Electronic Supplementary Material (ESI) for Polymer Chemistry.
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Supplementary Information

Hydrolytically Degradable Poly(β-thioether ester ketal) Thermosets via Radical-Mediated Thiol-ene Photopolymerization

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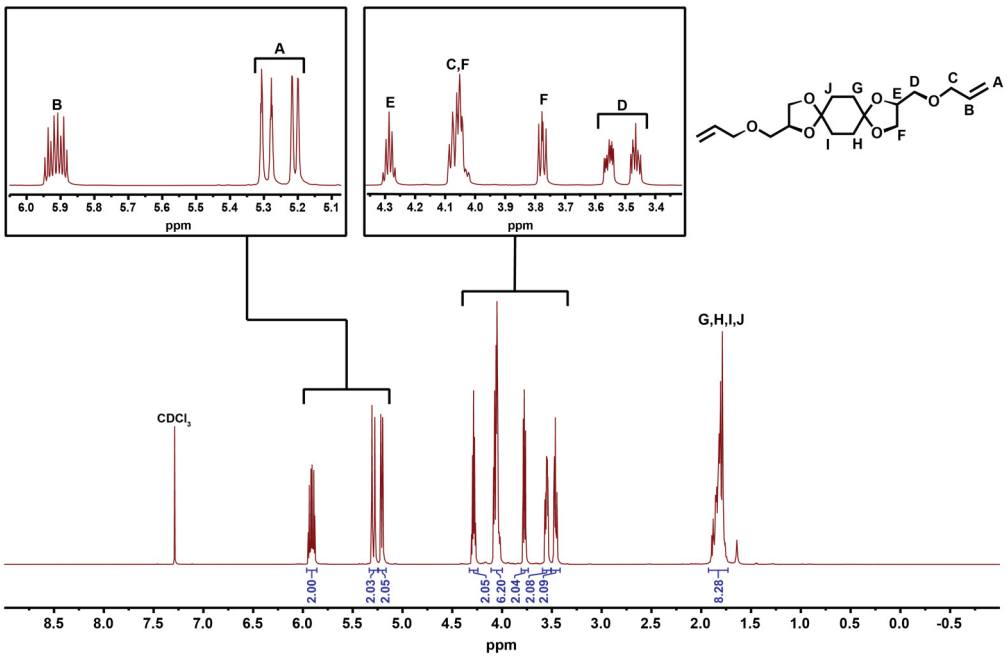
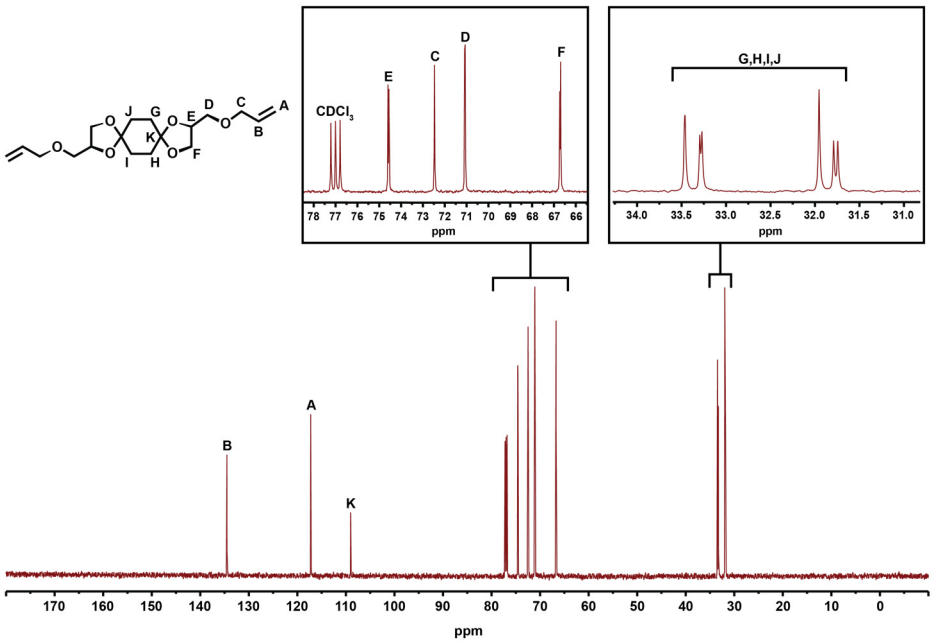


^{1}H NMR (600 MHz, Chloroform-d) δ 5.91 (ddt, J = 17.3, 10.4, 5.6 Hz, 2H), 5.29 (dt, J = 17.2, 1.6 Hz, 2H), 5.21 (dd, J = 10.4, 1.5 Hz, 2H), 4.29 (p, J = 6.0 Hz, 2H), 4.10 – 4.01 (m, 6H), 3.78 (dd, J = 8.3, 6.3 Hz, 2H), 3.57 – 3.54 (m, 2H), 3.46 (ddd, J = 9.8, 5.6, 3.6 Hz, 2H), 1.91 – 1.75 (m, 8H).

Fig. S1. ^{1}H-NMR Spectrum of Monomer **3**.



13C NMR (151 MHz, CDCl3) δ 134.51 (CH), 117.25 (CH_2), 109.02 (C), 74.61 (CH_2), 74.56 (CH_2), 72.48 (CH_2), 71.10 (CH_2), 71.07 (CH_2), 66.75 (CH_2), 66.71 (CH_2), 33.46 (CH_2), 33.29 (CH_2), 33.27 (CH_2), 31.95 (CH_2), 31.79 (CH_2), 31.74 (CH_2).

Fig. S2. ^{13}C-NMR Spectrum of Monomer **3**.

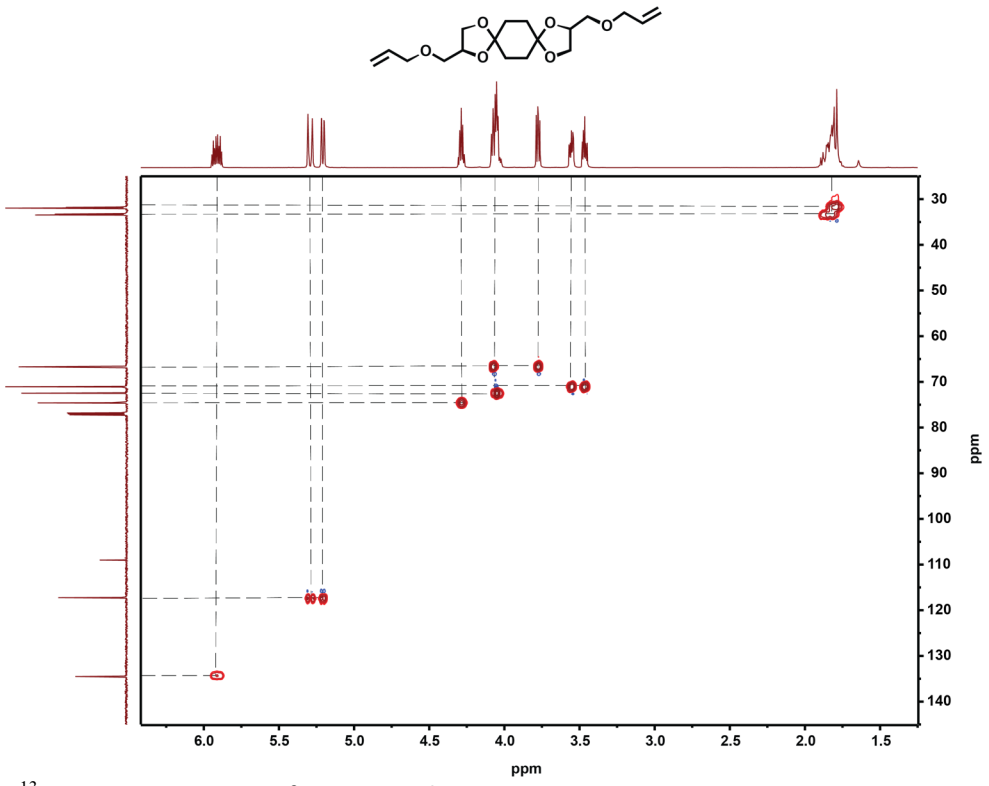


Fig. S3. ^{1}H -^{13}C HSQC Spectrum of Monomer **3**.

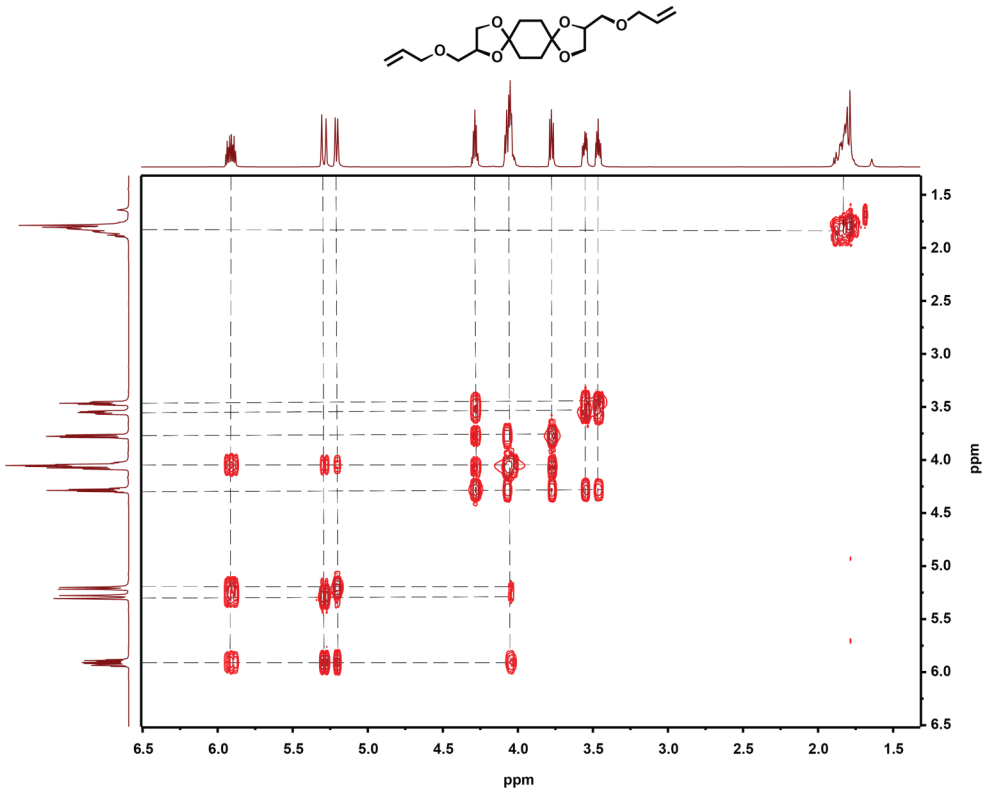
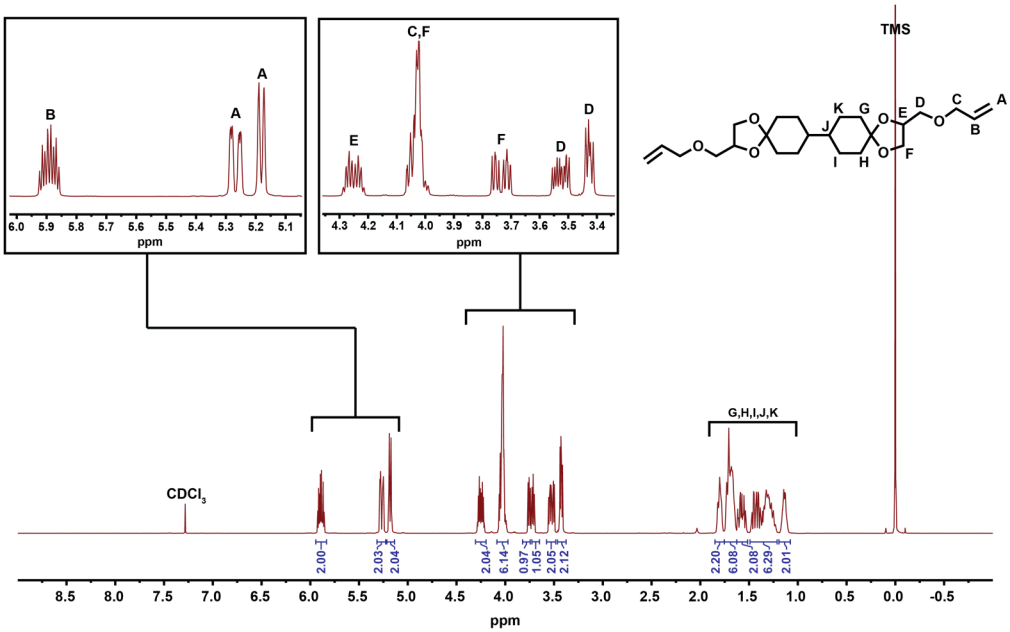
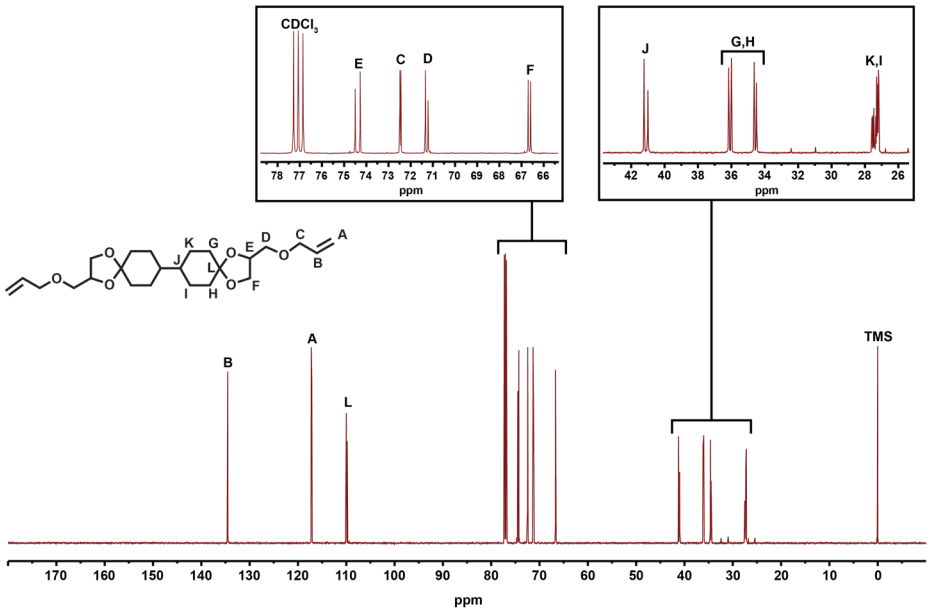


Fig. S4. COSY Spectrum of Monomer **3**.



^{1}H NMR (600 MHz, Chloroform-d) δ 5.94 – 5.85 (m, 2H), 5.31 – 5.23 (m, 2H), 5.18 (d, J = 10.4 Hz, 2H), 4.30 – 4.20 (m, 2H), 4.08 – 3.98 (m, 6H), 3.75 (dd, J = 7.8, 6.5 Hz, 1H), 3.74 – 3.68 (m, 1H), 3.57 – 3.49 (m, 2H), 3.45 – 3.41 (m, 2H), 1.85 – 1.76 (m, 2H), 1.75 – 1.63 (m, 6H), 1.63 – 1.51 (m, 2H), 1.50 – 1.21 (m, 6H), 1.19 – 1.08 (m, 2H).

Fig. S5. ^{1}H-NMR Spectrum of Monomer **5**.



^{13}C NMR (151 MHz, CDCl3) δ 134.59 (CH_2), 134.53 (CH_2), 117.25 (CH), 117.13 (CH), 110.00 (C), 109.80 (C), 74.50 (CH), 74.28 (CH), 72.49 (CH_2), 72.44 (CH_2), 71.34 (CH_2), 71.21 (CH_2), 66.70 (CH_2), 66.59 (CH_2), 41.23 (CH), 41.00 (CH), 36.16 (CH_2), 36.00 (CH_2), 34.63 (CH_2), 34.50 (CH_2), 27.58 (CH_2), 27.52 (CH_2), 27.47 (CH_2), 27.45 (CH_2), 27.35 (CH_2), 27.30 (CH_2), 27.25 (CH_2), 27.23 (CH_2), 27.20 (CH_2), 27.17 (CH_2).

Fig. S6. ^{13}C-NMR Spectrum of Monomer **5**.

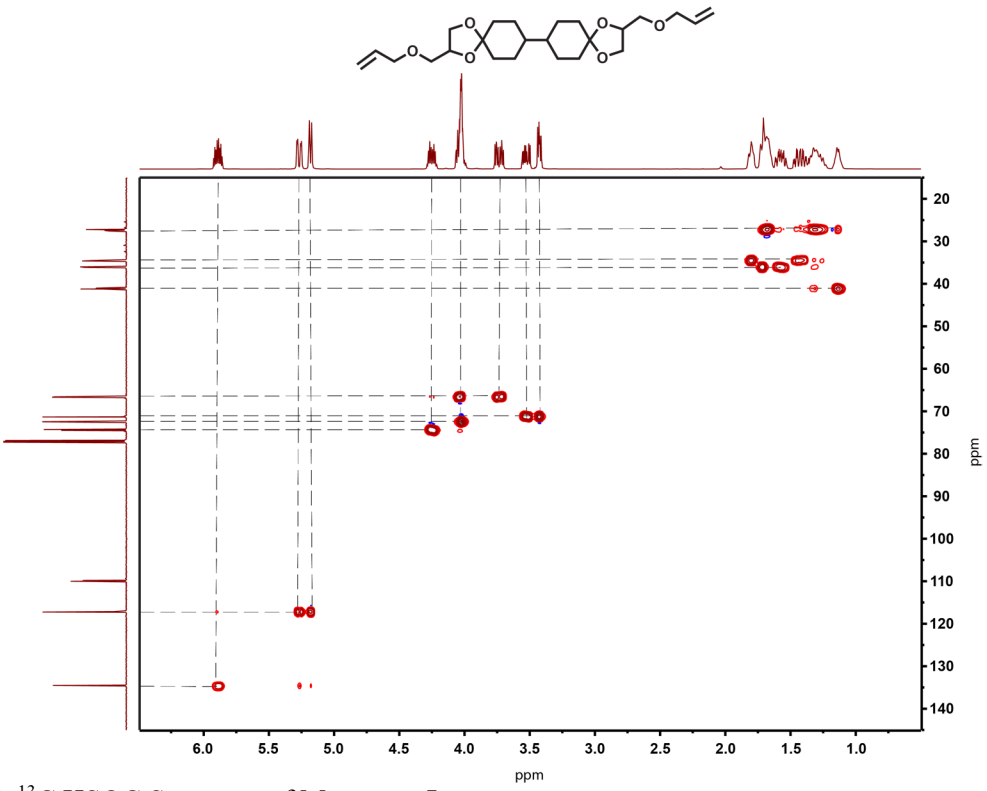


Fig. S7. ^{1}H -^{13}C HSQC Spectrum of Monomer **5**.

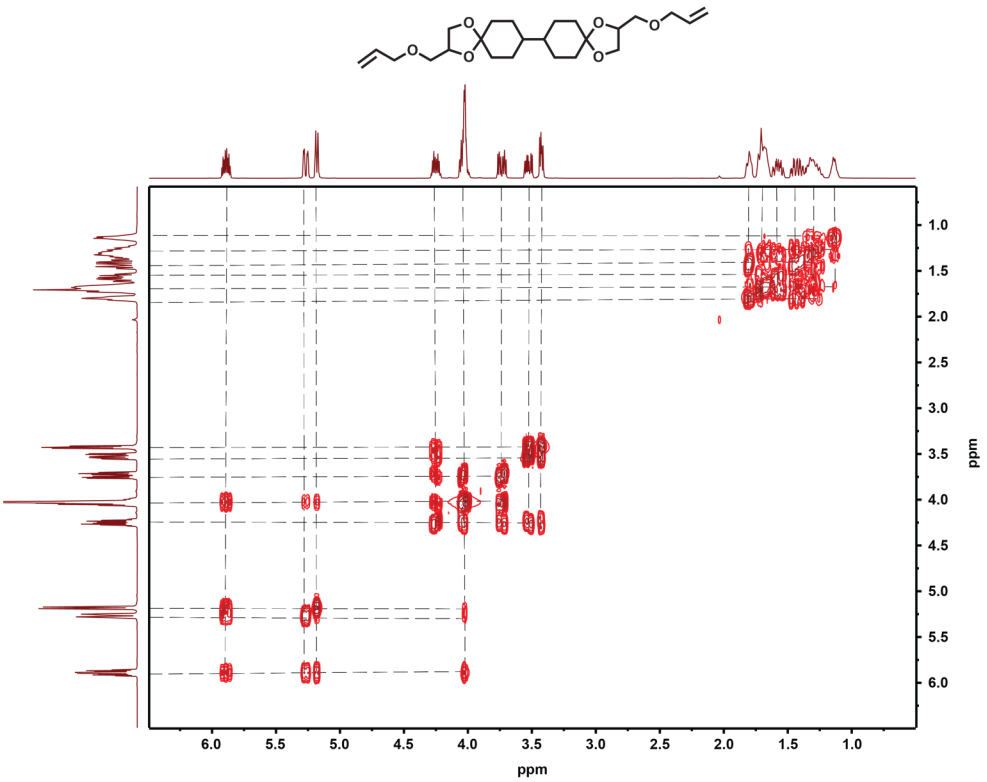
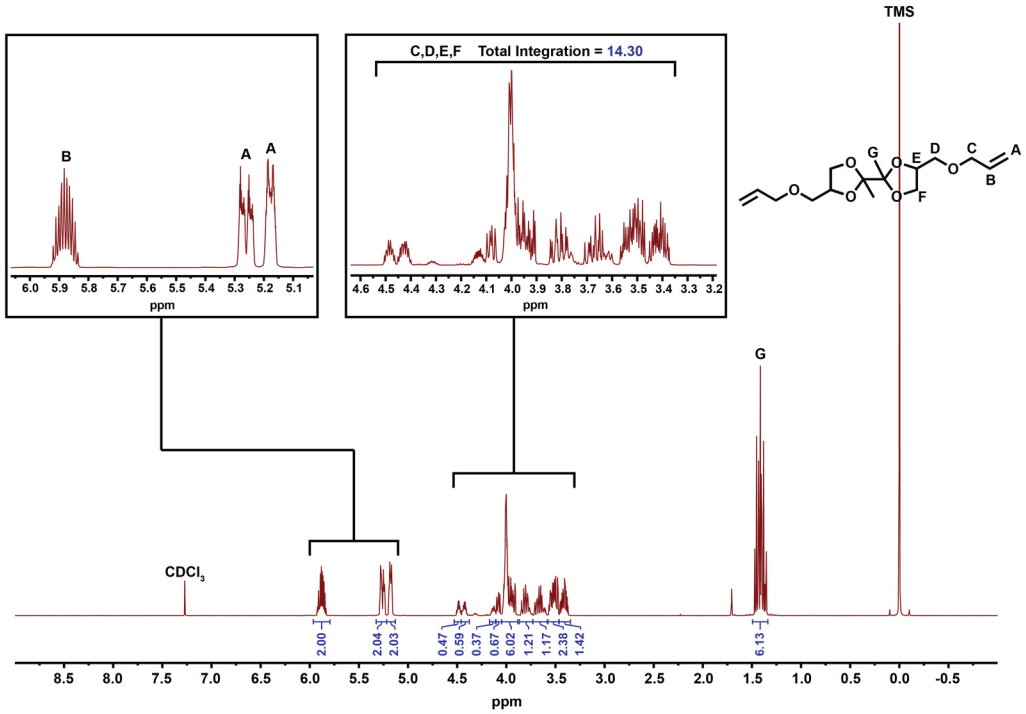
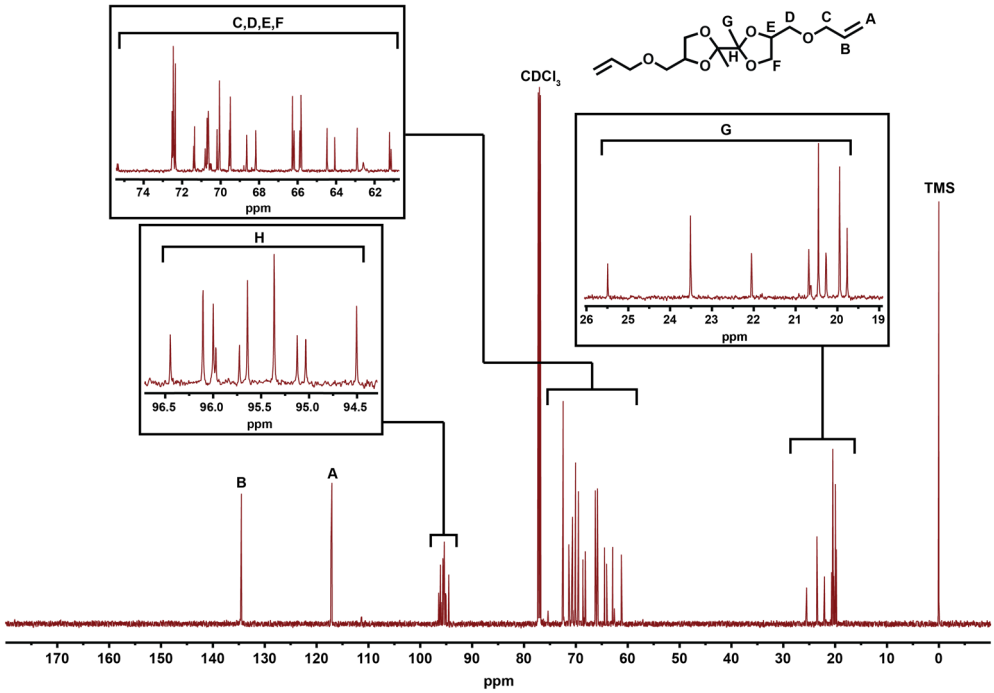


Fig. S8. COSY Spectrum of Monomer **5**.



[1]H NMR (600 MHz, Chloroform-d) δ 5.94 – 5.82 (m, 2H), 5.31 – 5.22 (m, 2H), 5.22 – 5.14 (m, 2H), 4.51 – 4.46 (m, 0.5H), 4.46 – 4.39 (m, 0.5H), 4.16 – 4.10 (m, 0.5H), 4.08 (dd, J = 11.6, 7.4 Hz, 0.5H), 4.05 – 3.90 (m, 6H), 3.85 – 3.74 (m, 1H), 3.72 – 3.59 (m, 1H), 3.58 – 3.46 (m, 2.5H), 3.46 – 3.37 (m, 1.5H), 1.48 -1.34 (m, 6H).

Fig. S9. [1]H-NMR Spectrum of Monomer **7**.



[13]C NMR (151 MHz, Chloroform-d) δ 134.51 (CH), 117.05 (CH_2), 96.45 (C), 96.11 (C), 96.00 (C), 95.73 (C), 95.64 (C), 95.36 (C), 95.12 (C), 95.04 (C), 94.50 (C), 72.52 (CH_2), 72.46 (CH_2), 72.35 (CH_2), 71.40 (CH_2), 71.36 (CH_2), 70.81 (CH_2), 70.70 (CH_2), 70.64 (CH_2), 70.18 (CH_2), 70.06 (CH_2), 69.55 (CH_2), 69.50 (CH_2), 68.65 (CH_2), 68.18 (CH_2), 66.27 (CH_2), 66.18 (CH_2), 65.89 (CH_2), 65.82 (CH_2), 64.47 (CH_2), 64.07 (CH_2), 62.91 (CH_2), 61.23 (CH_2), 61.15 (CH_2), 25.49 (CH_3), 23.51 (CH_3), 22.05 (CH_3), 20.68 (CH_3), 20.45 (CH_3), 20.27 (CH_3), 19.95 (CH_3), 19.77 (CH_3).

Fig. S10. [13]C-NMR Spectrum of Monomer **7**.

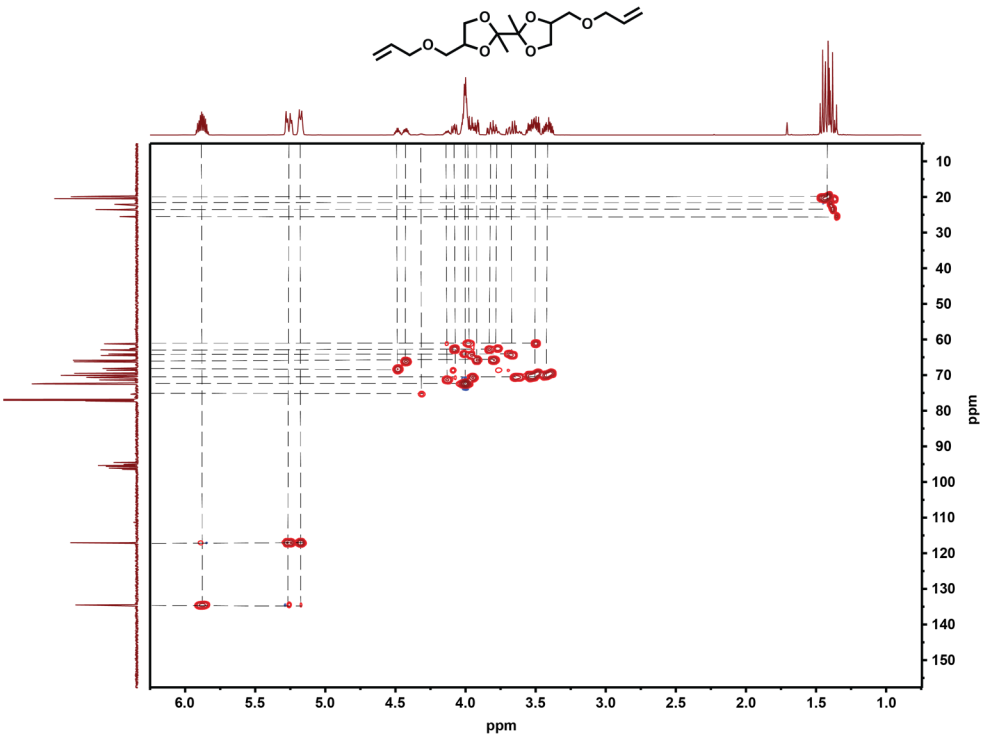


Fig. S11. ^{1}H -^{13}C HSQC Spectrum of Monomer **7**.

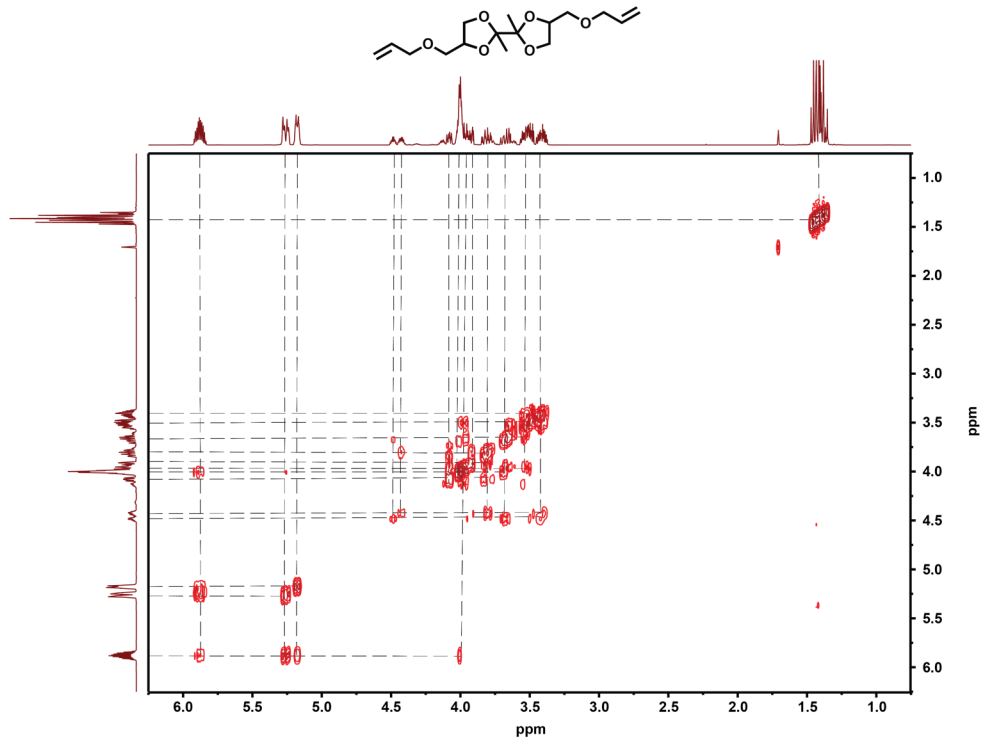
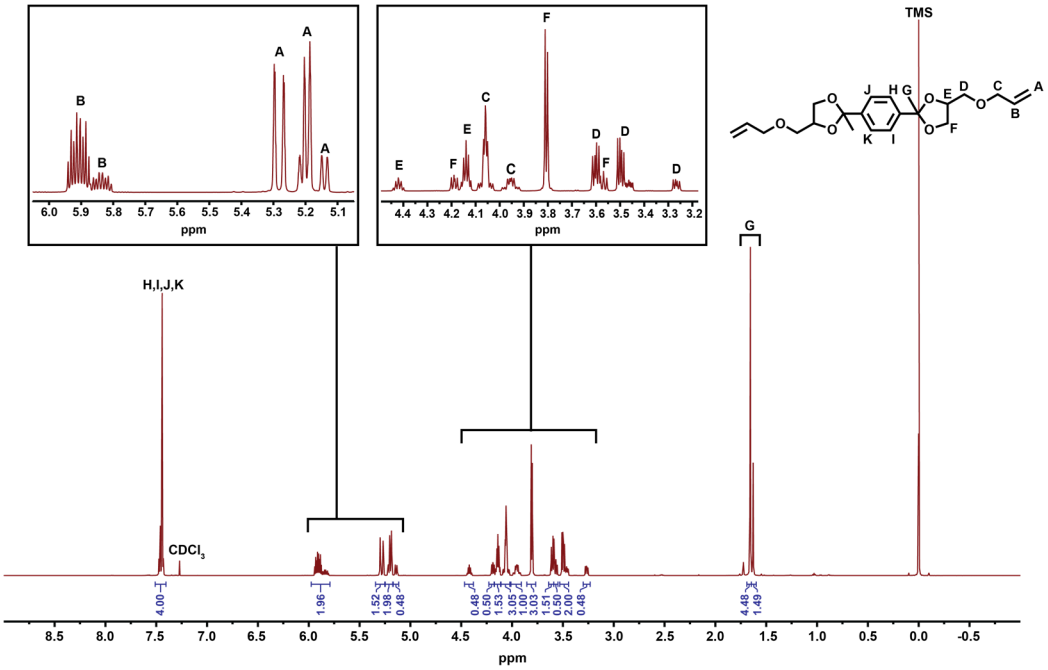
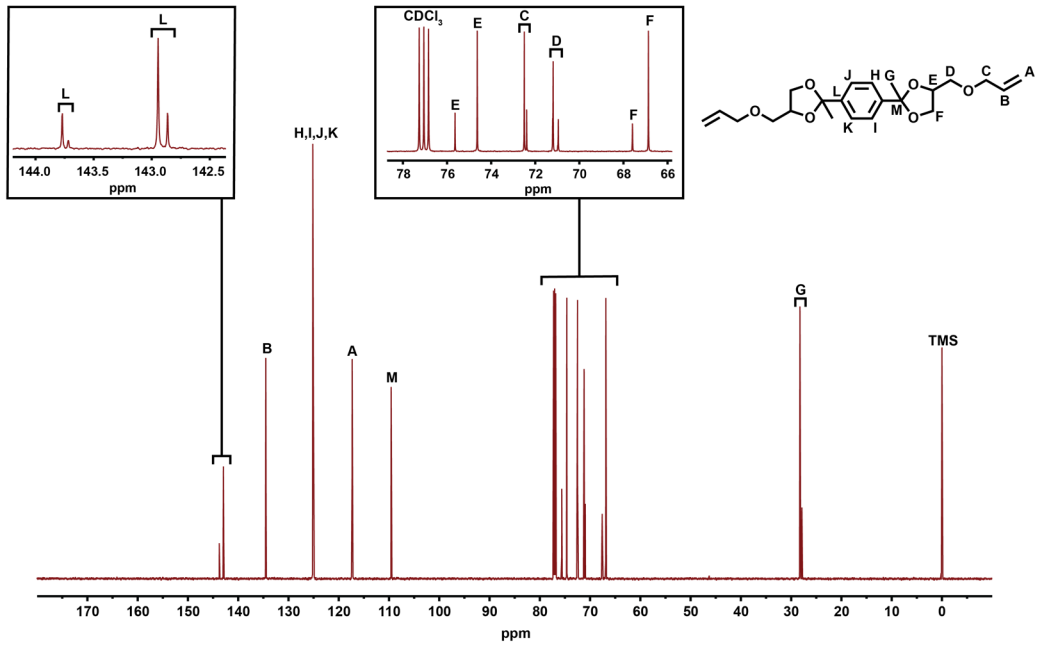


Fig. S12. COSY Spectrum of Monomer **7**.



¹H NMR (600 MHz, Chloroform-d) δ 7.48 – 7.42 (m, 4H), 5.95 – 5.80 (m, 2H), 5.28 (dd, J = 17.2, 1.6 Hz, 1.5H), 5.24 – 5.17 (m, 2H), 5.16 – 5.12 (d, 0.5H), 4.42 (quint, J = 7.5, 6.1 Hz, 0.5H), 4.19 (dd, J = 8.4, 6.3 Hz, 0.5H), 4.14 (quint, J = 5.9 Hz, 1.5H), 4.10-4.02 (m, J = 5.7, 4.2, 1.4 Hz, 3H), 4.00 – 3.91 (m, 1H), 3.81 (d, J = 6.1 Hz, 3H), 3.60 (m, 1.5H), 3.57 (t, J = 8.4, 7.4 Hz, 0.5H), 3.53 – 3.44 (m, 2H), 3.27 (dd, J = 9.9, 5.7, 0.9 Hz, 0.5H), 1.66 (s, J = 2.0 Hz, 4.5H), 1.63 (s, J = 1.9 Hz, 1.5H).

Fig. S13. [1]H-NMR Spectrum of Monomer **9**.



¹³C NMR (151 MHz, Chloroform-d) δ 143.77 (C), 143.72 (C), 142.95 (C), 142.87 (C), 134.51 (CH), 134.45 (CH), 125.15 (CH), 125.03 (CH), 124.91 (CH), 117.33 (CH2), 117.21 (CH2), 109.57 (C), 75.64 (CH), 74.63 (C), 72.50 (CH2), 72.39 (CH2), 71.19 (CH2), 70.95 (CH2), 67.59 (CH2), 66.87 (CH2), 28.25 (CH3), 27.87 (CH3).

Fig.S14. [13]C-NMR Spectrum of Monomer **9**.

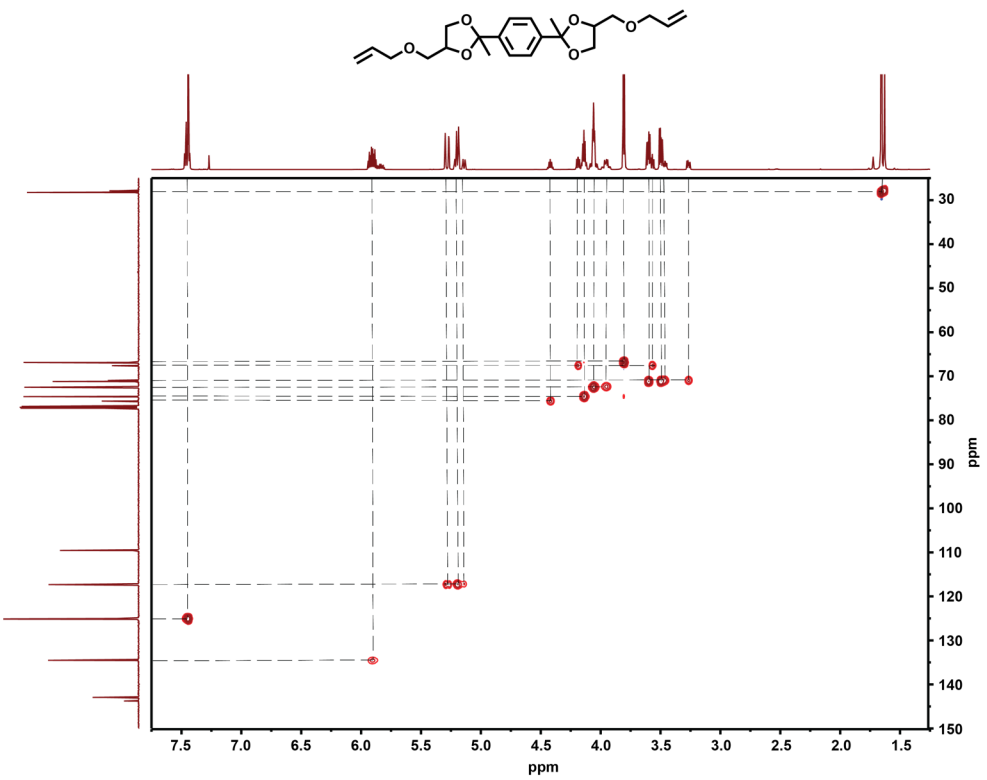


Fig. S15. ^{1}H -^{13}C HSQC Spectrum of Monomer **9**.

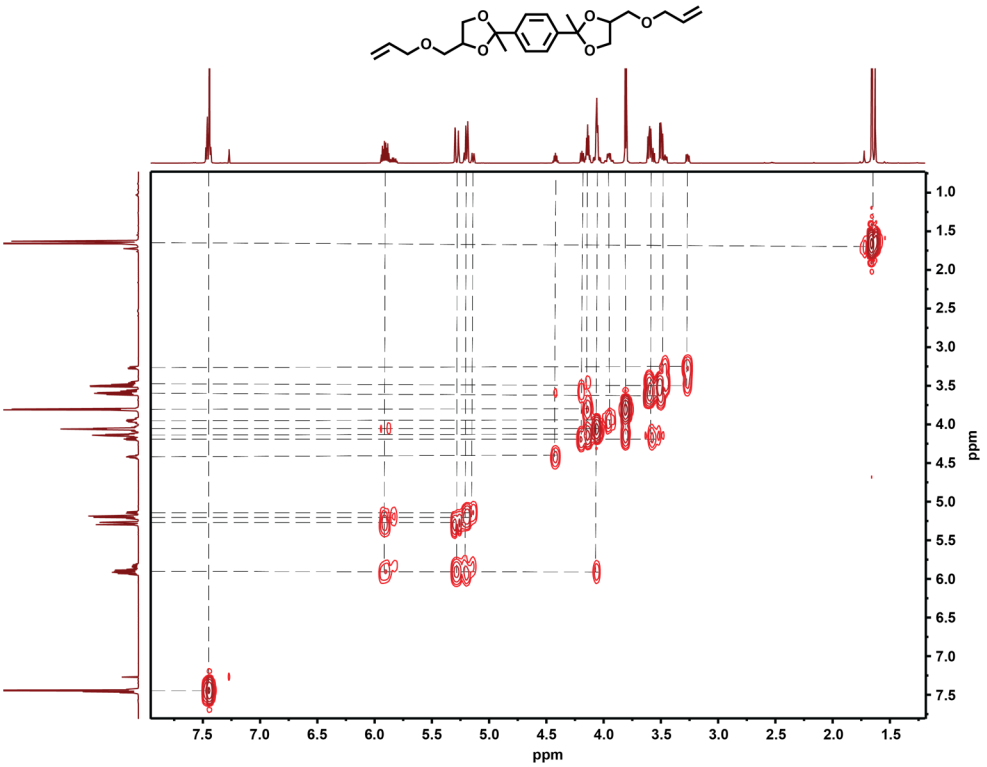


Fig. S16. COSY Spectrum of Monomer **9**.

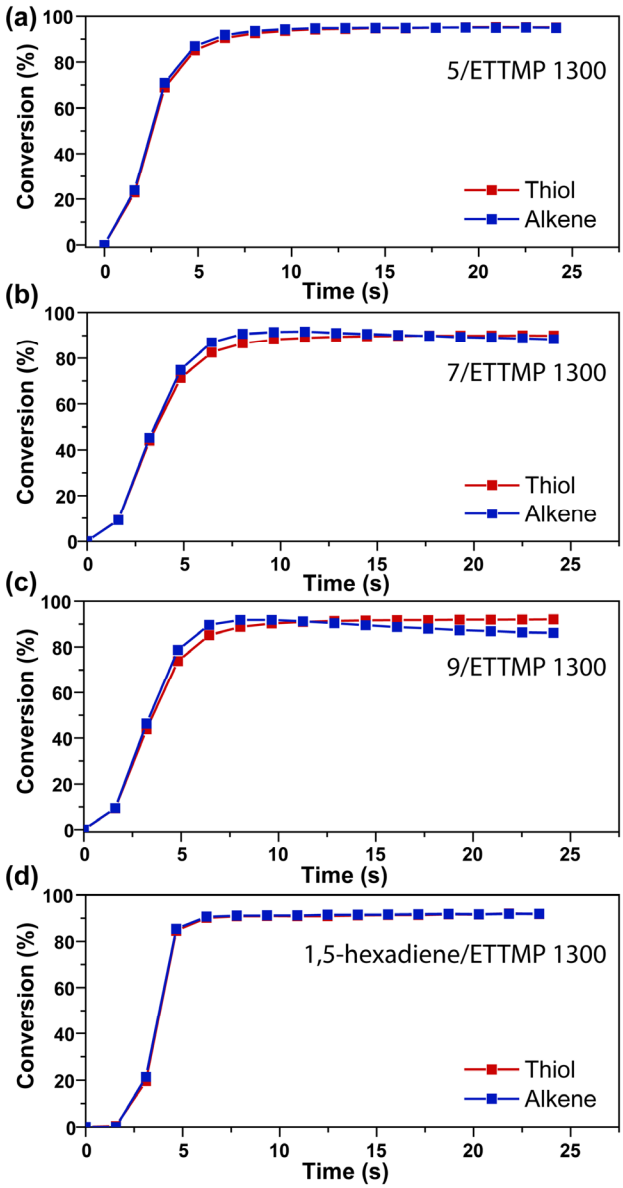


Fig. S17. Experiments resulted in respectable conversions of 94%, 95%, and 92% for thermosets 1a, 1b (a) and 1,5-hexadiene (d) respectively, while compositions based on 1c and 1d showed conversions of 91% (b,c).

Acidic degradation product analysis for P9

Experimental procedure: 900mg of P9 was degraded in 20 mL HCl/H_2O (pH 0.2) over the course of 12 h. Fine white crystals formed in the degradation solution. The crystals were washed with DI H_2O and ethanol and set aside for analysis. The remaining degradation solution was extracted 2x with chloroform, dried with sodium sulfate and vacuumed to yield a clear viscous oil. The crystals and viscous oil products were analyzed by ^{1}H-NMR and were confirmed as 1,4-diacetylbenzene (fine white crystals) and a multifunctional alcohol (clear viscous oil). Both products confirmed ketal hydrolysis to be the main mechanism of degradation for P9.

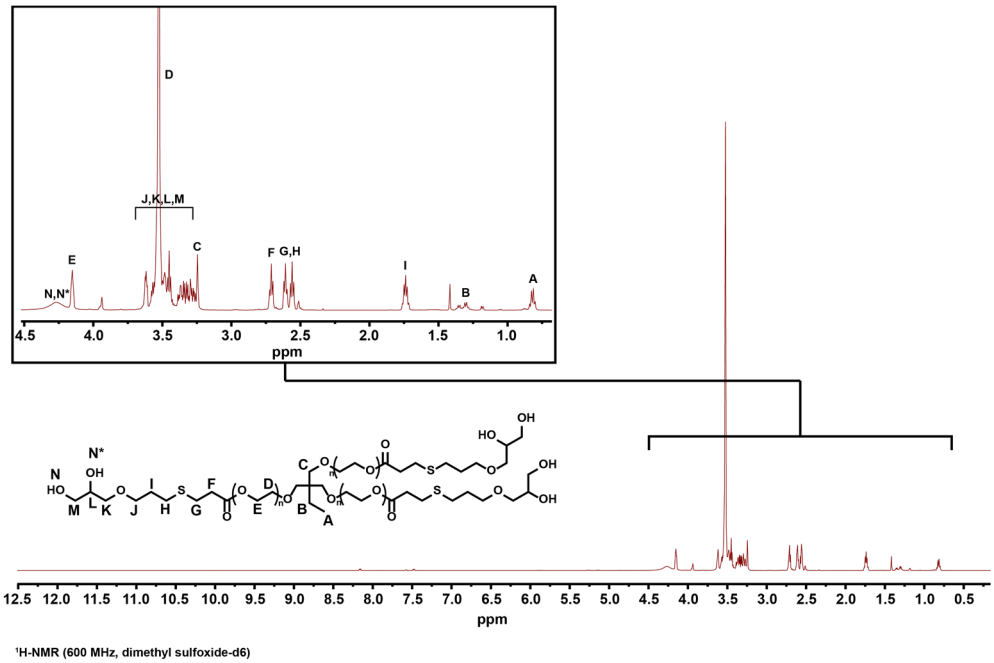


Fig S18. ^{1}H-NMR spectrum of water-soluble **P9** degradation by-products obtained under acidic conditions (pH 0.2).

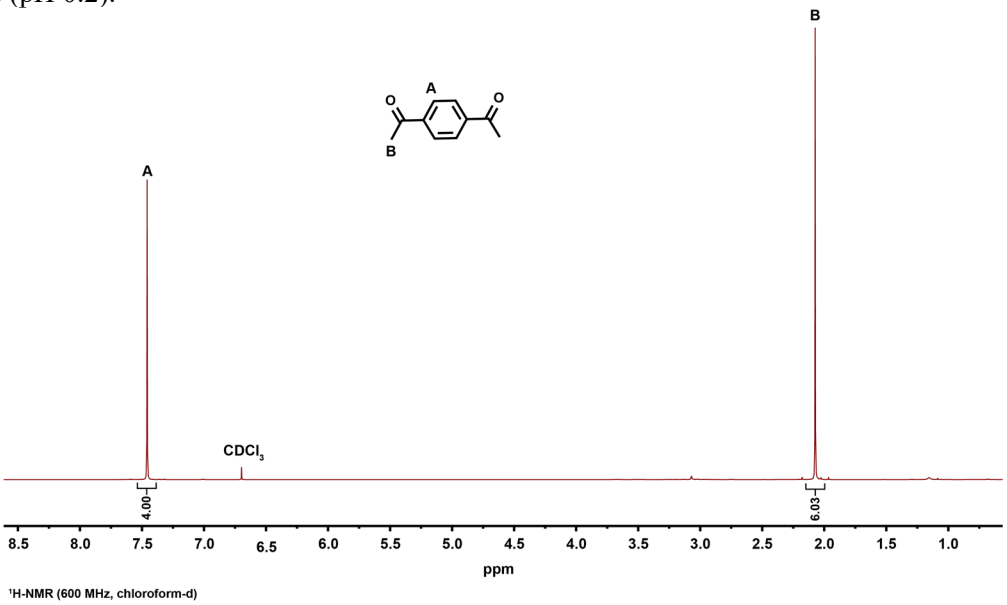


Fig S19. ^{1}H-NMR spectrum of water-insoluble **P9** degradation by-products obtained under acidic conditions (pH 0.2).

Basic degradation product analysis for P9

Experimental procedure: 900mg of P9 was degraded in 20 mL of NaOH/H_2O (pH 13.5) over 10 h. No precipitates or crystals were observed to form. The remaining degradation solution was neutralized with HCl/H_2O solution before being extracted 2x with chloroform, dried with sodium sulfate and vacuumed to yield a clear viscous oil. ^{1}H-NMR confirmed the products to be trimethylol propane ethoxylate and a carboxylic acid end-functionalized ketal crosslinker. Both products confirmed ester hydrolysis to be the main mechanism of degradation for P9.

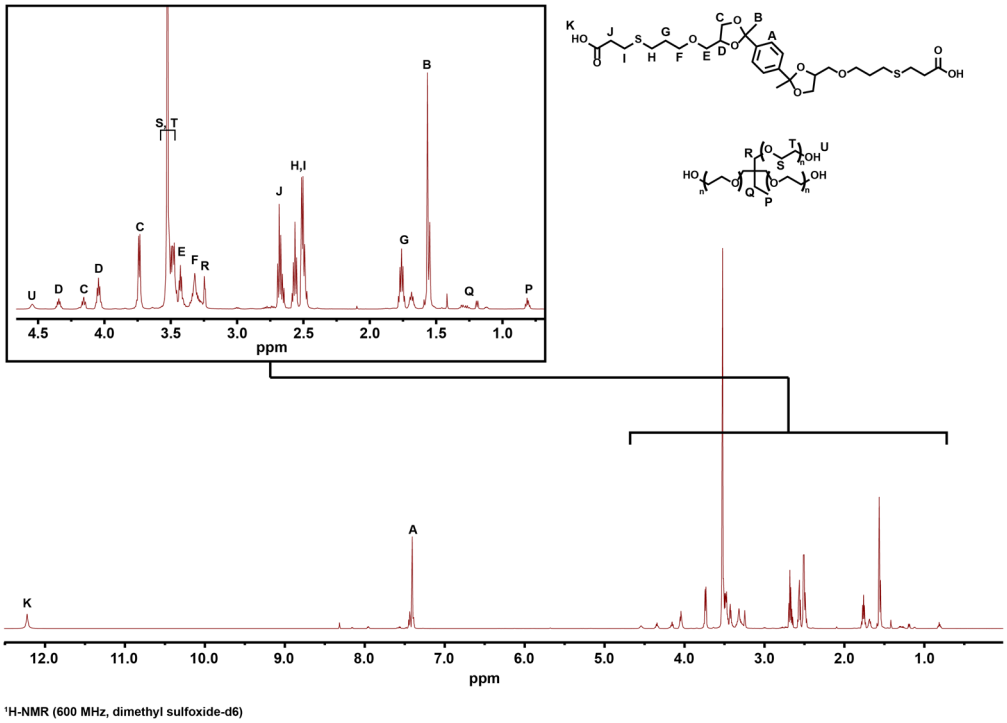
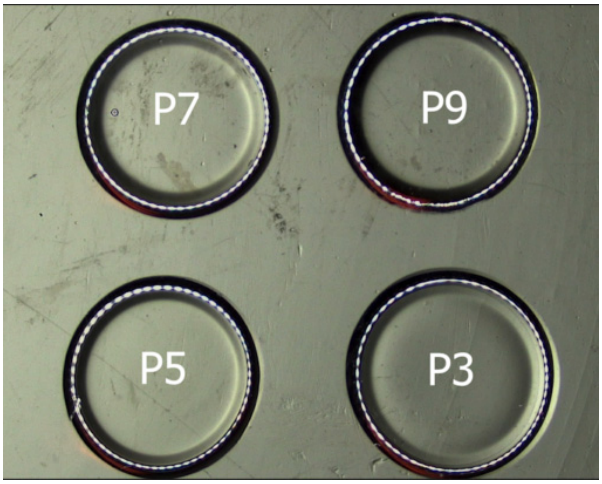


Fig S20. ^{1}H-NMR spectrum of **P9** degradation by-products obtained under basic conditions (pH 13.5).



Video S1. Degradation of poly(β-thioether ester ketal) thermosets P3, P5, P7, at pH 0.88 (HCl/H_2O). Full length video is 17h presented at approximately 1500x speed. Note: Thermoset disk size for video capture was based on 5µL droplets prior to photopolymerization. This disk size is much smaller than samples employed in mass loss experiments.