Supporting Information

Catalyst-free amino-alcoholysis depolymerization strategy: a facile and powerful tool for chemical recycling of poly(bisphenol A carbonate)

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Experimental section

Materials

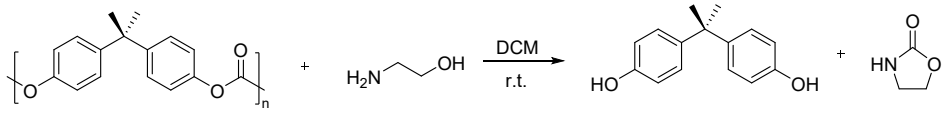
The BPA-PC (pellet, bowl, goggle, frame, disc, lampshade, bucket, veil, tube), PLA (cup), PBS (straw), PET (bottle) materials were purchased on Taobao.com and amazon.cn and used without further purification. Ethanolamine (> 99%, Aladdin), (*R*)-2-amino-1-propanol (97%, Macklin), D-phenylalaninol (98%, Macklin), (*R*)-2-amino-3,3-dimethyl-1-butanol (> 99%, Macklin), (1*S*,2*S*)-2-aminocyclohexanol (98%, Bidepharm), 2-methylaminoethanol (> 99%, TCI), as commercial grade depolymerizing reagents were used without further purification. Dibromomethane (98%, Energy Chemical) and hexamethylbenzene (98%, Energy Chemical) were used as internal standard. Toluene (> 99%), dichloromethane (> 99%), ethyl acetate (> 99%), tetrahydrofuran (> 99%), N,N-dimethylformamide (> 99%) and dimethyl sulfoxide (> 99%) were purchased as solvents at Sinopharm Chemical Reagent Co., Ltd. 2-Methyltetrahydrofuran (> 99%) was purchased as a solvent at Macklin. Chloroform-*d* (> 99%) was purchased at Cambridge Isotope laboratories, Inc. Dimethyl sulfoxide-d_6 (> 99%) was purchased at Energy Chemical. Chromatographic tetrahydrofuran (THF) was purchased from Honeywell LTD for the analysis of GPC measurements.

Instrumentation

Nuclear magnetic resonance measurements were performed at room temperature on Bruker Advance instrument at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR), using $CDCl_3$ and Dimethyl sulfoxide-d_6 as solvent and TMS as internal reference. Molecular weight (M_n) and dispersity (Đ) of the polymers were determined by gel permeation chromatography (GPC, Agilent 1260 LC, USA) using THF as the eluent (flow rate: 1 mL/min, at 40°C). DSC measurements were performed on a TA Instrument Q100 DSC equipped with a refrigerated cooling system (RCS) under a N_2 atmosphere. The instrument was operated in the standard DSC mode and was calibrated with an indium standard. Samples (about 5 mg) were heated from 25°C to 250°C at 10°C/min, hold for 10 minute and then cooled to 0 °C at 10°C/min, the data were then collected in the second heating ramp from 0°C to 250°C at 10°C/min. Glass transition temperatures (T_g) were read as the middle of the change in heat capacity. The

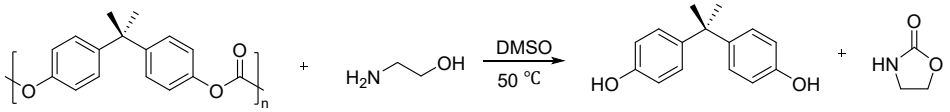
transmittance of BPA-PC was tested according to chemical industrial standard HG/T2503-1993.

General procedure for the depolymerization of BPA-PC (Fig. 1)



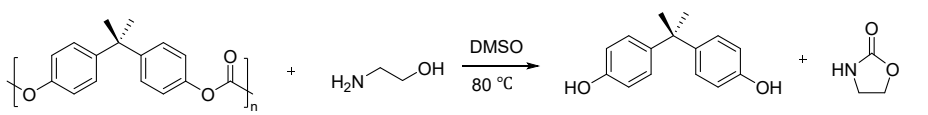
The depolymerization of BPA-PC was carried out in a Schlenk flask at 25°C. BPA-PC pellets (254 mg, 1 mmol based on BPA unit) were added first. Hexamethylbenzene (32 mg, 0.4 mmol) was then added as an internal standard. Then, adding DCM (1 mL) and ethanolamine (122 μL, 2 mmol) in sequence. The reaction was monitored by ^{1}H NMR spectrum. After 82 h, we calculated that the yield of BPA was 63%, and the yield of 2-oxazolidone was 73% by using hexamethylbenzene as an internal standard.

General procedure for the depolymerization of BPA-PC (Table 1, entry 7)



The depolymerization of BPA-PC was carried out in a Schlenk flask at 50°C. BPA-PC pellets (254 mg, 1 mmol based on BPA unit) was added first. Then, adding dimethyl sulfoxide (1 mL) and ethanolamine (61 μL, 1 mmol) in sequence. The reaction was monitored by ^{1}H NMR spectrum, aliquot was taken for ^{1}H NMR spectroscopic analysis with acetic acid as quenching reagent. After 3 h, we calculated that the yield of BPA was 99%, and the yield of 2-oxazolidone was 99% by using hexamethylbenzene as an internal standard.

General procedure for gram-scale depolymerization in DMSO (Fig. S4)



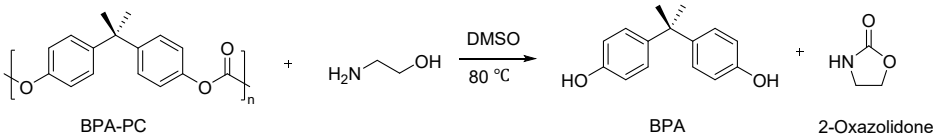
The depolymerization of 100 g BPA-PC tubes was carried out in a round-bottomed flask at 80°C. BPA-PC tubes (100 g, 1 equiv.) were added first. Dimethyl sulfoxide (394 mL) and ethanolamine (24 mL, 1.03 equiv.) were then added. The reaction was monitored by ^{1}H NMR spectrum, aliquot was taken for ^{1}H NMR spectroscopic

analysis. After 2 h, we calculated that the conversion was 100%. Then, DMSO was recovered by vacuum distillation (70°C, 0.23 mbar) with a recovery rate of 93%. The NMR spectra showed that the recovered DMSO was pure without impurities. After that, a certain amount of water was introduced to the remaining solids, stirring uniformly. The suspension was filtered to collect the precipitate and filtrate. The precipitate was vacuum dried, 88 g of BPA with a yield of 96% was obtained. After evaporative concentration and ether washing of filtrate, 28 g of 2-oxazolidone was obtained in 83% yield.

2-Oxazolidone : ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.46 (s, 1H), 4.32-4.25 (m, 2H), 3.42-3.46 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 155.4, 141.5, 127.8, 115.0, 41.4, 31.4.

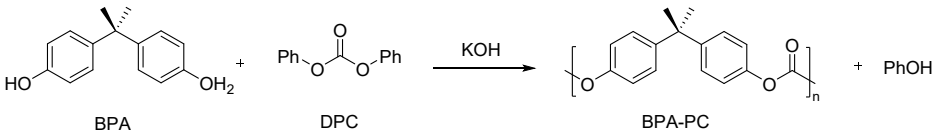
BPA : ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.12 (s, 2H), 7.00-6.94 (m, 4H), 6.68-6.59 (m, 4H), 1.52 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.1, 64.6, 40.4.

General procedure for gram-scale depolymerization under solvent-free condition (Fig. 4)



The depolymerization of 30 g BPA-PC tubes was carried out in a round-bottomed flask at 120°C. BPA-PC tubes (30 g, 1 equiv.) were added first. Ethanolamine (7.6 mL, 1.06 equiv.) was then added. The reaction was monitored by ^{1}H NMR spectrum, aliquot was taken for ^{1}H NMR spectroscopic analysis. After 47 h, we calculated that the conversion was 100%. The reaction system was cooled to room temperature. After that, a certain amount of water was introduced to the reaction, stirring uniformly. The suspension was filtered to collect the precipitate and filtrate. The precipitate was vacuum dried, 26.5 g of BPA with a yield of 98% was obtained. After evaporative concentration and column chromatography (chloroform as eluent), 7.3 g of 2-oxazolidone was obtained in 71% yield.

General procedure for the synthesis of BPA-PC (Fig. 5)



To a round-bottom flask, 8.1 g bisphenol A (35.6 mmol, 1 equiv.) and 8.4 g diphenyl carbonate (39.2 mmol, 1.1 equiv.) were weighed and added, followed by 0.2 mg potassium hydroxide (0.003 mmol, 0.01 mol%). The air was removed from the system by a vacuum pump. The reaction was divided into two stages. The transesterification reaction stage was carried out under the protection of argon. The reaction was stirred slowly at 130°C for 30 minutes, and then heated to 170°C for 120 minutes. In the polycondensation reaction stage, the temperature was rapidly increased to 220℃, and the reaction was slowly reduced to 70 mbar for 30 minutes. Then continue to reduce the pressure to 0.001 mbar, and increase the temperature to 260℃. Continue to react for 30 minutes and then stop heating, keep the pressure naturally cooling to room temperature, and finally get colorless and transparent solid.

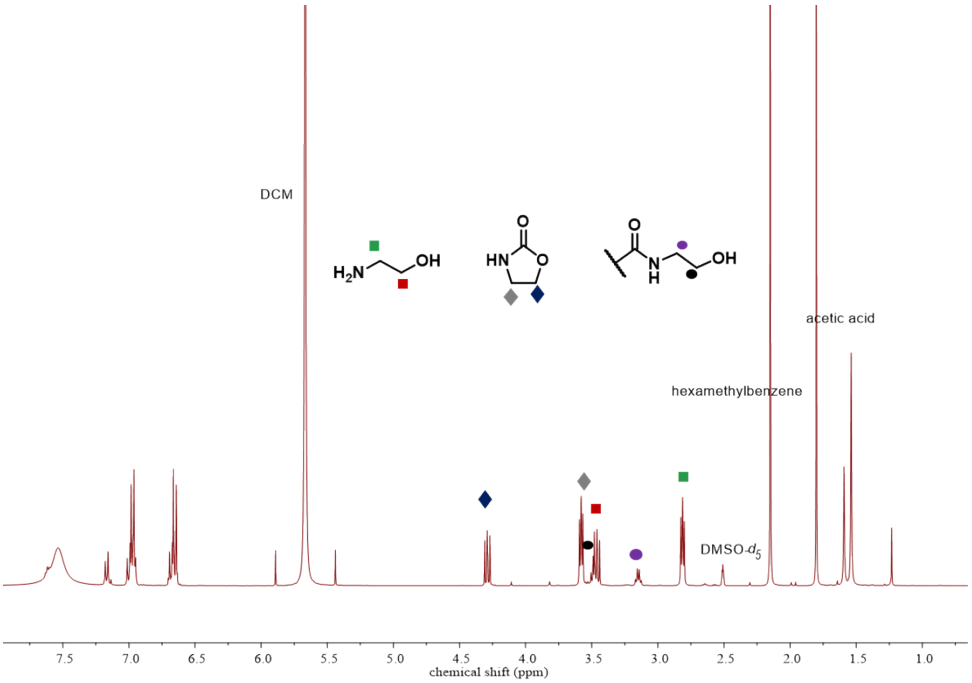
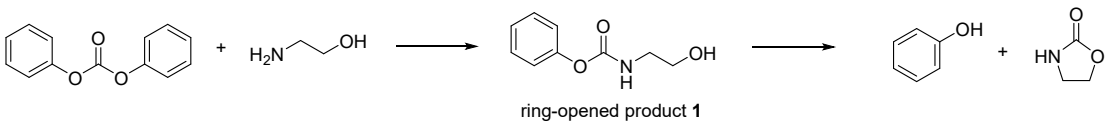
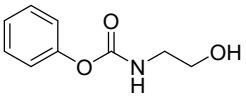
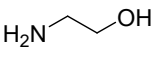


Figure S1. ^{1}H NMR spectrum of the degradation product in DCM. (400 MHz, DMSO-d_6, 298 K).

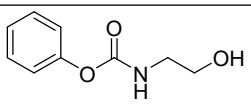
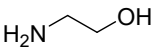


Tables S1. Results of the reaction of diphenyl carbonate with 1 equiv. of ethanolamine in DMSO.

Time			
30 min	78.7%	21.3%	0%
1 h	88.5%	11.5%	0%
6 h	100%	0%	0%

Reaction conditions: diphenyl carbonate (2 mmol), ethanolamine (2 mmol), $V_{solvent}$ = 1 mL, 50 °C.

Tables S2. Results of the reaction of diphenyl carbonate with 1 equiv. of ethanolamine in chloroform.

Time			
30 min	0%	87.8%	12.2%
1 h	0%	91.7%	8.3%
6 h	1.1%	97.0%	1.9%

Reaction conditions: diphenyl carbonate (2 mmol), ethanolamine (2 mmol), $V_{solvent}$ = 1 mL, 50 °C.

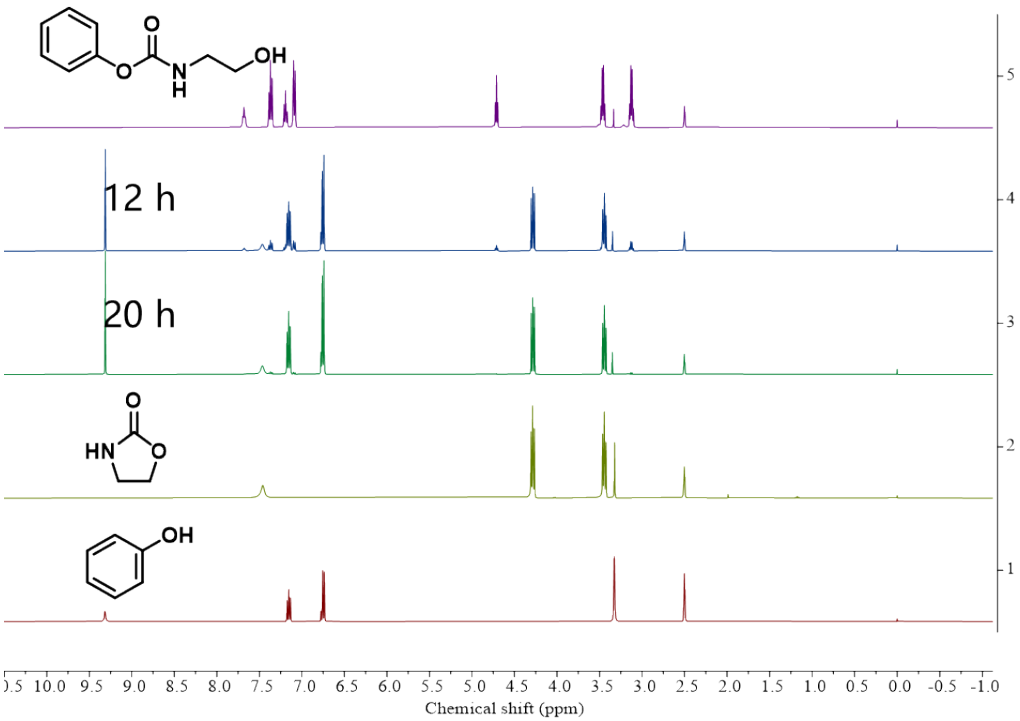


Figure S2. ^{1}H NMR spectra changes of ring-opened product **1** in DMSO-d_6.

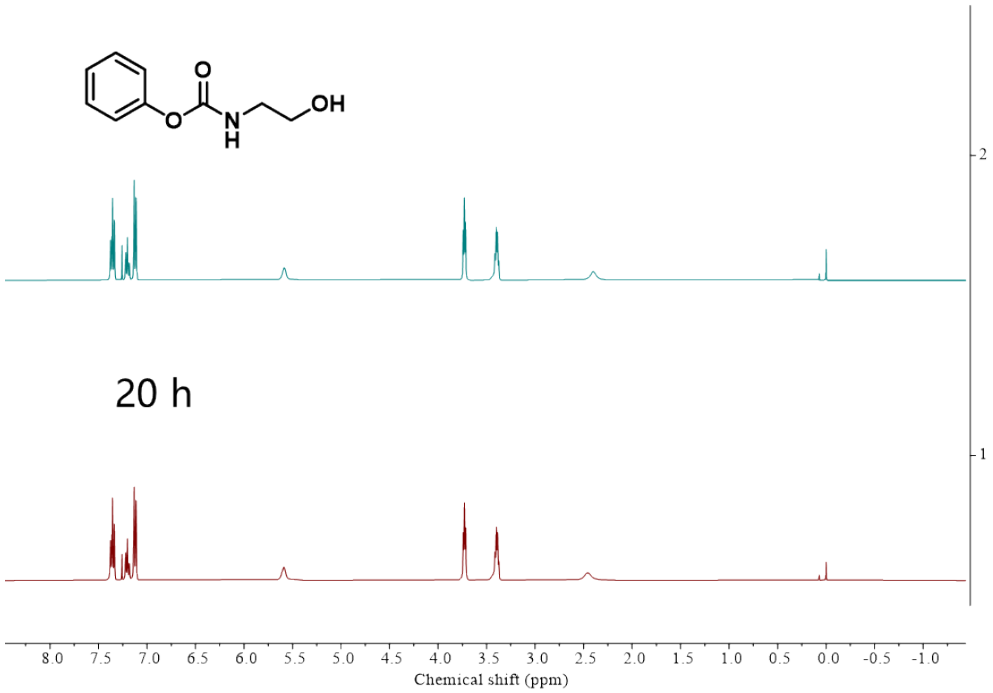


Figure S3. ^{1}H NMR spectra changes of ring-opened product **1** in $CDCl_3$.

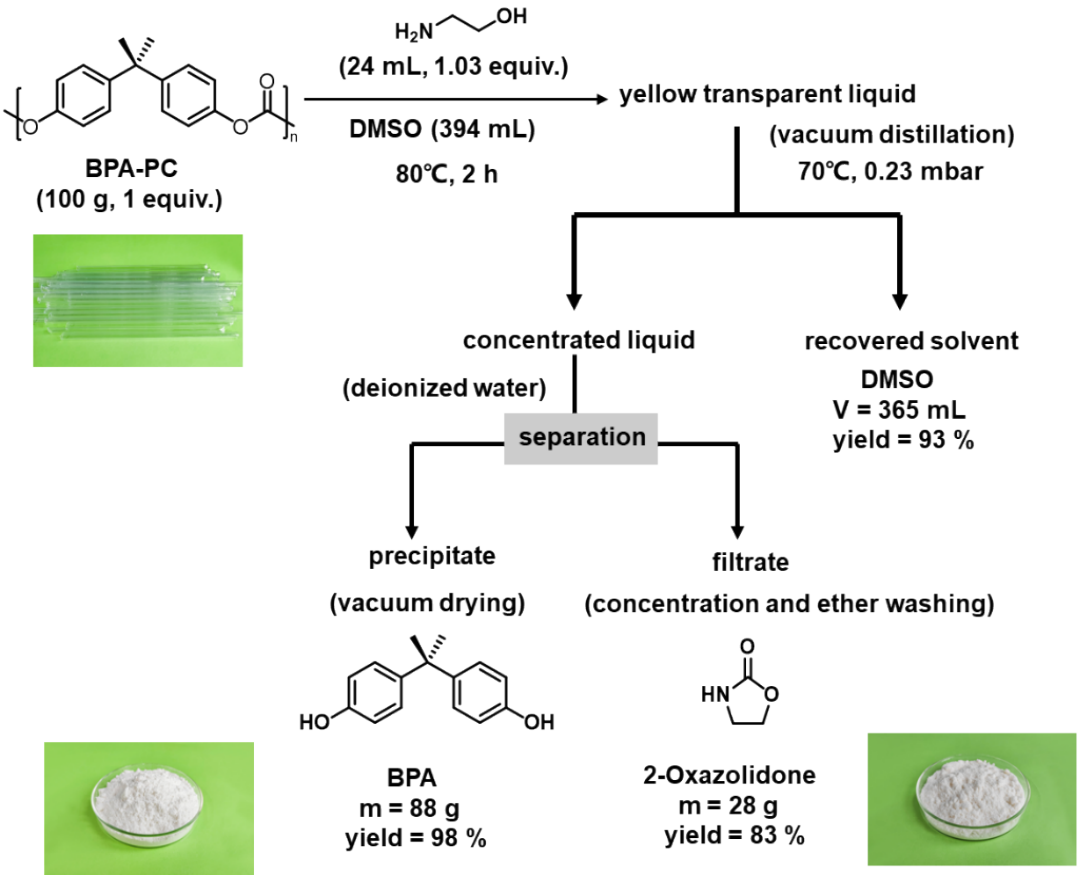


Figure S4. The gram-scale depolymerization of BPA-PC tube by using ethanolamine in DMSO.

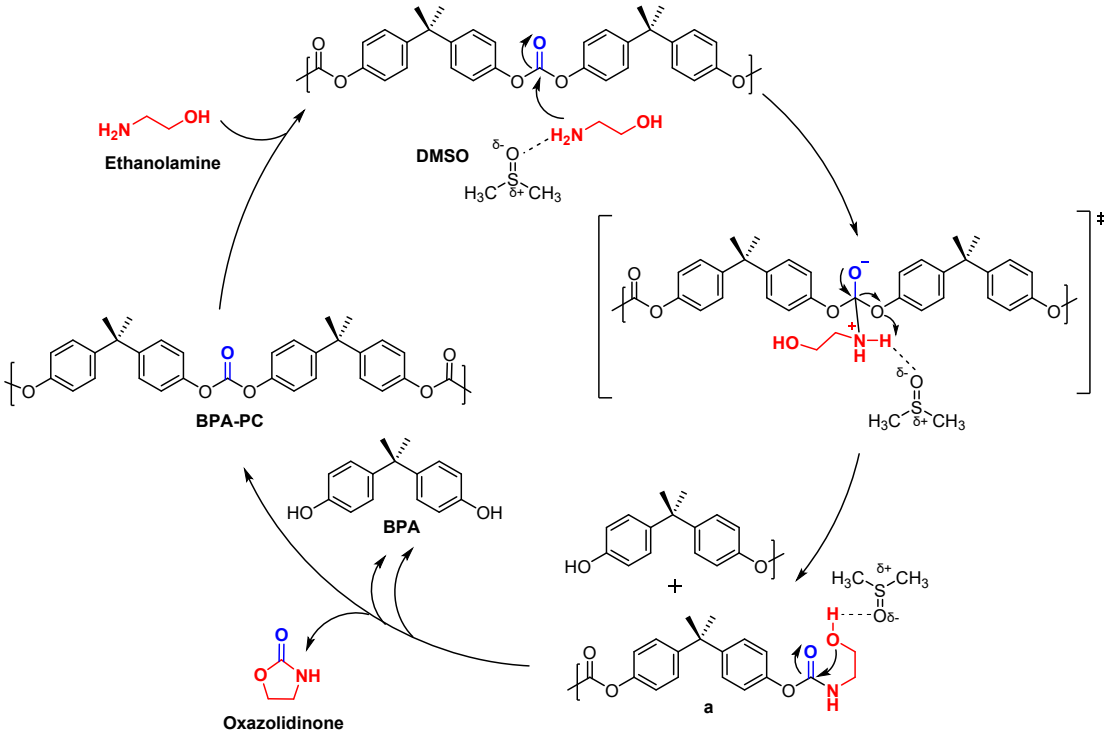
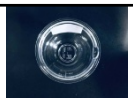
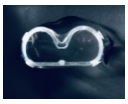
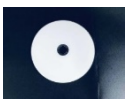
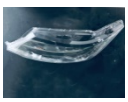
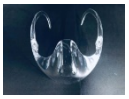


Figure S5. Proposed mechanism.

Table S3. Results of PC materials depolymerization with ethanolamine.

Entry[a]	Material	Name	Time (h)	Conv.[b] (%)	BPA[b] (%)	2-Oxazolidone[b] (%)
1		bowl	2	99	99	99
2		goggle	2	99	99	99
3		frame	2	99	97	97
4		disc	2	99	94	93
5		lampshade	2	99	99	99
6		bucket	3	99	98	99

7		veil	2	99	99	99
8		tube	3	99	99	99

a. The degradation of BPA-PC commodities. Depolymerization conditions: BPA-PC commodities (254 mg, 1 mmol based on BPA unit), ethanolamine (61 μL, 1 mmol) in DMSO (1 mL) at 50°C. b. Determined by ^{1}H NMR spectroscopy in DMSO-d_6 using dibromomethane (145 μL, 2 mmol) as an internal standard, acetic acid as quencher.

Table S4. The hardness of BPA-PC materials.

Sample	bowl	goggle	frame	disc	lampshade	bucket	veil	tube
Hardness/HD	79	68	82	84	79	62	74	67

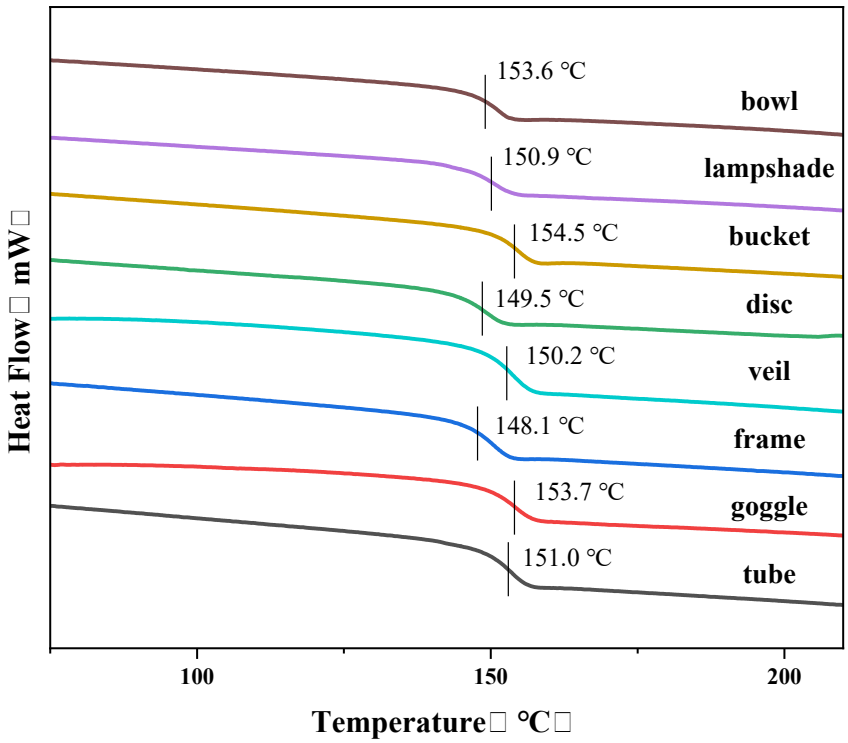


Figure S6. DSC analysis of glass transition temperature of bowl, lampshade, bucket, disc, veil, frame, goggle and tube.

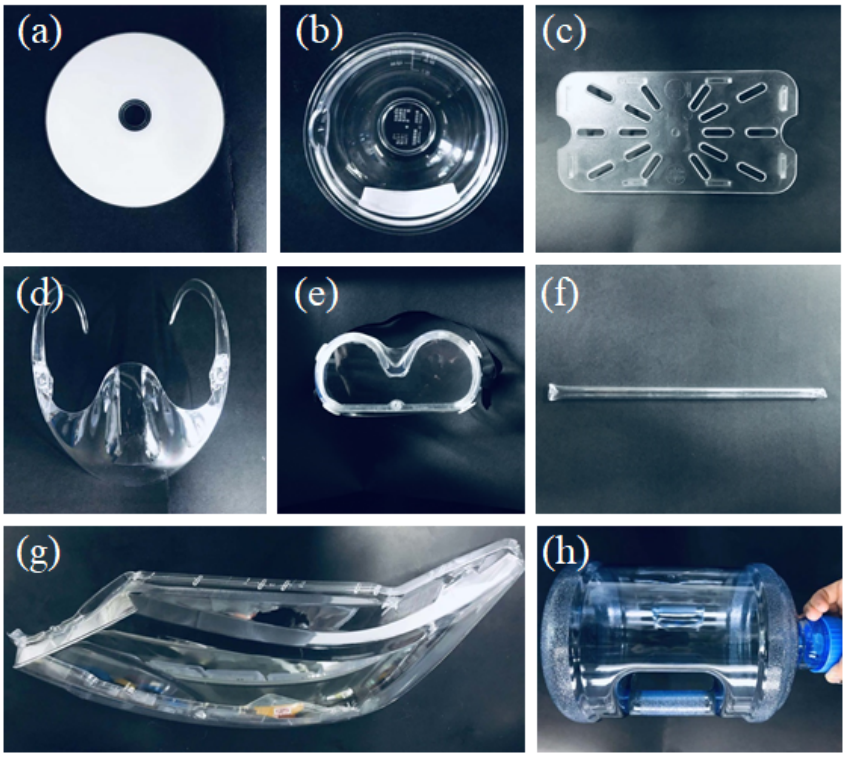


Figure S7. BPA-PC samples: (a) disc, (b) bowl, (c) fixed frame, (d) veil, (e) goggle, (f) tube, (g) lampshade, (h) bucket.

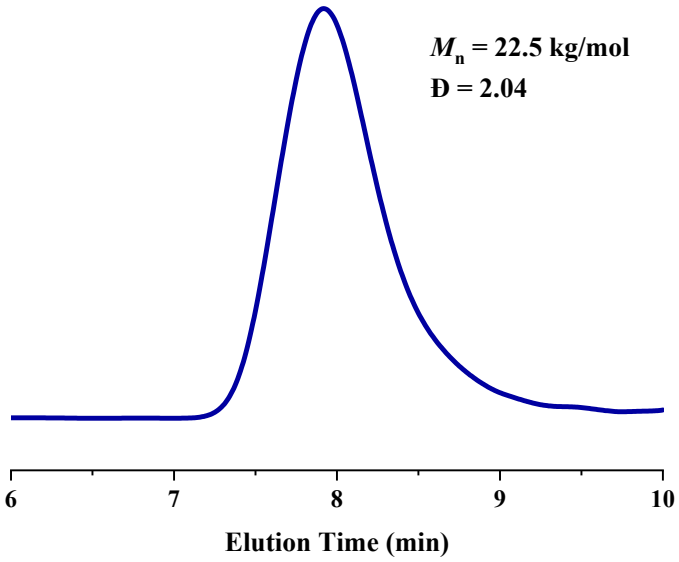


Figure S8. GPC analysis for BPA-PC disc.

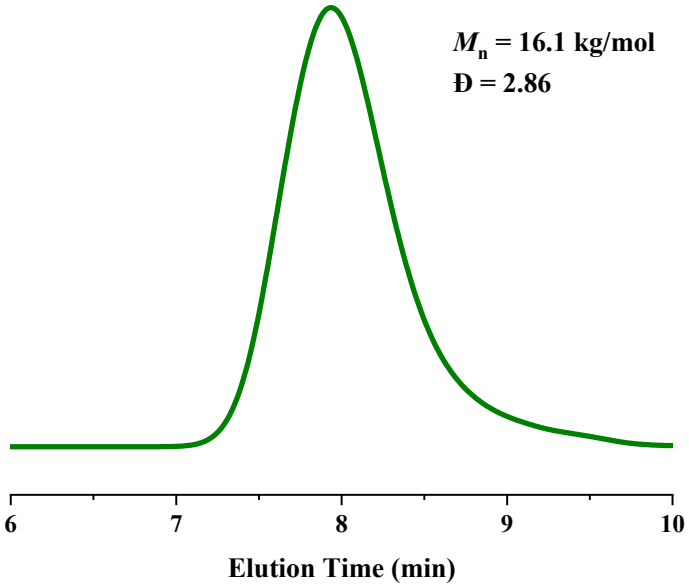


Figure S9. GPC analysis for BPA-PC bowl.

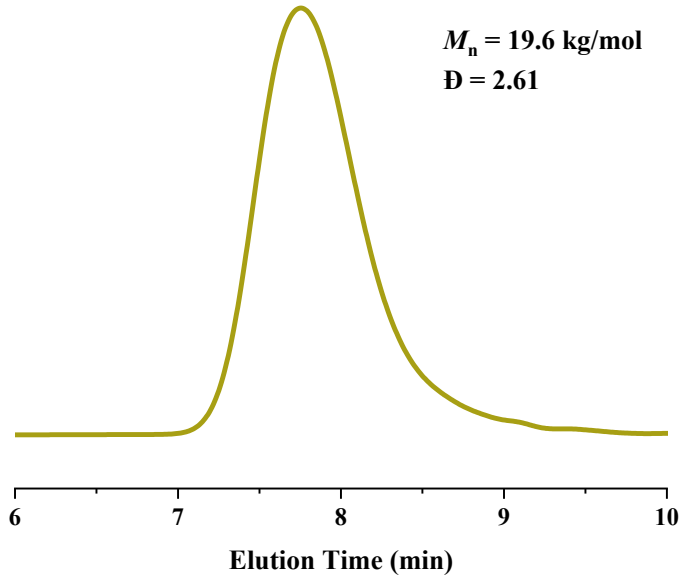


Figure S10. GPC analysis for BPA-PC fixed frame.

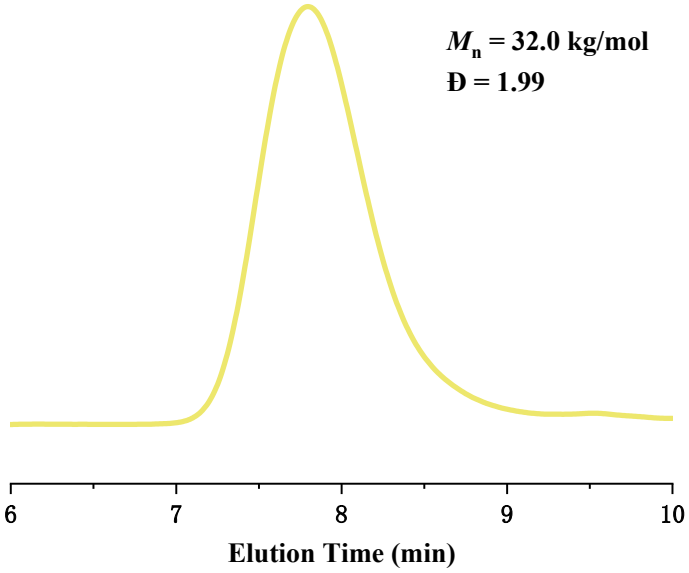


Figure S11. GPC analysis for BPA-PC veil.

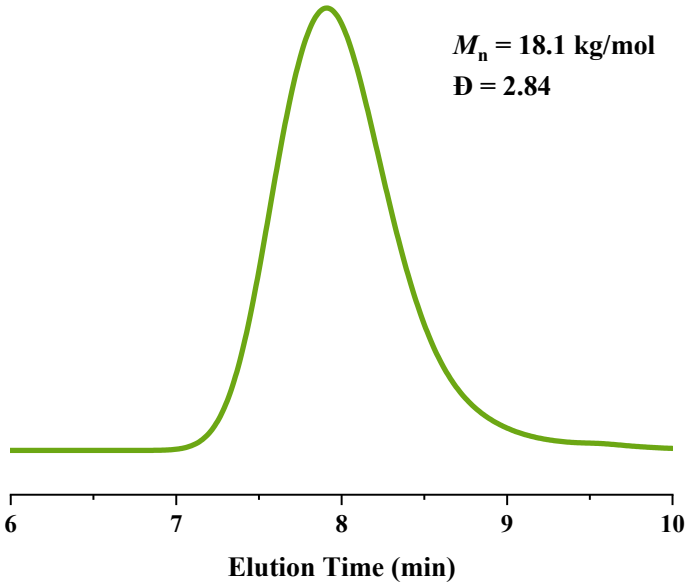


Figure S12. GPC analysis for BPA-PC goggle.

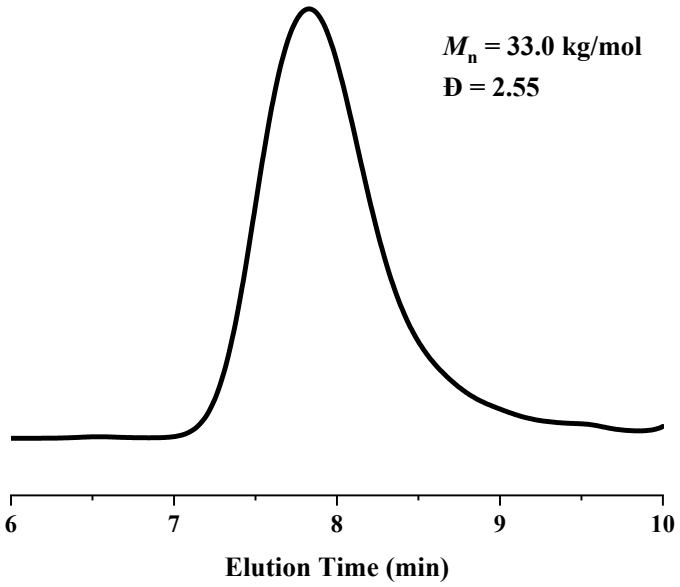


Figure S13. GPC analysis for BPA-PC tube.

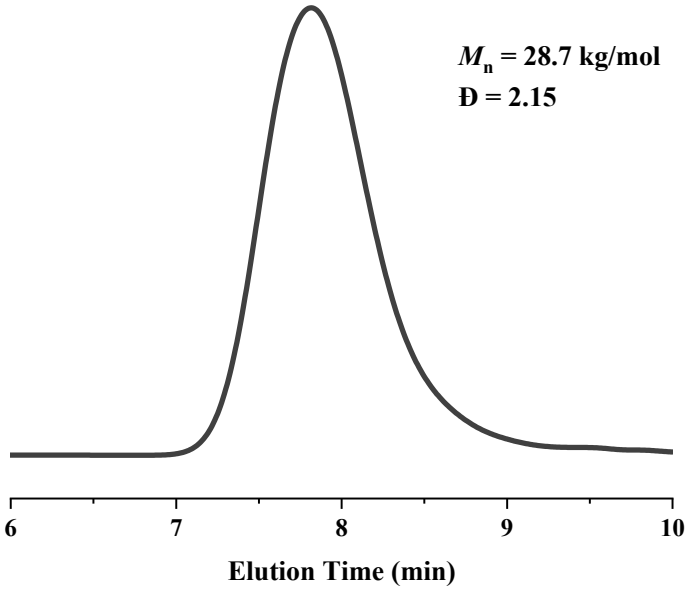


Figure S14. GPC analysis for BPA-PC lampshade.

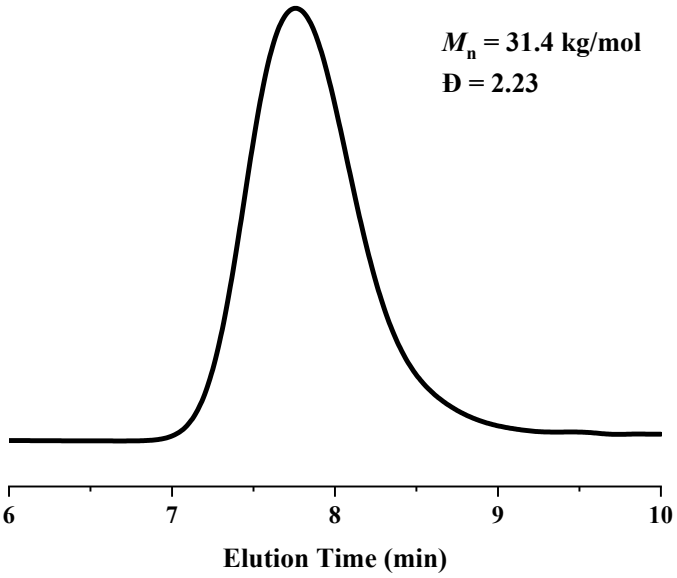


Figure S15. GPC analysis for BPA-PC bucket.

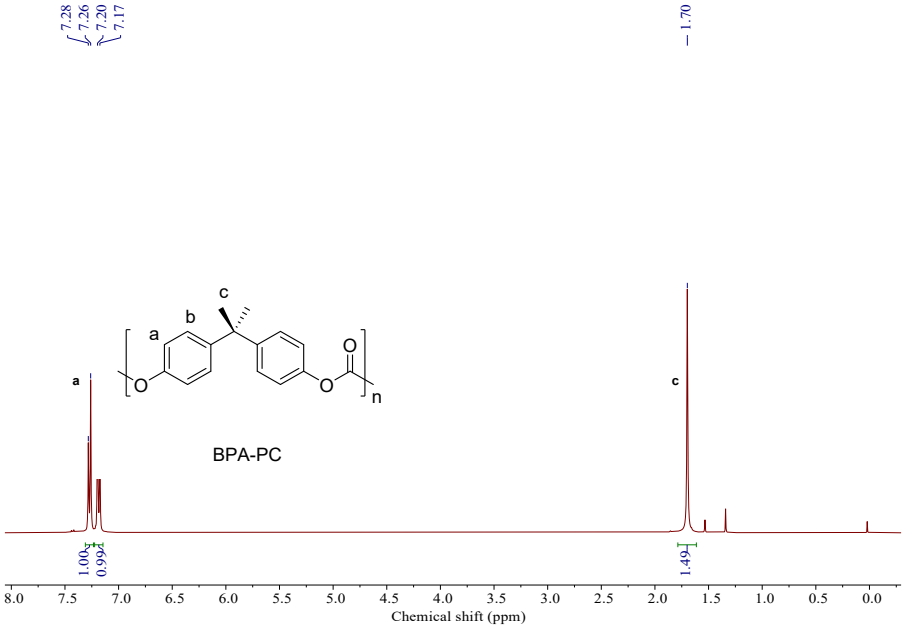


Figure S16. ^{1}H NMR spectrum of BPA-PC (400 MHz, Chloroform-*d*, 298 K).

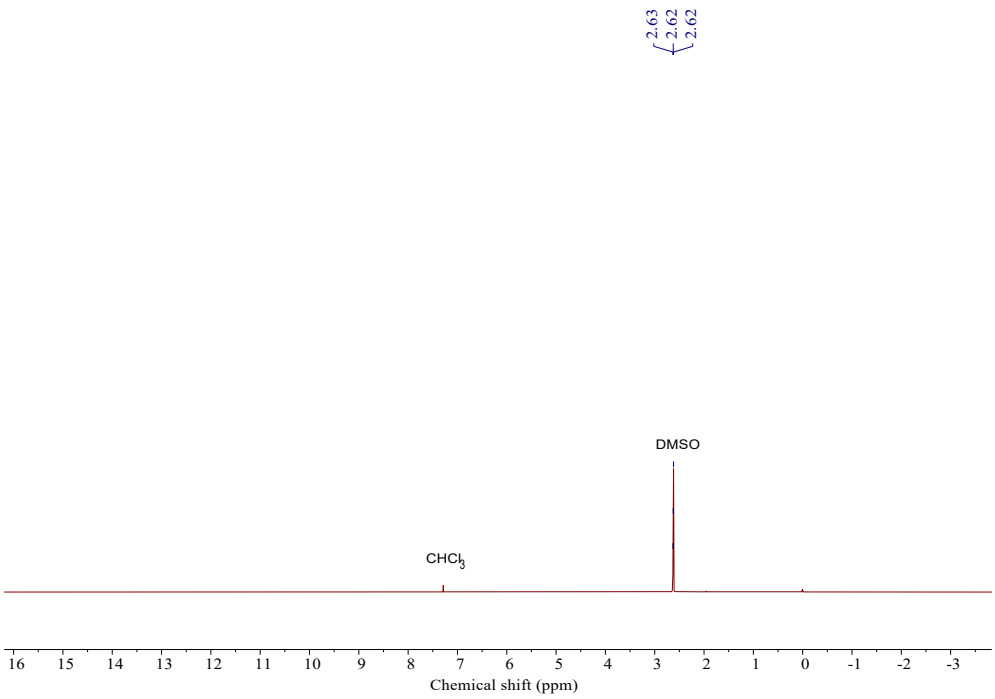


Figure S17. ^{1}H NMR spectrum of recovered DMSO (400 MHz, Chloroform-*d*, 298 K).

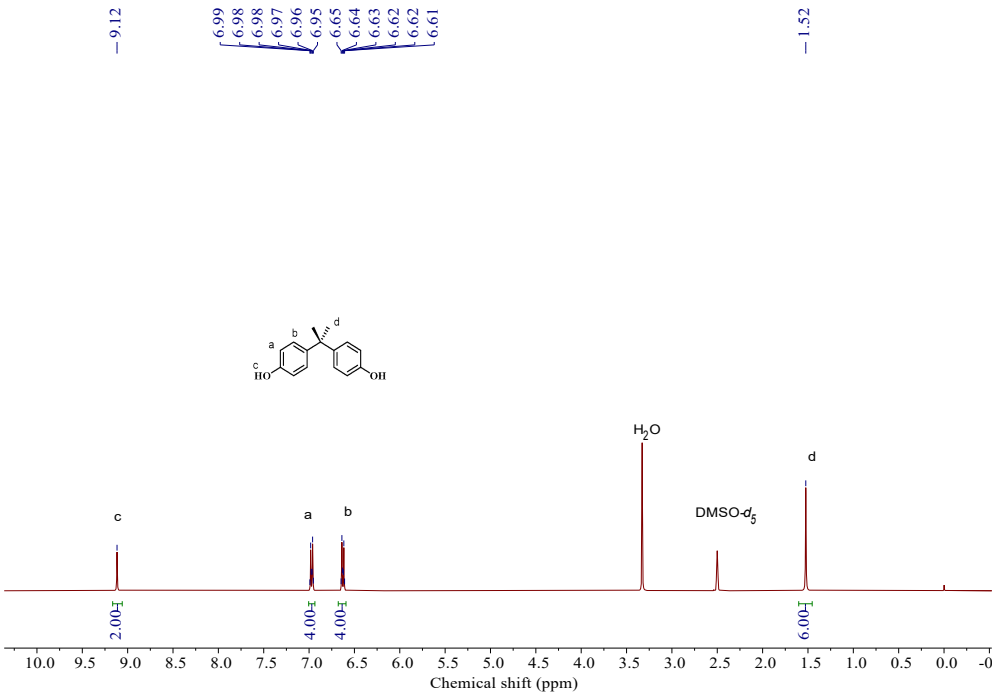


Figure S18. ^{1}H NMR spectrum of recovered BPA (400 MHz, DMSO-d_6, 298 K).

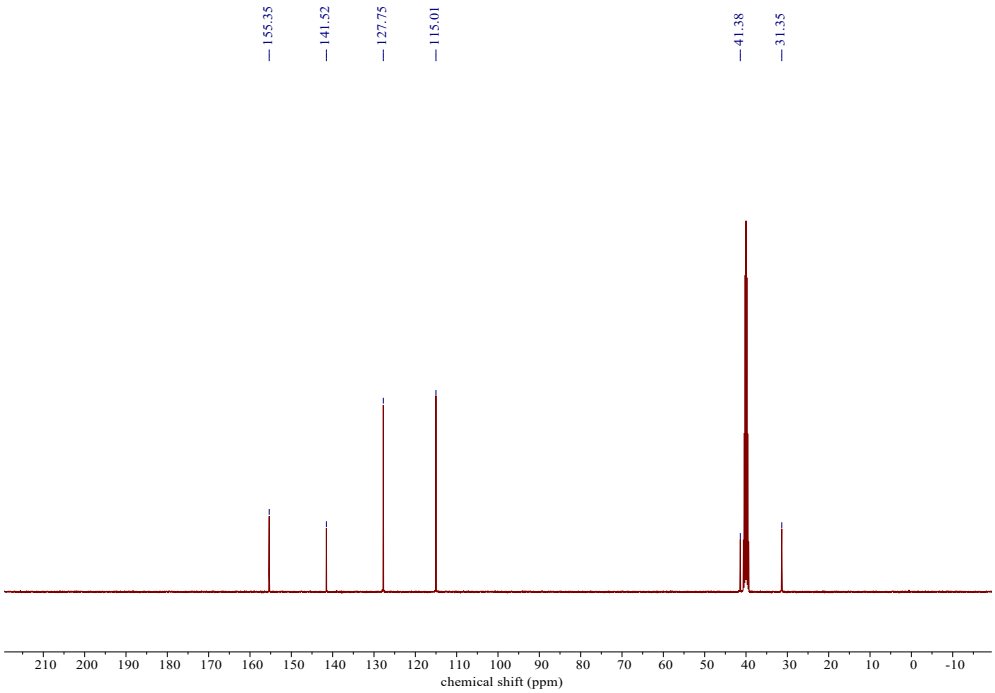


Figure S19. ^{13}C NMR spectrum of recovered BPA (400 MHz, DMSO-d_6, 298 K).

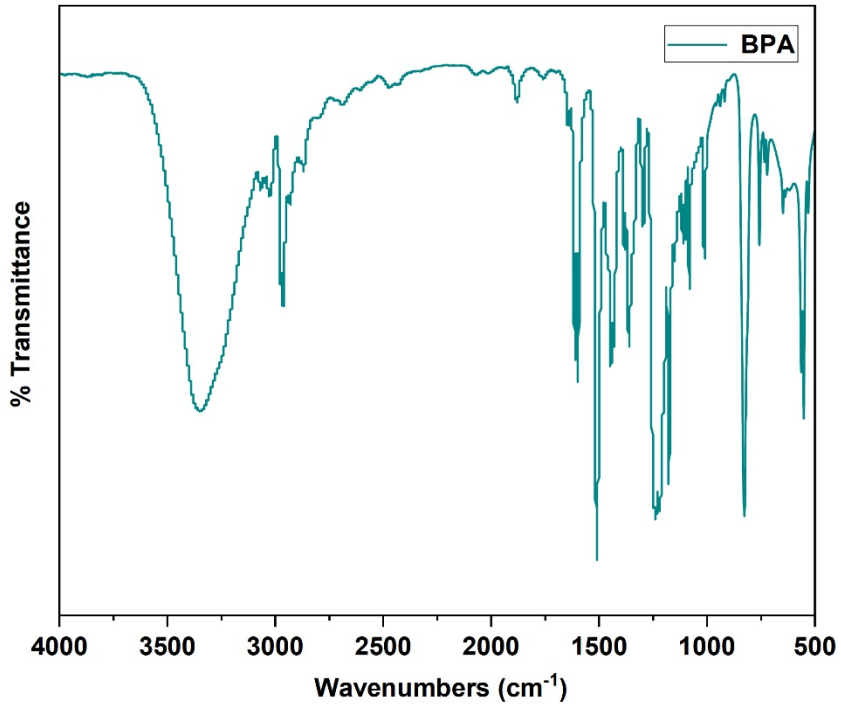
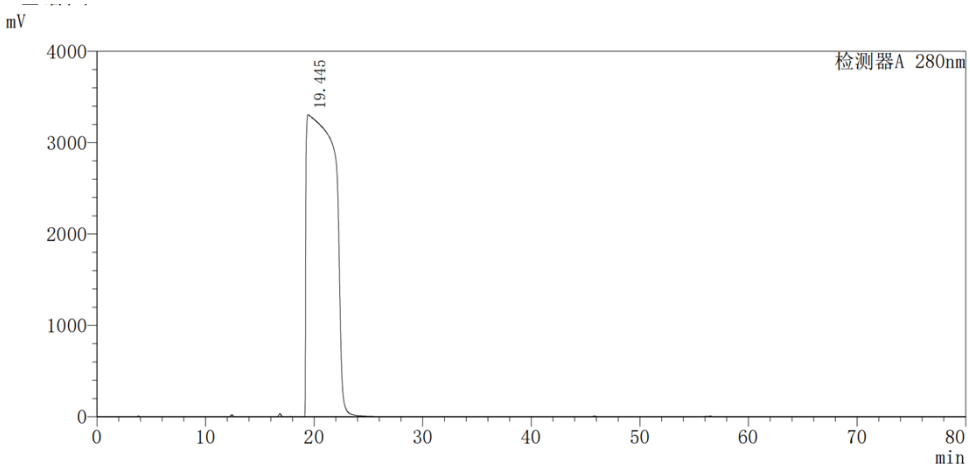


Figure S20. IR spectrum of recovered BPA.



Methods: column, C18; flow rate, 1 mL/min;

eluent, 0-30 min: (0.1%) phosphoric acid/acetonitrile/methanol = 65/25/10; 30-50 min: (0.1%) phosphoric acid/acetonitrile/methanol = 50/40/10; 50-60 min: (0.1%) phosphoric acid/acetonitrile/methanol = 30/50/20; 60-80 min: (0.1%) phosphoric acid/acetonitrile/methanol = 0/70/30;

detector, UV (280 nm).

Figure S21. HPLC analysis of BPA.

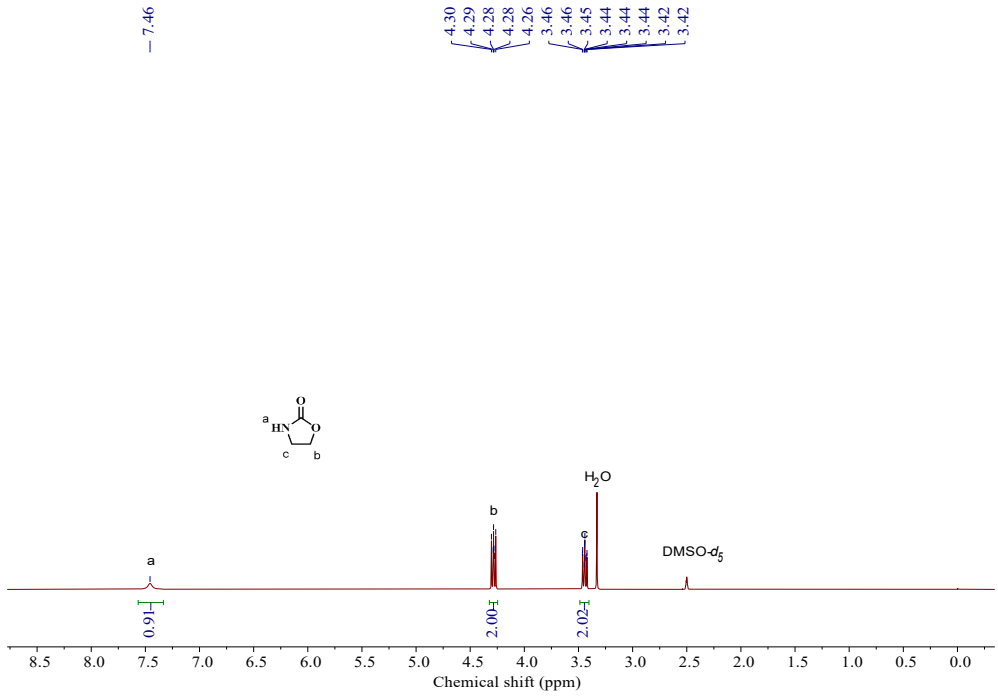


Figure S22. ^{1}H NMR spectrum of recovered 2-oxazolidone (400 MHz, DMSO-d_6, 298 K).

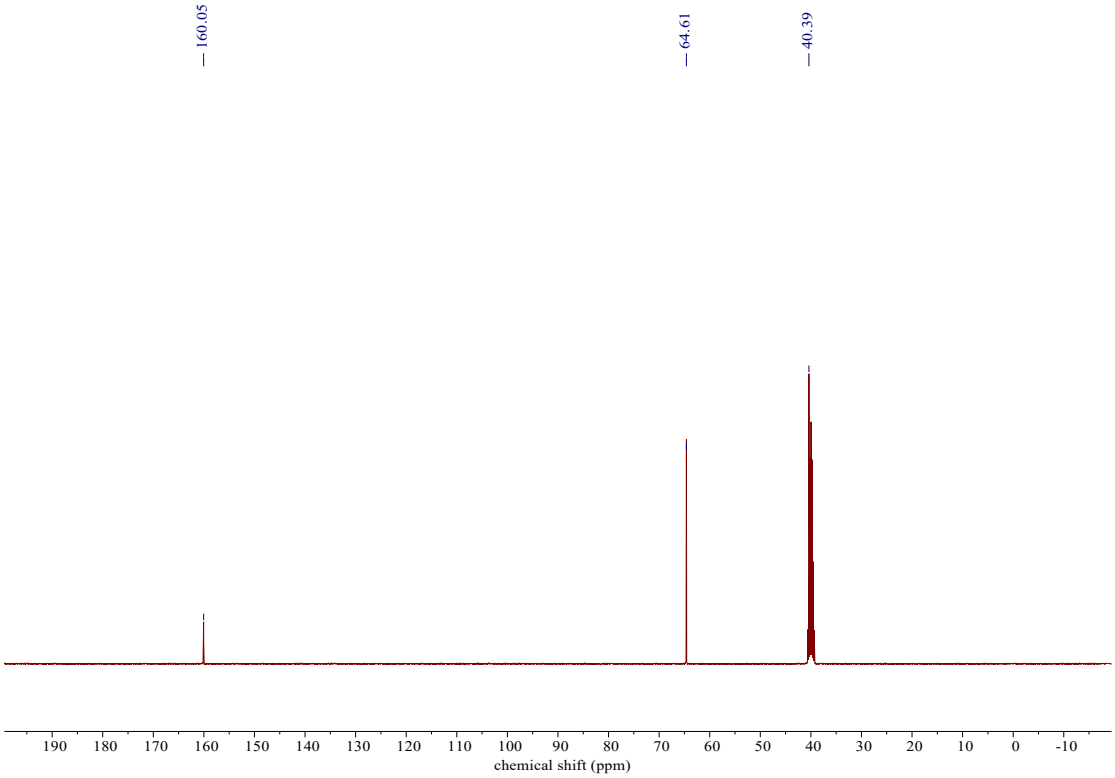


Figure S23. ^{13}C NMR spectrum of recovered 2-oxazolidone (400 MHz, DMSO-d_6, 298 K).

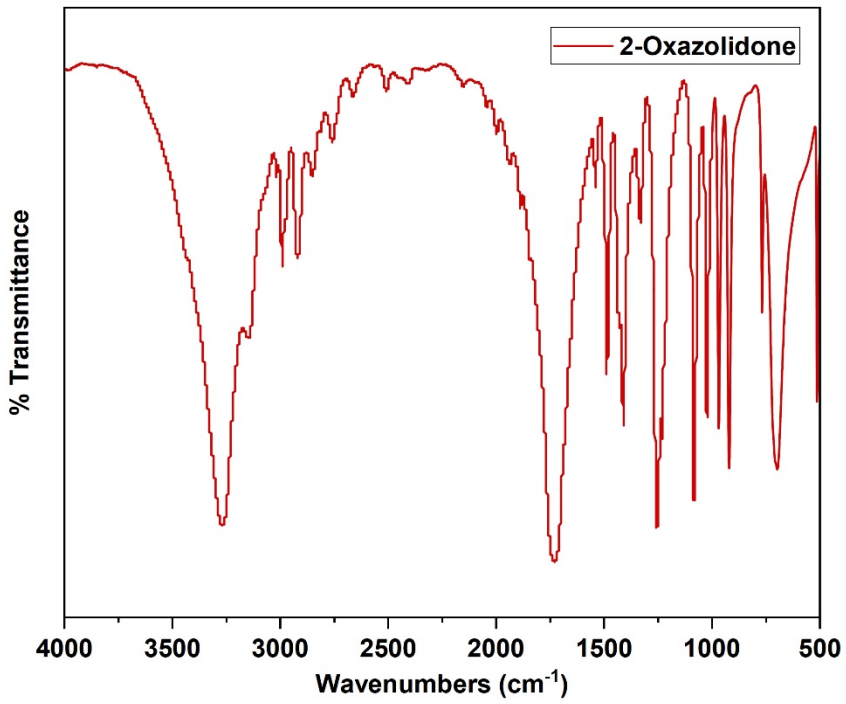


Figure S24. IR spectrum of recovered 2-oxazolidone.

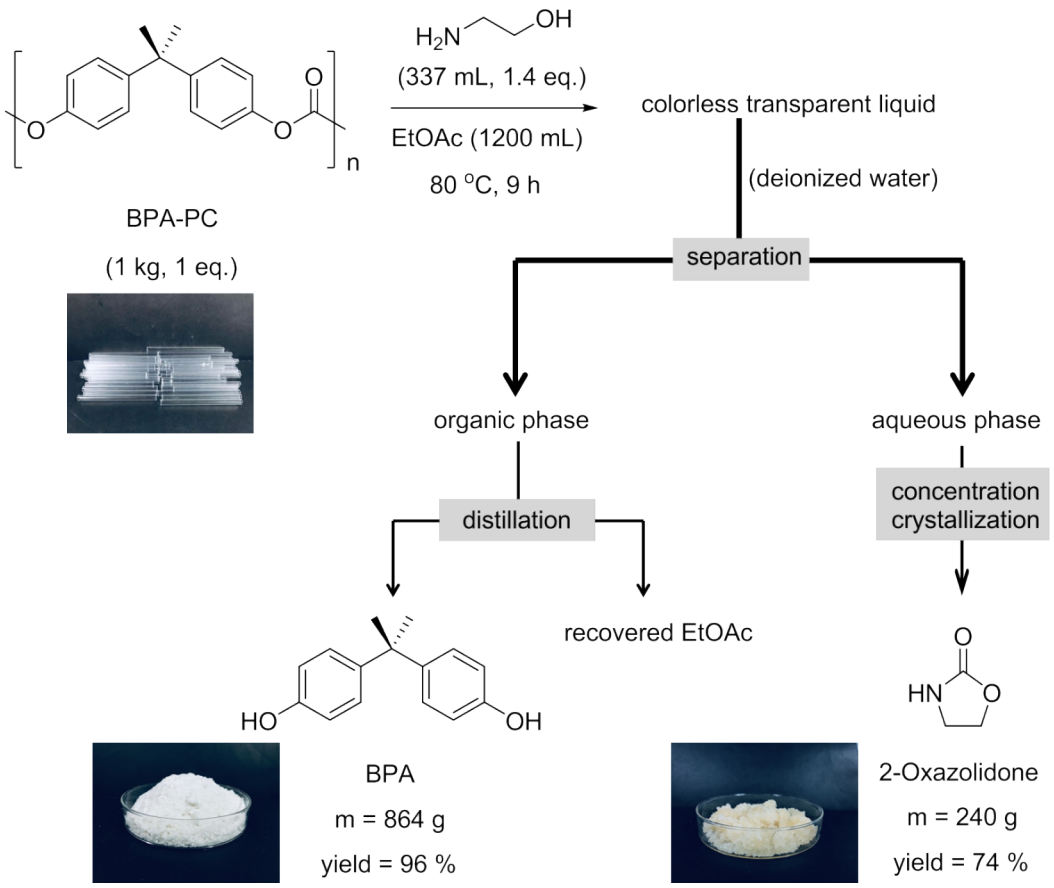


Figure S25. The kilogram-scale depolymerization of BPA-PC tube by using ethanolamine. BPA-PC (m = 1 kg, 1 equiv.), ethanolamine (337 mL, 1.4 equiv.), EtOAc (1200 mL).

Table S5. The prices of ethanolamine and 2-oxazolidone.

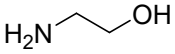
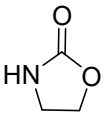
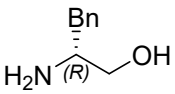
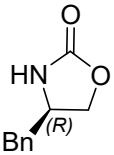
Chemical	Structure	Brand	Grades	Price
Ethanolamine		TCI	500 g	$ 23.00
2-Oxazolidone		TCI	500 g	$ 284.00
D-Phenylalaninol		TCI	25 g	$ 178.00
(R)-4-Benzyl-2-oxazolidinone		TCI	25 g	$ 322.00

Table S6. The transmittance of regenerated BPA-PC and original BPA-PC.

Entry	BPA-PC	Transmittance/%
1	Original BPA-PC tube	99.10
2	Prepared from recovered BPA	98.17
3	Prepared from commercialized BPA	98.19

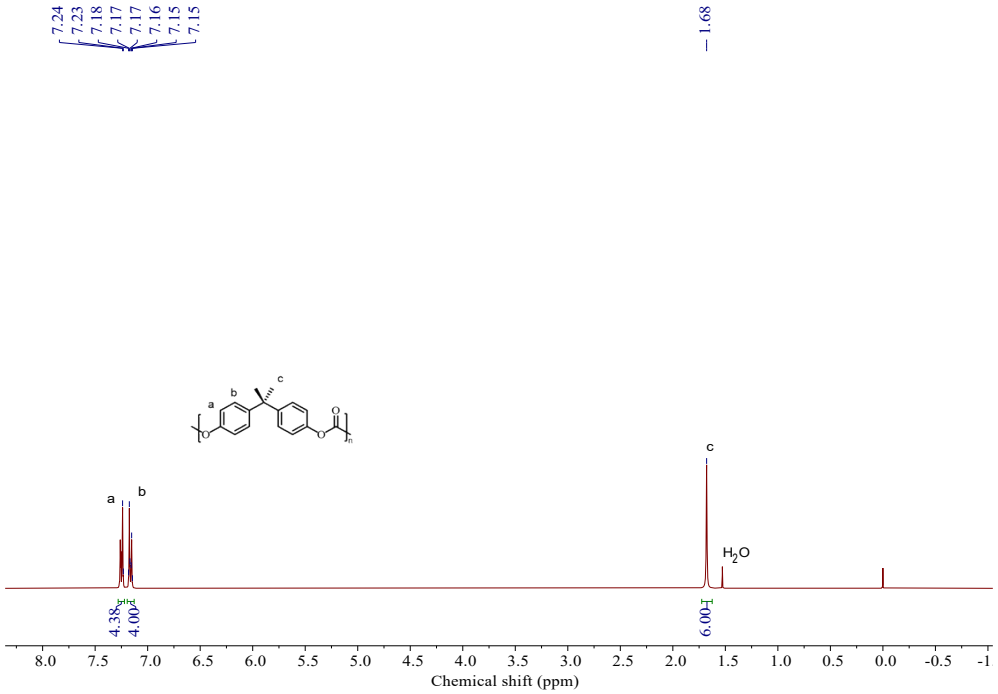


Figure S26. ^{1}H NMR spectrum of BPA-PC synthesized from recycled BPA. (400 MHz, Chloroform-*d*, 298 K).

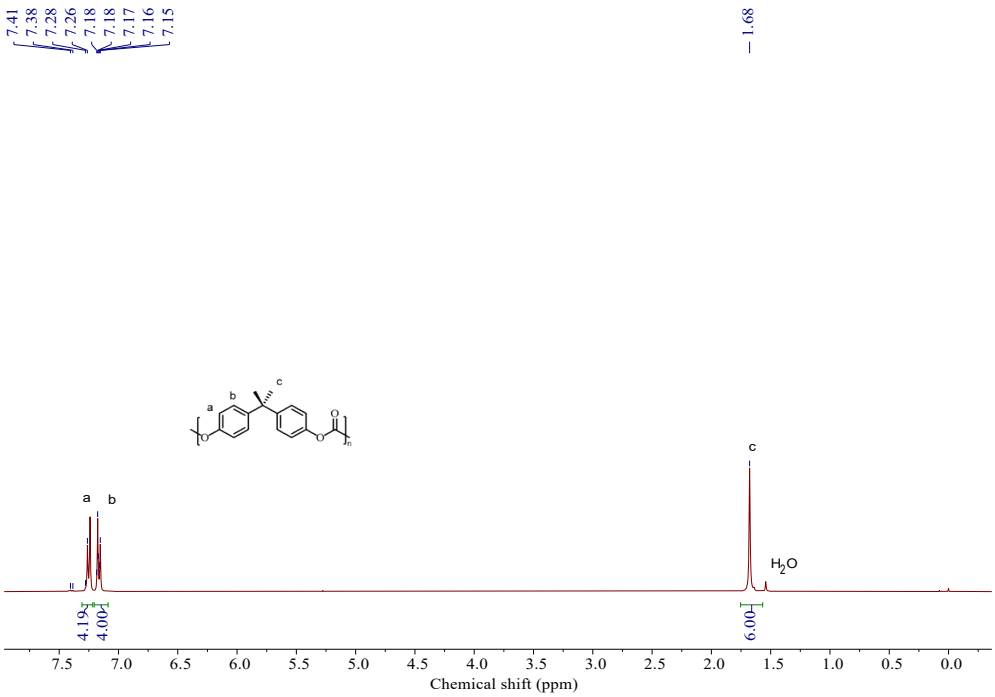


Figure S27. ^{1}H NMR spectrum of BPA-PC synthesized from commercialized BPA. (400 MHz, Chloroform-*d*, 298 K).

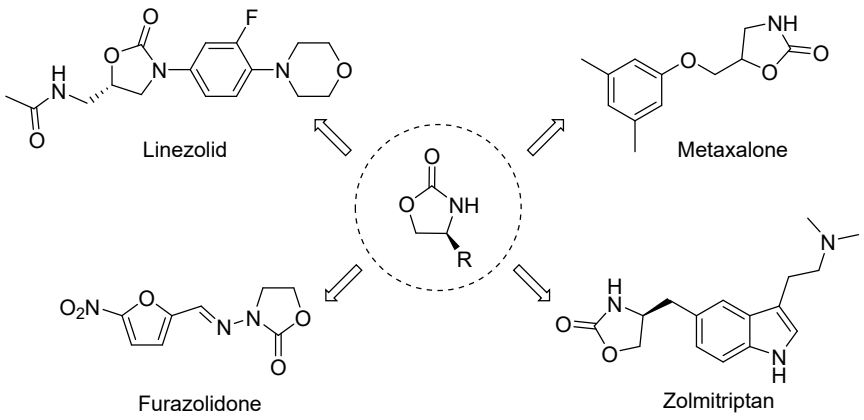
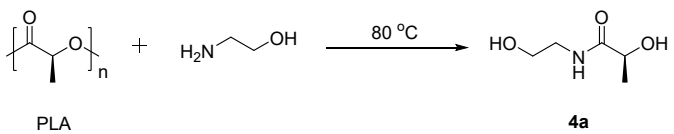


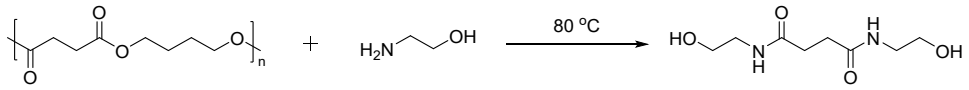
Figure S28. Oxazolidinones were important synthetic intermediate in the fields of medicine and pesticides.

General procedure for the depolymerization of PLA cup



The depolymerization of PLA cup was carried out in a Schlenk flask at 80°C. PLA cup (2 g) was added first. Ethanolamine (5 mL) wa then added. The reaction was monitored by ^{1}H NMR spectrum, aliquot was taken for ^{1}H NMR spectroscopic analysis. After 1 h, we calculated that the conversion was 100 %. The solvent was removed under vacuum. Removed excess ethanolamine by vacuum distillation to obtain oily liquid product **4a** (3.58 g, 97%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.60 (t, J = 5.8 Hz, 1H), 5.49 (s, 1H), 4.70 (s, 1H), 3.95 (q, J = 6.8 Hz, 1H), 3.40 (t, J = 6.0 Hz, 2H), 3.14 (qd, J = 6.0, 2.5 Hz, 2H), 1.19 (d, J = 6.8 Hz, 3H).[1]

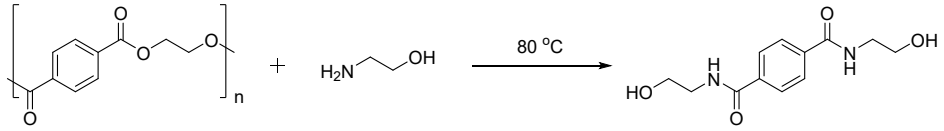
General procedure for the depolymerization of PBS straw



PBS **4b**

The depolymerization of PBS straw was carried out in a Schlenk flask at 80°C. PBS straw (2 g) was added first. Ethanolamine (5 mL) were then added. The reaction was monitored by ^{1}H NMR spectrum, aliquot was taken for ^{1}H NMR spectroscopic analysis. After 5 h, we calculated that the conversion was 100%. Dichloromethane was added to the reaction system, then filtered, the filtered solid was vacuum dried to remove residual dichloromethane to obtain a pure white solid product **4b** (2.32 g, 98%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.79 (t, J = 5.6 Hz, 2H), 4.61 (t, J = 5.4 Hz, 2H), 3.41 – 3.35 (q, 4H), 3.08 (q, J = 6.0 Hz, 4H), 2.29 (s, 4H).

General procedure for the depolymerization of PET bottle



PET **4c**

The depolymerization of PET bottle was carried out in a Schlenk flask at 80°C. PET bottle (2 g) was added first. Ethanolamine (5 mL) were then added. The reaction was monitored by ^{1}H NMR spectrum, aliquot was taken for ^{1}H NMR spectroscopic analysis. After 24 h, we calculated that the conversion was 100%. Dichloromethane was added to the reaction system, then filtered, the filtered solid was vacuum dried to

remove residual dichloromethane to obtain a pure white solid product **4c** (2.53 g, 96%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.54 (t, J = 5.6 Hz, 2H), 7.91 (s, 4H), 4.74 (t, J = 5.6 Hz, 2H), 3.52 (q, J = 5.9 Hz, 4H), 3.34 (d, J = 6.3 Hz, 4H). [2]

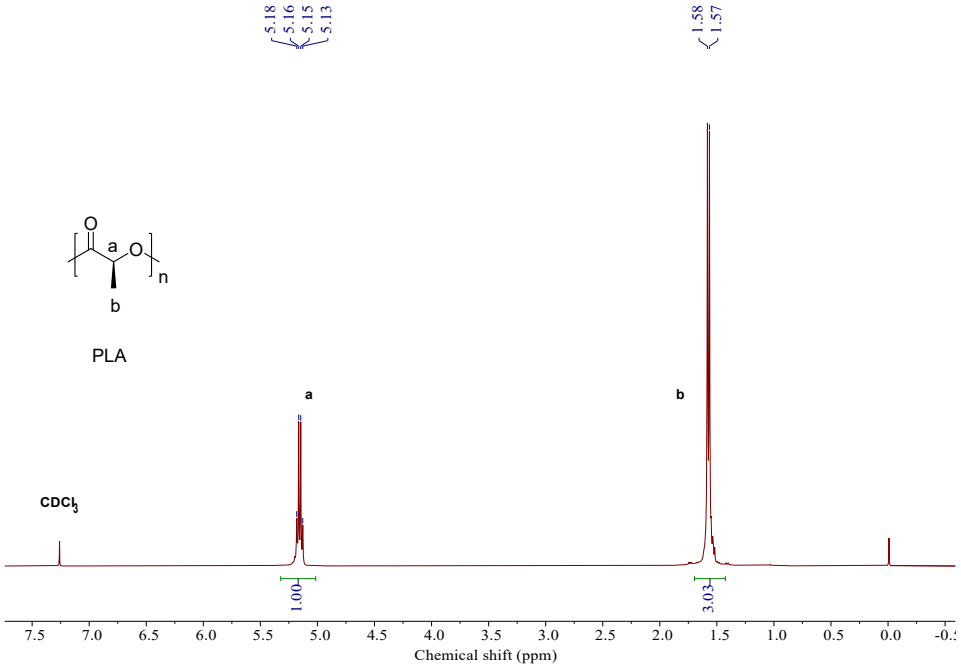


Figure S29. ^{1}H NMR spectrum of PLA cup. (400 MHz, Chloroform-*d*, 298 K).

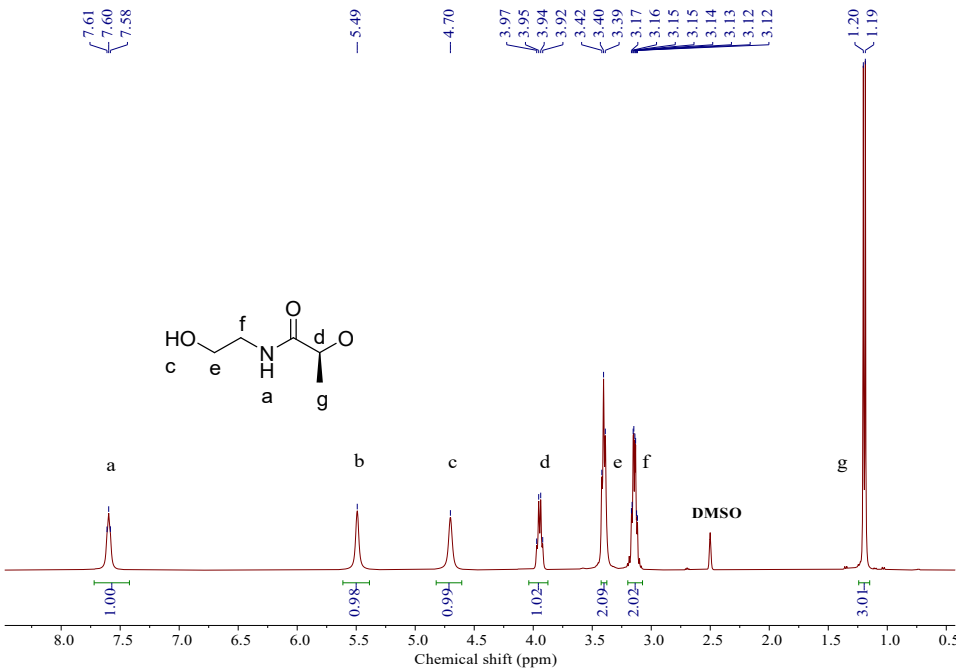


Figure S30. ^{1}H NMR spectrum of PLA depolymerization product (400 MHz, DMSO-

d_6, 298 K).

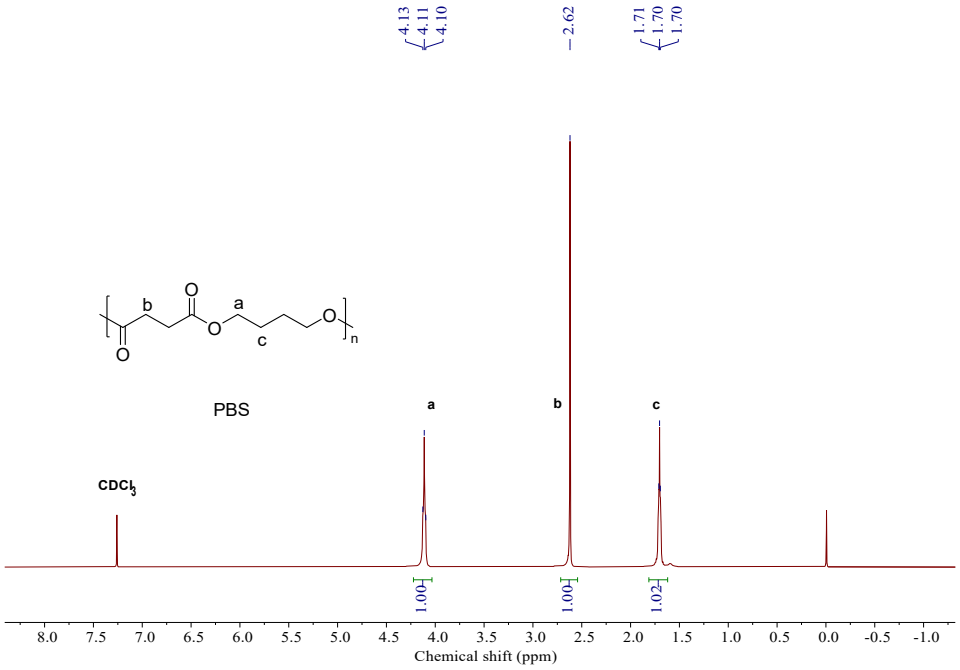


Figure S31. [1]H NMR spectrum of PBS straw. (400 MHz, Chloroform-*d*, 298 K).

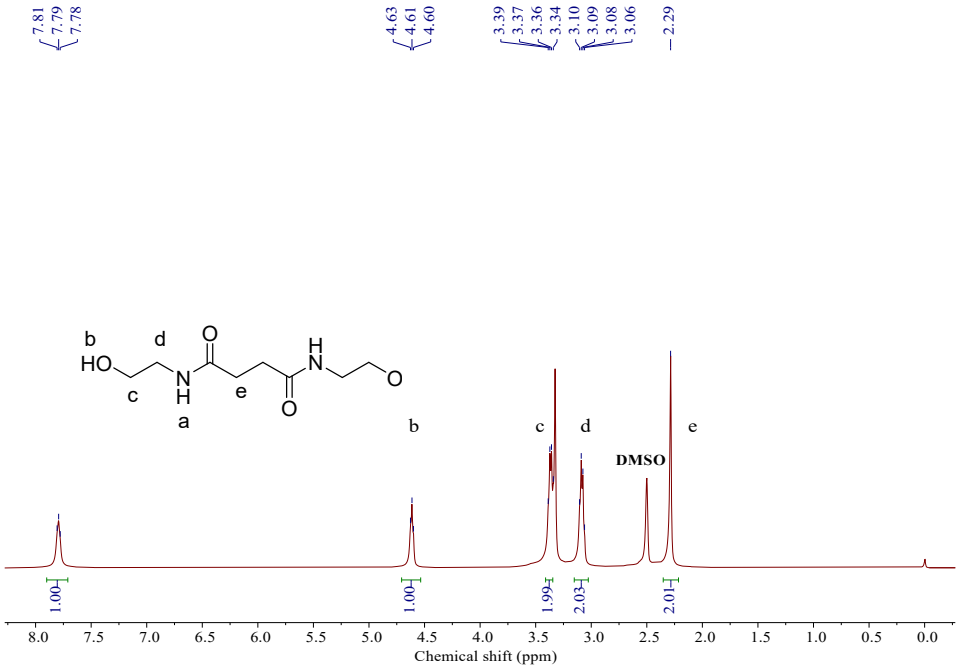


Figure S32. [1]H NMR spectrum of PBS depolymerization product (400 MHz, DMSO-d_6, 298 K).

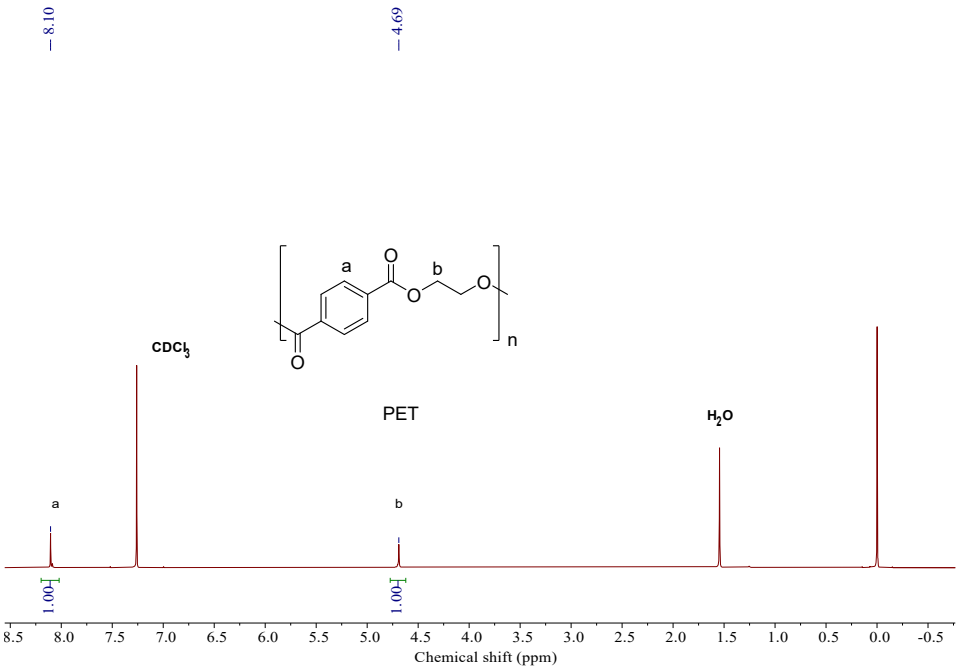


Figure S33. [1]H NMR spectrum of PET bottle. (400 MHz, Chloroform-*d*, 298 K).

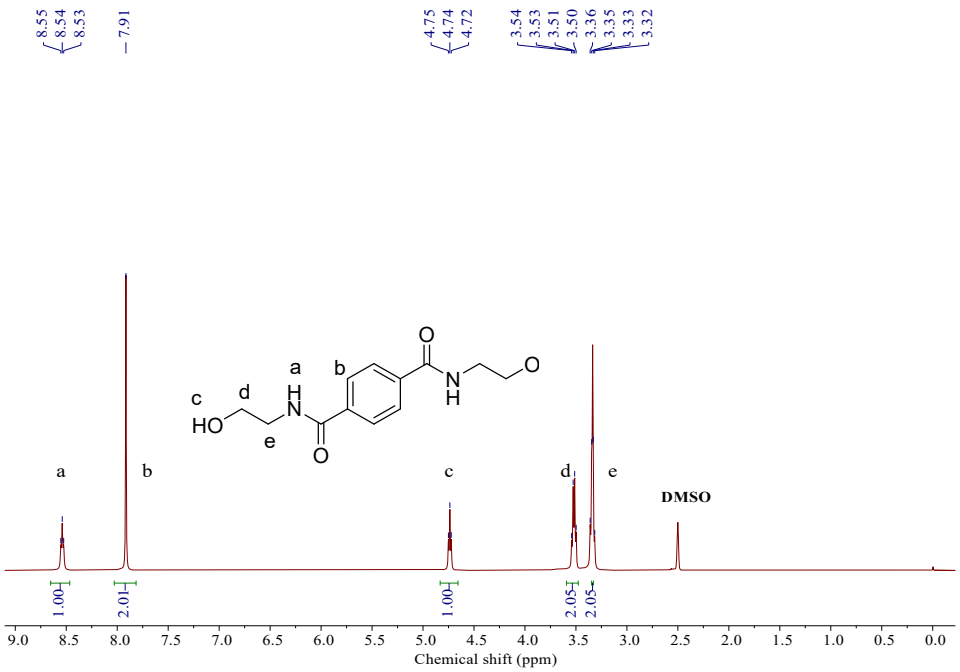


Figure S34. [1]H NMR spectrum of PET depolymerization product (400 MHz, DMSO-d_6, 298 K).

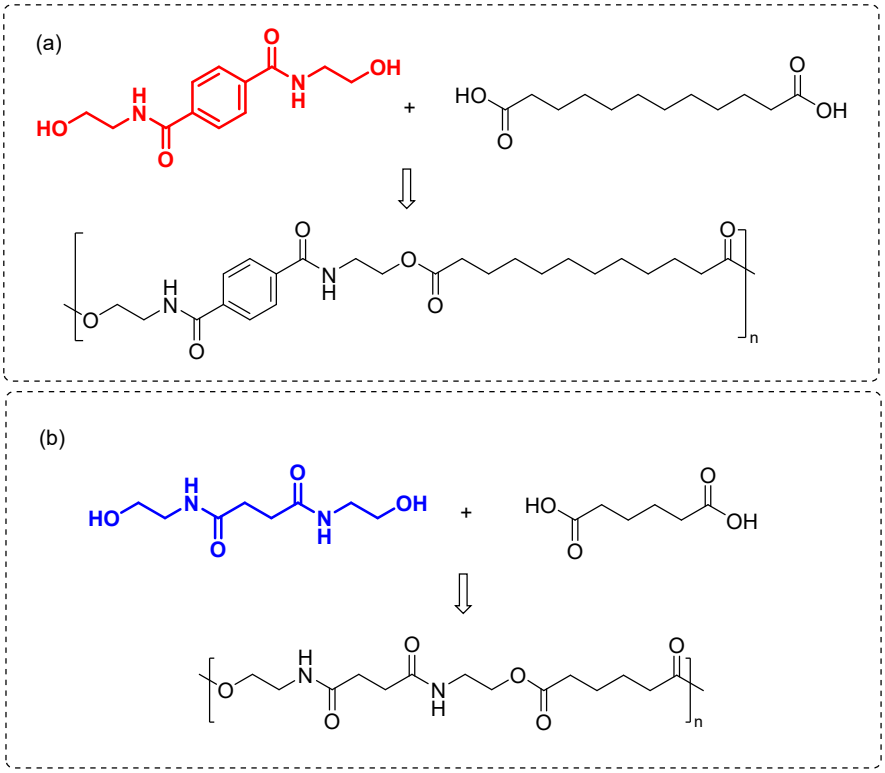


Figure S35. The application of aminolysis products.[3,4]

References

[1] Y. Nishikawa, K. Takemoto, K. Matsuda, R. Tanaka, A. Arashima, K. Ito, Y. Kamezawa, Y. Hori, O. Hara, *Org. Lett.,* 2018, **20**, 3367-3371.

[2] S. R. Shukla, A. M. Harad, *Polym. Degrad. Stabil.,* 2006, **91**, 1850-1854.

[3] J. Natarajan, G. Madras and K. Chatterjee, *ACS Appl. Mater. Interfaces*, 2017, **9**, 28281-28297.

[4] T. H. N. Nguyen, F. Balligand, A. Bormann, V. Bennevault and P. Guégan, *Eur. Polym. J.*, 2019, **121**, 10314.