

Efficient catalytic degradation of anhydride-cured epoxy resin by amphiphilic molecule catalysts

Ning Zhang^{a,b,d,1}, *Shaodi Wu*^{a,b,d,1}, *Chizhou Wang*^{a,b,d}, *Xiaojing Cui*^e, *Ting Zhao*^f, *Liye Yuan*^d,
Yongqin Qi^{a,b,d}, *Xianglin Hou*^{*a,b,d}, *Haibo Jin*^{*c}, *Tiansheng Deng*^{*a,b,d}

^a *Shanxi Engineering Research Center of Biorefinery, Institute of Coal Chemistry, Chinese Academy of Sciences, 27 South Taoyuan Road, Taiyuan 030001, China.*

^b *Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China.*

^c *Beijing Key Laboratory of Fuels Cleaning and Advanced Catalytic Emission Reduction Technology/College of New Materials and Chemical Engineering, Beijing Institute of Petrochemical Technology, Beijing 102617, China*

^d *CAS key laboratory of carbon materials, Institute of Coal Chemistry, Chinese Academy of Sciences, 27 South Taoyuan Road, Taiyuan 030001, China.*

^e *Department of Chemistry and Chemical Engineering, Taiyuan Institute of Technology, Taiyuan, Shanxi, 030008, P. R. China.*

^f *Key Laboratory of China Research Institute of Daily Chemistry Co., Ltd., Sinolight Corporation, Taiyuan, 030001, China.*

¹ *These authors contributed equally to this work.*

**E-mail: dts117@sxicc.ac.cn; jinhaibo@bipt.edu.cn; houxianglin@sxicc.ac.cn*

1. Experimental section

1.1 Materials

The anhydride-cured epoxy resin applied in this work was bisphenol-A diglycidyl ether epoxy resin (DGEBA) cured with methyl-tetrahydrophalic anhydride (ACEP) and cross-linked by ester bonds, which was provided by CAS Key Laboratory of Carbon Materials, Institute of Coal Chemistry, Chinese Academy of Sciences. DGEBA (grade: C204, epoxy value: 0.5) and methyl-tetrahydrophalic anhydride were purchased from Tianjin Sigu Synthetic Material Co., LTD. Dodecylbenzene sulfonic acid (DBSA, 90%), p-toluenesulfonic acid monohydrate (PTSA, $\geq 98.5\%$) and aluminum chloride (AlCl_3 , 98%) were purchased from Aladdin. Methanesulfonic acid (MSA, 99.5%), zinc chloride (ZnCl_2 , 98%), deuterated acetone (acetone- d_6 , D, 99.9%+0.03% (V/V) TMS) and deuterated dimethyl sulfoxide (DMSO- d_6 , D, 99.9%) were purchased from Macklin. Acetone (AR) and phosphotungstic acid hydrate (HPW, AR) were purchased from Sinopharm Chemicals Reagent Co., Ltd. Linear aliphatic alcohol polyoxyethylene ether (A_{12}EO_5) with the purity higher than 99 % was purchased from Uself Chemical Technology Co., Ltd. (Shandong, China). The water applied in all of the experiments was distilled water.

1.2 Preparation of ACEP

DGEBA and methyl-tetrahydrophalic anhydride with the mass ratio of 5:4 (the molar ratio of epoxy group to methyl-tetrahydrophalic anhydride was 1:1) were fully mixed in a beaker at 80 °C by agitation. The mixture was transferred into a Teflon mold and cured. The curing condition was 90 °C for 2 h, 120 °C for 2 h, and 150 °C for 2 h. Then the resulting ACEP was cooled down to room temperature.

1.3 Degradation of ACEP

One piece of ACEP, and 4.0 g of aqueous solution with 0.28 mmol of catalyst were added into a Teflon-lined autoclave with a volume of 10 mL. For the ACEP piece of 0.35 (± 0.02) g, the dimension was ca. 8 mm \times 10 mm \times 4 mm, while for that of 0.55 (± 0.02) g, the dimension was about 12 mm \times 10 mm \times 4 mm. The degradation reaction was carried out at 170 °C.

ACEP is a thermoset resin, which cannot dissolve in either H₂O or the organic solvents. It exists as a solid in the organic solvents. When the ester bonds of ACEP was cleaved via hydrolysis with acidic DBSA, the degradation products including linear bisphenol-A diglycidyl ether and tetrahydromethylphthalic acid were obtained. Both of them dissolve well in acetone. The mass variation of ACEP before and after the decomposition process can be indicative of the degradation degree of ACEP. After reaction, the degradation system was dissolved in acetone. After filtration and washing for three times with acetone, the residue was dried at 80 °C. The degradation ratio was calculated based on the following formula:

$$\text{Degradation ratio (R}_d\text{, \%)} = \frac{W_0 - W_1}{W_0} \times 100\%$$

Where, W_0 and W_1 were the masses of raw ACEP and ACEP residue after degradation, respectively.

1.4 Adsorption experiment of catalyst on ACEP surface

0.069 mol/L of DBSA aqueous solution and PTSA aqueous solution were diluted 100 times separately. 0.5 g of ACEP (100 mesh) was added into the 100 mL of diluted solution at 30 °C. 4 mL of the mixture was sampled at different times and analyzed by a visible ultraviolet spectrophotometer.

1.5 The recycle of degradation system

0.55 g of ACEP piece and 4.0 g of 1.25 wt.% DBSA aqueous solution were added into the Teflon-lined autoclave. The degradation reaction was carried out at 170 °C for 12 h. The upper aqueous phase was separated and collected for the next run of degradation reaction.

1.6 Characterization and testing

The dynamic mechanical properties of ACEP were measured using a dynamic mechanical analyzer (DMA, Discovery 850). The dimension of the specimen was 10.7 mm × 7.0 mm × 3.0 mm. The frequency was 1 Hz with an oscillating amplitude of 20 μm. ACEP was scanned from 30 °C to 190 °C at a heating rate of 3 °C/min. Nuclear magnetic resonance (NMR) data were collected on an AVANCE IIIITM (Bruker, Switzerland) spectrometer (400MHz). The deuterated solvents used for NMR were acetone-d₆ and DMSO-d₆. To explore the structure of the degradation products, FT-IR spectra were collected on a Vertex 80V (VRUKER, Germany) spectrometer in a wavenumber range of 4000-400 cm⁻¹ with a resolution of 4 cm⁻¹, and 40 times scan were accumulated to form 1 spectrum. A JSM-7001F scanning electron microscope (SEM) was used to observe the morphology transformation of resin during the degradation reaction. In the absorption experiments, the catalyst concentration in the aqueous solutions was analyzed by an UV-Vis spectroscopy at 260.5 nm. The contact angles of water on the resin surface with different catalysts were determined at 25 ± 0.1 °C using a KRÜSS DSA255 Drop Shape Analyzer. The molecular weight of degradation product was measured on a matrix-assisted laser analytical ionization time-of-flight mass spectrometer (MALDI-TOF-MS) in the range of 0-4000 m/z with an acceleration voltage of 25 kV (BRUKER, Germany), and the solvent used for MALDI-TOF-MS was acetone.

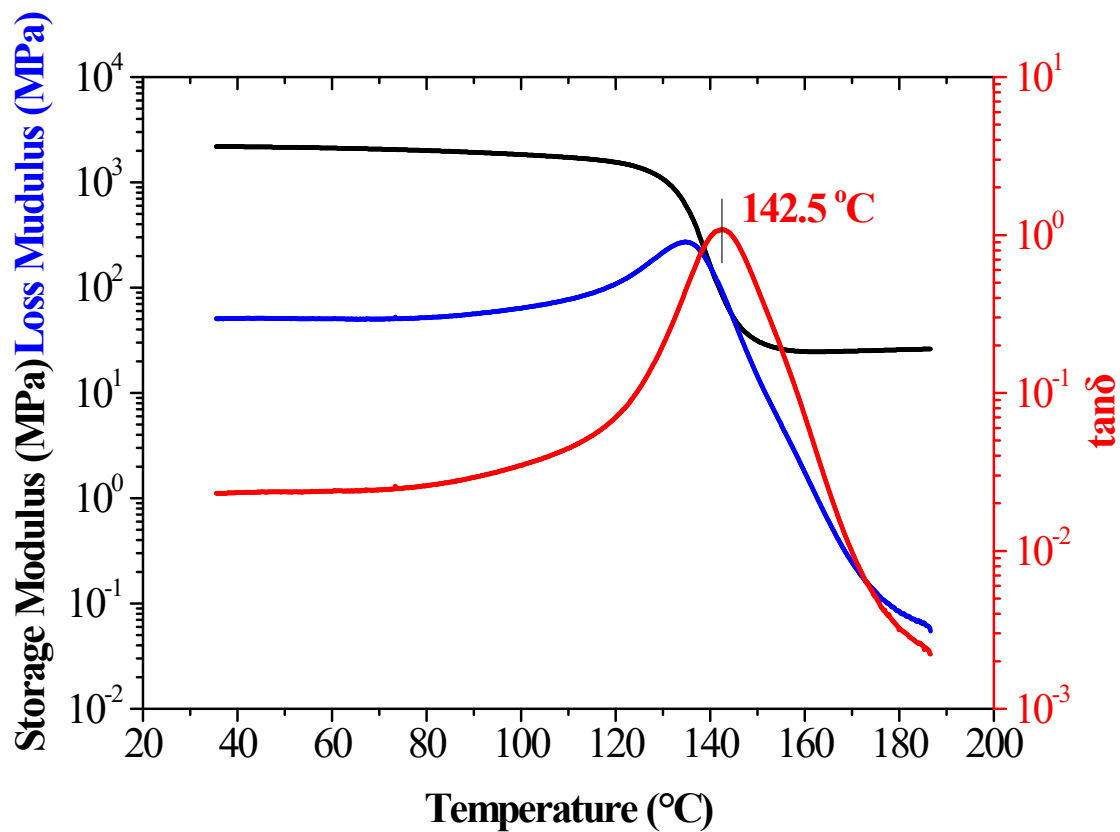


Figure S1 DMA curves of ACEP

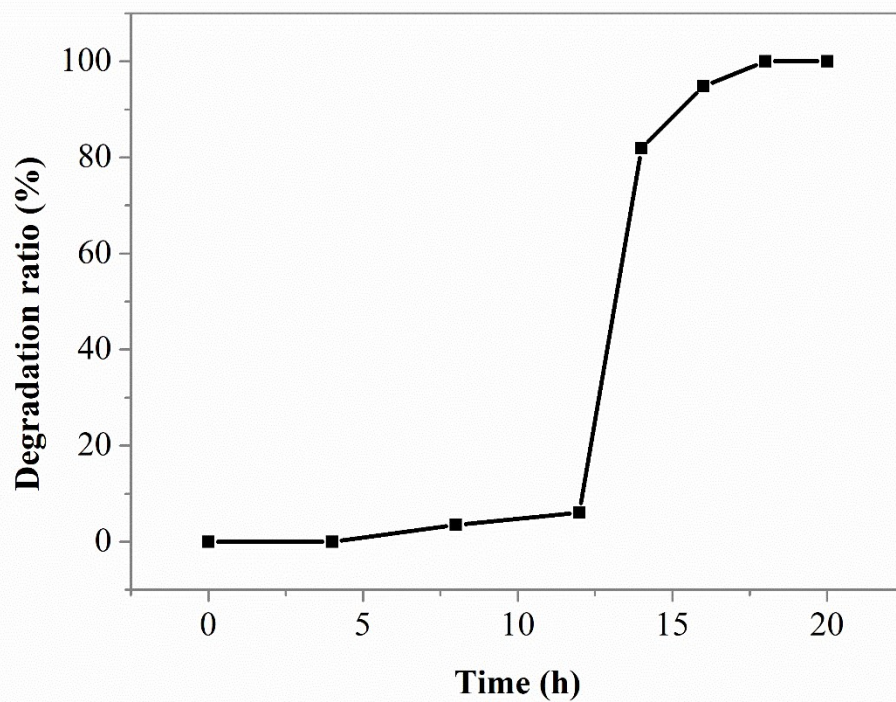


Figure S2 The degradation ratio of ACEP with time in the HPW-H₂O solution (0.09 mmol of HPW, 4.0g of the HPW-H₂O solution) at 170 °C.

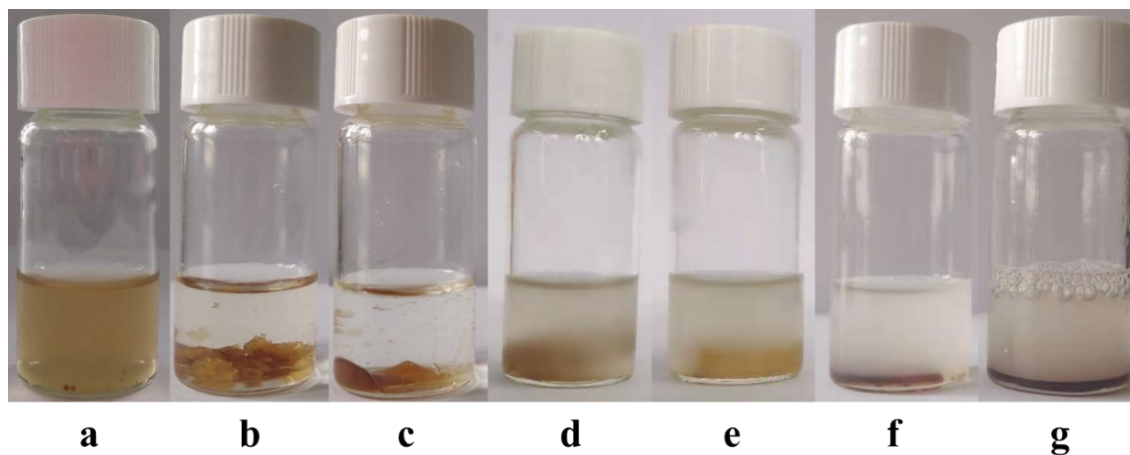


Figure S3 The pictures of a) 0.28 mmol of DBSA system; b) 0.28 mmol of PTSA system; c) 0.28 mmol of MSA system; d) 0.28 mmol of MSA+0.05 g of $A_{12}EO_5$; e) 0.05 g of $A_{12}EO_5$; f) 0.014 mmol of DBSA+0.266 mmol of MSA; g) 0.042 mmol of DBSA+0.238 mmol of MSA degradation system. Degradation ratio: 100%. Reaction conditions: 0.35 g of ACEP, 4.0 g of the aqueous solution.

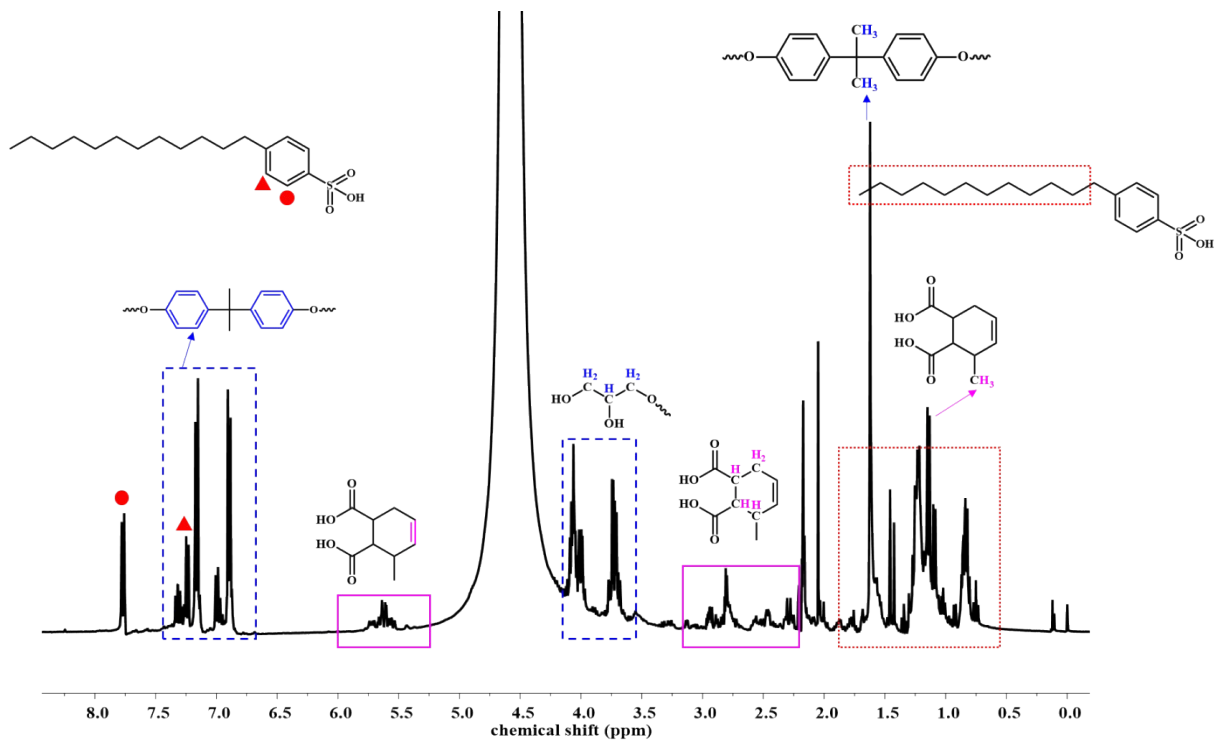


Figure S4 $^1\text{H-NMR}$ spectrum of degradation products for ACEP

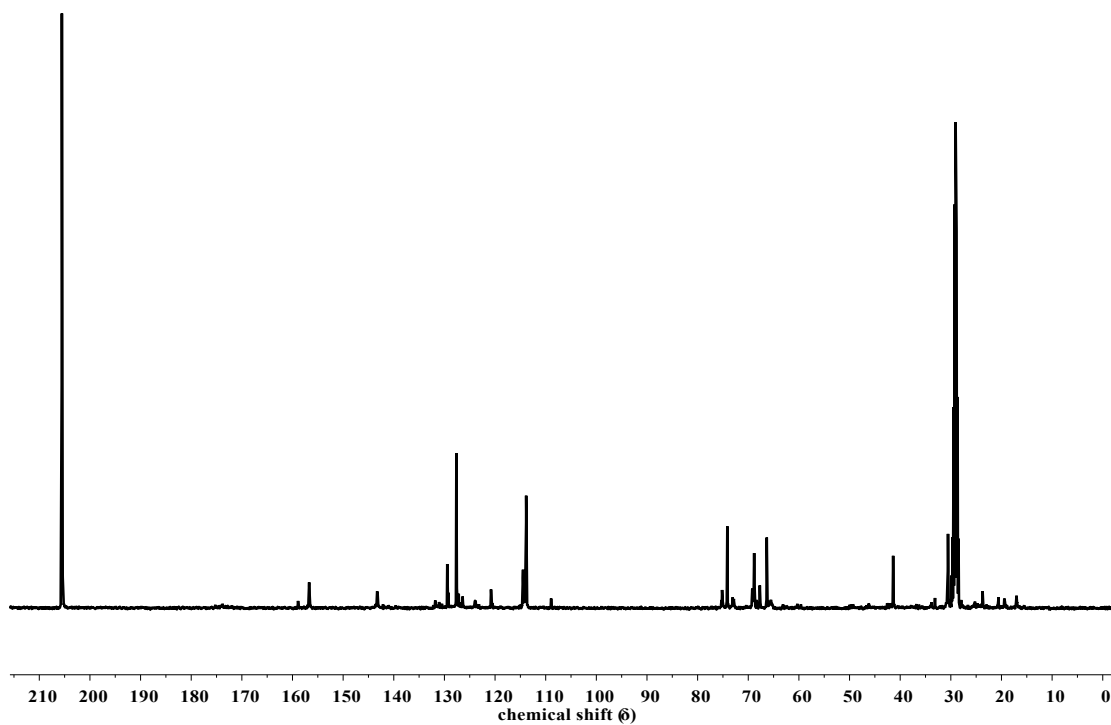


Figure S5 ¹³C-NMR spectrum of the degradation product in the organic phase.

The main organic degradation product was bisphenol-A diglycidyl ether. There existed no carbonyl peaks at 175-177 ppm, indicating the absence of carboxylic acid product.

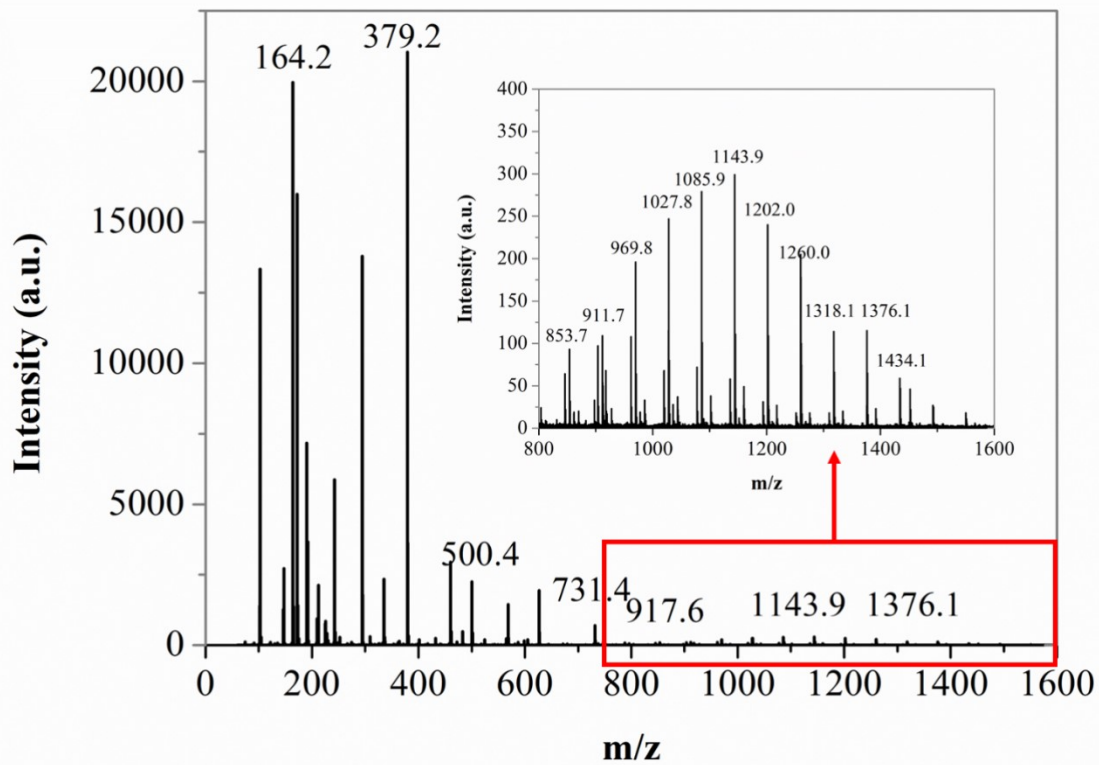


Figure S6 MALDI-TOF-MS spectra of the organic degradation product.

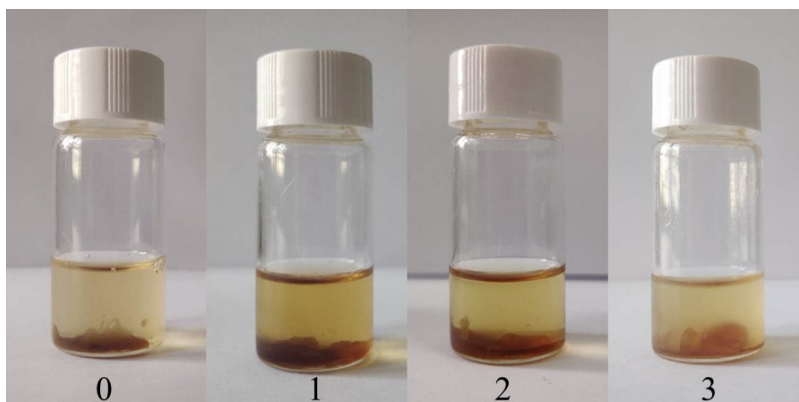


Figure S7 Photos of the degradation system after recycling for different times.

Table S1 The gel content of ACEP

Solvent	Reaction vessel	Gel content/%
Acetone	Soxhlet extractor ^a	-
Acetone	Teflon-lined autoclave ^b	97.5
Toluene	Soxhlet extractor ^c	99.9
Toluene	Teflon-lined autoclave ^d	99.3

Reaction conditions: ^a The ACEP was cut into the particles of 20-40 mesh. 2.92 g of the ACEP particles and 100 g of acetone were added into Soxhlet extractor at 70 °C and kept for 24 h. Then the remaining solid particles were separated, dried at 80 °C for 72 h and weighed to calculate the gel content of ACEP. The weight of the remaining solid particles was not decreased. It is likely that some components are difficult to diffuse from resin to solvent due to the high crosslinked ACEP at a low temperature.

^b 0.40 g of the 20-40 mesh ACEP particles and 4.0 g of acetone were added into a Teflon-lined autoclave with a volume of 10 mL and carried out at 170 °C for 12 h. Then the remaining solid particles were separated, dried at 80 °C for 72 h and weighed to calculate the gel content of ACEP. The gel content of ACEP was 97.5%.

^c 2.92 g of 20-40 mesh ACEP particles and 100 g of toluene were added into Soxhlet extractor at 125 °C and kept for 24 h. Then the remaining solid particles were separated, dried at 120 °C for 72 h and weighed to calculate the gel content of ACEP.

^d 0.40 g of 20-40 mesh ACEP particles and 4.0 g of toluene were added into a Teflon-lined autoclave with a volume of 10 mL and carried out at 170 °C for 12 h. Then the remaining solid particles were separated, dried at 120 °C for 72 h and weighed to calculate the gel content of ACEP.

Table S2 The swelling ratio of ACEP in different solvents at 170 °C for 12 h ^a

Solvent	Swelling ratio/%
Water	2.2
Acetone	23.2
Toluene	32.5

^a Mass of ACEP: 0.55 g.

Table S3 The effect of surfactant on degradation of ACEP in MSA aqueous solution

Entry	Moles of MSA/mmol	Mass of A ₁₂ EO ₅ /g	R _d /%
1	0.28	0	39.6
2	0.28	0.05	76.7
3	0	0.05	11.7

Reaction conditions: 0.35 g of ACEP, 4.0 g of aqueous solutions, 170 °C, reaction for 20 h.

The structure of A₁₂EO₅ is as follows:

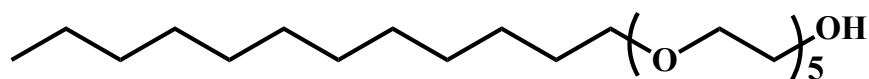


Table S4 The quality of recycled bisphenol-A diglycidyl ether

Entry	Mass of ACEP/g	Mass of recycled bisphenol-A diglycidyl ether /g	Mass ratio/%	Yield/%
1	0.55	0.30	54.5	84.5

After the degradation reaction, the aqueous phase at the top layer was removed, and the organic phase at the bottom layer mainly consisted of bisphenol-A diglycidyl ether was washed by water and dried at 80 °C for 24 h.