

Supporting information

High Performance Polyurethanes Derived from Aromatic Acetal-Containing Polyols Enabling Closed-Loop Recycling

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1. Materials & Characterization

Materials

1,6-Hexanediol (99%), benzaldehyde (98%) and 1,4-bis(2-hydroxyethoxy)benzene (95%) were purchased from TCI Europe. 4,4'-diphenylmethane diisocyanate (4,4'-MDI) and Basolite C-300 MOF were kindly provided by BASF (Germany). Paraformaldehyde (for synthesis), *p*-Toluenesulfonic acid monohydrate (98.5%), 1,4-diazabicyclo[2.2.2]octane (DABCO, 99%), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 98%), 1 M HCl solution and orthophosphoric acid (crystals) were purchased from Sigma Aldrich. Siral 70 was kindly provided by SASOL (Germany). Chloroform-*d* (99.8%), acetone-*d*₆ and dimethylsulfoxide-*d*₆ (DMSO-*d*₆, 99.9%) were purchased from Cambridge Isotope Laboratories. All chemical compounds were used without further purification, unless stated otherwise. All solvents were ACS Reagent Grade, purchased from Acros Organics, Fisher Scientific or Sigma–Aldrich and used without further purification.

Characterization

¹H nuclear magnetic resonance (NMR) spectroscopy was performed using a Bruker UltraShield 400 MHz at room temperature. ¹H NMR spectra were taken using 32 scans and a relaxation time of 2 seconds. The kinetic curves of the polyol hydrolysis were based on ¹H NMR analysis performed on a Varian unit Inova 500 MHz spectrometer using THF-*d*₈ as a solvent with TMS as an internal standard. The spectra were taken at 50 °C with a delay time of 2 s and 32 scans. The polyol (0.1 g) and the THF-*d*₈ (1 ml) were first added in an NMR tube. The measurements were started after addition of 0.2 ml 20 mM PTSA solution to the NMR tube.

The titration of the hydroxy end groups of the APs was performed on a 916 Ti-touch machine from Metrohm equipped with an electrode using 0.4 mol/L tetraethylammonium bromide in ethylene glycol as the electrolyte. The hydroxy groups of the polyol (1-2 g) were reacted with excess acetic acid anhydride (5 ml 21 vol% in pyridine) for 1 hour at 120 °C, then the unreacted anhydride was hydrolyzed by the addition of excess amounts of water (10 ml). After 10 min, the reaction mixture was cooled to room temperature and diluted with 100 ml MeOH/toluene (1:1 v/v) solution. The mixture was titrated with 1 M KOH solution in methanol as the titrant. After getting the volume of KOH solution at the end of titration of sample (*V*₁) and the volume of the blank sample titration using the same condition (*V*₀), the OH value in mg KOH/g could be determined using the following equation:

$$OH_v = \frac{56.1 \cdot (V_0 - V_1)}{W_{\text{sample}}} \quad (\text{eq. S1})$$

where *W*_{sample} is the weight of the AP sample in grams, and both *V*₁ and *V*₀ are expressed in ml.

Matrix-assisted laser desorption and ionization-time of flight-mass spectroscopy (MALDI-TOF-MS) was employed to investigate the repeating unit structure of the prepared polyacetal polyols, using a PerSeptive Biosystems Voyager-DE STR equipped with a 337 nm nitrogen laser with a 3 ns pulse

duration. Spectra were recorded in positive mode with an accelerating voltage of 20 kV. The polyols were dissolved in THF at a 1.5 mg/ml concentration, cesium triiodide was added as an ionization agent, and α -Cyano-4-hydroxycinnamic acid was used as a matrix.

Gel permeation chromatography (GPC) measurements of acetal containing polyols were performed on LC-250C (Shimazu) equipped with two PSS GRAM liner 5 μ m columns and a refractive index (RI) detector. The polyols were dissolved in THF with 1 vol% acetic acid (2 mg/ml), the solution was filtered with 0.2 μ m PTFE filter before analysis. THF was used as the eluent with a flow rate of 1 ml/min. The GPC traces were calibrated with a PEG standard to calculate the molecular weight. The GPC measurements of the acetal containing PUs were performed on LC-250C (Shimazu) equipped with two PSS GRAM liner 10 μ m columns and a refractive index (RI) detector. The PU materials were dissolved in DMF with 0.1 M LiBr (1.5 mg/ml), and the solution was filtered with 0.2 μ m PTFE filter before analysis. DMF was used as the eluent with a flow rate of 1 ml/min and the GPC traces were calibrated with a PMMA as standard to calculate the molecular weight.

Viscosity of the polyols were determined using a Physica MCR 301 rheometer (Anton Paar GmbH) with a plate-plate configuration with a diameter of 50 mm and a gap of 0.5 mm. The polyol (2 ml) was applied to the plate system, and the viscosity was determined via a shear rate sweep from 0.01 to 1000 1/s at 65 °C.

Fourier transformation infrared spectroscopy (FT-IR) was carried out in attenuated total reflection mode on a Thermo-Scientific NICOLET iS20 FTIR Spectrometer. 8 scans were performed over the wavenumber range of 4000 to 450 cm^{-1} .

Thermogravimetric analysis (TGA) was performed using TGA550 (TA instruments). Small pieces of PU bulk cast material (5 - 15 mg) were cut and put on the platinum pan for measurement. The samples were first equilibrated at 100 °C for 30 minutes, followed by heating from 100 to 800 °C with a rate of 10 °C /min under a nitrogen atmosphere.

Differential scanning calorimetry (DSC) was performed on TA Q2000 (TA instruments). 5 - 10 mg samples were used in an aluminum pan. The experiments were carried out from -80 to 200 °C at a rate of 20 °C/min under argon atmosphere. Glass transition temperatures (T_g) were determined by taking the midpoint of the reversible endotherm of the 2nd heating.

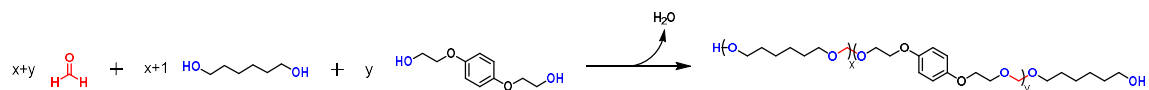
Tensile tests were performed on Zwick/Roell Intelligent testing with a 200 N load cell and a strain rate of 20 mm/min using dumbbell-shaped specimens (effective length: 12 mm, width: 2 mm, and measured thickness around 0.5 mm). The Young modulus of the materials was determined by calculating the slope of the derivative of the stress-strain curves within the range of 3% to 5% elongation. The Young's moduli and elongation at break reported are the mean values of at least four different samples.

Dynamic mechanical analysis (DMA) was performed on a DMA850 (TA instruments) with a film tension setup. Samples were cut from PU films with a dimension of width of 4.2 mm and a thickness of 0.5 mm. The experiments were carried out from $-80\text{ }^{\circ}\text{C}$ to $150\text{ }^{\circ}\text{C}$ with a heating rate of $3\text{ }^{\circ}\text{C}/\text{min}$ under an oscillatory strain of 0.5% and a frequency of 1 Hz. The glass transition temperature (T_g) of the samples was determined by the peak maximum of $\tan(\delta)$.

Static contact angle measurements were conducted on a OCA30 goniometer (Dataphysics), using MilliQ water (resistivity of $18.2\text{ M}\Omega \cdot \text{cm}$) as probe liquid with a droplet volume of $2\text{ }\mu\text{L}$ and measurements were performed on at least four different spots per coating, recording the contact angle for at least 20 s using the OCA20 software. Values reported are the average of all individual left and right contact angle values after 20 s measurement time.

2. Synthesis & Characterization of Acetal-Containing Polyols

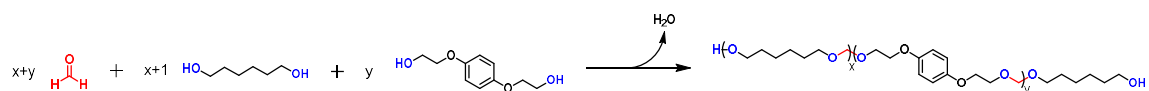
Synthesis of acetal-containing polyol from the reaction between 1,6-hexanediol, 1,4-bis(2-hydroxyethoxy)benzene and formaldehyde (AP1)



Scheme S1. Synthesis of **AP1** from the condensation of formaldehyde, H16 and HEB. * Formaldehyde is synthesized in-situ via the decomposition of paraformaldehyde.

H16 (80.3 g, 0.68 mol), 1,4-bis(2-hydroxyethoxy)benzene (26.9 g, 0.14 mol) and Siral 70 (6.6 g) were added to a 250 ml one neck flask equipped with a water-cooled short-path vacuum condenser and a receiving flask, and heated to $110\text{ }^{\circ}\text{C}$ under argon. Paraformaldehyde (25.1 g, 0.84 eq) was then added, and the mixture was stirred vigorously under vacuum. After 2 h, the reaction mixture was cooled, diluted with acetone to reduce viscosity and vacuum filtered to remove the solid catalyst. The filtrate was then dried in a vacuum oven at $80\text{ }^{\circ}\text{C}$ for 2 h. The resulting product is a clear, colorless polyacetal polyol which slowly crystallizes at room temperature, exhibiting an OH value of 77 mg KOH/g and an acid value below 0.1 mg KOH/g.

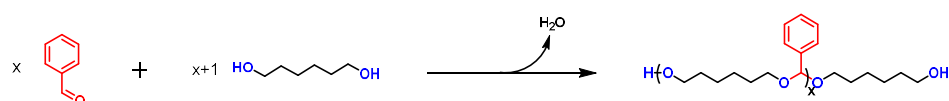
Synthesis of acetal-containing polyol from the reaction between 1,6-hexanediol, 1,4-bis(2-hydroxyethoxy)benzene and formaldehyde (AP2)



Scheme S2. Synthesis of **AP2** from the condensation of formaldehyde, H16 and HEB. * Formaldehyde is synthesized in-situ via the decomposition of paraformaldehyde.

H16 (53.5 g, 0.45 mol), 1,4-bis(2-hydroxyethoxy)benzene (71.7 g, 0.36 mol) and Siral 70 (7.5 g) were added to a 250 ml one neck flask equipped with a water-cooled short-path vacuum condenser and a receiving flask, and heated to 110 °C under argon. Paraformaldehyde (25.2 g, 0.84 eq) was then added, and the mixture was stirred vigorously under vacuum. After 2 h, the reaction mixture was cooled, diluted with acetone to reduce viscosity and vacuum filtered to remove the solid catalyst. The filtrate was then dried in a vacuum oven at 80 °C for 2 h. The resulting product is a clear, colorless polyacetal polyol which slowly crystallizes at room temperature, exhibiting an OH value of 81 mg KOH/g and an acid value below 0.1 mg KOH/g.

Synthesis of acetal-containing polyol from the reaction between 1,6-hexanediol and benzaldehyde (AP3)



Scheme S3. Synthesis of **AP3** from the condensation of benzaldehyde and H16.

1,6-Hexanediol (H16) was melted in an oven at 80 °C. H16 (90 g, 0.76 mol) and MOF C-300 (2.12 g) were added to a 250 ml three-neck flask equipped with a Dean-Stark condenser and an argon inlet. A 1:1 hexane/pentane mixture and benzaldehyde (80.6 g, 0.76 mol) were introduced to the flask. With an oil bath set at 90 °C, the internal temperature reached 75 °C, resulting in continuous reflux. After 30 h, the reaction mixture was cooled, diluted with acetone to reduce viscosity, and vacuum filtered to remove the solid catalyst. The filtrate was then dried at 100 °C under 1 mbar for 2 hours. The resulting product is a clear, colorless polyacetal polyol, exhibiting an OH value of 106 mg KOH/g and an acid value below 0.1 mg KOH/g.

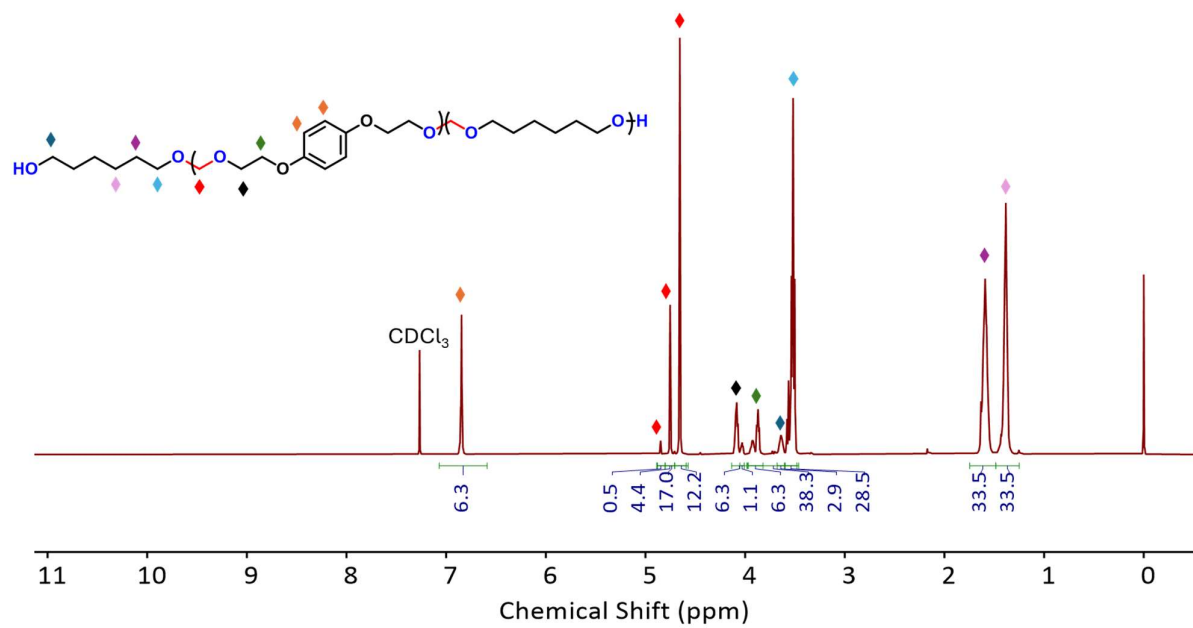


Figure S1. ¹H NMR spectrum (400 MHz, chloroform-*d*) of AP1.

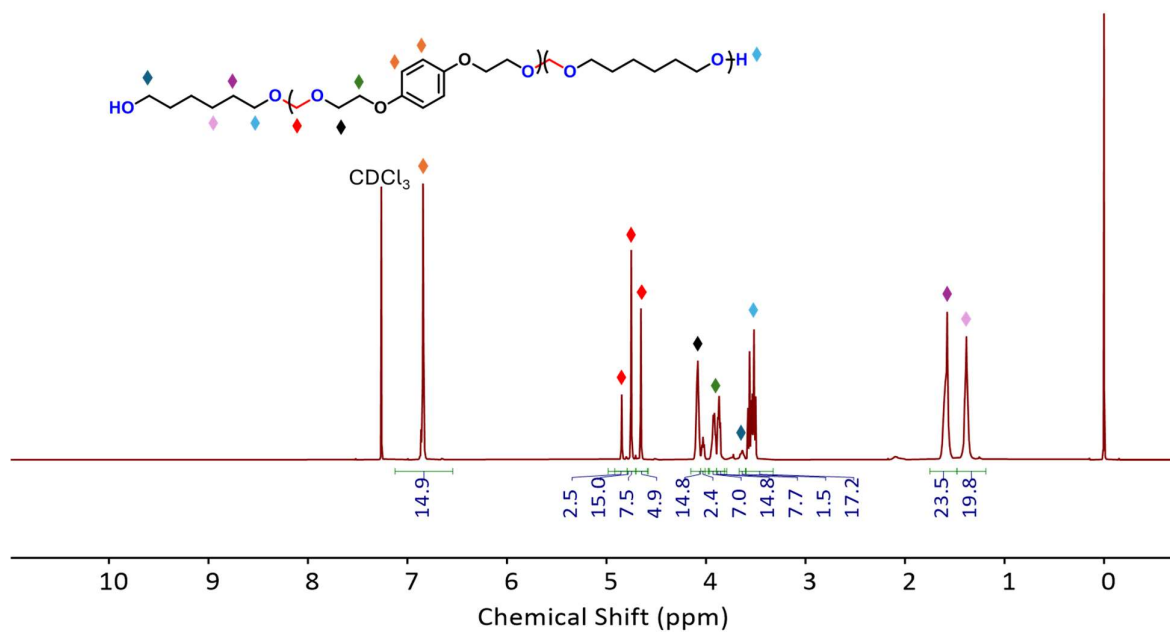


Figure S2. ¹H NMR spectrum (400 MHz, chloroform-*d*) of AP2.

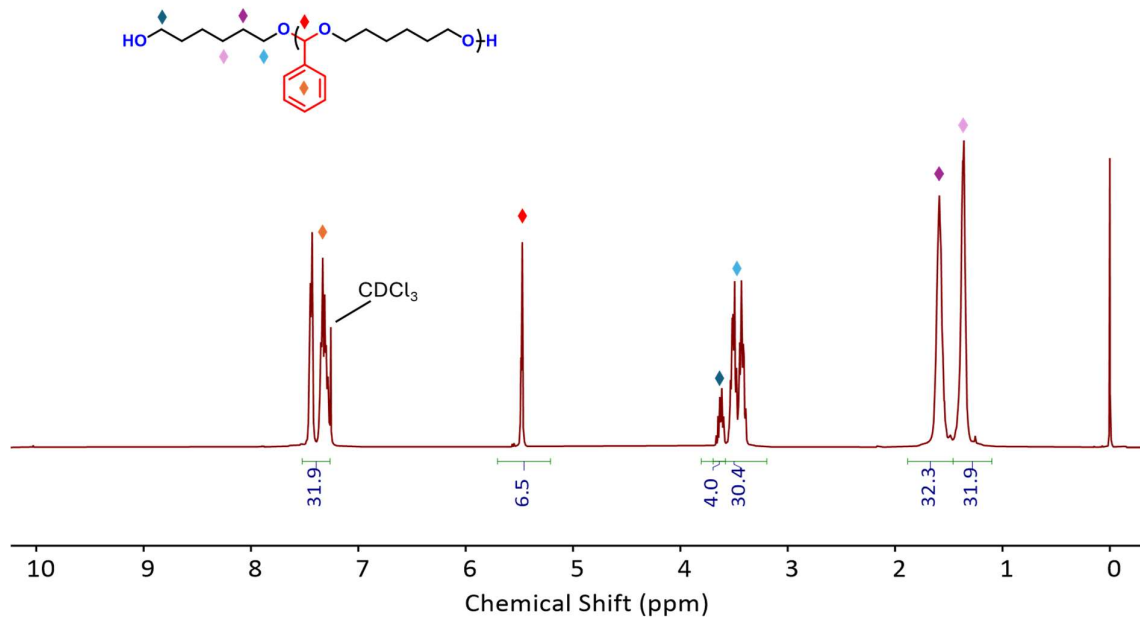


Figure S3. ^1H NMR spectrum (400 MHz, chloroform-*d*) of **AP3**.

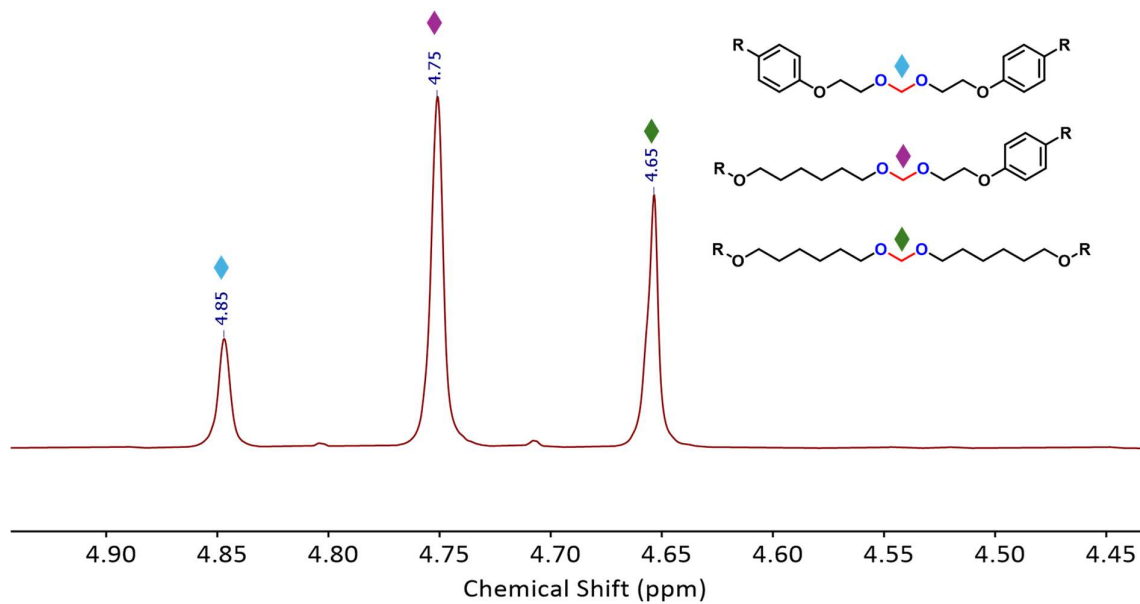


Figure S4. ^1H NMR spectrum (400 MHz, chloroform-*d*) zoom in of the acetal region of **AP2**.

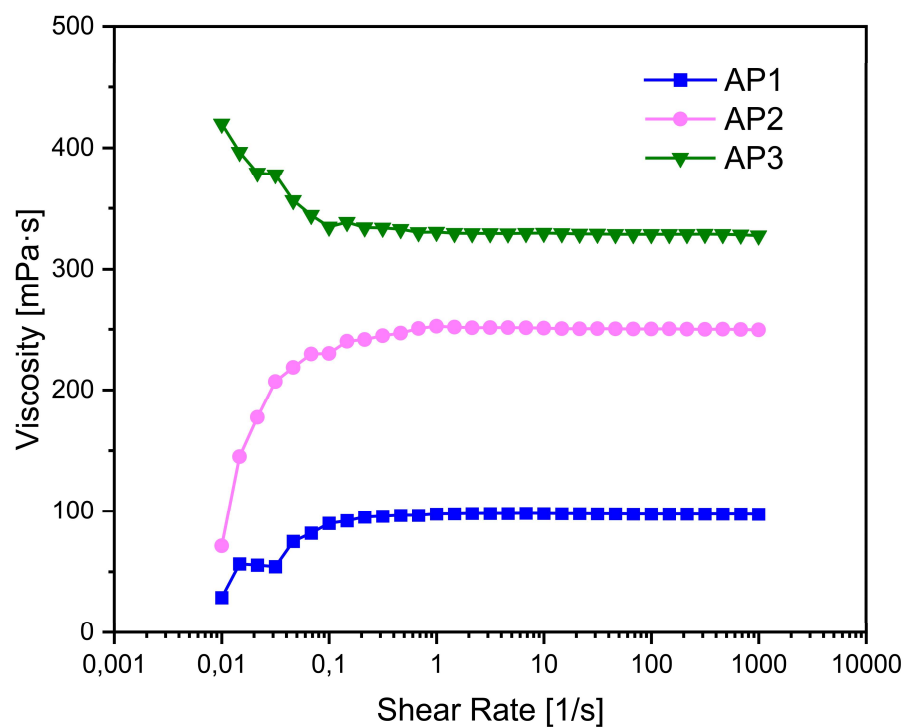


Figure S5. Viscosity measurements of acetal polyols **AP1-3** at 65 °C as a function of shear rate.

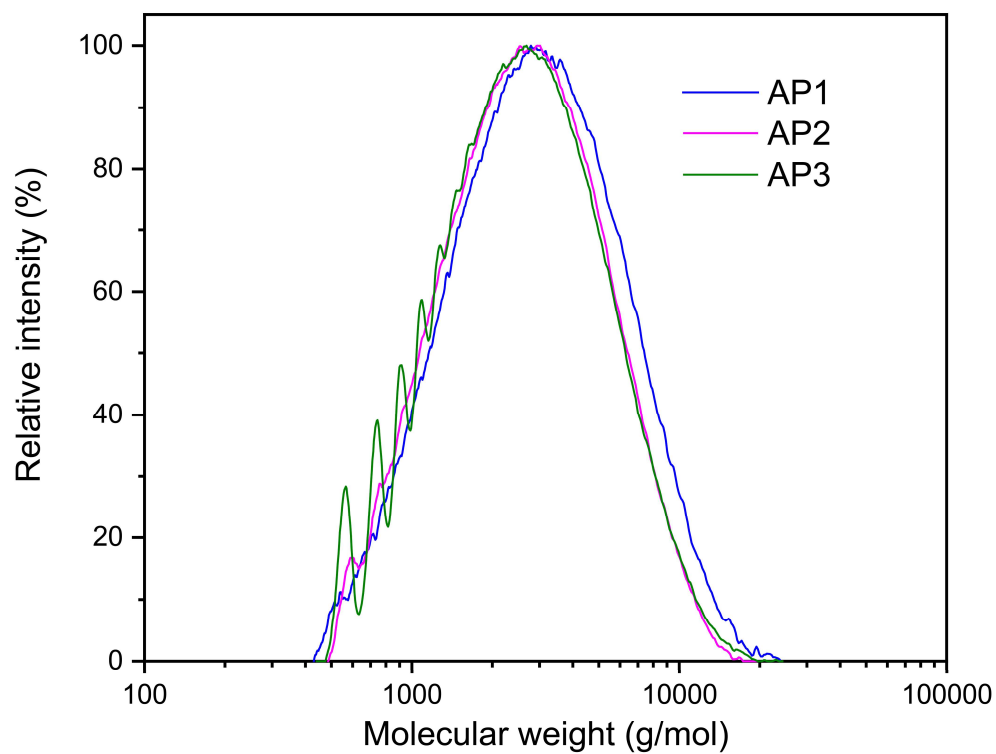


Figure S6. GPC traces of acetal polyols **AP1-3**.

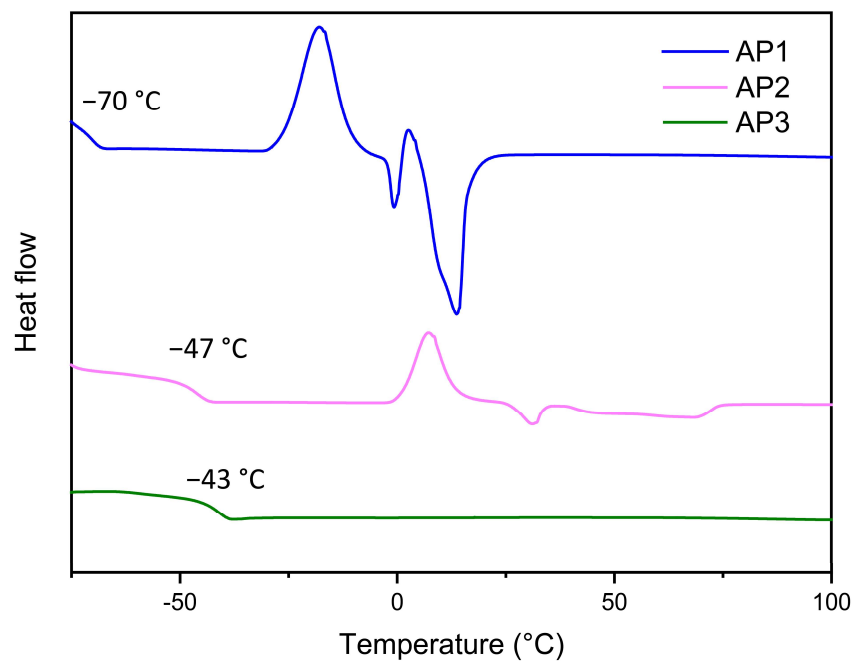


Figure S7. DSC curves of **AP1-3**

3. Kinetics of AP Hydrolysis

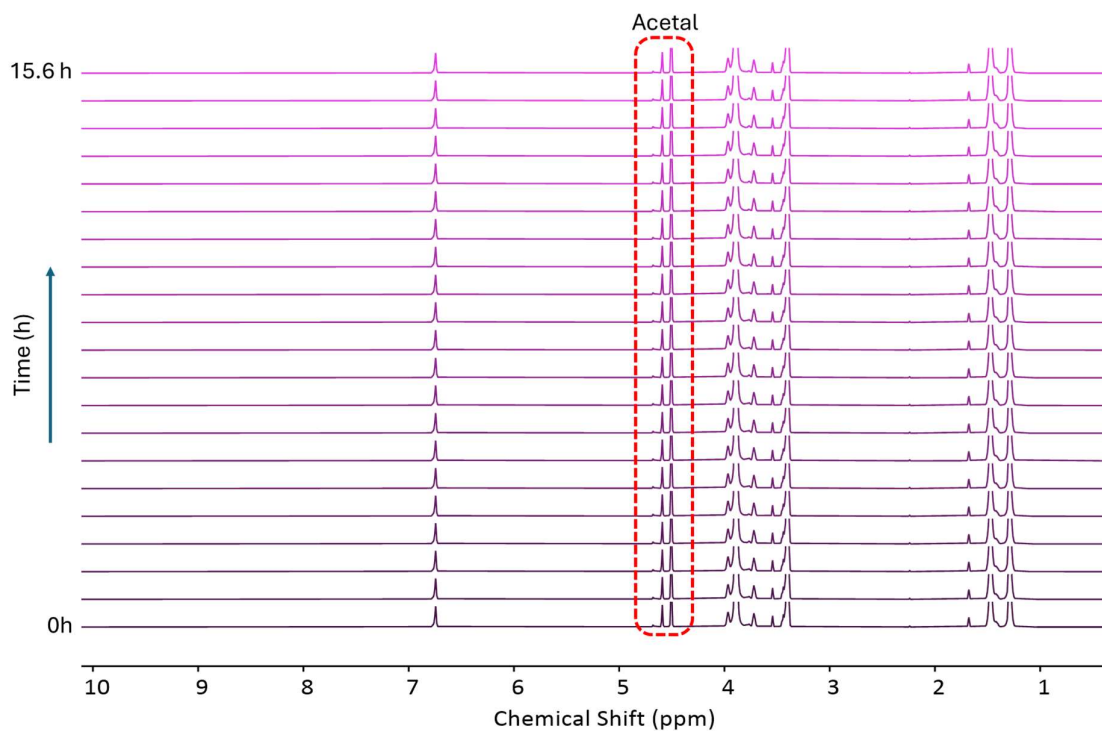


Figure S8. Time-resolved ¹H NMR spectra of **AP1** under acid catalyzed hydrolysis (500 MHz, THF-d₈, 50 °C).

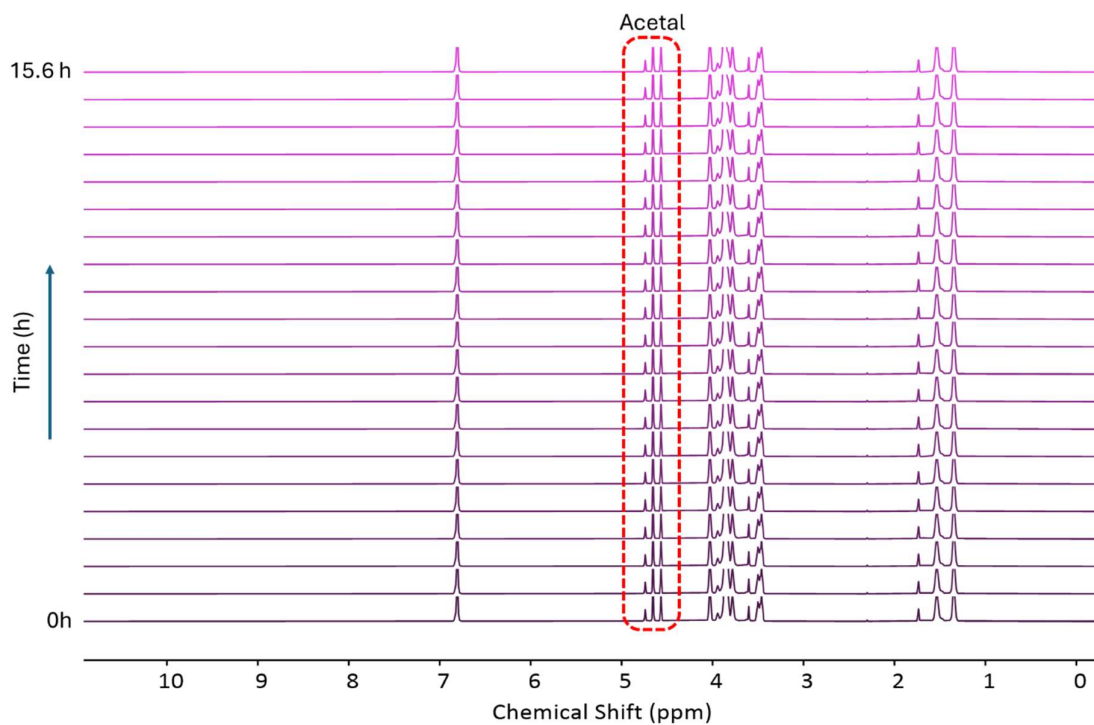


Figure S9. Time-resolved ^1H NMR spectra of **AP2** under acid catalyzed hydrolysis (500 MHz, THF-d_8 , $50\text{ }^\circ\text{C}$).

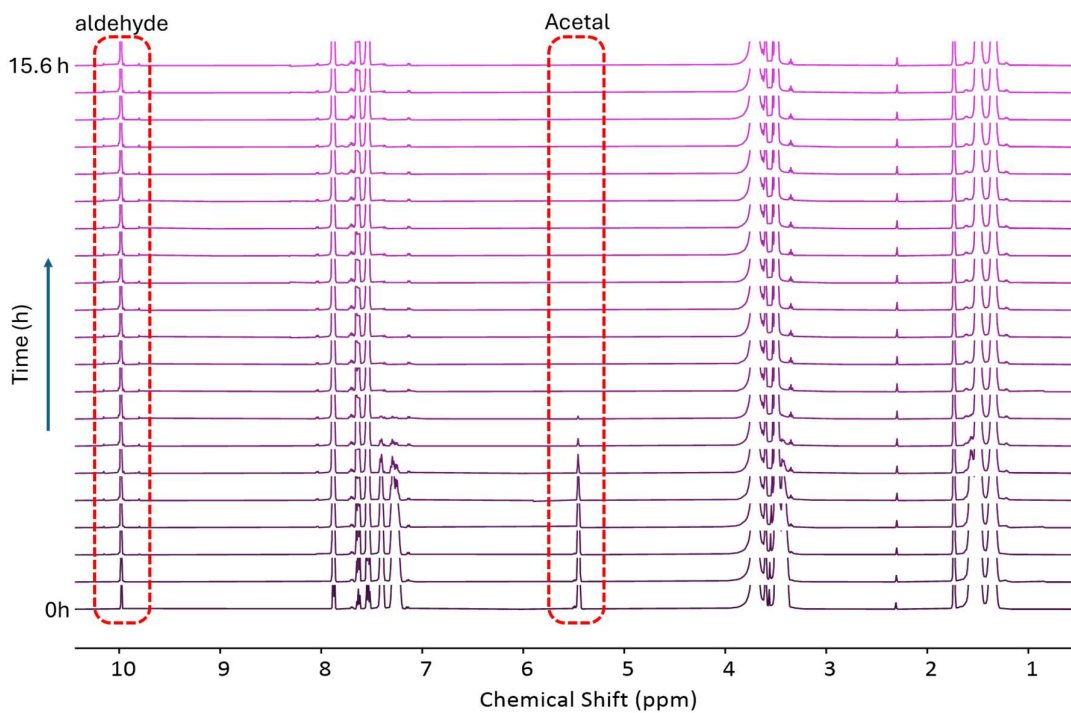


Figure S10. Time-resolved ^1H NMR spectra of **AP3** under acid catalyzed hydrolysis (500 MHz, THF-d_8 , $50\text{ }^\circ\text{C}$).

4. Synthesis & Characterization of Acetal-Containing PU Materials

Synthesis of acetal-containing thermoplastic polyurethane materials

The preparation of acetal-containing **PU AP1** is used as an example to illustrate the synthetic route:

AP1 was dried at 80 °C in a vacuum oven for 4 hours prior to use. **AP1** (17.5 g, 12 mmol), 1,6-hexanediol (1.5 g, 12 mmol) and 1,4-diazabicyclo[2.2.2]octane (DABCO, (2.5 mg, 0.01 wt%) were added into a 50 ml polypropylene cup, heated to 80 °C and mixed using a vacuum speedmixer (DAC 250.4 VAC-P LR from Hauschild speedmixer) set at 2500 RPM with 1250 RPM counter rotations for 2 minutes, and then placed in a 50 °C nitrogen oven. Meanwhile, 4,4'-MDI (6.1 g, 24 mmol) was melted at 50 °C and added in the cup. The reaction mixture was mixed using the speedmixer set at 2500 RPM with 1250 RMP counter rotations for 45 seconds, and poured into a preheated Teflon mold at 80 °C, and kept in an 100°C nitrogen oven for 2 days.

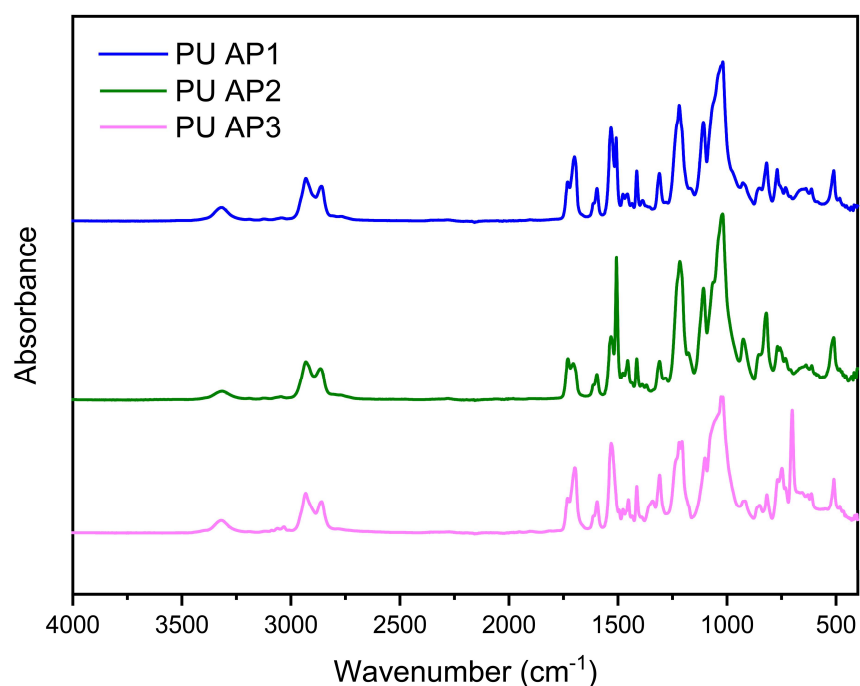


Figure S11. FT-IR spectra of the acetal-containing PUs after curing.

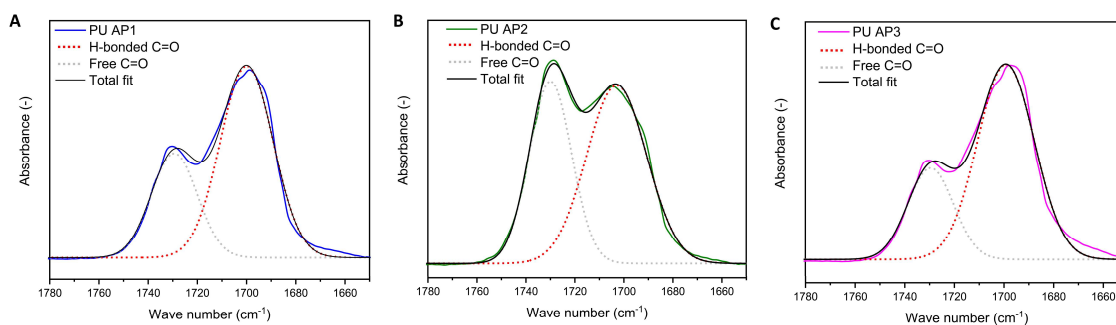


Figure S12. FT-IR spectra at the carbonyl region deconvoluted into two Gaussian curves for PU AP1 (A), PU AP2 (B), PU AP3 (C).

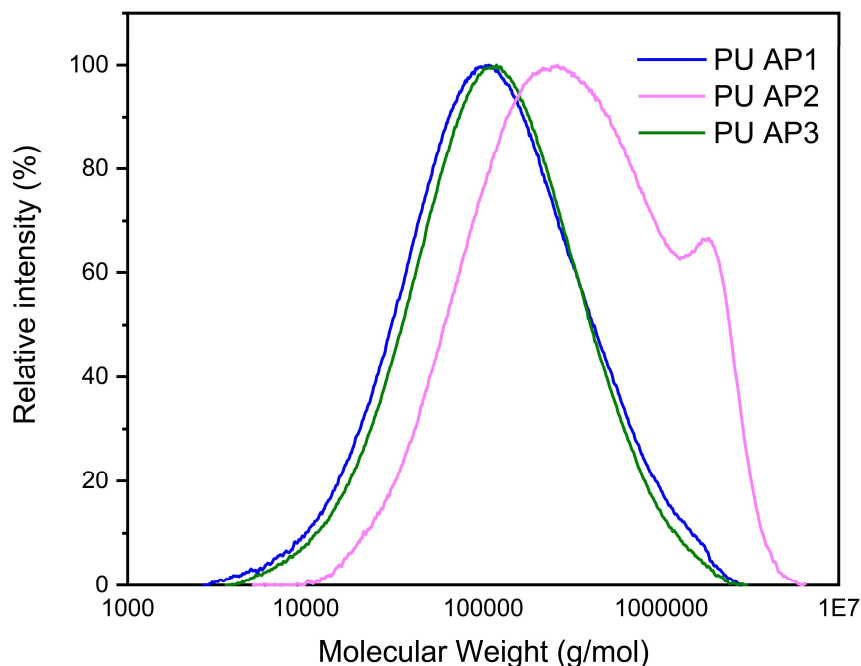


Figure S13. GPC traces of the acetal-containing PUs.

5. Closed-Loop Recycling of Acetal Polyol-Containing PU Material

Chemical depolymerization of AP-containing PU materials

The hydrolysis of acetal-containing **PU AP3** is used as an illustrative example:

PU AP3 (5 g) and 0.3 M HCl solution (20 ml) were added into a 50 ml flask equipped with a condenser. The mixture was stirred for 20 h at 50 °C, and then vacuum filtered to remove the hard phase as a fine powder. H16 and benzaldehyde remain in the aqueous solution and could be isolated via extraction in ethyl acetate.

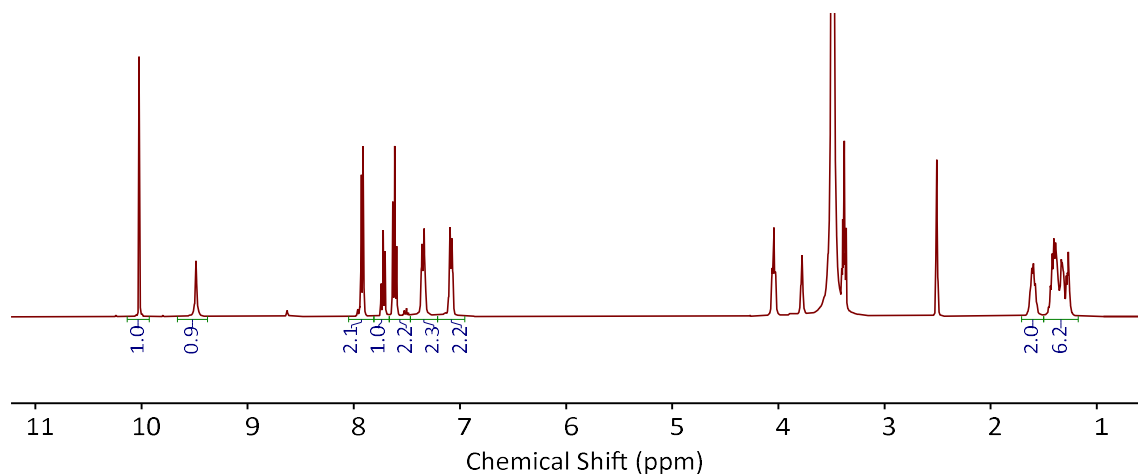


Figure S14. ^1H NMR spectrum (400 MHz, $\text{DMSO-}d_6$) of the depolymerization mixture of **PU AP3** in 1 M H_3PO_4 in water at 50 °C after 24 h.

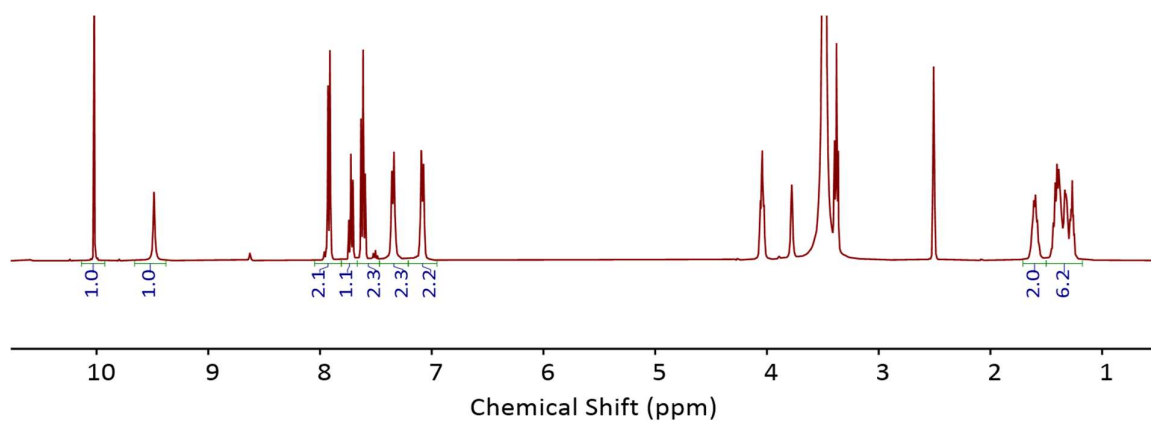


Figure S15. ^1H NMR spectrum (400 MHz, $\text{DMSO-}d_6$) of the depolymerization mixture of **PU AP3** in 0.3 M HCl in water at 50 °C after 24 h.

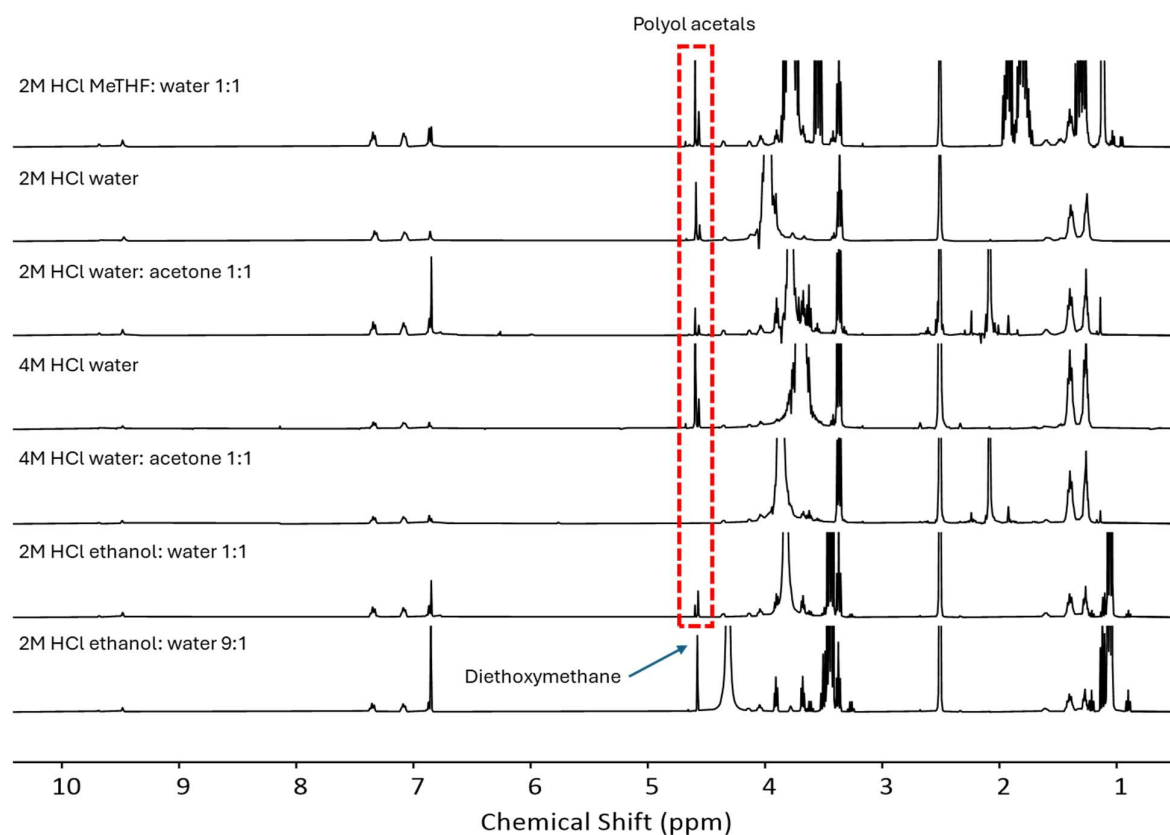
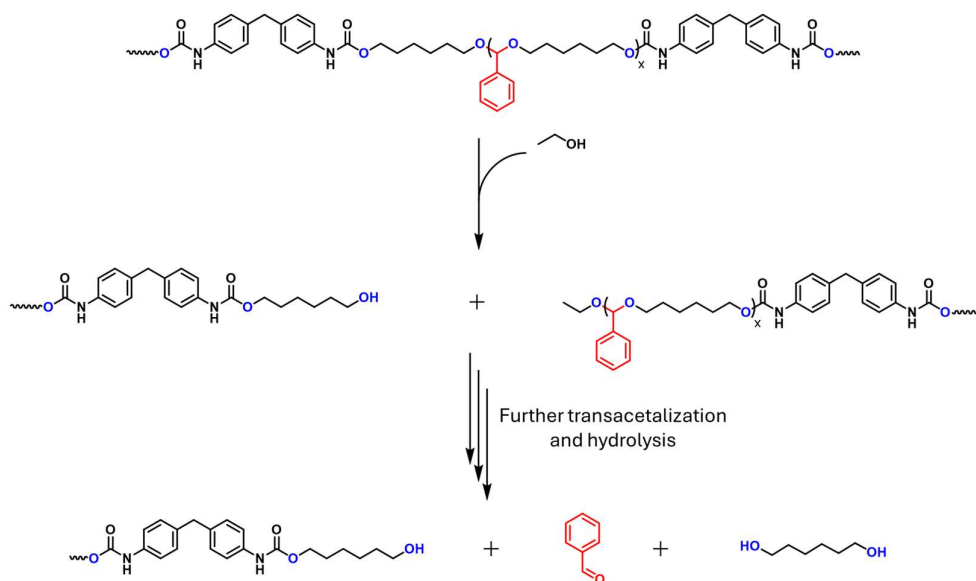


Figure S16. Stacked ^1H NMR spectra (400 MHz, $\text{DMSO-}d_6$) of the depolymerization mixture of **PU AP2** using various reaction solvent mixtures at 80 °C after 24h.

Ethanol assisted chemical depolymerization of AP-containing PU materials

The hydrolysis of PU AP2: PU AP2 (20 g) and ethanol:2 M H₃PO₄ (9:1 by vol.) (80 ml) were added into a 250 ml flask equipped with a condenser. The mixture was stirred for 20 h at 80 °C. After that, water (80 ml) was added to induce the precipitation of the hard phase. The resulting mixture was vacuum filtered to remove the hard phase as a fine powder (9.1 g). The filtrate, containing 1,6-Hexanediol (H16) and 1,4-bis(2-hydroxyethoxy)benzene (HEB), was set aside for further processing. The dried hard phase (9.1 g) was added to a 50 ml flask along with water (2.5 g) and TBD (0.9 g). After 36 h of stirring at 130 °C, the reaction mixture was cooled and washed with water. The water insoluble phase was vacuum-distilled to yield MDA (3.6 g), which was recrystallized from hot water to improve purity. The water-soluble mixture was combined with the aqueous solution of the acetal depolymerization. H16 and HEB were isolated by vacuum distillation yielding 5 g and 4.6 g, respectively. Resulting in final yields of 69%, 79% and 74% for HEB, H16 and MDA, respectively.

The hydrolysis of PU AP3: PU AP3 (44 g) and ethanol:2 M H₃PO₄ (9:1 by vol.) (100 ml) were added into a 250 ml flask equipped with a condenser. The mixture was stirred for 5 h at 80 °C. After that water (100 ml) was added to induce the precipitation of the hard phase. The resulting mixture was vacuum filtered to remove the hard phase as a fine powder (19 g). The filtrate, containing benzaldehyde and the H16, was extracted with ethyl acetate recover benzaldehyde in a yield of 8.2 g. The filtrate, containing 1,6-Hexanediol (H16) was set aside for further processing. The dried hard phase (19g) added to a 50 ml flask along with water (3 g) and TBD (1.5 g) . After 36 h of stirring at 130 °C, the reaction mixture was cooled and washed with water. The water insoluble phase was vacuum-distilled to yield MDA (5.9 g), which was recrystallized from hot water to improve purity. The water-soluble mixture was combined with the aqueous solution of the acetal depolymerization. H16 was isolated by vacuum distillation yielding 18.8 g. Resulting in final yields of 90%, 57% and 68% for H16, benzaldehyde and MDA, respectively.



Scheme S4. Depolymerization of **PU AP3** into hard phase, benzaldehyde and H16 via synergistic ethanol-mediated transacetalization and hydrolysis of the acetal bonds.

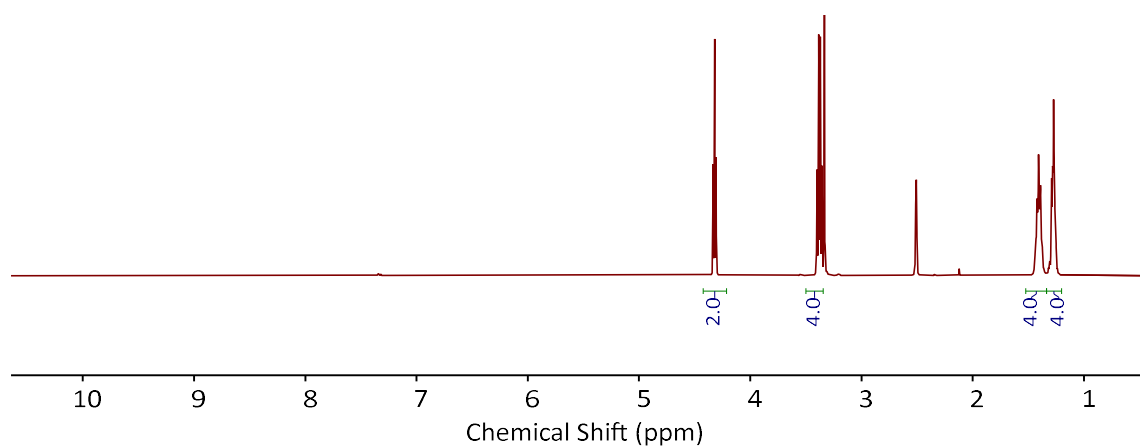


Figure S17. ^1H NMR spectrum (400 MHz, $\text{DMSO-}d_6$) of the isolated and dried H16 from the depolymerization of **PU AP3** in ethanol: 2M H_3PO_4 mixture (9:1).

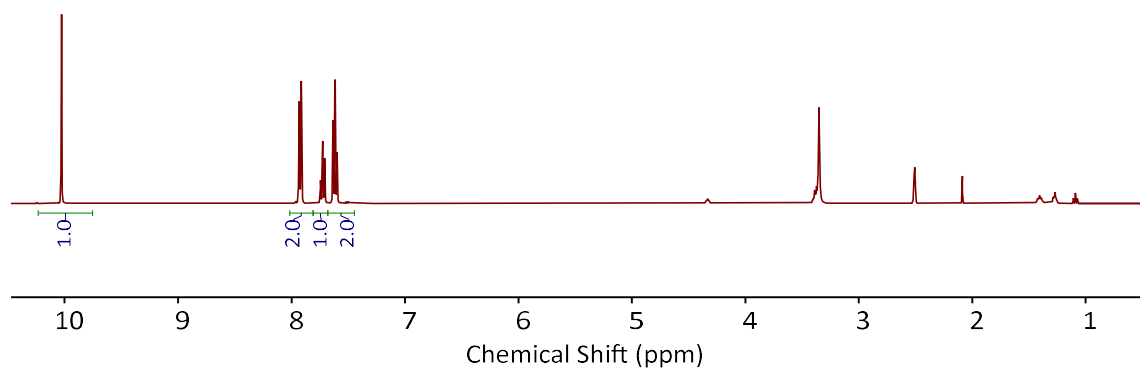


Figure S18. ^1H NMR spectrum (400 MHz, $\text{DMSO-}d_6$) of the isolated benzaldehyde from the depolymerization of **PU AP3** in ethanol: 2M H_3PO_4 mixture (9:1).

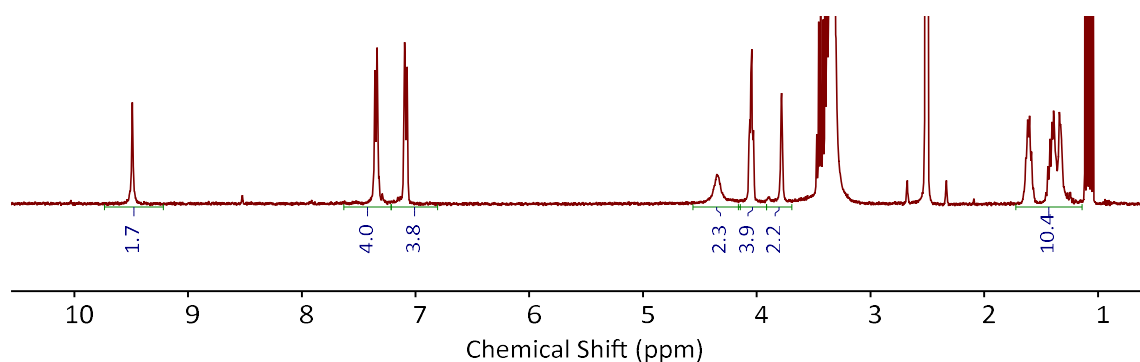


Figure S19. ^1H NMR spectrum (400 MHz, $\text{DMSO-}d_6$) of the filtered hard phase from the depolymerization of **PU AP3** in ethanol: 2M H_3PO_4 mixture (9:1).

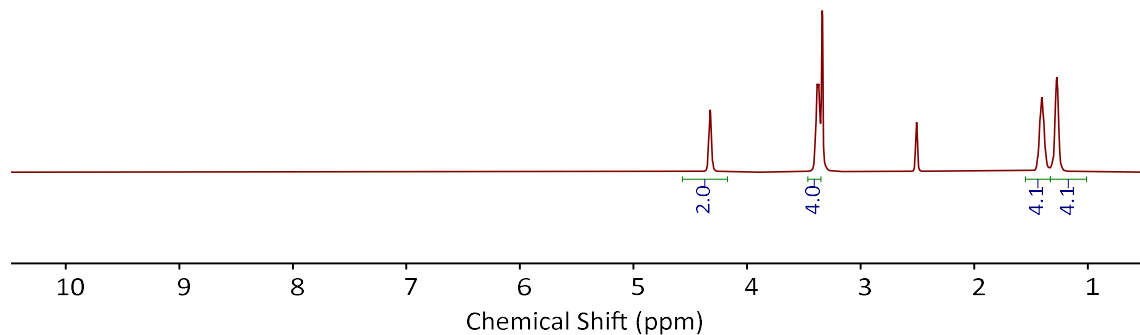


Figure S20. ^1H NMR spectrum (400 MHz, $\text{DMSO-}d_6$) of the isolated and distilled H16 from the hydrolysis of **PU AP3** hard phase.

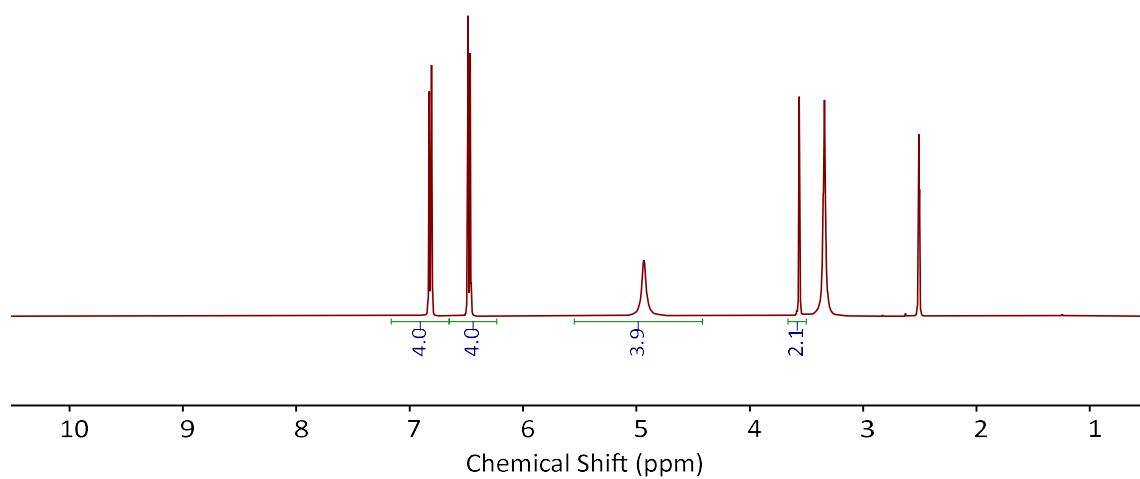


Figure S21. ^1H NMR spectrum (400 MHz, $\text{DMSO-}d_6$) of the distilled and recrystallized MDA from the hydrolysis of **PU AP3** hard phase.

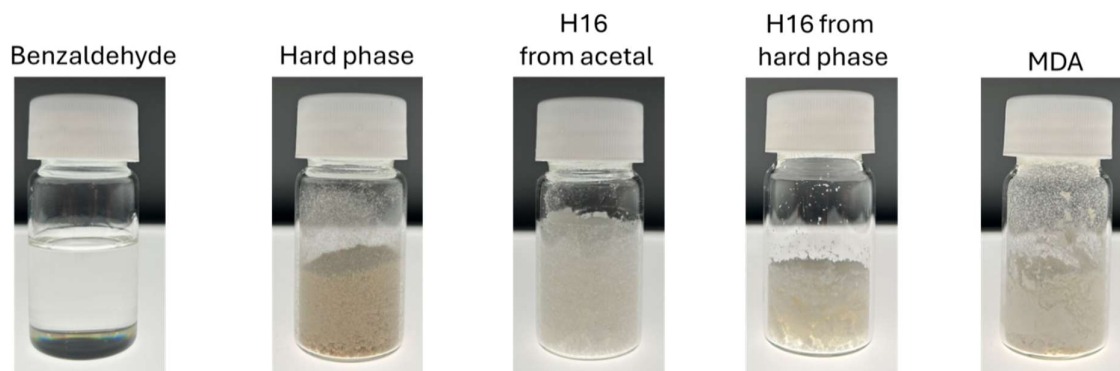


Figure S22. Photographs of the recovered monomers from the depolymerization of **PU AP3**.

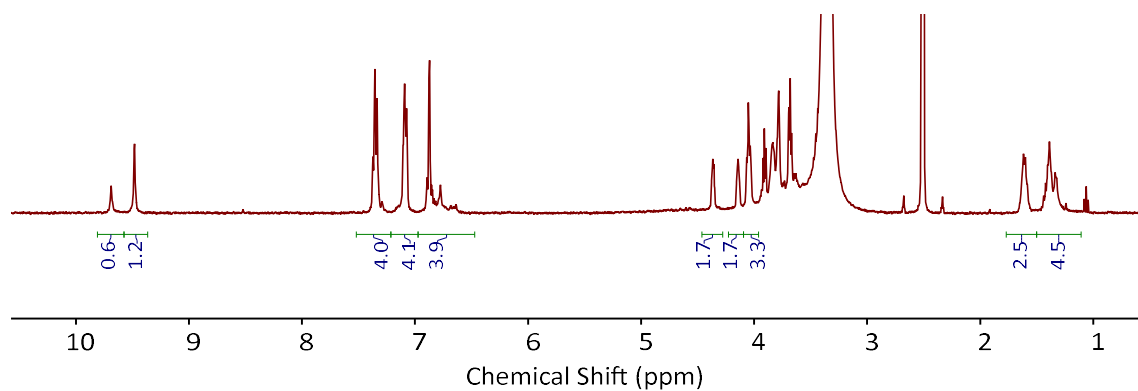


Figure S23. ^1H NMR spectrum (400 MHz, $\text{DMSO-}d_6$) of the filtered hard phase from the depolymerization of **PU AP2** in ethanol: 2M H_3PO_4 mixture (9:1).

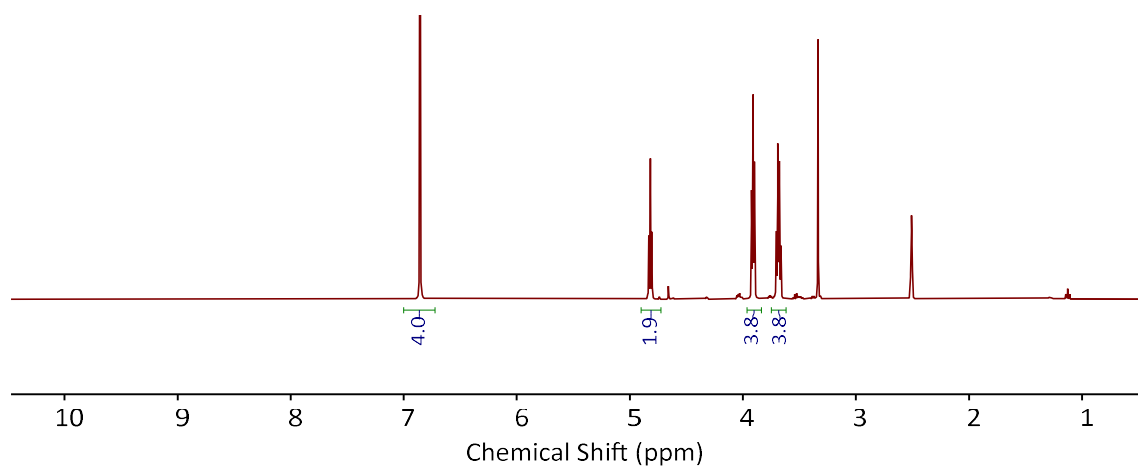


Figure S24. ^1H NMR spectrum (400 MHz, $\text{DMSO-}d_6$) of the HEB recovered from the depolymerization of **PU AP2** in ethanol: 2M H_3PO_4 mixture (9:1) and the subsequent hard phase hydrolysis.

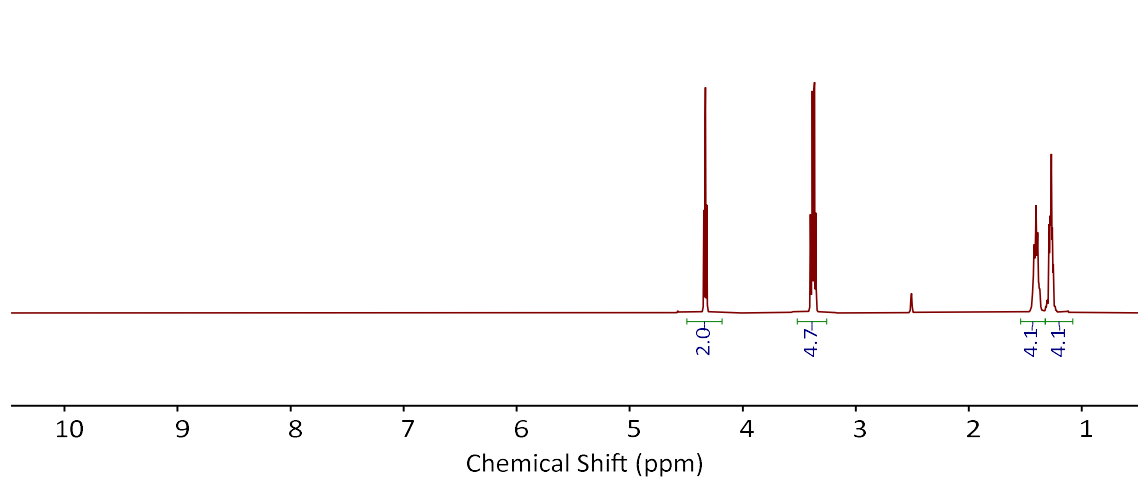


Figure S25. ^1H NMR spectrum (400 MHz, $\text{DMSO-}d_6$) of the H16 recovered from the depolymerization of **PU AP2** in ethanol: 2 M H_3PO_4 mixture (9:1) and the subsequent hard phase hydrolysis.

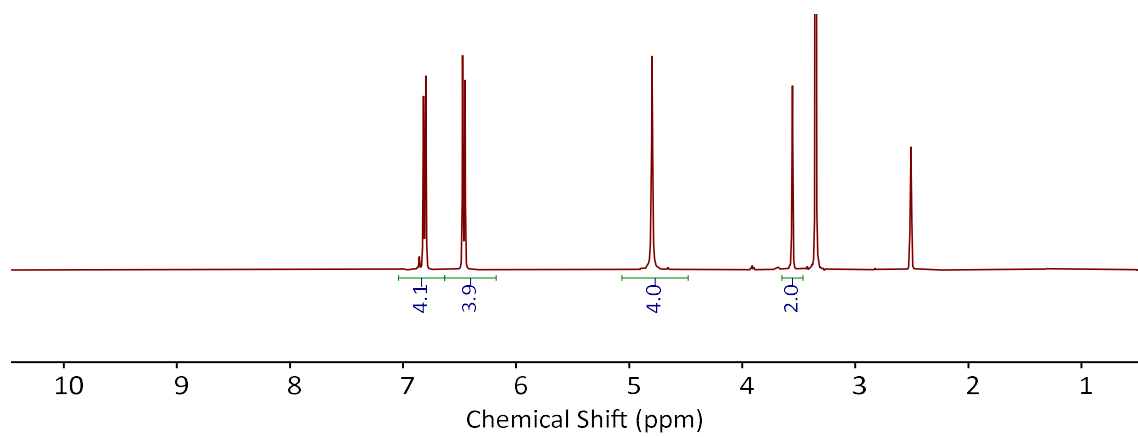


Figure S26. ^1H NMR spectrum (400 MHz, $\text{DMSO-}d_6$) of the distilled and recrystallized MDA from the hydrolysis of **PU AP2** hard phase.

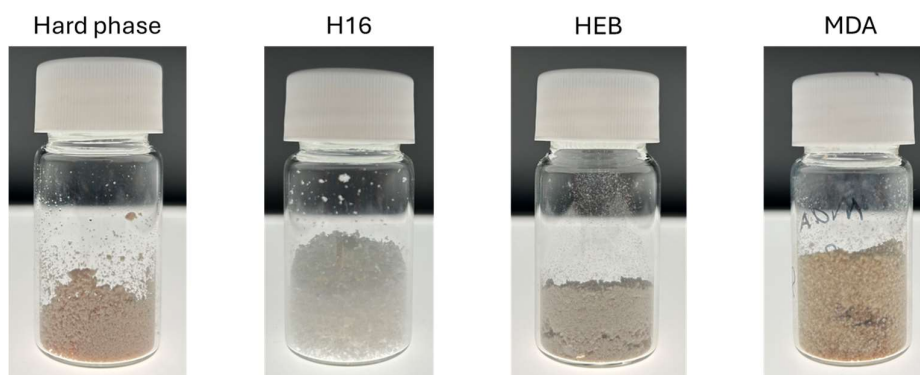


Figure S27. Photographs of the recovered monomers from the depolymerization of **PU AP2**.