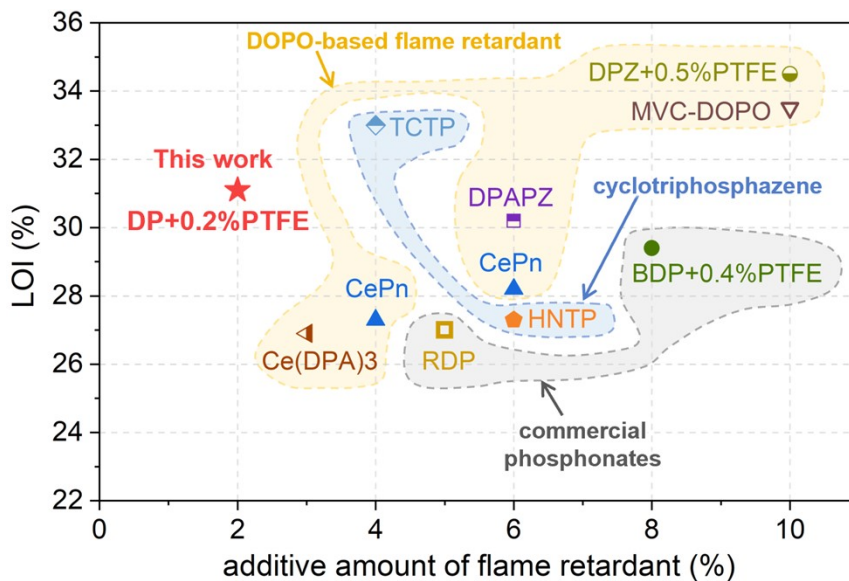
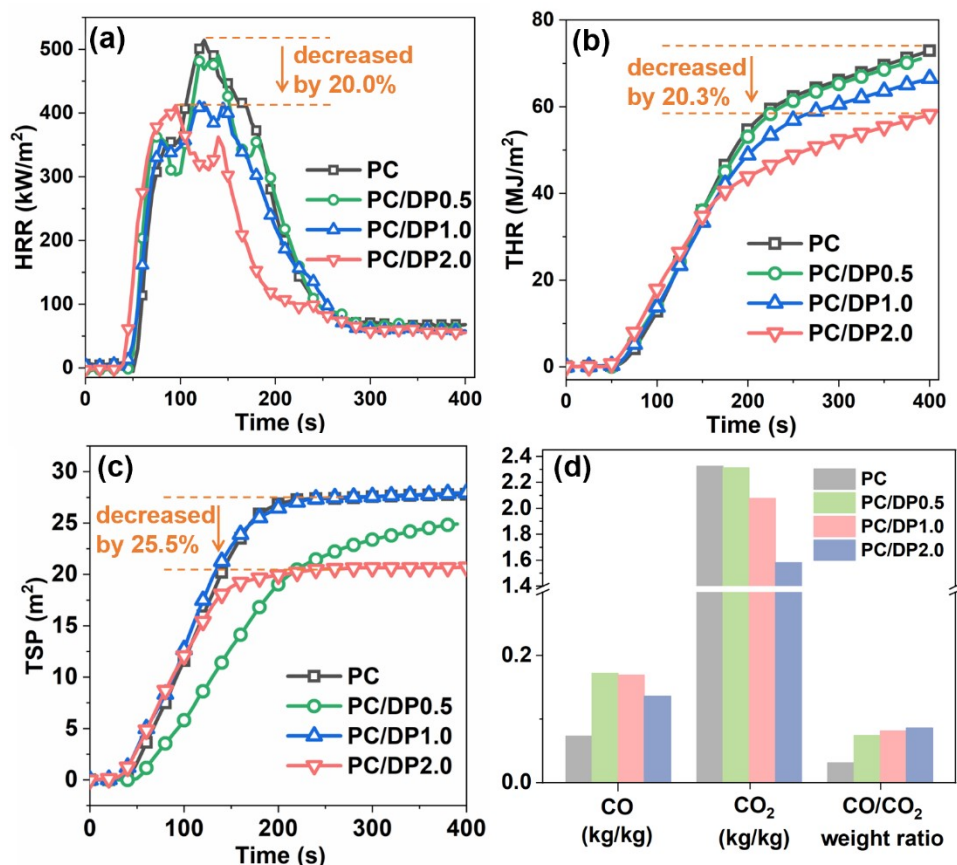


Fig. S10. Combustion process of PC and PC/DP2.0 during UL-94 vertical burning



**Fig. S11.** Comparison of the additive amount and LOI for phosphorus-containing flame-retarded PC that pass the UL-94 V-0 rating without dripping

As shown in **Table S5** and **Fig. S11**, commonly used flame retardants for polycarbonate mainly include phosphonates (number 1-5), 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) containing flame retardants (number 6-13) and cyclotriphosphazenes (number 15-17). Among them, resorcinol bis(diphenyl phosphate) (RDP) and bisphenol A bis(diphenyl phosphate) (BDP) are already commercial flame retardants. Compared with these literatures, the DP in this work can achieve the UL-94 V-0 rating of polycarbonate at a lower addition amount (2 wt%), while the reported phosphorus-containing flame retardants require higher addition (3 wt%~13.5 wt%).



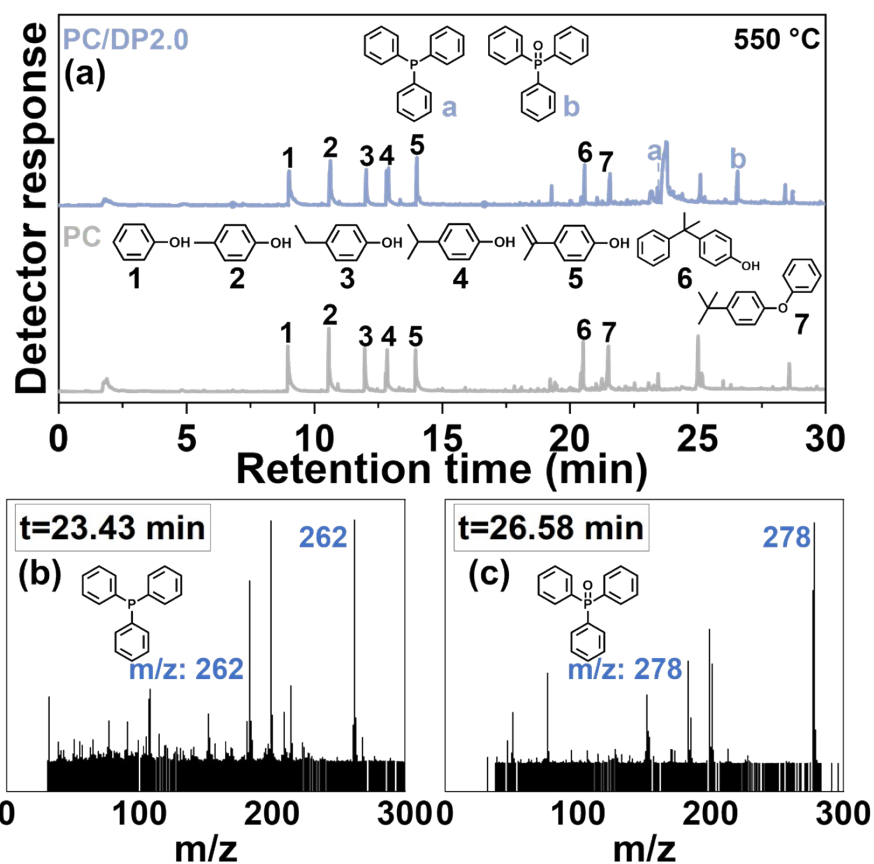
**Fig. S12.** HRR, THR and TSP curves of PC and PC/DP in cone calorimetry test

The heat release and smoke release of the PC/DP are researched by the cone calorimetry. **Fig. S12a-c** are the curves of heat release rate (HRR), total heat release (THR) and total smoke production (TSP), the relevant data are listed in **Table S6**. Peak heat release rate (p-HRR), THR and TSP are important parameters for judging the flame-retardant performance. The lower the p-HRR, THR and TSP values, the less heat and smoke released when the polymer burns, and the lower the fire hazard is.

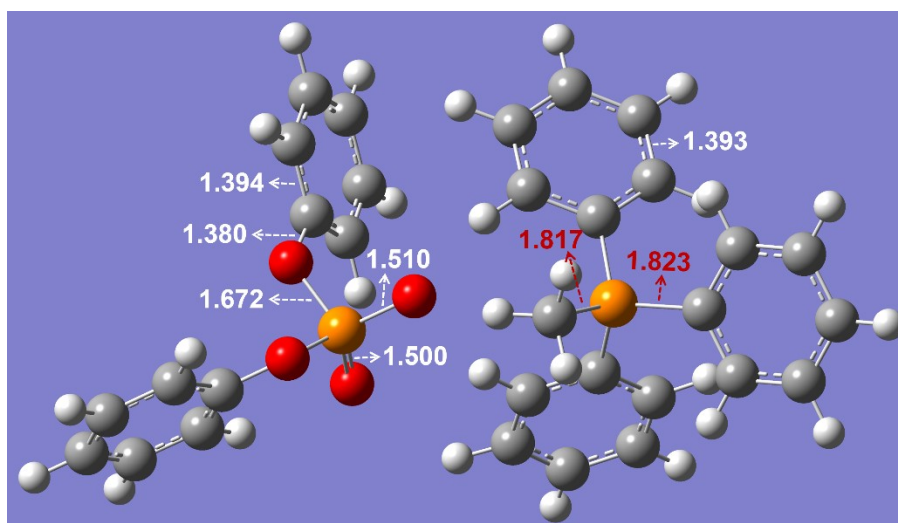
The addition of DP can reduce the p-HRR, THR and TSP of PC. The p-HRR, THR and TSP of PC are 514 kW/m<sup>2</sup>, 72.9 MJ/m<sup>2</sup> and 27.8 m<sup>2</sup>, respectively. As the content of DP increases, the p-HRR and THR of PC/DP gradually decrease. The p-HRR of PC/DP0.5, PC/DP1.0 and PC/DP2.0 are 490, 416 and 411 kW/m<sup>2</sup>, respectively. The THR of PC/DP0.5, PC/DP1.0 and PC/DP2.0 are 71.0, 66.5 and 58.1 MJ/m<sup>2</sup>, respectively. With only 2.0 wt% DP, the p-HRR, THR and TSP of PC/DP2.0 decreased

by 20.0%, 20.3% and 25.5%, respectively. The results show that PC/DP exhibits lower heat release, decreased smoke release and better fire safety.

After adding DP flame retardant, the CO/CO<sub>2</sub> ratio of PC/DP is higher than that of PC (**Fig. S12d**). This suggests an increased degree of incomplete combustion in the PC/DP system, indicating that DP flame retardant hinders the conversion of CO to CO<sub>2</sub>. This is because triphenylphosphine produced by DP decomposition at high temperature is more easily reacted with oxygen, thereby hindering the conversion of CO to CO<sub>2</sub> to some extent.



**Fig. S13.** (a) Total ion chromatograms of pyrolysis products of PC and PC/DP2.0; mass spectrum for the pyrolysis product of triphenylphosphine (b) and triphenylphosphine oxide (c)



**Fig. S14.** Optimized molecular structure of DP at B3LYP/6-31G(d) basis set.



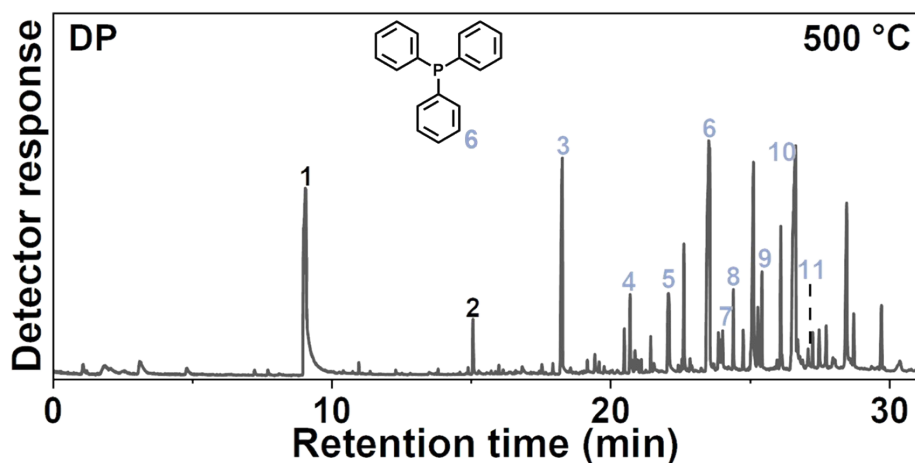


Fig. S15. Total ion chromatograms of products when DP is pyrolysed at 500 °C

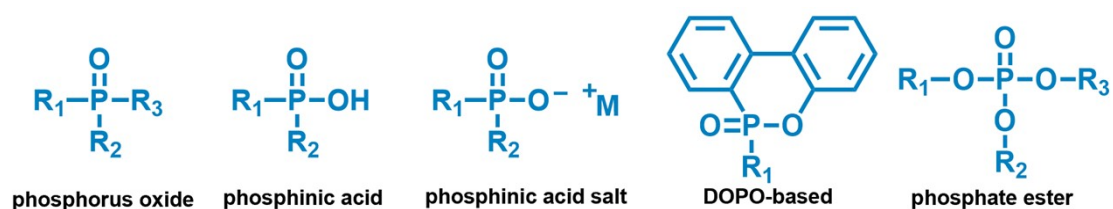


Fig. S16. Structural general formula of traditional phosphorus-containing flame retardants

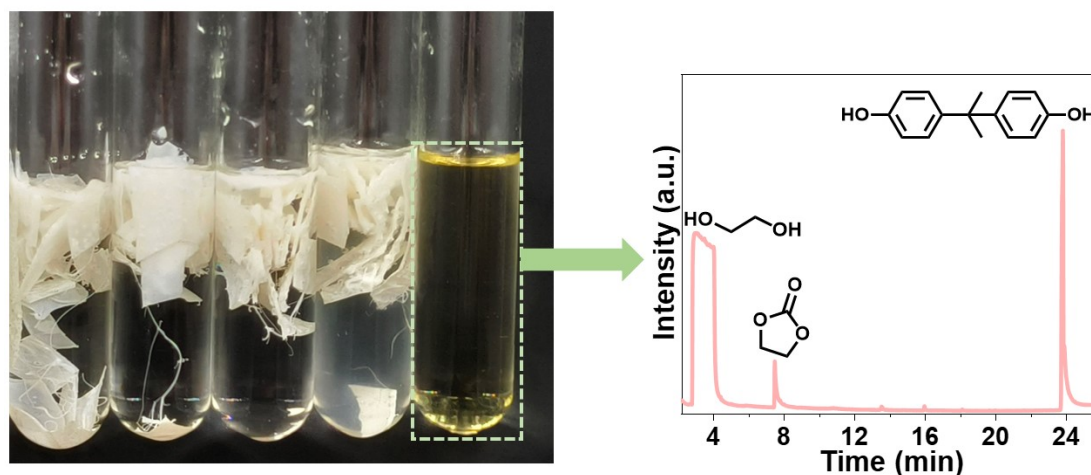
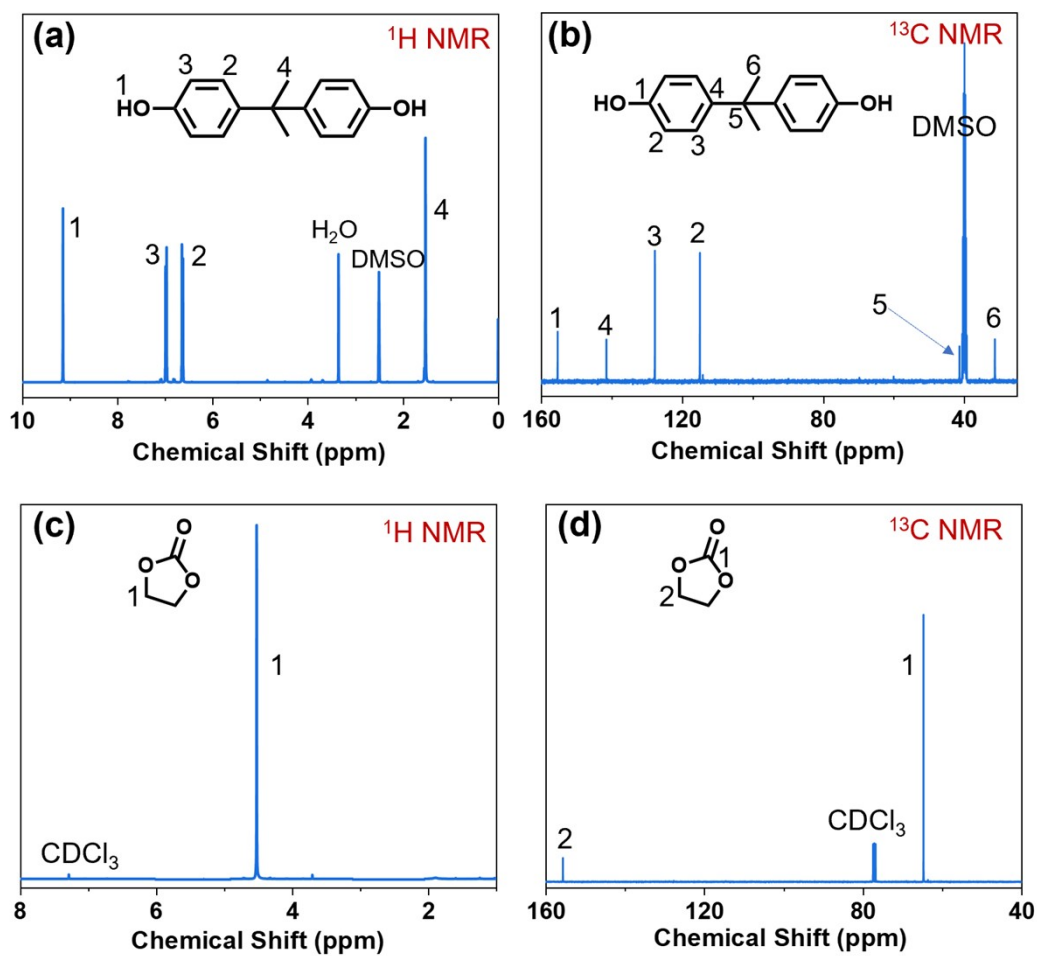
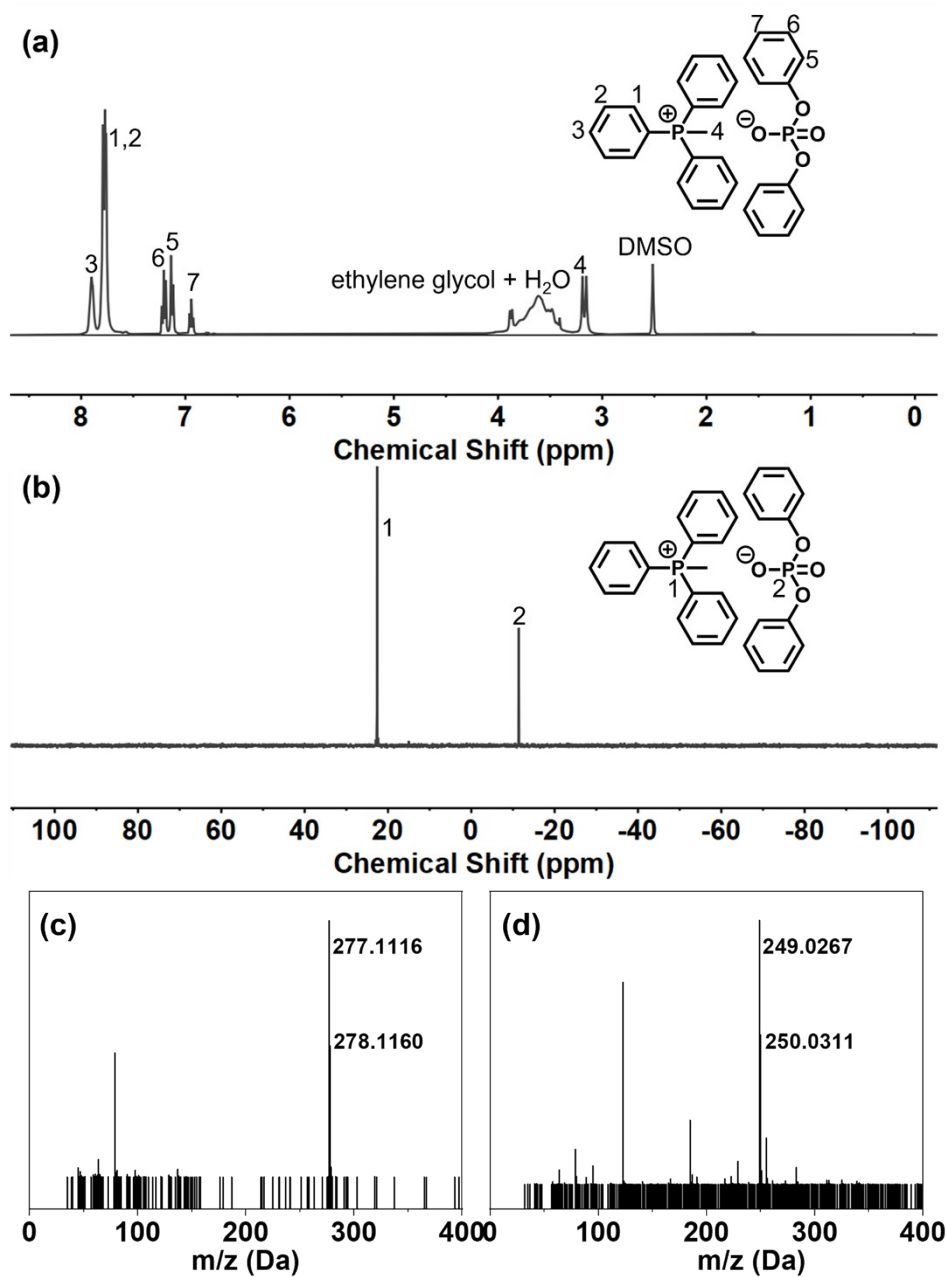


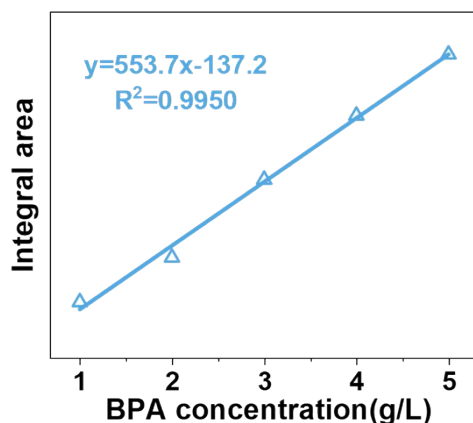
Fig. S17. GC-MS analysis of reaction mixture after PC/DP2.0 reacted with ethylene glycol at 180 °C for 1 h



**Fig. S18.** NMR spectra of recycled BPA (a-b, 400 MHz, DMSO, 298 K) and recycled EC from PC/DP2.0 (c-d, 400 MHz, CDCl<sub>3</sub>, 298 K)

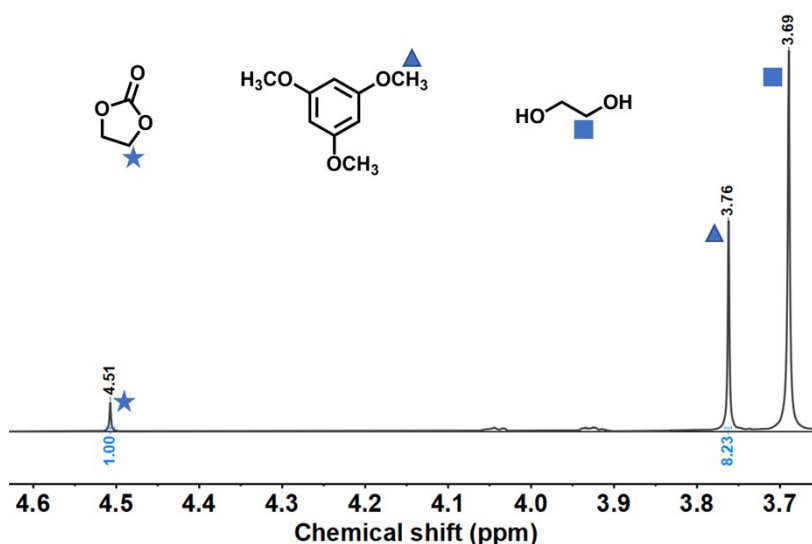


**Fig. S19.**  $^1\text{H}$  NMR,  $^{31}\text{P}$  NMR (a-b, 400 MHz, DMSO, 298 K) and mass spectra (c-d) of recycled DP

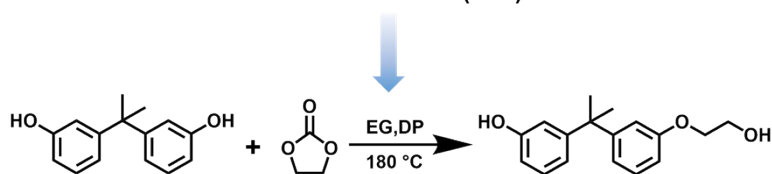
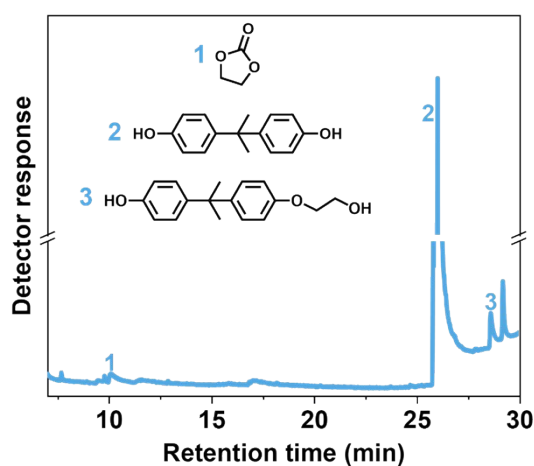


**Fig. S20.** BPA standard curve in gas chromatography

**Calculation of yield for recycled products.** When the reaction mixture was completely cooled, an aliquot was kept for gas chromatography (Agilent 7890B) analysis. Meanwhile, BPA standard with equal concentration gradient were detected under the same conditions, which was to obtain a standard curve of BPA integral area relative to its concentration (**Fig. S20**). Eventually, according to the standard curve equation, the concentration and the yield of BPA in the reaction solution could be calculated. On the other hand, when the reaction mixture was completely cooled, an aliquot was kept for  $^1\text{H}$  NMR spectroscopic analysis to determine the yield of EC, in which 1,3,5-trimethoxybenzene was used as internal standard (**Fig. S21**).

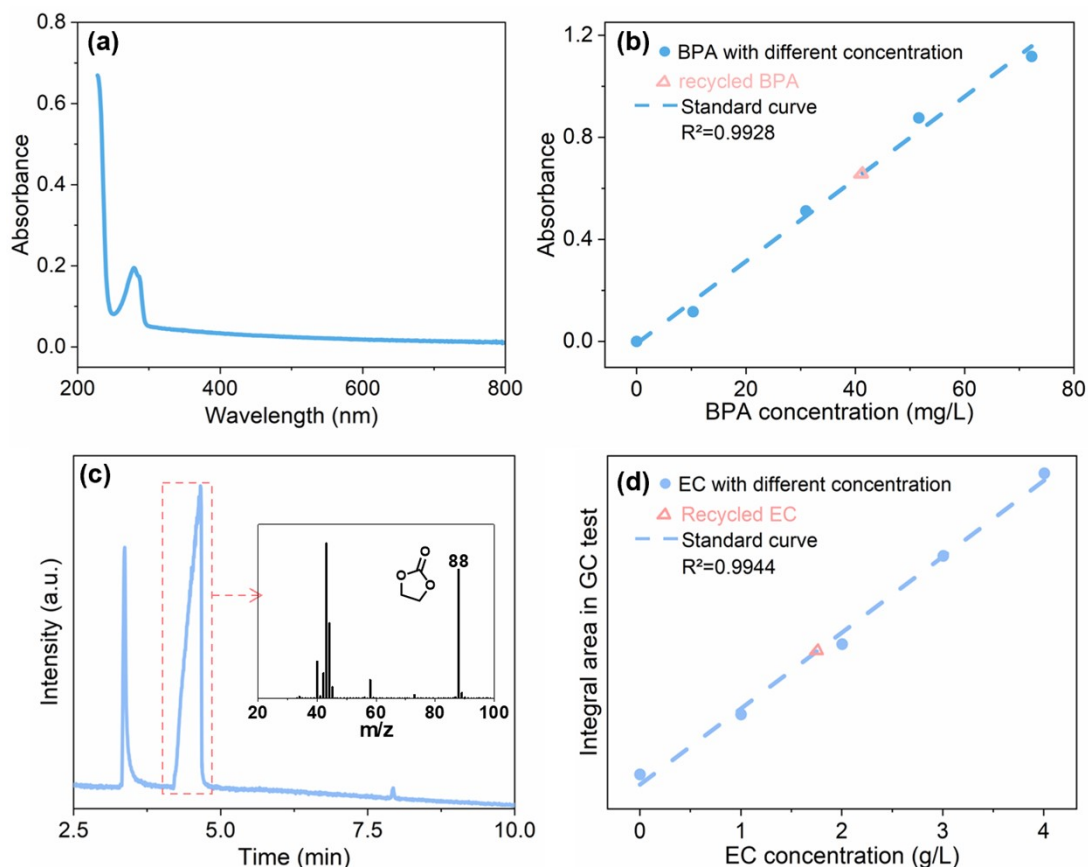


**Fig. S21.**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ , 298 K) of the reaction mixture with 1,3,5-trimethoxybenzene as internal standard



**Fig. S22.** GC-MS test results of the reaction mixture after BPA reacted with EC

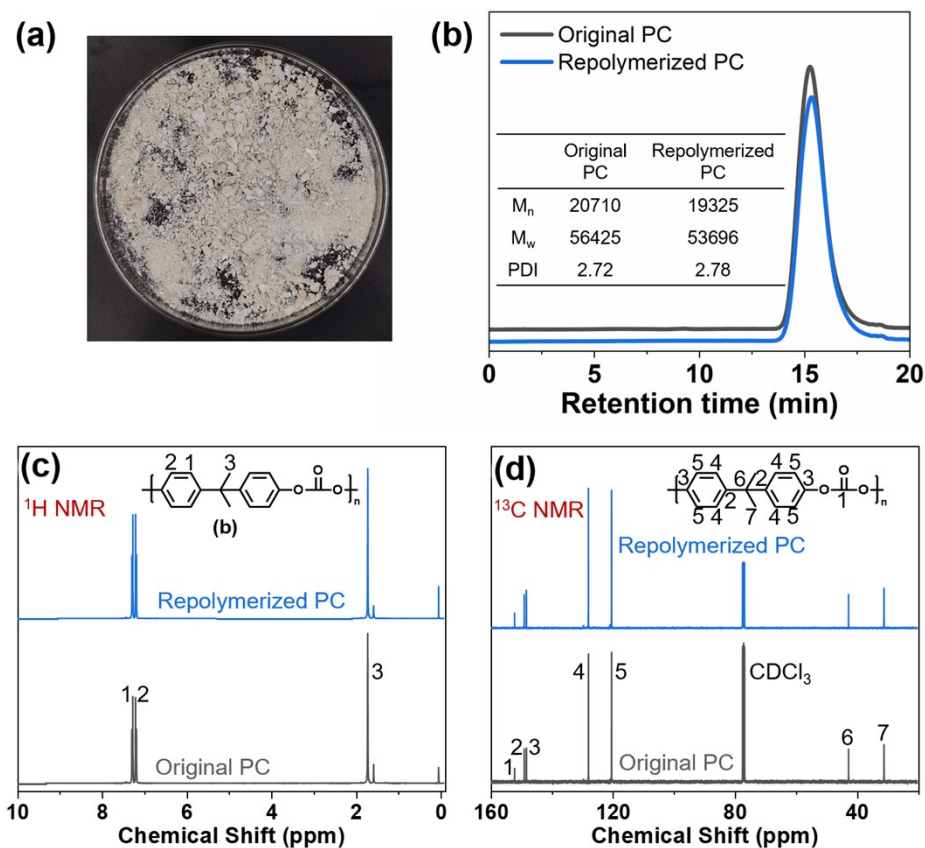
**The model reaction of BPA and EC.** The reaction was carried out at 180 °C for 8 h with 2.28 g BPA (10 mmol), 0.88 g EC (10 mmol), 0.046 g DP (2 wt% of BPA) and 11.4 g EG. When the reaction mixture was completely cooled, an aliquot was kept for GC-MS test.



**Fig. S23.** UV-Vis absorption spectrum of purchased BPA standard in methanol (a) and standard curve of BPA (b); GC-MS test results of purchased EC standard in methanol (c) and standard curve of EC (d)

After chemical depolymerization of 1.0 g PC/DP2.0 at 180 °C for 3 h, the theoretical weights of bisphenol A, ethylene carbonate and DP are 0.877 g, 0.338 g and 0.02 g, respectively. Since ethylene carbonate is a liquid, the mass loss during experimental operation is relatively large. The actual recycled bisphenol A, ethylene carbonate and DP are 0.772 g, 0.137 g and 0.013 g. Thus, as shown in **Table S9**, the isolated yields of bisphenol A, ethylene carbonate and DP are 88.0%, 40.5% and 65%, respectively. The purity of the recovered product is calculated from the standard curve of the purchased standard material, as shown in **Fig. S23**. The purity of recovered bisphenol A and ethylene carbonate reach 98.1% and 97.3%, respectively. Because DP is synthesized in the laboratory, standard material cannot be purchased to calculate the purity of recycled DP.

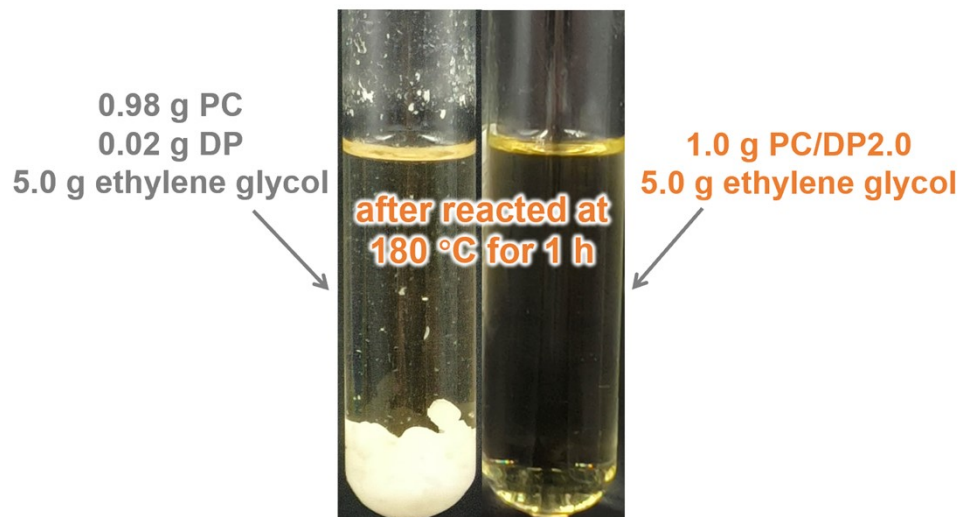
The detailed calculation process of the purity for bisphenol A and ethylene carbonate is as follows. (1) In the UV-Vis test, the characteristic absorption peak of BPA in methanol solvent is located at 279 nm (**Fig. S23a**). A standard curve of BPA is drawn based on the absorbance of purchased BPA standard with different concentrations in methanol at 279 nm (**Fig. S23b**). Then, the recycled BPA and methanol solvent are prepared into a solution with a concentration of 42 mg L<sup>-1</sup>. By substituting the absorbance of the recycled BPA solution at 279 nm into the standard curve, the actual concentration of the recycled BPA is calculated to be 41.2 mg L<sup>-1</sup>. Thus, the purity of recycled BPA is 98.1%. (2) In the GC-MS test (**Fig. S23c**), according to the integral area of purchased EC standard in methanol solvent at different concentration, the standard curve of EC is obtained. Then, the recycled EC and methanol solvent are prepared into a solution with a concentration of 1.8 g L<sup>-1</sup>. By substituting the integral area of the recycled EC solution into the standard curve, the actual concentration of the recycled EC is calculated to be 1.752 g L<sup>-1</sup> (**Fig. S23d**). Thus, the purity of recycled EC is 97.3%.



**Fig. S24.** (a) Digital photo of the repolymerized PC; (b) Gel permeation chromatography (GPC) test of repolymerized PC and original PC; (c-d)  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of repolymerized PC and original PC

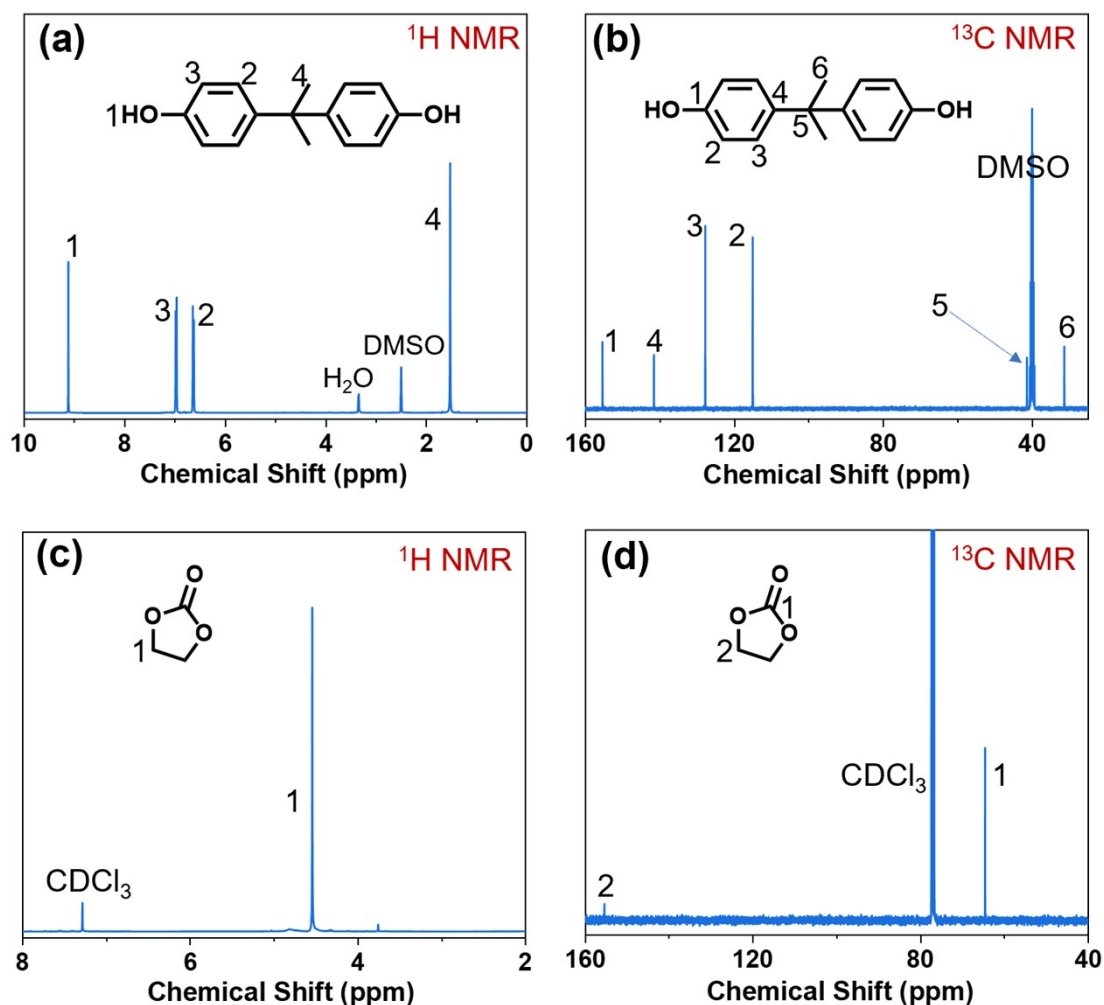
For the recycled products, bisphenol A can be used as a raw material for PC polymerization, and ethylene carbonate is mainly used in battery electrolytes, organic intermediates, etc. Therefore, we use recycled bisphenol A to repolymerize to obtain virgin PC. Recycled bisphenol A (BPA, 22.8 g, 0.1 mol), diphenyl carbonate (DPC, 21.4 g, 0.1 mol) and NaOH (catalyst, 600 ppm) were used as raw materials for repolymerization synthesis of virgin PC. Firstly, the mixtures were reacted at 170 °C for 2 h under  $\text{N}_2$  atmosphere to carry out the transesterification reaction. Then, the polycondensation reaction was carried out at 220 °C for 2 h, and the vacuum was kept below 100 Pa. Finally, the temperature was raised to 270 °C for 2 h. As shown in **Fig. S24**, the chemical structure and molecular weight of the repolymerized PC are consistent with the original PC, indicating that the recycled BPA exhibits good polymerization activity.





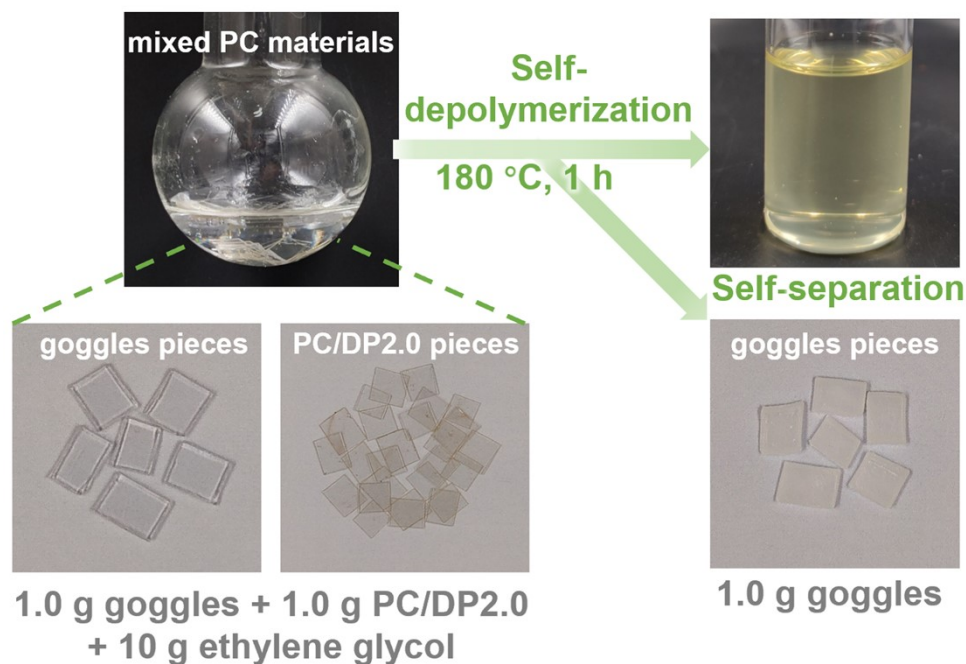
**Fig. S25.** Digital photos of samples after reacted at 180 °C for 1 h

0.98 g PC, 0.02 g (2 wt%) DP and 5 g ethylene glycol were mixed and reacted at 180 °C for 1 h. PC was not completely depolymerized and still maintained the granular morphology. Under the same reaction condition (180 °C, 1 h), PC/DP2.0 is completely depolymerized into small molecules bisphenol A and ethylene carbonate.



**Fig. S26.**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of recycled BPA (a-b, 400 MHz, DMSO, 298 K) and recycled EC (c-d, 400 MHz,  $\text{CDCl}_3$ , 298 K) from mixed plastics

**Selective self-recycling and self-separation of PC/DP in mixed plastics.** 1.0 g PET, 1.0 g PVC, 1.0 g HDPE, 1.0 g PP, 2.0 g PC/DP2.0 pieces and 10.0 g EG were added to a 25 mL single-neck round bottom flask equipped with a magnetic stirrer. Then the mixture was heated and stirred at 180 °C for 2 h. After the mixture was cooled to room temperature, PC/DP2.0 completely disappeared in the reaction bottle and was directly self-separated from the other waste plastics. The degradation products BPA, EC, and additive DP were recovered according to the steps mentioned above.



**Fig. S27.** Selective self-recycling and self-separation of PC/DP2.0 in mixed PC-based materials

**Selective self-recycling and self-separation of PC/DP in PC-based materials.** 1.0 g goggles pieces, 1.0 g PC/DP2.0 pieces and 10.0 g EG were added to a 25 mL single-neck round bottom flask equipped with a magnetic stirrer. Then the mixture was heated and stirred at 180 °C for 1 h. After the mixture was cooled to room temperature, PC/DP2.0 completely disappeared in the reaction bottle was self-separated from the goggles. The PC material (goggles) without DP maintains its original physical shape and can be separated by filtration.

**Table S1.** Formulation for preparation of PC, PC/DP and PC/(TPPO+DPPA)

Sample	PC (wt%)	DP (wt%)	TPPO+DPPA (wt%)	PTEF (wt%)	A1010 (wt%)
PC	99.7	0	0	0	0.3
PC/DP0.5	99.2	0.5	0	0	0.3
PC/DP1.0	98.7	1.0	0	0	0.3
PC/DP2.0	97.7	2.0	0	0	0.3
PC/DP2.0/PTEF0.2	97.5	2.0	0	0.2	0.3
PC/(TPPO+DPPA)0.5	99.2	0	0.5	0	0.3
PC/(TPPO+DPPA)1.0	98.7	0	1.0	0	0.3
PC/(TPPO+DPPA)2.0	97.7	0	2.0	0	0.3

**Table S2.** Theoretical and actual phosphorus content of PC and PC/DP

Sample	Theoretical phosphorus content (wt%)	Actual phosphorus content (wt%)
PC	0	0
PC/DP0.5	0.06	0.05
PC/DP1.0	0.12	0.11
PC/DP2.0	0.24	0.26

**Table S3.** Classification standards for UL-94 rating

Test content	Rating		
	V-0	V-1	V-2
The flaming combustion time (s) of each sample after each ignition is not more than	10	30	30
The flaming combustion time (s) of 5 samples after 10 times of ignition is not more than	50	250	250
The flameless combustion time (s) of a single sample after the second ignition is not more than	30	60	60
Whether each sample flame combustion or flameless combustion spread to the clamp	No	No	No
Whether the droplet of each sample ignite absorbent cotton	No	No	Yes

**Table S4.** Experiment details of sample in UL-94 vertical burning test

sample	after first ignition		after second ignition		cotton ignited	average weight loss (%)	rating
	burning time (t <sub>1</sub> )	dripping	burning time (t <sub>2</sub> )	dripping			
PC	3±1s	0~1 drop	5±2s	1~2 drop	Yes	2.6%	V-2
PC/DP2.0	2±1s	No	2±1s	1~2 drop	No	2.3%	V-0
PC/DP2.0/PTFE0.2	0 s	No	1±1s	No	No	0.4%	V-0

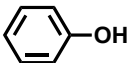
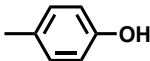



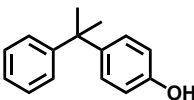
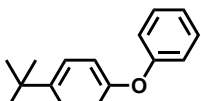
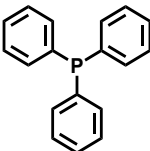
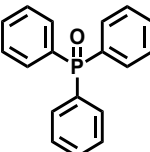
**Table S5.** Dataset of phosphorus-containing flame-retarded PC materials

number	flame retardant (FR)	FR amount	PTFE	LOI (%)	UL-94 (3.2 mm)		Ref
					rating	dripping	
1	resorcinol bis(diphenyl phosphate) (RDP)	3 wt%	/	Not given	V-2	Yes	1, 2
		5 wt%	/	27	V-0	No	
2	bisphenol A bis(diphenyl phosphate) (BDP)	8 wt%	0.4 wt%	29.4	V-0	No	3
		12.5 wt%	/	34	V-1	1 drop	4
3	Phloroglucinol tris(cyclic 2,2-dimethyl-1,3-propanediol phosphate) (PCDMPP)	3 wt%	/	Not given	V-2	Yes	2
		5 wt%	/	Not given	V-0	No	
4	Phloroglucinol tris(cyclic 1,3-propanediol phosphate) (PCPP)	3 wt%	/	Not given	V-0	No	
5	Rigid steric hindering spiro-bisphosphates (PDMPPD)	5 wt%	/	Not given	V-0	No	5
6	DOPO-containing polyhedral oligomeric silsesquioxanes (DPOP-POSSs)	2 wt%	/	26.1	V-2		6
		4 wt%	/	29.8	V-2	Yes	
		6 wt%	/	30.1	V-2		
7	DOPO-containing cerium (CePn)	2 wt%	/	26.5	V-1	Yes	7
		4 wt%	/	27.3	V-0	No	
		6 wt%	/	28.2	V-0	No	
8	Cerium-based P, N-Containing complex (Ce(DPA) <sub>3</sub> )	1 wt%	/	25.5	V-2	Yes	8
		3 wt%	/	26.9	V-0	No	
9	DOPO-based phosphoramidate (DPAPZ)	3 wt%	/	27.6	V-1	Yes	9
		6 wt%	/	30.2	V-0	No	
10	multi-phosphaphenanthrene compound (TDBA)	6 wt%	/	30.3	V-2	Yes	10
		8 wt%	/	31.3	V-2	Yes	
		10 wt%	/	33.7	V-0	Yes	
11	DOPO-based cyclo-tetrasiloxane (MVC-DOPO)	6 wt%	/	30.6	V-1	No	11
		10 wt%	/	33.5	V-0	No	
12	DOPO-formaldehyde-piperazine (DFPZ)	1 wt%	/	26.8	V-2	Yes	12
		3 wt%	/	32.3	V-0	severe	
		3 wt%	0.5 wt%	29.1	V-2	Yes	
13	DOPO-piperazine (DPZ)	10 wt%	/	34.5	V-0	severe	
		10 wt%	0.5 wt%	34.7	V-0	No	
14	triphenyl phosphite (TPP)	4 wt%	/	35	V-2	Not given	13
15	hexakis(4-nitrophenoxy) cyclotriphosphazene (HNTP)	6 wt%	/	27.3	V-0	No	14
16	tris(phenoxy)trifluorocyclotriphosphazenes (TCTP)	4 wt%	/	33	V-0	No	15
17	phosphazene-triazine bi-group flame retardant (A3)	13.5 wt%	/	29.3	V-0	Yes	16
18	methyltriphenylphosphonium diphenylphosphate (DP)	2.0 wt%	/	31.1	V-0	Yes	This work
		2.0 wt%	0.2 wt%	30.8	V-0	No	

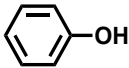
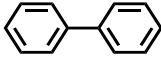
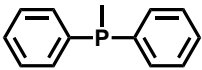
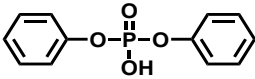
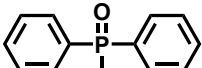
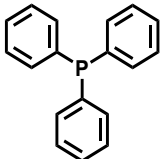
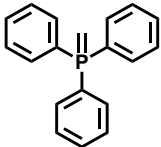
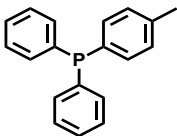
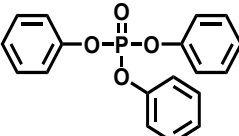
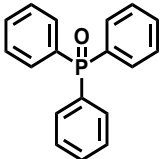
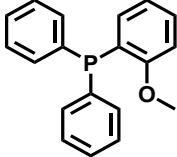
**Table S6.** Relevant data of PC and PC/DP in cone calorimetry test

sample	p-HRR	THR	TSP
PC	514	72.9	27.8
PC/DP0.5	490	71.0	24.9
PC/DP1.0	416	66.5	27.5
PC/DP2.0	411	58.1	20.7

**Table S7.** Major pyrolysis products detected from Py-GC-MS of PC and PC/DP2.0

peak	retention time (min)	molecular weight	compound	major mass fragments
1	9.03	94		39,40,66,94,95
2	10.65	108		77,79,107,108
3	12.06	122		77,107,108,122,123
4	12.93	136		77,91,120,121,136
5	14.09	134		91,119,133,134
6	20.61	212		197,198,212,213
7	21.60	226		119,211,212,226,227
a	23.43	262		108,183,199,262
b	26.58	278		51,77,152,183,199,277,278

**Table S8.** Major pyrolysis products detected from Py-GC-MS of DP.

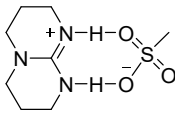
peak	retention time	molecular weight	compound	major mass fragments
1	9.06	94		65,66,94,95
2	15.08	154		152,153,154,155
3	18.29	200		183,185,200,201
4	20.72	250		77,94,170,248,249
5	22.09	216		201,215,216
6	23.50	262		107,108,184,185,262,263
7	24.05	276		108,183,275,276,277
8	24.44	276		183,197, 275,276,277
9	25.44	326		77,215,325,326
10	26.58	278		51,77,152,183,199,278,279
11	27.10	292		277,291,292



**Table S9.** Yield, isolated yield and purity of recycled products when PC/DP2.0 was depolymerized at 180 °C for 3 h

recycled product	yield (%)	isolated yield (%)	purity (%)
bisphenol A	98.6	88.0	98.1
ethylene carbonate	60.2	40.5	97.3
DP	/	65.0	/

**Table S10.** Dataset of PC chemical recycling by alcoholysis with ethylene glycol

catalyst	catalyst amount <sup>a</sup>	reaction condition	yield of BPA	yield of EC	isolated yield of BPA	isolated yield of EC	Ref
NaOH	10 mol%	180 °C, 45 min	6%	Not given	Not given	Not given	17
Na <sub>2</sub> CO <sub>3</sub>	2 mol%	180 °C, 20 min	28%	Not given	Not given	Not given	18
KOH			29.7%				
NaOH			31.8%				
Na <sub>2</sub> CO <sub>3</sub>	3 mol%	Microwave-assisted	14.3%	Not given	Not given	Not given	19
CaO		200 °C, 10 min	33%				
Al <sub>2</sub> O <sub>3</sub>			18.8%				
ZnO			5.6%				
TBD:MSA	15mol%	130 °C, 5 h	89%	83%	82%	79%	20
	15mol%	130 °C, 10 h	95%	Not given	Not given	Not given	21
	15mol%	180 °C, 20 min	96%	Not given	Not given	Not given	
DP	1 mol% (or 2 wt%)	180 °C, 3 h	98.6%	60.2%	88%	40.5%	This work

<sup>a</sup> mol% is calculated by dividing the molar amount of catalyst by the molar amount of carbonate groups in PC.

## Reference

1. E. A. Murashko, G. F. Levchik, S. V. Levchik, D. A. Bright and S. Dashevsky, *J. Fire Sci.*, 1998, **16**, 278-296.
2. H. Vothi, C. Nguyen, K. Lee and J. Kim, *Polym. Degrad. Stabil.*, 2010, **95**, 1092-1098.
3. J. Feng, J. Hao, J. Du and R. Yang, *Polym. Degrad. Stabil.*, 2010, **95**, 2041-2048.
4. Y. Yang, W. Kong and X. Cai, *Polym. Degrad. Stabil.*, 2016, **134**, 136-143.
5. K. Huang and Q. Yao, *Polym. Degrad. Stabil.*, 2015, **113**, 86-94.
6. X. Wang, W. Zhang, Z. Qin and R. Yang, *Compos. Part A-Appl. S.*, 2019, **117**, 92-102.
7. T. Sai, S. Ran, Z. Guo, H. Yan, Y. Zhang, H. Wang, P. Song and Z. Fang, *Chem. Eng. J.*, 2021, **409**, 128223.
8. T. Sai, Y. Su, H. Shen, S. Ran, S. Huo, Z. Guo and Z. Fang, *ACS Appl. Mater. Interfaces*, 2021, **13**, 30061-30075.
9. B. Cai, Q. Jiang, W. Xu, L. Wang, Z. Luo and B. Wang, *J. Appl. Polym. Sci.*, 2023, **140**, e54513.
10. Y. Qiu, Z. Liu, L. Qian and J. Hao, *Rsc Adv.*, 2017, **7**, 51290-51297.
11. P. Ni, Y. Fang, L. Qian and Y. Qiu, *J. Appl. Polym. Sci.*, 2018, **135**, 45815.
12. C. Liu and Q. Yao, *Ind. Eng. Chem. Res.*, 2017, **56**, 8789-8796.
13. B. Swoboda, S. Buonomo, E. Leroy and J. M. L. Cuesta, *Polym. Degrad. Stabil.*, 2008, **93**, 910-917.
14. Y. Yang, H. Luo, X. Cao, W. Kong and X. Cai, *J. Therm. Anal. Calorim.*, 2017, **129**, 809-820.
15. Y. Yang, W. Kong, Y. Wang and X. Cai, *J. Therm. Anal. Calorim.*, 2015, **122**, 805-816.
16. Y. Chen, X. Wu and L. Qian, *J. Appl. Polym. Sci.*, 2020, **137**, e49523.
17. A. Oku, S. Tanaka and S. Hata, *Polymer*, 2000, **41**, 6749-6753.
18. C.-H. Lin, H.-Y. Lin, W.-Z. Liao and S. A. Dai, *Green Chem.*, 2007, **9**, 38-43.
19. L. Rosi, M. Bartoli, A. Undri, M. Frediani and P. Frediani, *J. Mol. Catal. A: Chem.*, 2015, **408**, 278-286.
20. C. Jehanno, J. Demarteau, D. Mantione, M. C. Arno, F. Ruiperez, J. L. Hedrick, A. P. Dove and H. Sardon, *Acs Macro Lett.*, 2020, **9**, 443-447.
21. C. Jehanno, J. Demarteau, D. Mantione, M. C. Arno, F. Ruiperez, J. L. Hedrick, A. P. Dove and H. Sardon, *Angew. Chem. Int. Ed.*, 2021, **60**, 6710-6717.