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Concurrent Thiol-ene Competitive Reactions Enable Reprocessable, Degradable and Creep-resistant Dynamic-permanent Hybrid Covalent Networks

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Contents

Experimental

Materials

N-butyl mercaptan (N-btSH) (99%), methyl 3-mercaptopropionate (98%), pentaerythritol tetra(3-mercaptopropionate) (PTMP) (95%), 1,4-cyclohexanedimethanol divinyl ether (CDVE, mixture of isomers) were obtained from Sigma-Aldrich Co., China. n-Butyl vinyl ether (IBVE), cyclohexyl vinyl ether (CHVE), 2,2'-azobis(2-methylpropionitrile) (AIBN) were supplied by Aladdin Reagent Co., China. Methyl ethyl ketone (MEK), acetone, tetrahydrofuran (THF), N, N-dimethylformamide (DMF), toulene, ethanol and methanol were from Sinopharm Chemical Reagent Co., Ltd., China. Isobutyl vinyl ether are distilled under reduced pressure before use. All other chemicals were used as received.

Methods

Synthesis of S,O-acetal AB

The reaction was initiated by the addition of IBVE (2.5, 25 mmol) via a dry syringe into a solution containing N-btSH (2.25 mL, 25 mmol), PTSA (9.51 mg, 0.05 mmol) in CH_2Cl_2 (6 mL) and THF (0.5ml) in a 20 mL small bottle at -78 °C for 20 min, and then the reaction was terminated with methanol containing a small amount of triethylamine. The quenched reaction mixture was washed with sodium hydroxide aqueous solution and distilled water. The organic layer was concentrated to dryness under reduced pressure and vacuum-dried to give the product[1]. The synthetic route is illustrated in Scheme S1.

^{1}H NMR (400 MHz, DMSO-d6) δ 4.73 – 4.63 (m, 1H), 3.35 (dd, J = 15.8, 1.1 Hz, 1H), 3.19 – 3.09 (m, 1H), 2.65 – 2.49 (m, 2H), 1.76 (dt, J = 13.3, 6.6 Hz, 1H), 1.59 – 1.38 (m, 6H), 1.38 – 1.28 (m, 2H), 0.86 (dt, J = 6.9, 1.5 Hz, 9H).

^{13}C NMR (100 MHz, DMSO-d6) δ 81.08 , 73.40 , 32.31 , 28.32 , 27.47 , 22.81 , 22.00 , 19.78 , 13.93 .

Synthesis of S,O-acetal CD

Synthetic steps are the same as above, as shown in Scheme S2.

^{1}H NMR (400 MHz, DMSO-d6) δ 4.87 – 4.76 (m, 1H), 3.60 (d, J = 1.1 Hz, 4H), 2.83 – 2.65 (m, 2H), 2.61– 2.54 (m, 2H), 1.86 – 1.78 (m, 1H), 1.74 (q, J = 9.6, 7.7 Hz, 1H), 1.65 (q, J = 5.7, 4.7 Hz, 2H), 1.52 – 1.39 (m, 3H), 1.32 – 1.11 (m, 6H).

^{13}C NMR (101 MHz, DMSO-d6) δ 172.34 , 78.21 , 73.99 , 51.82 , 35.30 , 33.10 , 31.51 , 25.73 , 24.13 , 23.89 , 23.66 , 22.73 .

Mechanism of S,O-acetal exchange reactions via model compounds

A 5-mL vial containing model S,O-acetal **AB** (1 mmol) and S,O-acetal **CD** (1 mmol) was placed in a preheated oil bath at 100, 120, 140,160 ºC, and aliquot 2 μL was taken every 30 min and diluted in 1000 μL $CHCl_2$ for GC-MS spectroscopy. Rates of exchange were calculated by monitoring the change in concentration of acetal **AB** ([**1**]).

Synthesis of S,O-covalent adaptable networks (PTCD)

Covalent adaptable networks (PTCD) were prepared by mixing 1 equivalent Pentaerythritol Tetra(3-mercaptopropionate) (PTMP) with 2 equivalent 1,4-cyclohexanedioethylene ether (CDVE) at 80 ºC for 4h to form a gel. The gelled PTCD was pressed at 160 ºC for 30 min and then postcured at 160 ºC for 2 h to obtain PTCD films with a thickness of ~ 300 μm for examination of thermal, mechanical, and recycling property.

Synthesis of the control AIBN-PTCD network

The control AIBN-PTCD were prepared by mixing 1 equivalent PTMP, 2 equivalent CDVE with 0.01 equivalent AIBN and poured into the PTFE mold. The mixture was heated 80 ºC for 4 h, a 120 ºC for 2 h and followed postcured at 160 ºC for 2 h at oven.

Gel Content Test

PTCD (around 200 mg) was separately put into a Soxhlet extractor for extraction with tetrahydrofuran for 48 h and then dried in a vacuum oven at 70 °C for 12 h. m_0 is the initial mass, and m1 is the final mass after drying; the gel content is calculated by 100% × m_1/m_0.

Swelling Ratio Measurements.

PTCD (around 200 mg) were separately immersed in, THF, DMF, acetone, MEK, ethanol, methanol, and deionized water at 50 °C for 48 h. m_0 is the initial mass, and m_1 is the mass after swelling; the swelling ratio was calculated by 100% × $(m_1 - m_0)/m_0$

Reprocess Recycling

The reprocess recycling tests were implemented with a plate vulcanizer at elevated temperature and pressure. The original films were cut into small pieces; placed between two steel sheets covered with two polyimide films to avoid adherence of PTCD on the steel sheets; and hot-pressed under a pressure of 10 MPa at 180 °C for 1 h. After cooling the films to room temperature, reprocessed films were obtained. The remodeling experiment was repeated twice by the same procedure.

Chemical degradation

Chemical degradation was examined by immersing around 300 mg of PTCD in 10 mL vial containing corresponding solutions at 50 or 25 ºC. Degradation times refer to the times when the samples were completely dissolved in the solution. The degradation rate was calculated based on the starting weight, the final weight, the degradation time and the volume of the acidic solutions used for the degradation. 1 M HCl solutions with different volume ratio of water to MEK or THF was added into vials at 50 ºC. 0.01 M, 0.1 M, 0.5 M, 1.0 M HCl solutions with water and different type of main solvents in different proportions at 50 ºC, and 1 M acetic acid solution, sulfuric acid solution, and phosphoric acid solution were also used to measure the degradation of PTCD in different acid. Different ratio of main solvent to water at 1M HCl was also used to measure.

Instrumentation

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance II spectrometer at 400 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR), respectively, using DMSO-d_6 as the solvent. Fourier-transform infrared (FTIR) spectra were recorded with a Nicolet 6700 FTIR spectrometer (Nicolet) using the KBr pellet method. FTIR spectra of PTCD were recorded on a Micro-FTIR Cary 660 spectrometer (Agilent), and the absorbance mode was used.

Differential scanning calorimetry (DSC) was implemented using a Mettler-Toledo Star 1 under a nitrogen atmosphere. The cured samples (around 6−8 mg) were heated from −100 to 150 °C at a heating rate of 20 °C min^{-1}, kept at 100 °C for 3 min, cooled to 20 °C at a cooling rate of 50 °C min^{-1}, and then heated to 100 °C at a heating rate of 20 °C min^{-1}. Glass transition temperatures were found by taking the midpoint of the reversible endotherm of the second heating curve for each sample.

Thermogravimetric analyses (TGA) were performed on a Mettler Toledo TGA/SDTA 851e in a temperature window of 50-700 °C at a heating rate of 10 °C/min under a nitrogen atmosphere.

Dynamic mechanical analysis (DMA) was performed on a Q800 DMA (TA Instruments) in a tension mode with dimensions of around 20 mm (length) × 5 mm (width) × 0.3 mm (thickness) to measure the dynamic mechanical properties of PRCs from −100 to 100 °C at a heating rate of 3 °C min^{-1} at a frequency of 1 Hz.

Rheology experiments were performed on an Anton Paar MCR 302. The experiments were performed in parallel plate geometry using 0.5 mm sample disks. Unless specified, the experiments were performed using a normal force of 5 N, a frequency of 1 Hz. For stress relaxation experiments, a strain of 5% was applied to the material, and the relaxation modulus was followed over time at a constant temperature. For frequency sweep experiments, the frequency was varied from 100 to 0.1 Hz.

Creep experiments were performed on the Q800 DMA. The samples were stretched by a constant force of 1 MPa at a preset temperature for 10 min, followed by a 90 min recovery period.

Tensile testing was done by a universal mechanical testing machine (Instron 5569A). The samples with dimensions of 30 mm (length) × 0.5 mm (width) × 0.3 mm (thickness) were measured at a cross-head speed of 1 mm min^{-1}. The tensile properties of each sample were reported as the average of five repeated measurements.

Calculation of Activation energies (*E_a*) and Topology-freezing temperatures (*T_v*)

E_a of exchange reaction and T_v of PTCD were determined using the methodology reported in literature[2]. The characteristic relaxation times (τ*s) were fit to the Arrhenius law in supplementary equation 1[1].

Supplementary equation 1: $$\tau^{*}(T) = \tau_0^{*}\, e^{E_a/RT}$$

(R: universal gas constant; 8.314 J K^{-1} mol^{-1})

Supplementary equation 2: $$\ln \tau^{*}(T) = \ln \tau_0^{*} + {}^{Ea}\!/_{RT}$$

T_v is the temperature at which the relaxation time τ* is 10^6 s according to the same method from Capelot et al[2]. The measured values of characteristic relaxation times (τ*s) were plotted versus 1000/T.

PTCD: y=16.8x-29.8 E_a= 140 kJ mol^{-1} T_v= 113 °C

Supporting Figures and Tables

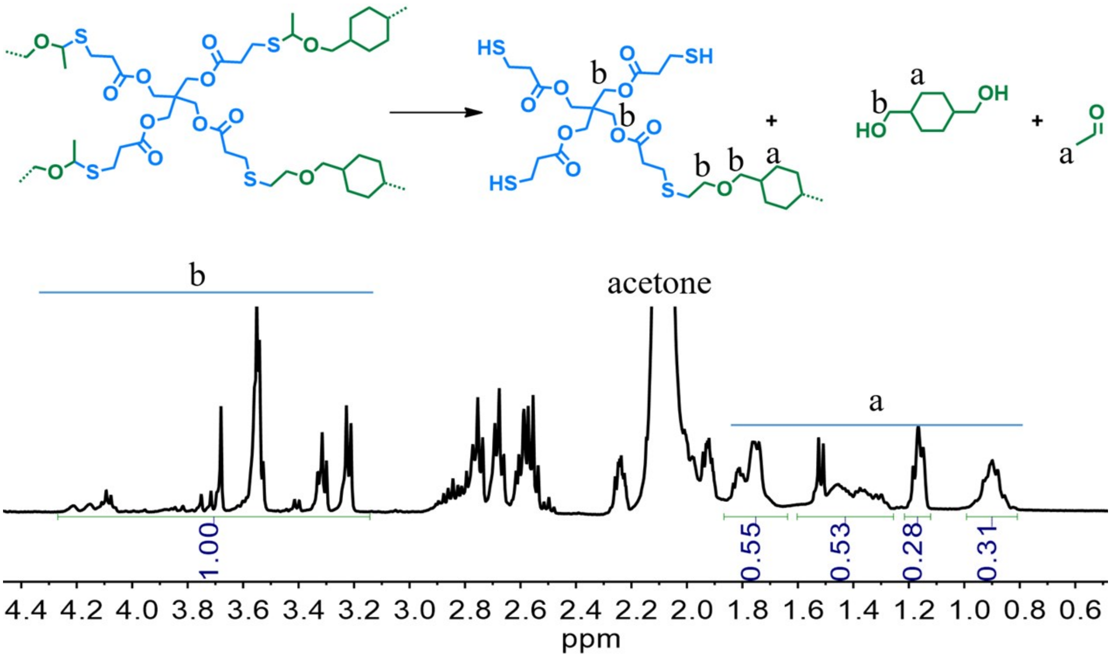


Fig. S1 ^{1}H NMR spectrum of the 0.1 M HCl acetone-d6/H_2O (9/1, v/v) solution after adding PTCD.

Assuming that the proportion of Markovnikov products is n, the proportion of anti-Markovnikov products is 1-n.

$$\frac{4n + 6 \times (1 - n)}{3n + 5} = \frac{1}{0.55 + 0.53 + 0.28 + 031} \qquad n = 0.79$$

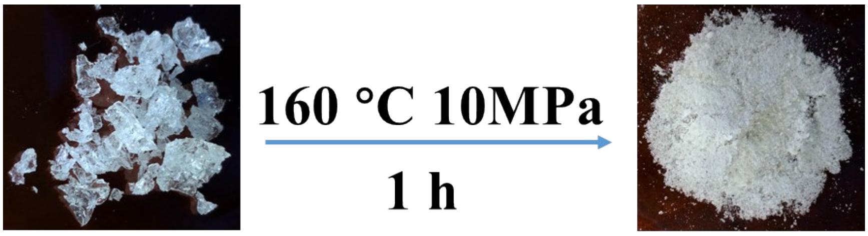


Fig. S2 Hot-pressing of the precured PTMP and CDVE with AIBN at 160 °C for 1 h under a pressure of 10 MPa.

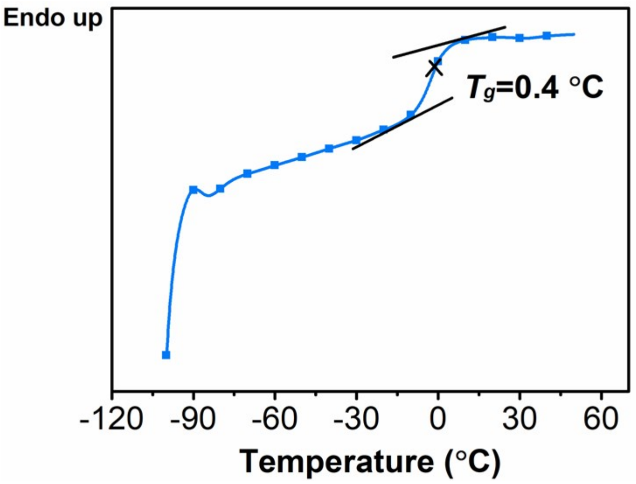


Fig. S3 Non-isothermal DSC curve of PTCD.

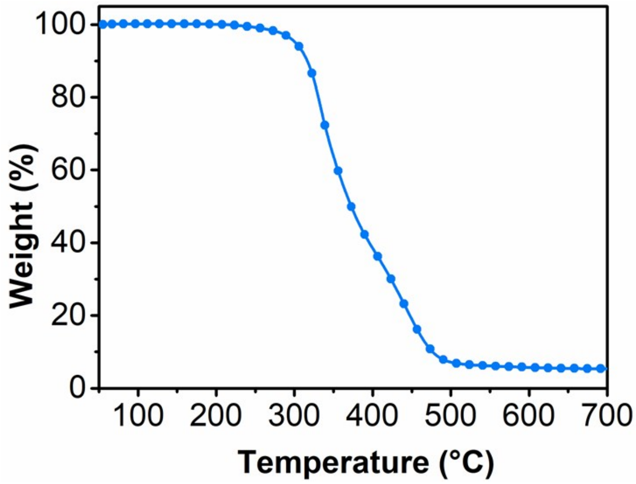


Fig. S4 TGA curve of PTCD.

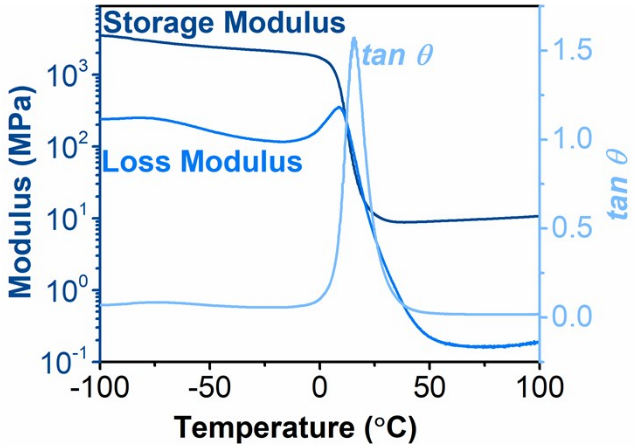


Fig. S5 DMA curves of PTCD.

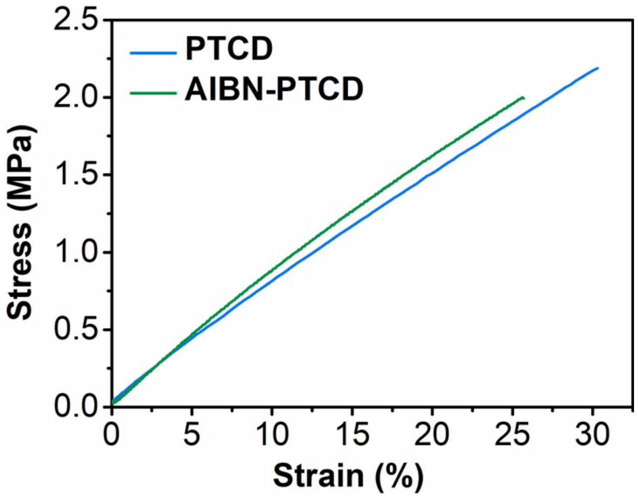


Fig. S6 Representative tensile stress-strain curve of PTCD and the controlled AIBN-PTCD.

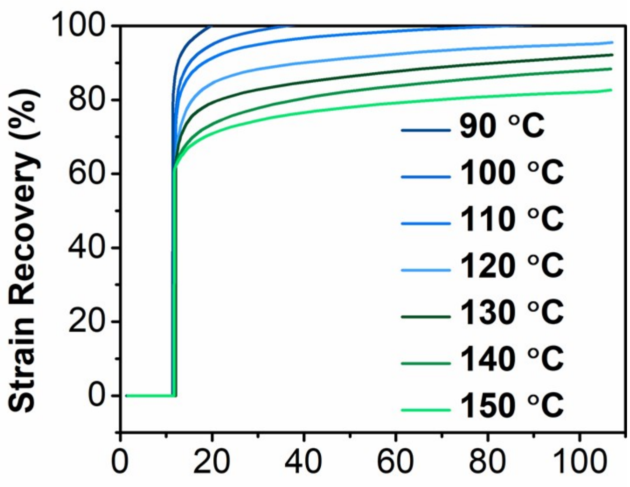
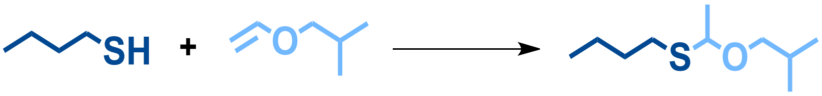
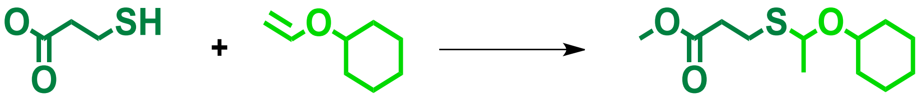


Fig. S7 Creep recovery curves of PTCD at different temperatures.



Scheme S1 Synthesis of model S,O-acetal **AB**.



Scheme S2 Synthesis of model S,O-acetal **CD**.

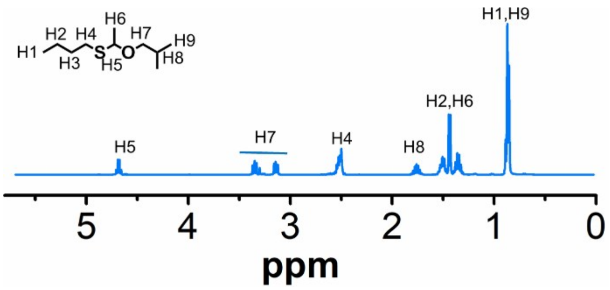


Fig. S8 ^{1}H NMR spectrum of model S,O-acetal **AB**.

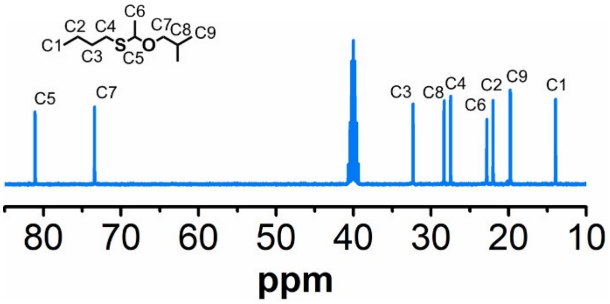


Fig. S9 ^{13}C NMR spectrum of model S,O-acetal **AB**.

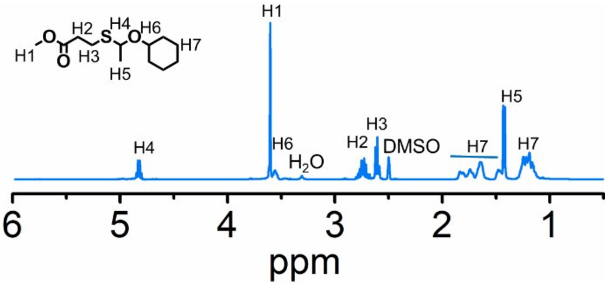


Fig. S10 ^{1}H NMR spectrum of model S,O-acetal **CD**.

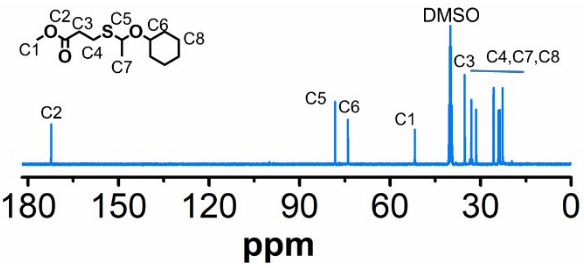


Fig. S11 ^{13}C NMR spectrum of model S,O-acetal **CD.**

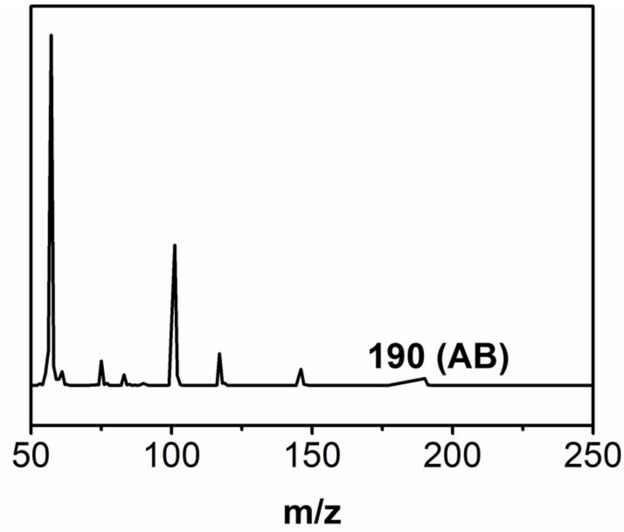


Fig. S12 MS spectrum of **AB.**

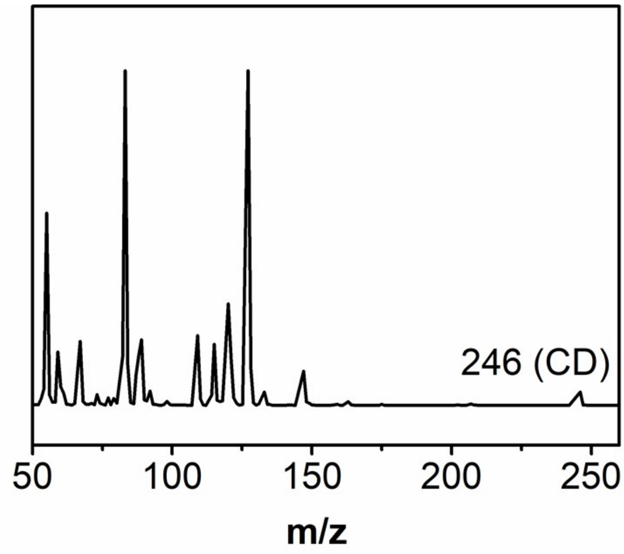


Fig. S13 MS spectrum of **CD.**

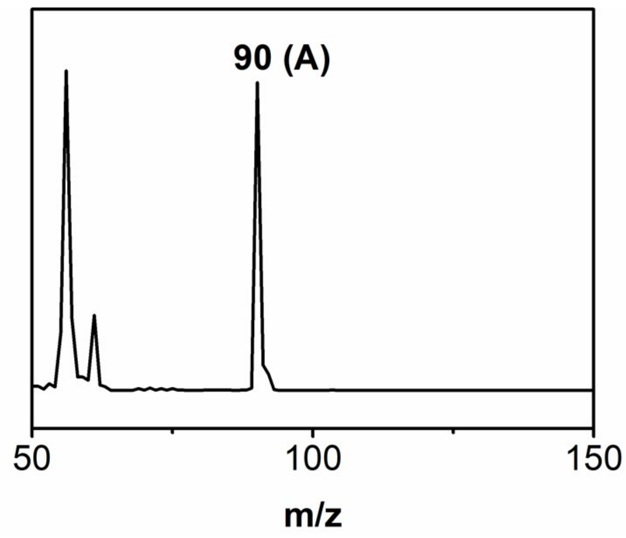


Fig. S14 MS spectrum of **A.**

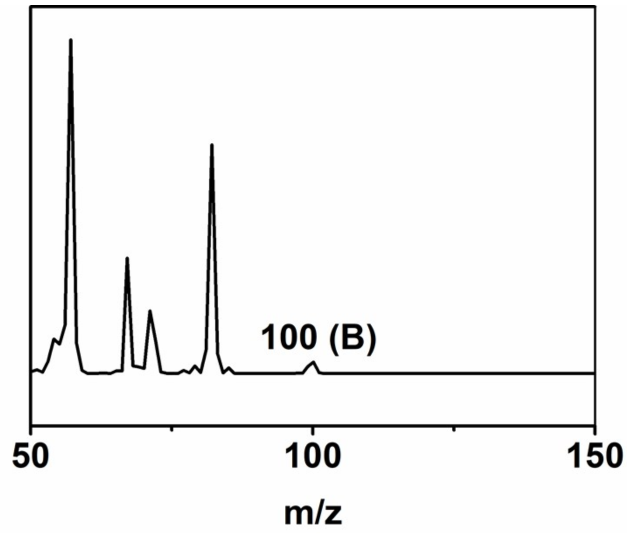


Fig. S15 MS spectrum of B**.**

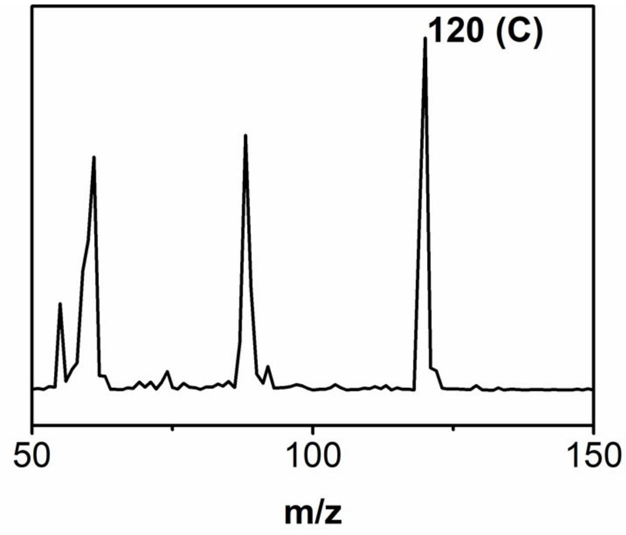


Fig. S16 MS spectrum of **C.**

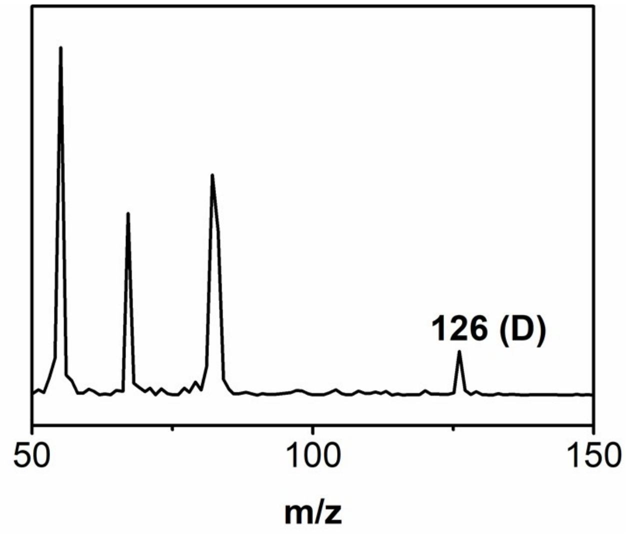


Fig. S17 MS spectrum of **D.**

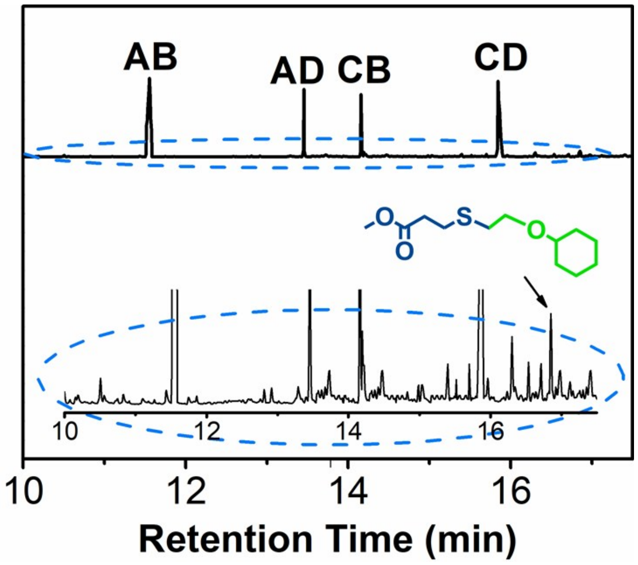


Fig.S18 Normalized GC spectra of S,O-thioacetal **AB** and S,O-thioacetal **CD** mixture at 160 ºC for 3 h.

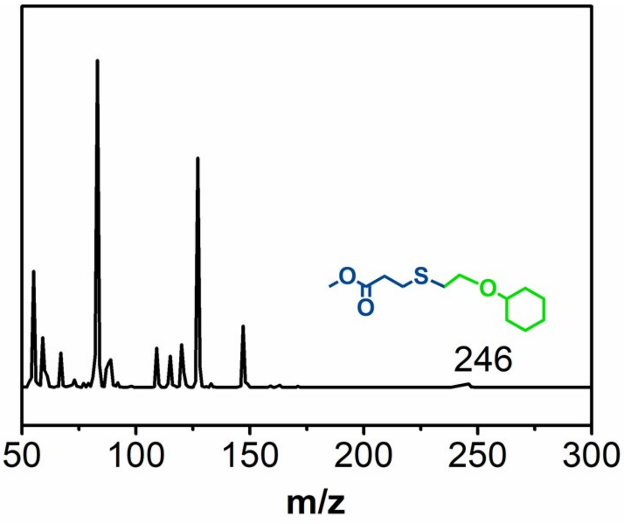


Fig. S19 MS spectrum of CD's radical products.

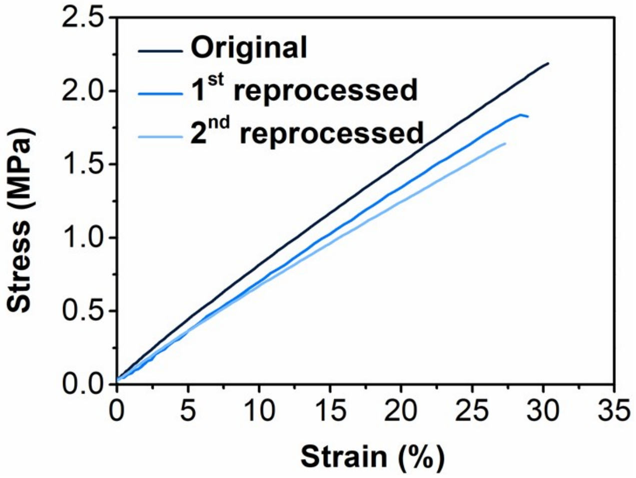


Fig. S20 Representative tensile stress-strain curves of the orignal and reprocessed PTCD.

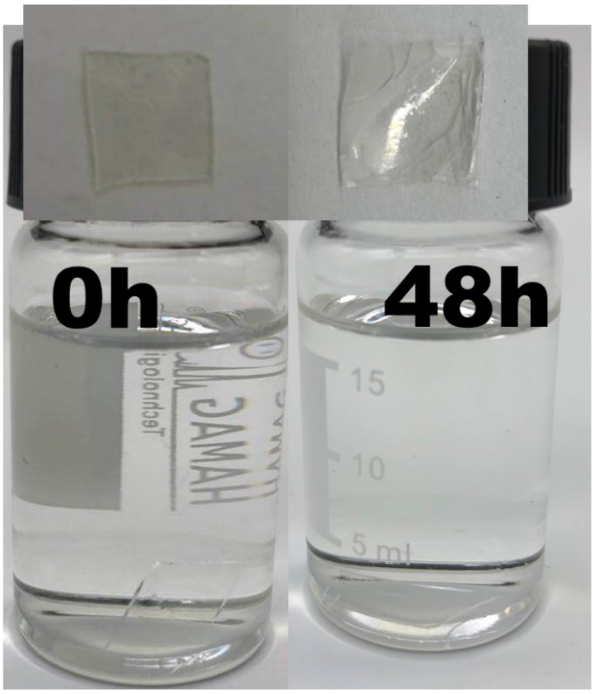


Fig. S21 Image of PTCD immersed in MEK at 50 ºC for 48 h.

Fig. S22 Degradation images of PTCD in 1 M HCl MEK solution at 50 °C.

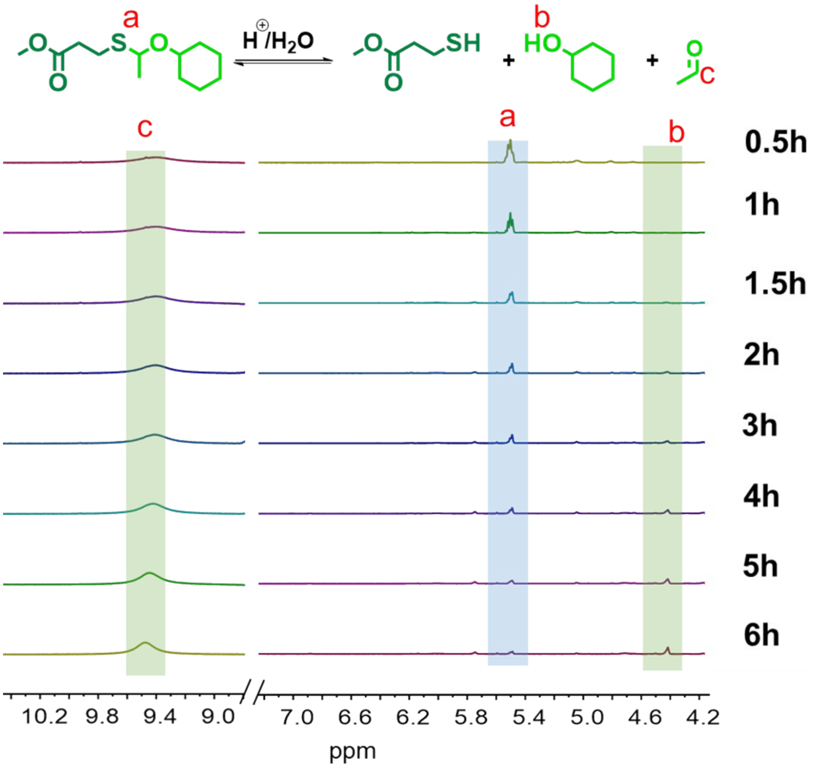


Fig. S23 Real-time ^{1}H NMR spectra of the 1 M HCl acetone-d6/H_2O (9/1, v/v) solution after adding S,O-acetal **CD** for different times at room temperature.

Table S1 Degradation rate of PTCD at different conditions.

Sample	Acid concerntration	Organic solvent	Organic solovent/H_2O (v/v)	Organic solvent (mL)	H_2O (mL)	37%HCl (mL)	Temperature (°C)	Degradation rate (g L^{-1} h^{-1})
1	1M	MEK	10/0	11	0	1	25	0.257
2	1M	MEK	10/0	11	0	1	50	1.834
3	1M	THF	10/0	11	0	1	50	1.09
4	1M	Acetone	10/0	11	0	1	50	0.872
5	1M	Methanol	10/0	11	0	1	50	0.21
6	1M	Ethanol	10/0	11	0	1	50	0.192
7	1M	DMF	10/0	11	0	1	50	-
8	1M	Water	10/0	11	0	1	50	-
9	1M	MEK	9/1	9.9	1.1	1	50	1.122
10	1M	THF	9/1	9.9	1.1	1	50	0.661
11	0.5M	MEK	9/1	10.35	1.55	0.5	50	0.673
12	0.5M	THF	9/1	10.35	1.55	0.5	50	0.353
13	0.1M	MEK	9/1	10.71	1.19	0.1	50	0.246
14	0.1M	THF	9/1	10.71	1.19	0.1	50	0.142
15	0.01M	MEK	9/1	10.79	1.11	0.01	50	-
16	0.01M	THF	9/1	10.79	1.11	0.01	50	-
17	1M	MEK	9/1	10.22	1.13	0.65 (H_2SO_4)	50	1.246
18	1M	THF	9/1	10.22	1.13	0.65 (H_2SO_4)	50	0.685
19	1M	MEK	9/1	10.06	1.12	0.82 (H_3PO_4)	50	-
20	1M	THF	9/1	10.06	1.12	0.82 (H_3PO_4)	50	-
21	1M	MEK	9/1	10.12	1.13	0.68 (CH_3COOH)	50	-
22	1M	THF	9/1	10.12	1.13	0.68 (CH_3COOH)	50	-
23	1M	MEK	8/2	8.8	2.2	1	50	0.762
24	1M	THF	8/2	8.8	2.2	1	50	0.511
25	1M	MEK	7/3	7.7	3.3	1	50	0.390
26	1M	THF	7/3	7.7	3.3	1	50	0.317
27	1M	MEK	6/4	6.6	4.4	1	50	0.183
28	1M	THF	6/4	6.6	4.4	1	50	0.136

References

1 M. Uchiyama, M. Osumi, K. Satoh and M. Kamigaito, *Angew. Chem. Int. Ed.*, 2020, **59**, 6832-6838.

2 M. Capelot, M. M. Unterlass, F. Tournilhac and L. Leibler, *ACS Macro Lett.*, 2012, **1**, 789-792.