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

Degradable and Renewably-sourced Poly(ester-thioethers) by Photo-initiated Thiol-ene Polymerization

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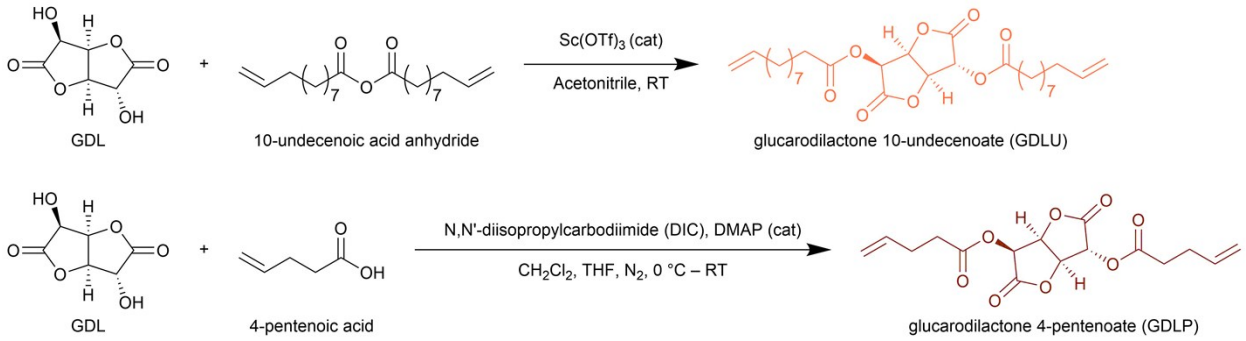
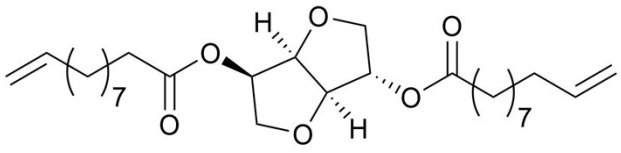
Contents

Synthesis Schemes and Molecular Structures



Scheme S1. Reaction schemes for the synthesis of Glucarodilactone 10-undecenoate (GDLU)[1] and glucarodilactone 4-pentenoate (GDLP).



isosorbide 10-undecenoate (IU)

Scheme S2. Molecular structure of isosorbide 10-undecenoate (IU).

Polymer Sample Pictures

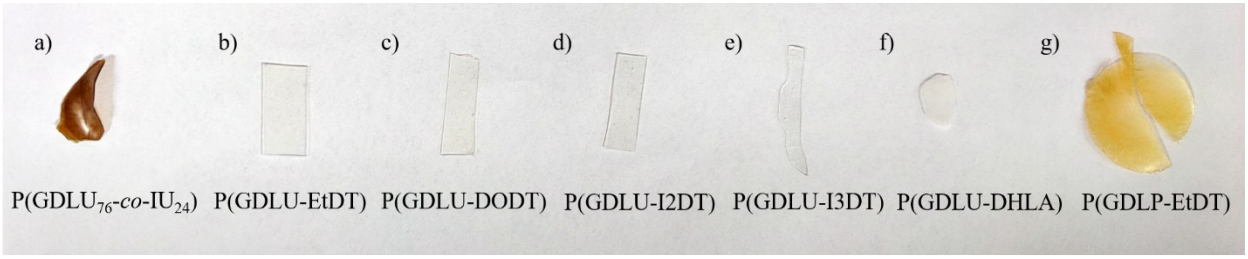


Figure S1. Visual comparison of an ADMET-derived GDL-containing polyester P($GDLU_{76}$-*co*-IU_{24}) (a)[1] and the GDL-containing poly(ester-thioethers) of this work. (b) P(GDLU- EtDT), (c) P(GDLU-DODT), (d) P(GDLU-I2DT), (e) P(GDLU-I3DT), (f) P(GDLU-DHLA), and (g) P(GDLP-EtDT).

Polymer Yield Information

Table S1. Yield information for the poly(ester-thioethers) reported in this work.

Polymer	Theoretical Yield (g)	Collected Yield (g)	Percent Theoretical Yield (%)
P(GDLU-EtDT)	3.6	3.2	89
P(GDLU-DODT)	4.1	3.6	88
P(GDLU-I2DT)	3.3	3.0	91
P(GDLU-I3DT)	3.3	3.0	91
P(GDLU-DHLA)	3.1	2.7	87
P(GDLP-EtDT)	1.6	1.0	63

^{1}H NMR Spectra

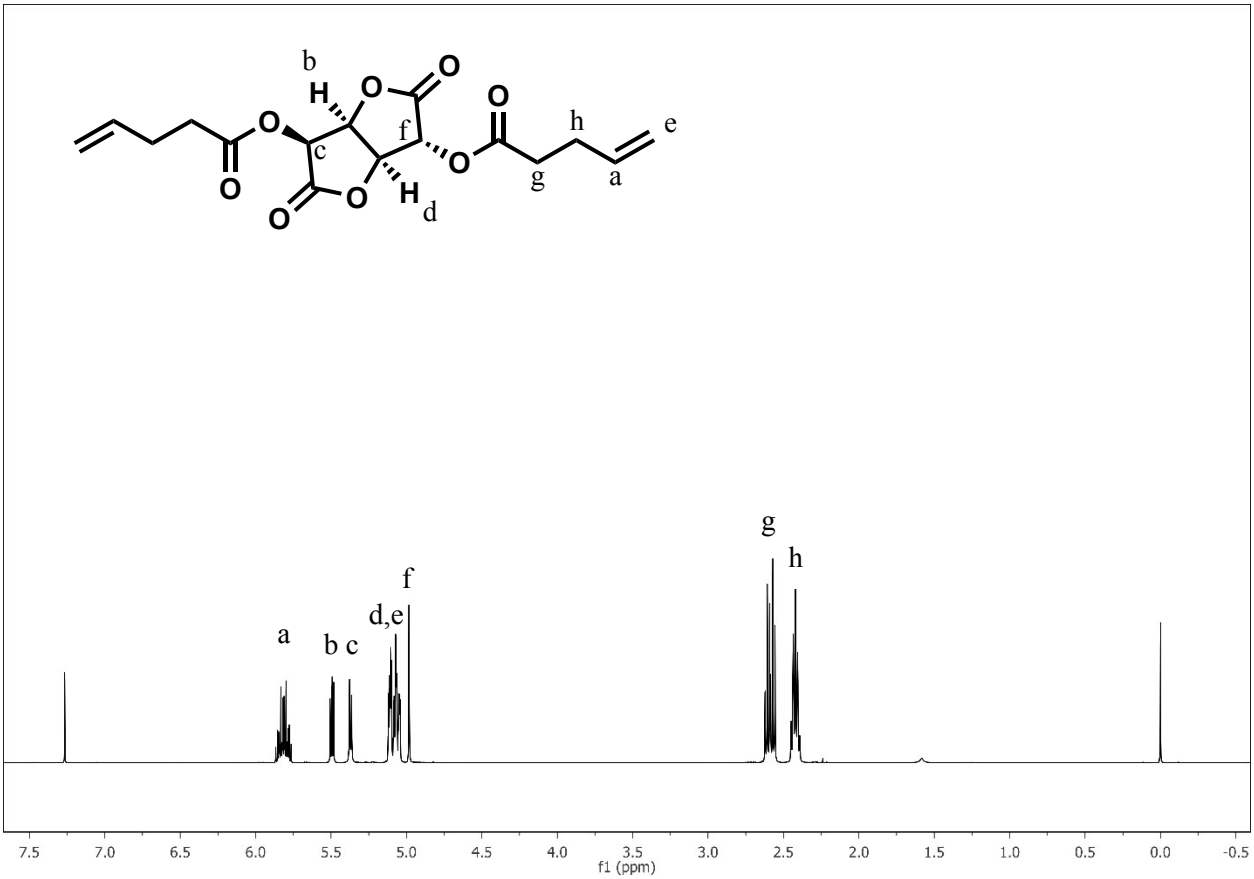


Figure S2. ^{1}H-NMR spectrum of glucarodilactone 4-pentenoate ($CDCl_3$, 500 MHz)

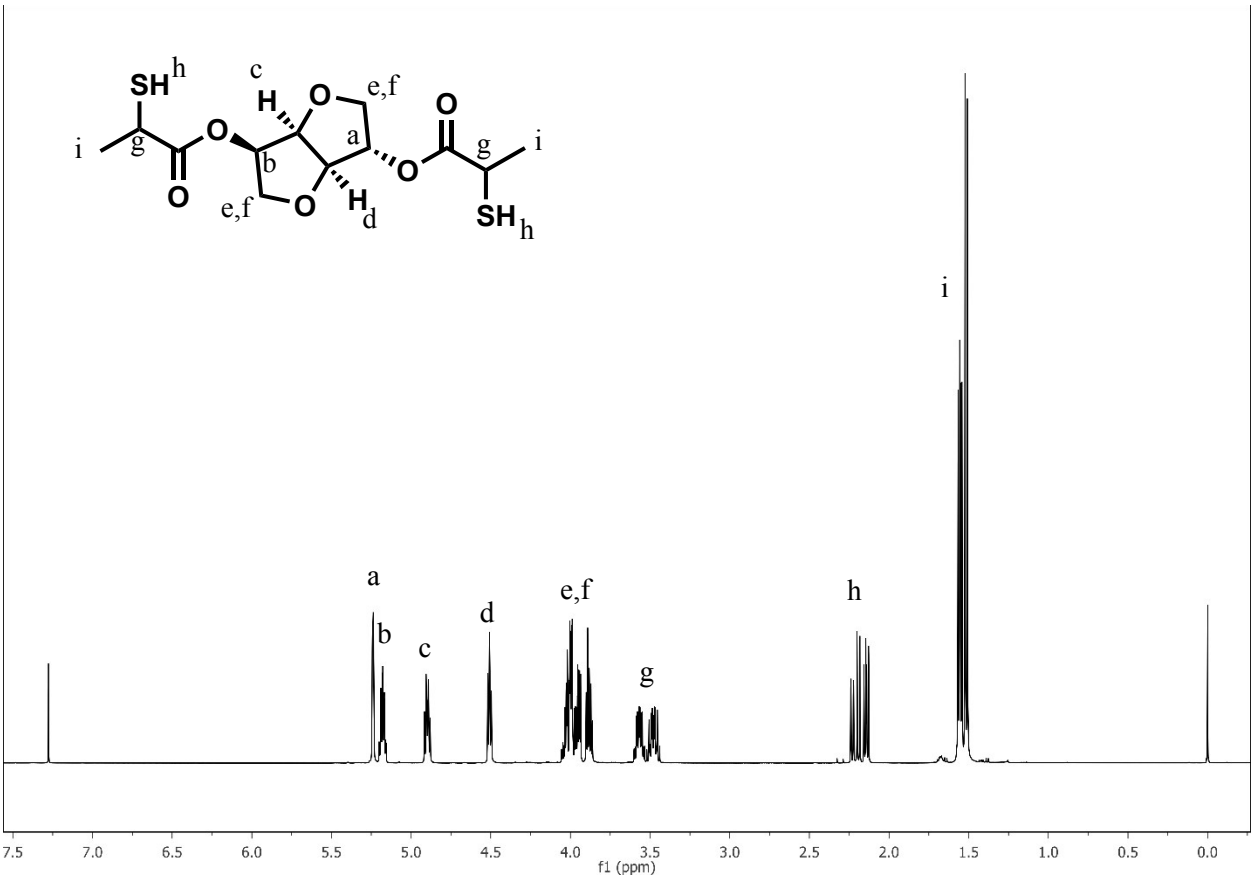


Figure S3. ^{1}H-NMR spectrum of isosorbide 2-mercaptopropionate ($CDCl_3$, 500 MHz)

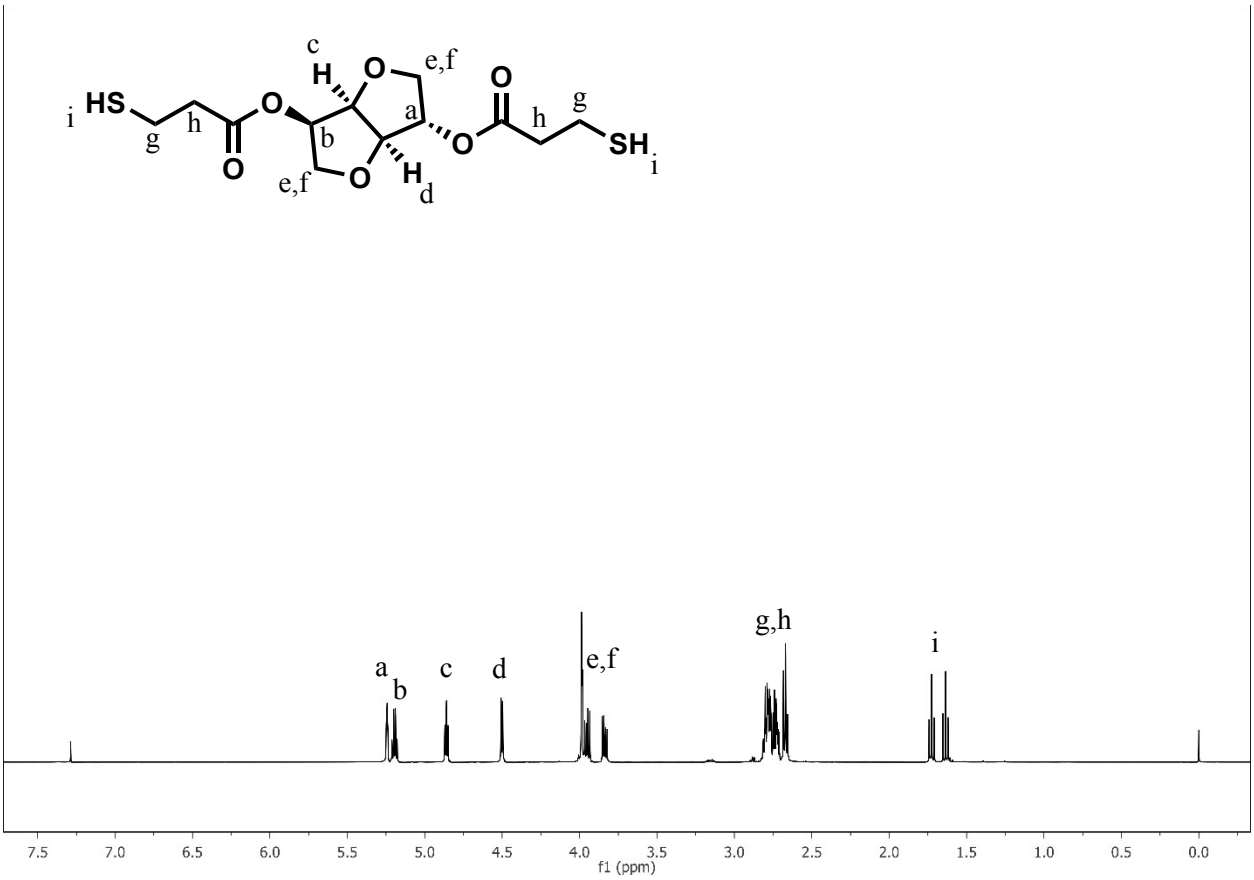


Figure S4. ^{1}H-NMR spectrum of isosorbide 3-mercaptopropionate ($CDCl_3$, 500 MHz)

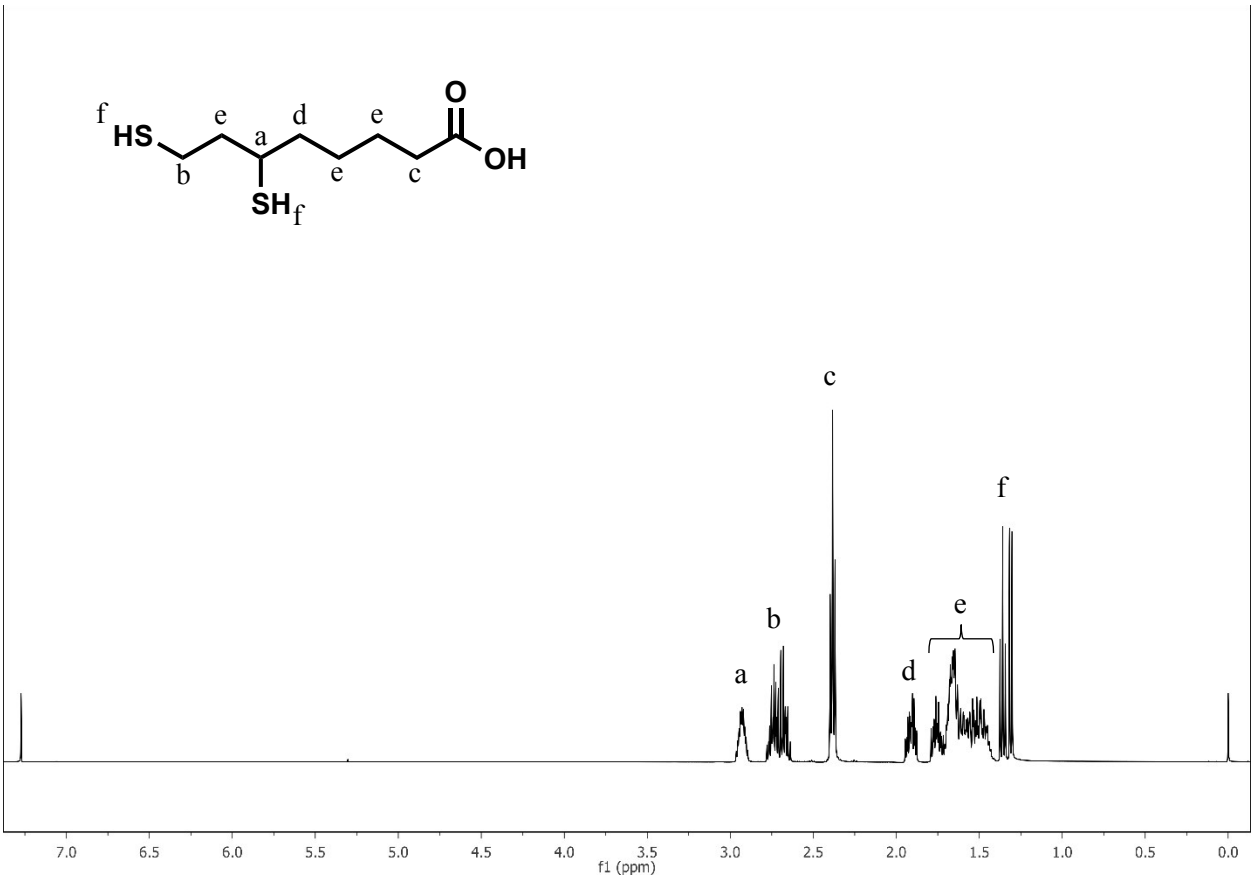


Figure S5. ^{1}H-NMR spectrum of *rac*-dihydrolipoic Acid ($CDCl_3$, 500 MHz)

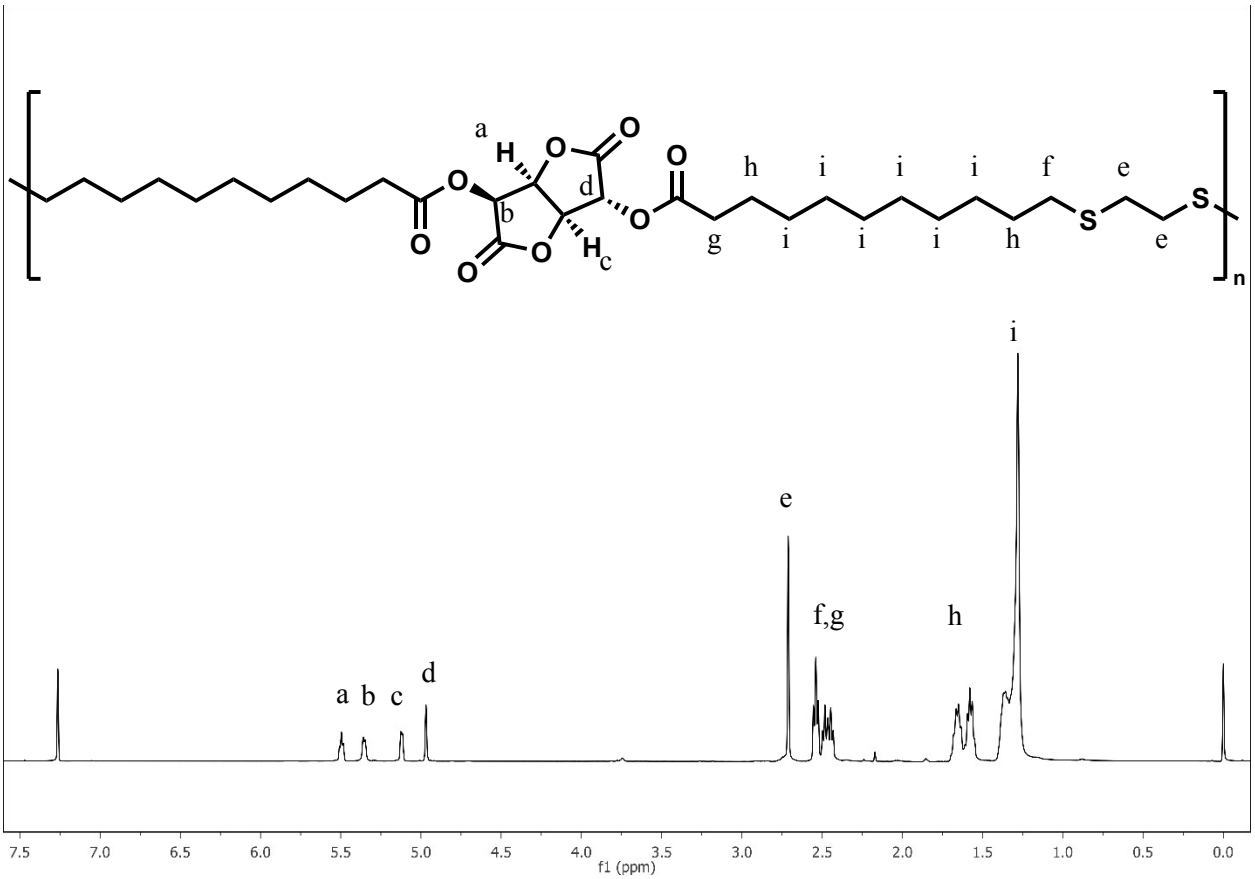


Figure S6. ^{1}H-NMR spectrum of P(GDLU-EtDT) ($CDCl_3$, 500 MHz)

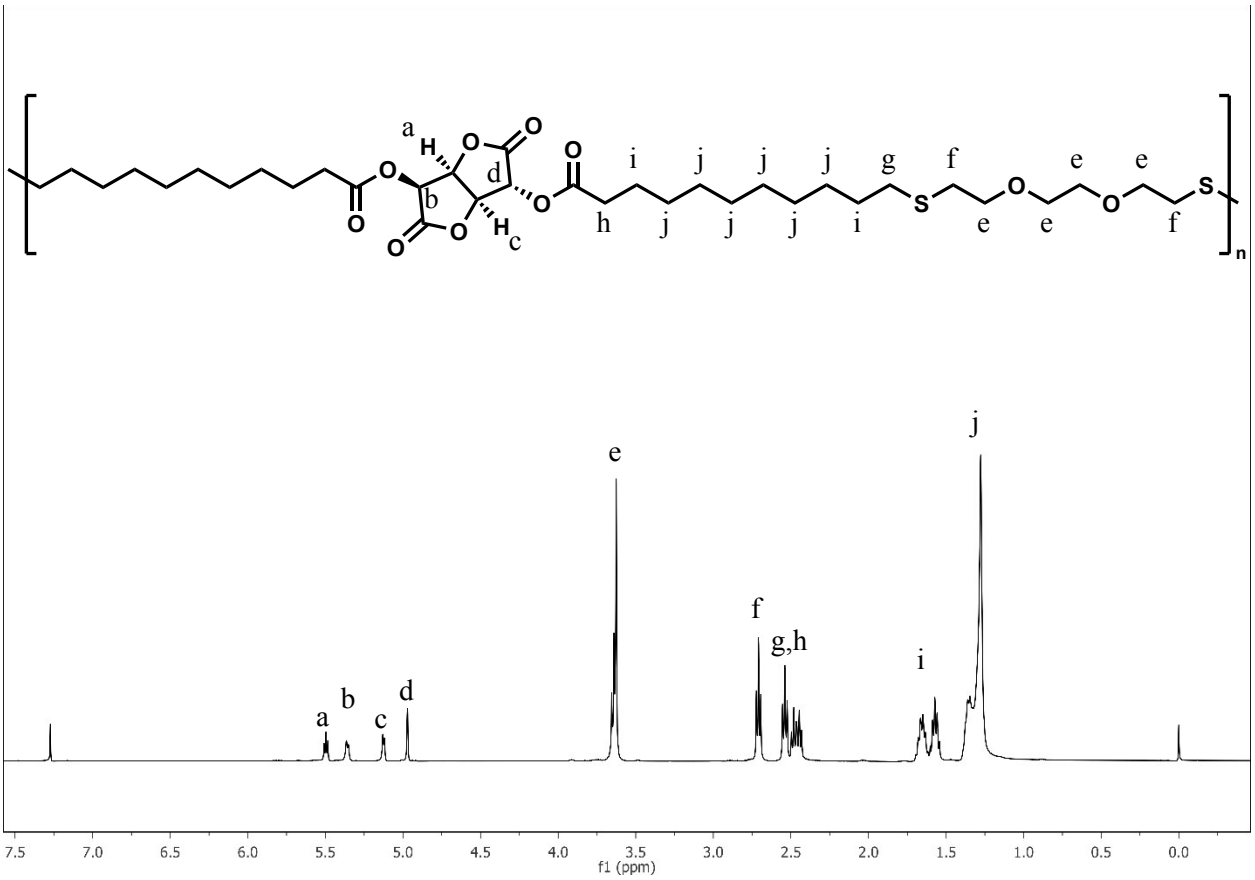


Figure S7. ^{1}H-NMR spectrum of P(GDLU-DODT) ($CDCl_3$, 500 MHz)

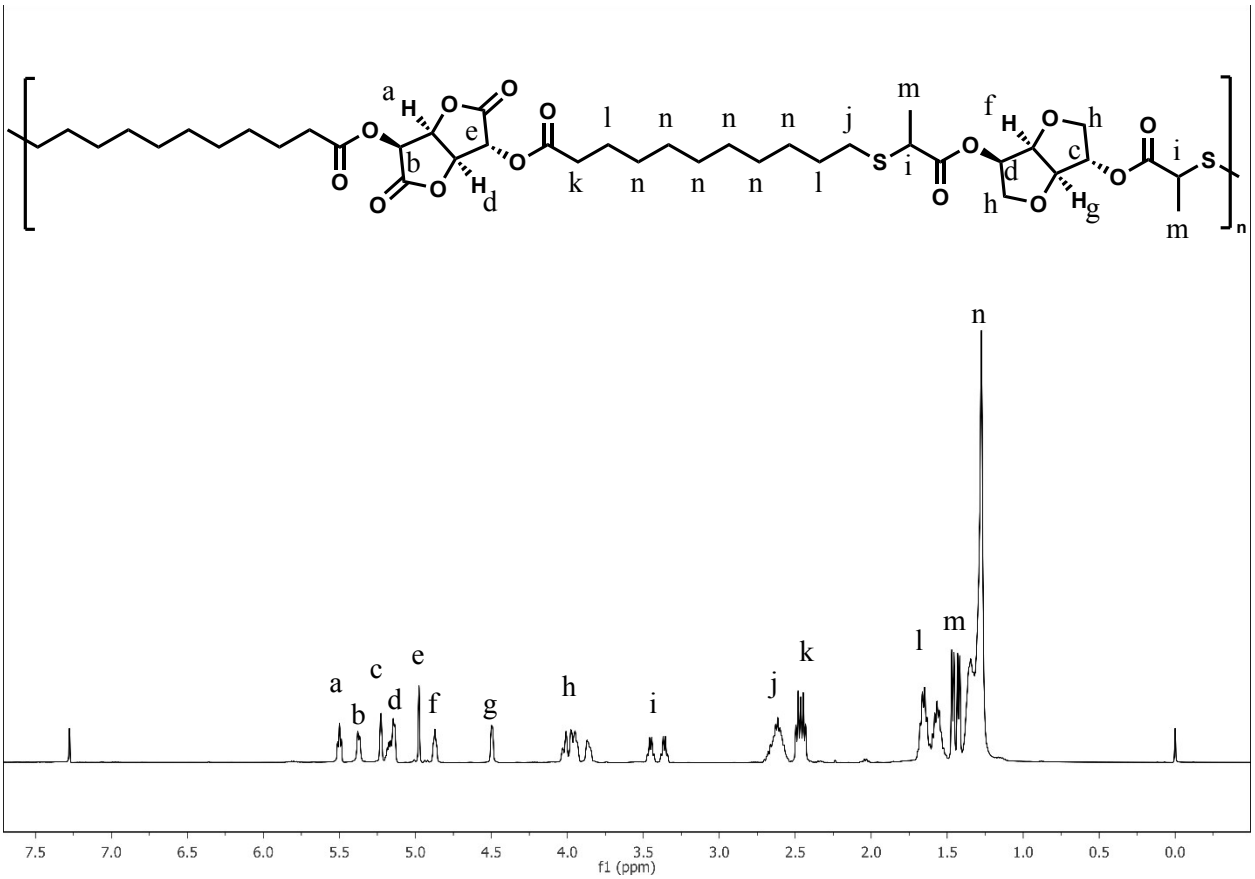


Figure S8. ^{1}H-NMR spectrum of P(GDLU-I2DT) ($CDCl_3$, 500 MHz)

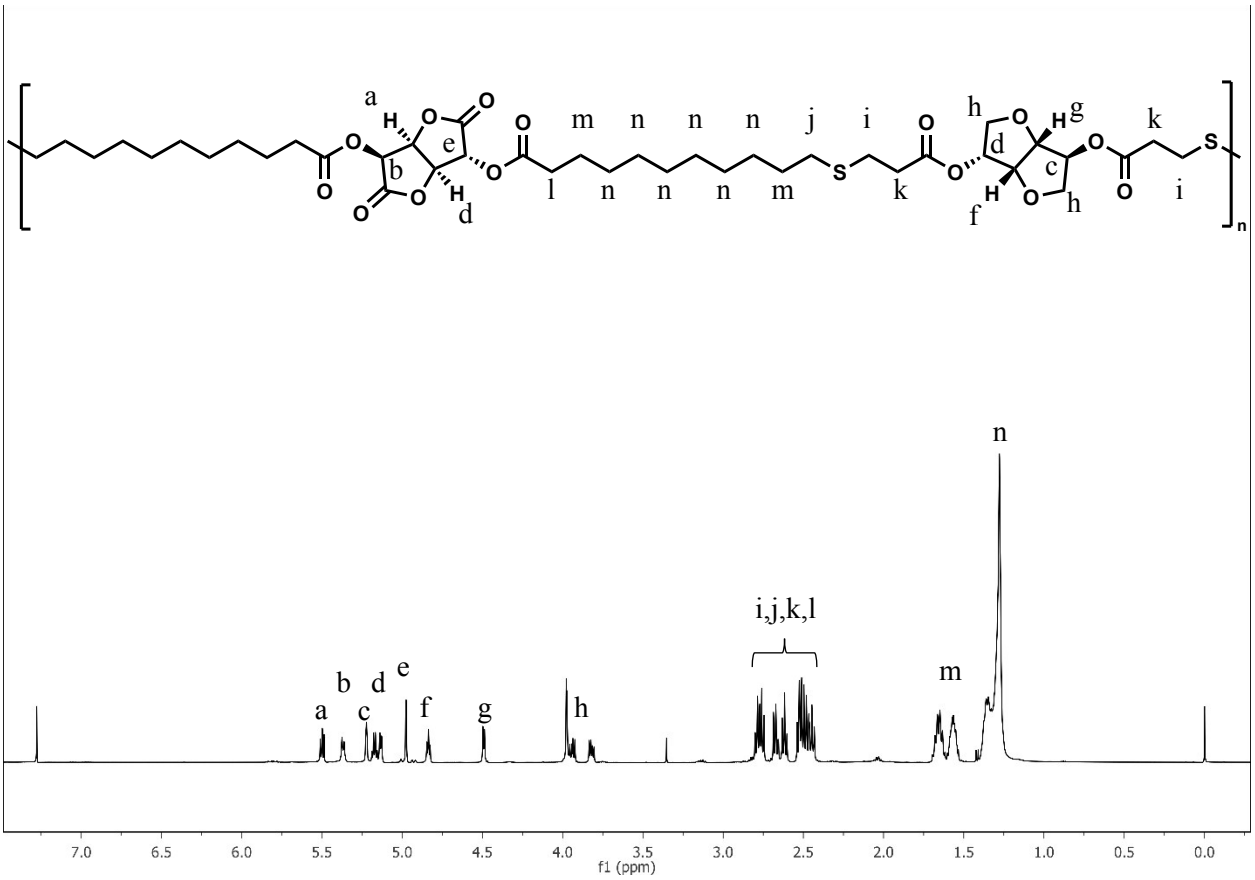


Figure S9. ^{1}H-NMR spectrum of P(GDLU-I3DT) ($CDCl_3$, 500 MHz)

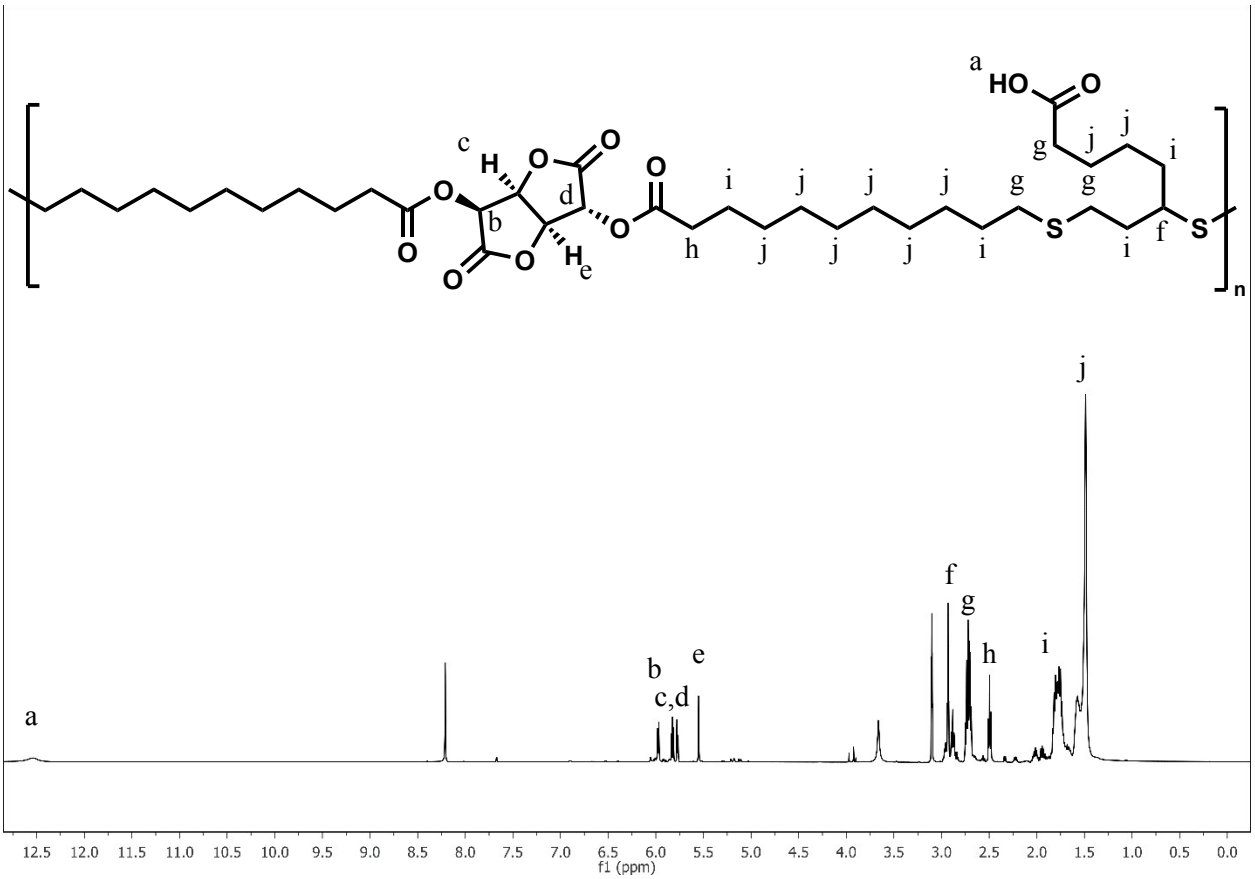


Figure S10. ^{1}H-NMR spectrum of P(GDLU-DHLA) (DMF-d_7, 500 MHz)

^{13}C NMR Spectra

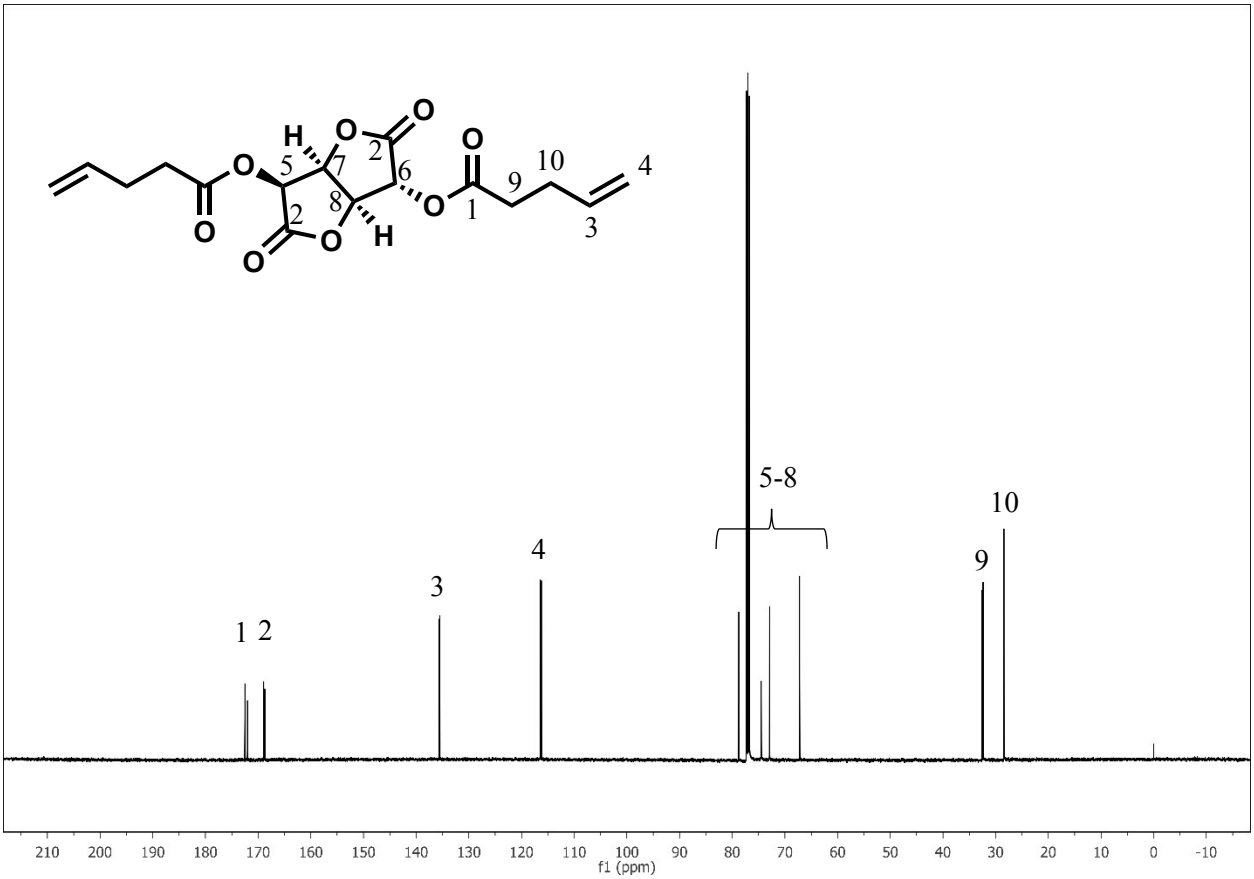


Figure S11. ^{13}C-NMR spectrum of glucarodilactone 4-pentenoate ($CDCl_3$, 126 MHz)

Figure S12. ^{13}C-NMR spectrum of isosorbide 2-mercaptopropionate ($CDCl_3$, 126 MHz)

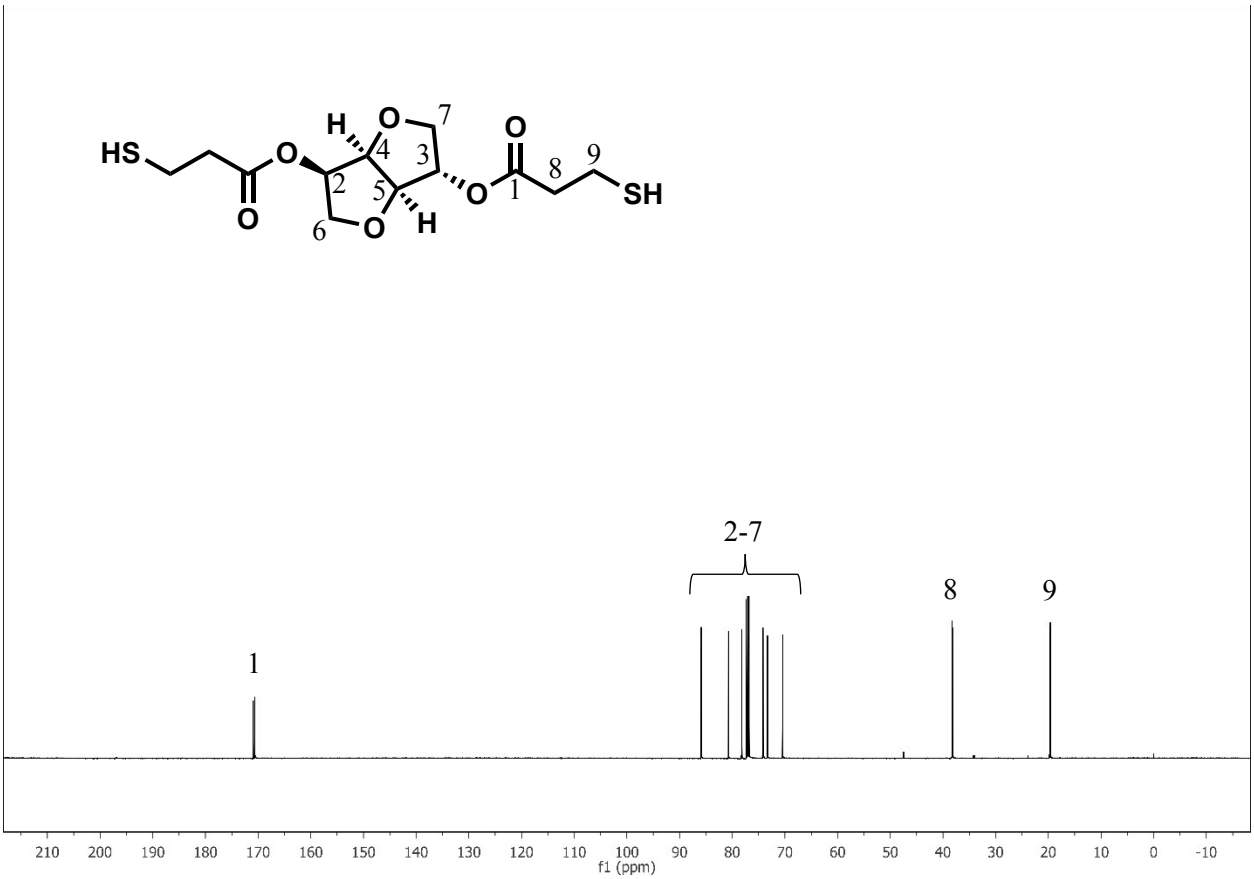


Figure S13. ^{13}C-NMR spectrum of isosorbide 3-mercaptopropionate ($CDCl_3$, 126 MHz)

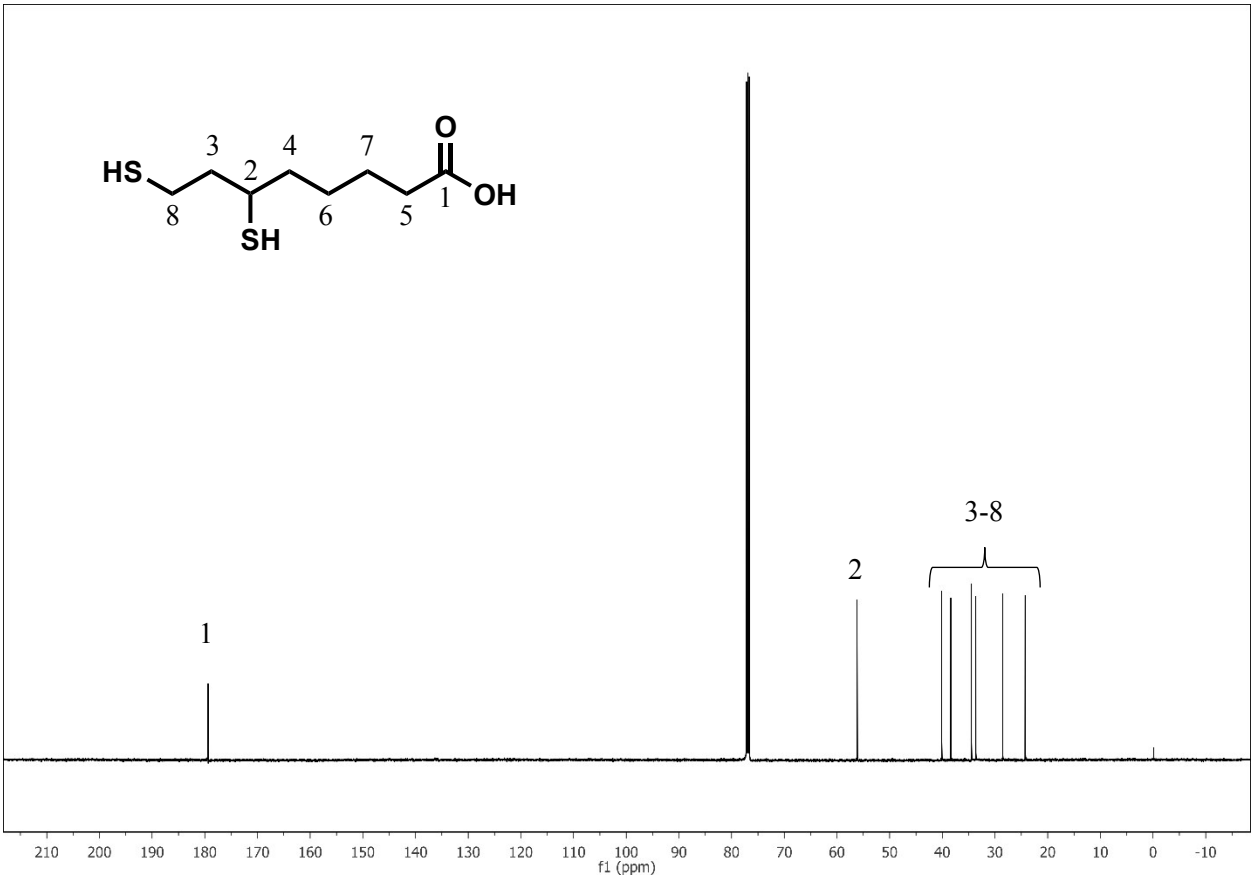


Figure S14. ^{13}C-NMR spectrum of *rac*-dihydrolipoic acid ($CDCl_3$, 126 MHz)

2D NMR Spectra (COSY)

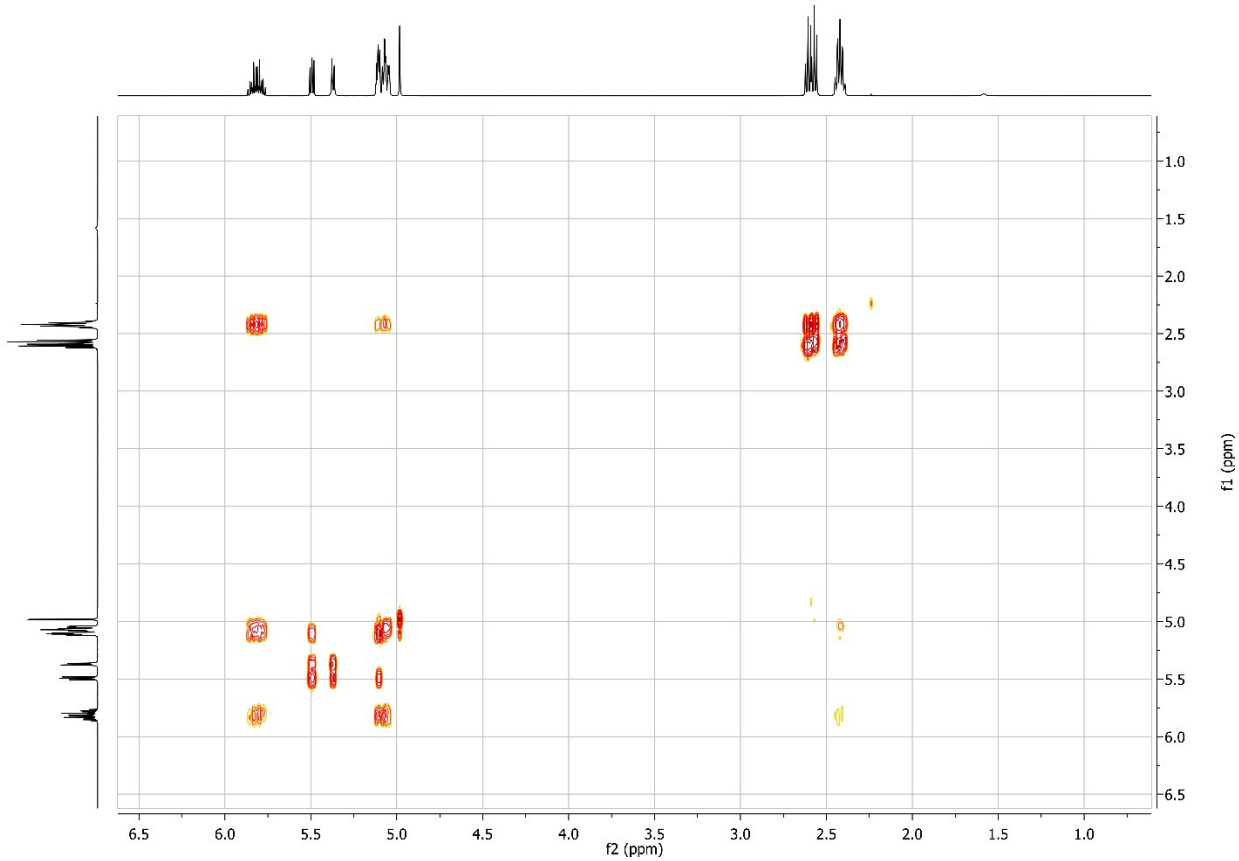


Figure S15. ^{1}H COSY NMR spectrum of glucarodilactone 4-pentenoate ($CDCl_3$, 500 MHz)

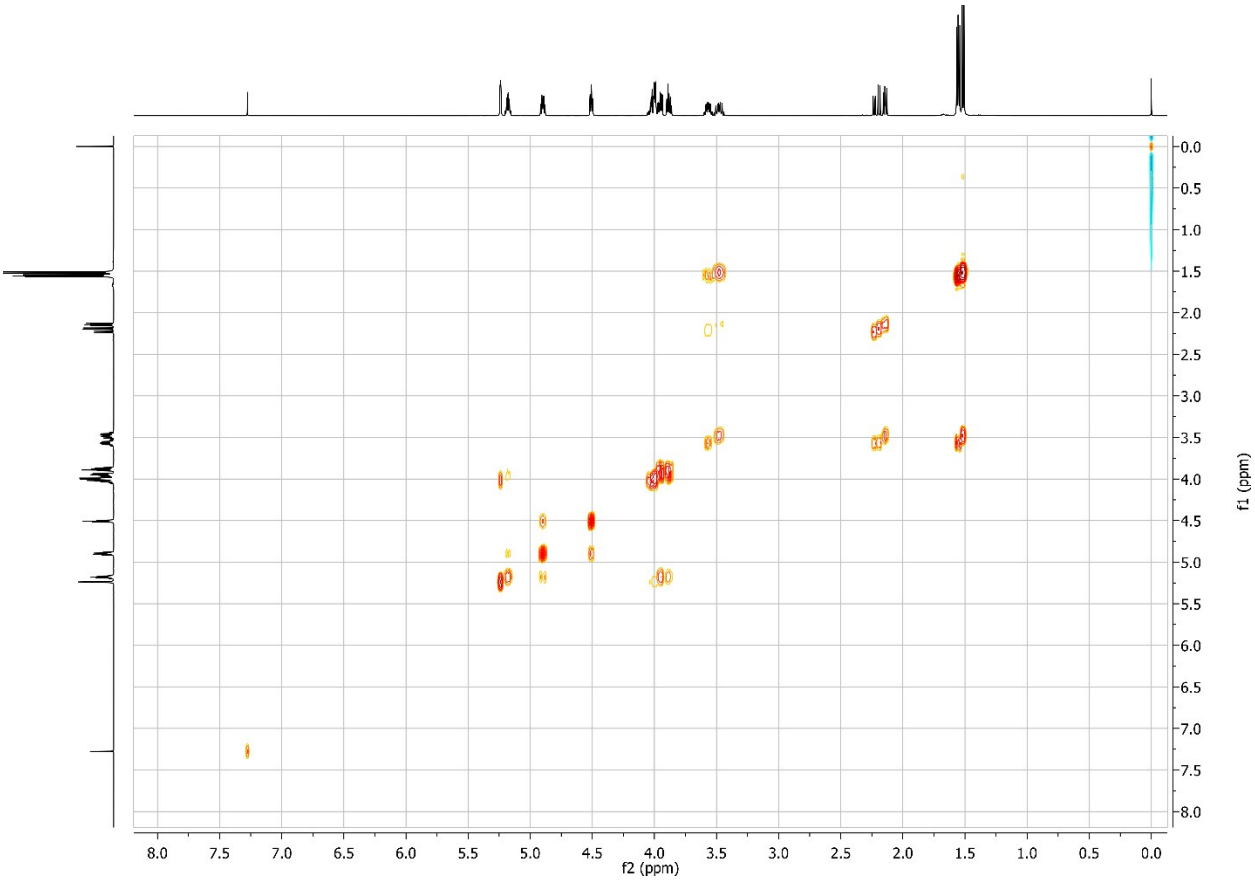


Figure S16. ^{1}H COSY NMR spectrum of isosorbide 2-mercaptopropionate ($CDCl_3$, 500 MHz)

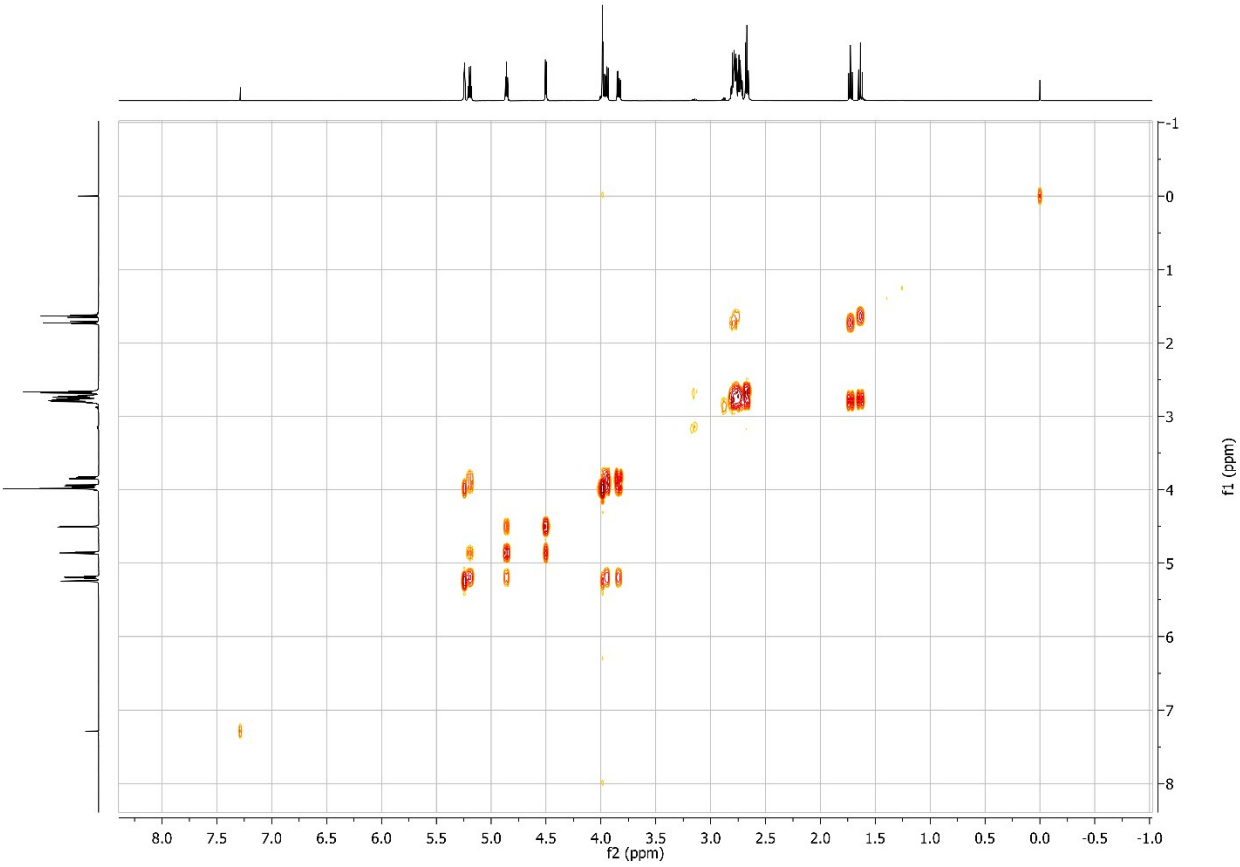


Figure S17. ^{1}H COSY NMR spectrum of isosorbide 3-mercaptopropionate ($CDCl_3$, 500 MHz)

Thermal Characterization Data

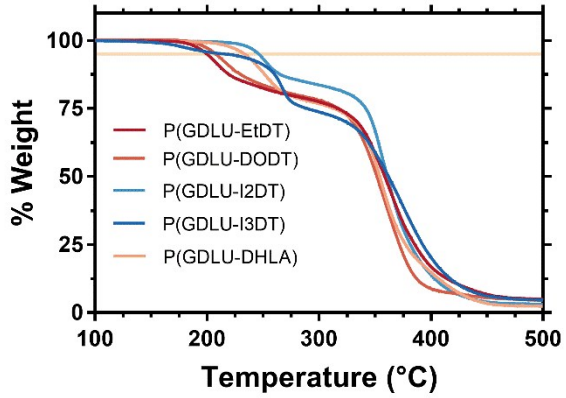


Figure S18. Thermogravimetric analysis of the GDLU-containing thiol-ene polymer system. Testing was performed under nitrogen atmosphere and reported degradation temperatures are recorded at 5% weight loss visualized by the orange line.

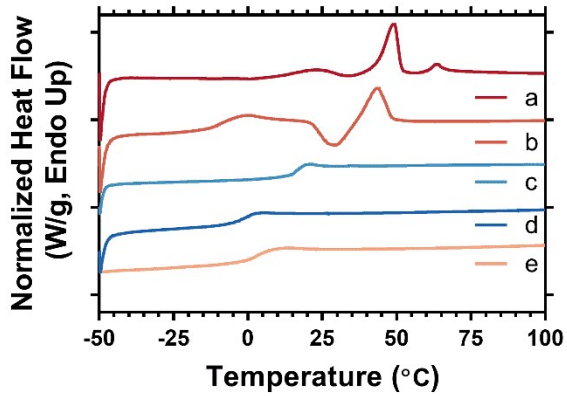


Figure S19. Differential scanning calorimetry of the GDLU-containing thiol-ene polymer system. Samples were heated from -50 °C to 100 °C and the second heating cycle are shown and used for the measurement of the glass transition and melting temperatures (if applicable) for the above materials. A) P(GDLU-EtDT), b) P(GDLU-DODT), c) P(GDLU-I2DT), d) P(GDLU-I3DT), and e) P(GDLU-DHLA).

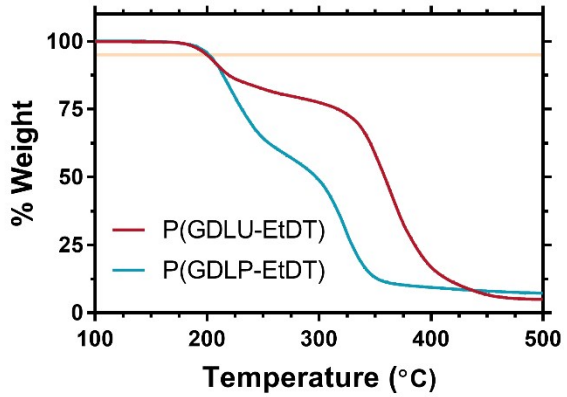


Figure S20. Thermogravimetric analysis of P(GDLU-EtDT) and P(GDLP-EtDT). Testing was performed under nitrogen atmosphere and reported degradation temperatures are recorded at 5% weight loss visualized by the orange line.

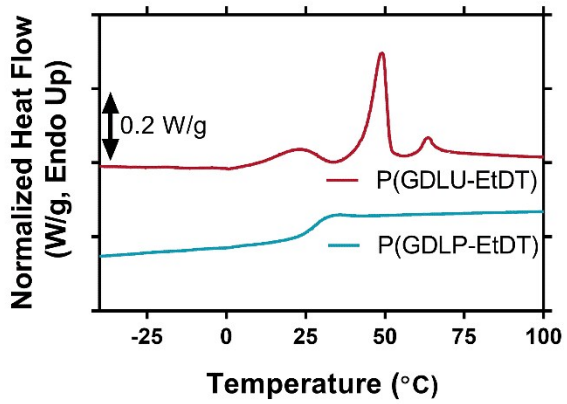


Figure S21. Differential scanning calorimetry of P(GDLU-EtDT) and P(GDLP-EtDT). Samples were heated from -50 °C to 100 °C and the second heating cycle are shown and used for the measurement of the glass transition and melting temperatures (if applicable) for the above materials.

Molecular Weight Characterization

Table S2. Instrument obtained refractive index increments for the family of polymers with 100 percent mass recovery assumption.

Polymer Name	*dn*/*dc*
P(GDLU-EtDT)	0.1029
P(GDLU-DODT)	0.0901
P(GDLU-I2DT)	0.0959
P(GDLU-I3DT)	0.1031
P(GDLU-DHLA)	0.0959
P(GDLP-EtDT)	0.1171

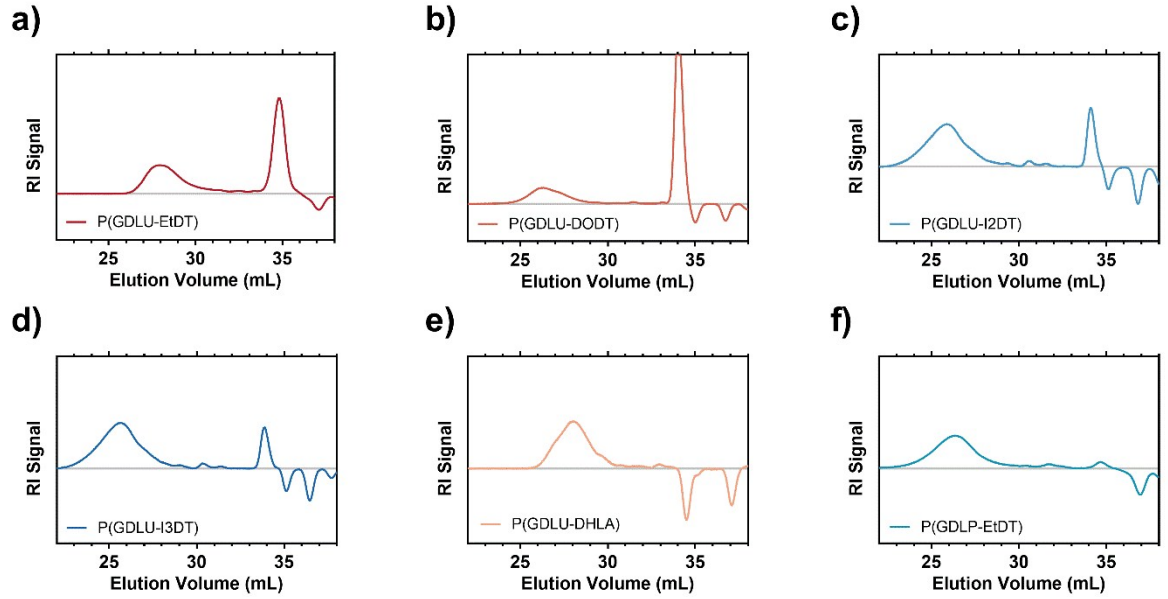


Figure S 22. Size exclusion chromatography profiles for a) P(GDLU-EtDT), b) P(GDLU-DODT), c) P(GDLU-I2DT), d) P(GDLU-I3DT), e) P(GDLU-DHLA), and f) P(GDLP-EtDT). Tetrahydrofuran was used as the mobile phase with a flow rate of 1 mL/min.

Strain Hardening in P(GDLU-EtDT)

Samples of P(GDLU-EtDT) were found to exhibit reversible strain hardening during tensile testing. Differential Scanning Calorimetry (DSC) of P(GDLU-EtDT) prior to deformation and gauge samples after deformation to break with uniaxial tensile testing. DSC, shown in **Figure S23**, shows reversible crystal formation in these materials, where upon testing a sample from the gauge section of a broken tensile sample, a new large melting temperature (77 °C) is observed. This new melting feature is lost upon heating of this sample above this new T_m, and recovery of the original features are observed. This hardening behavior has potential utilization in the formation of drawn fibers of this polymeric material.

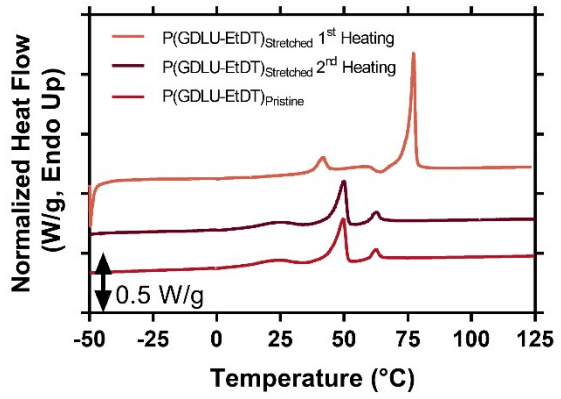


Figure S23. Differential scanning calorimetry of P(GDLU-EtDT) prior to ($P(GDLU\text{-}EtDT)_{Pristine}$) and after ($P(GDLU\text{-}EtDT)_{stretched}$) uniaxial tensile testing. Samples were heated from -50 °C to 125 °C. The second heating of P(GDLU-EtDT) is shown for the pristine sample.

Hydrolytic Stability Testing

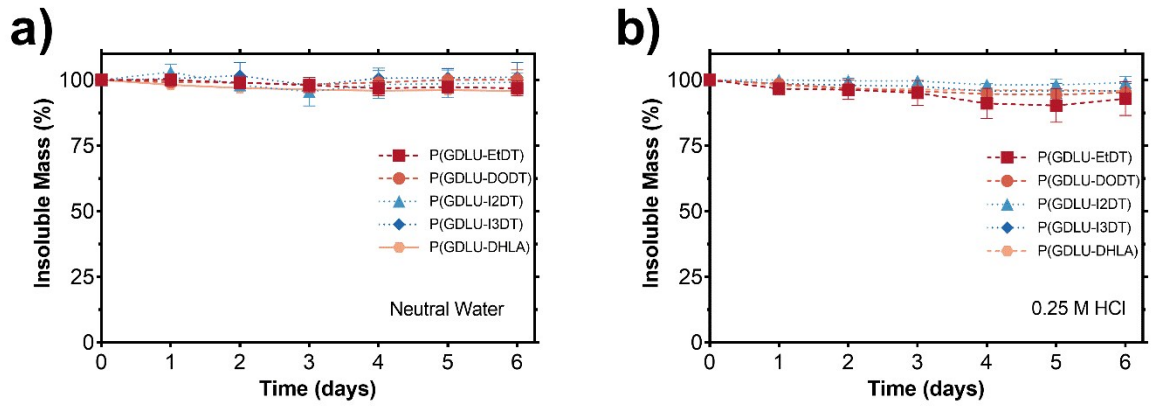


Figure S24. Hydrolytic stability testing of the GDLU-based poly(ester-thioether)'s in neutral (a), and acidic (b, 0.25 M HCl) aqueous conditions. Samples were characterized in triplicate and each sample was exposed to either neutral water or 0.25 M HCl aqueous solutions for 24-hour periods, dried and insoluble mass was massed. Then samples were exposed to new degradation solution for the next 24-hour period. This process was repeated over the course of six 24-hour timepoints.

[1] L. M. Lillie, W. B. Tolman and T. M. Reineke, *Polymer Chemistry*, 2017, **8**, 3746-3754.