

Electronic Supplementary Information (ESI) for:

Structure/Property Relationships in Copolymers Comprising Renewable Isosorbide, Glucarodilactone, and 2,5-Bis(hydroxymethyl)furan Subunits

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¹H NMR Spectra

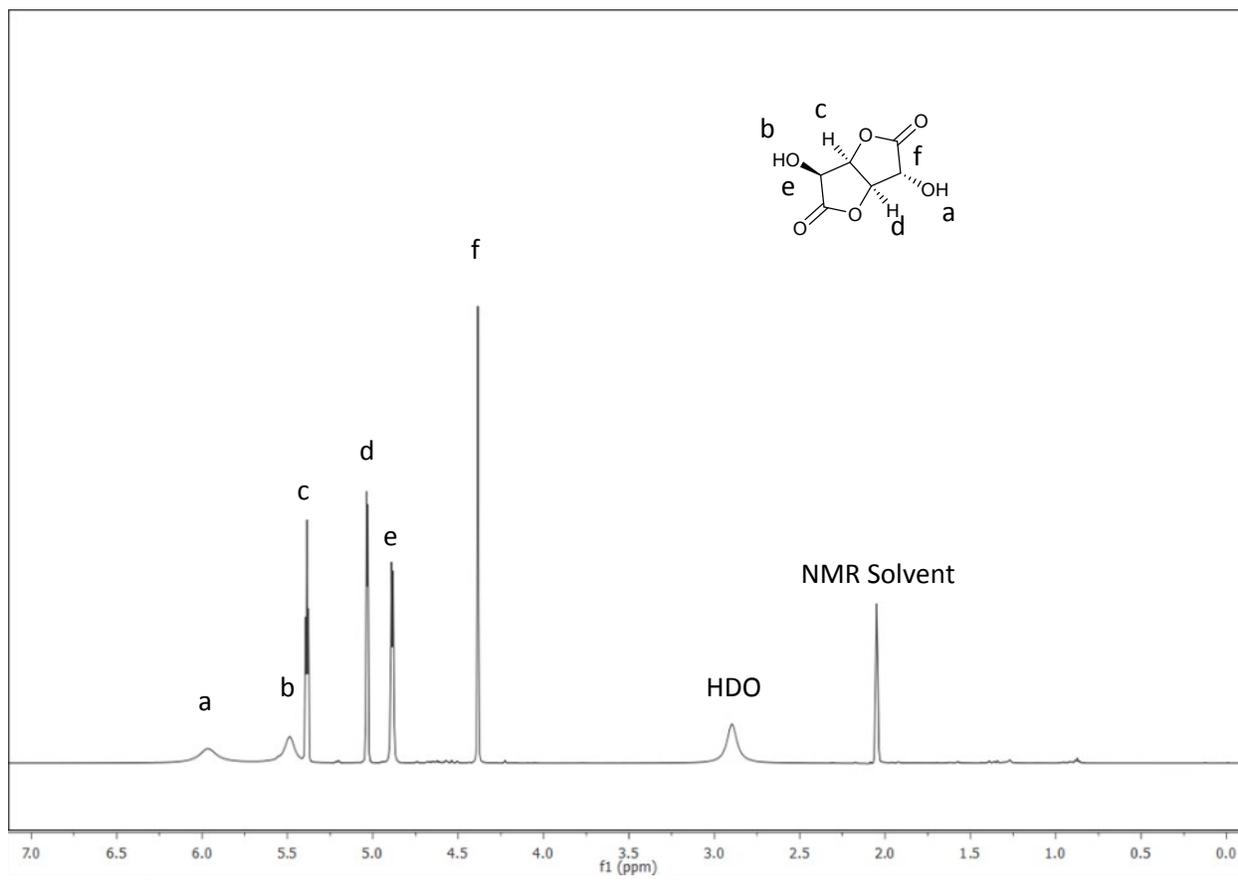


Figure S1. ¹H-NMR spectrum of D-glucaro-1,4:6,3-dilactone (**GDL**) ((CD₃)₂CO, 500 MHz).

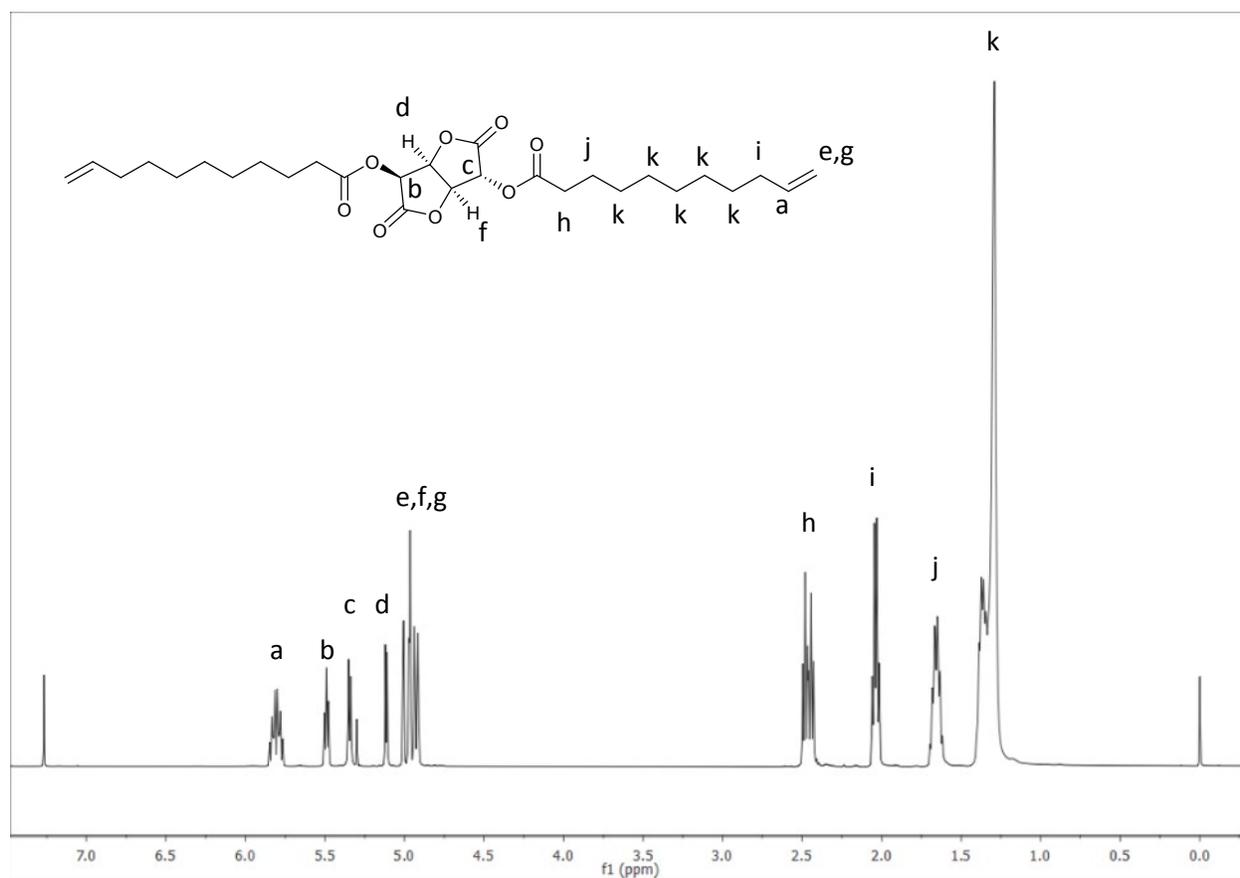


Figure S2. ¹H-NMR spectrum of glucarodilactone undecenoate (**GDLU**) (CDCl₃, 500 MHz).

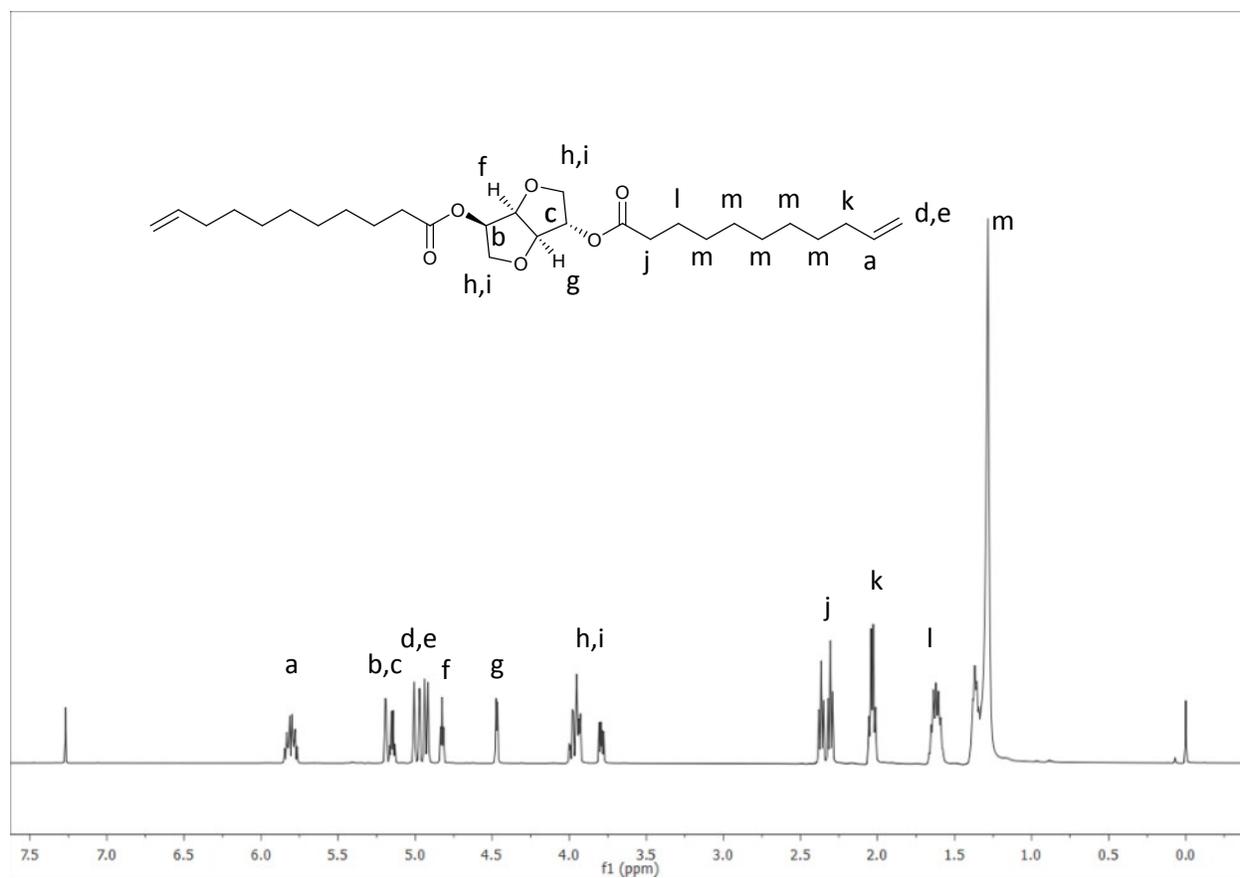


Figure S3. ¹H-NMR spectrum of isosorbide undecenoate (**IU**) (CDCl₃, 500 MHz).

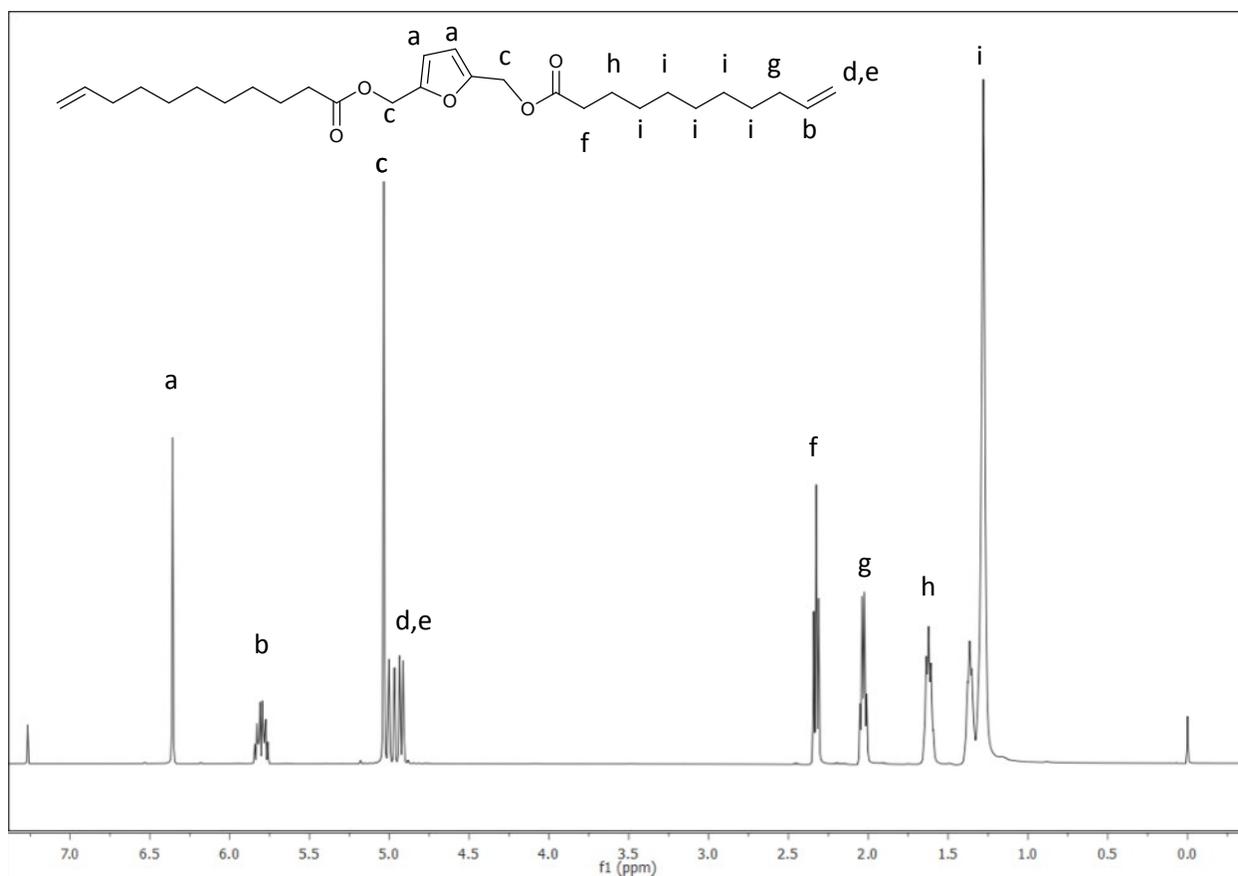


Figure S4. ¹H-NMR spectrum of 2,5-bis(hydroxymethyl)furan undecenoate (**BHMFU**) (CDCl₃, 500 MHz)

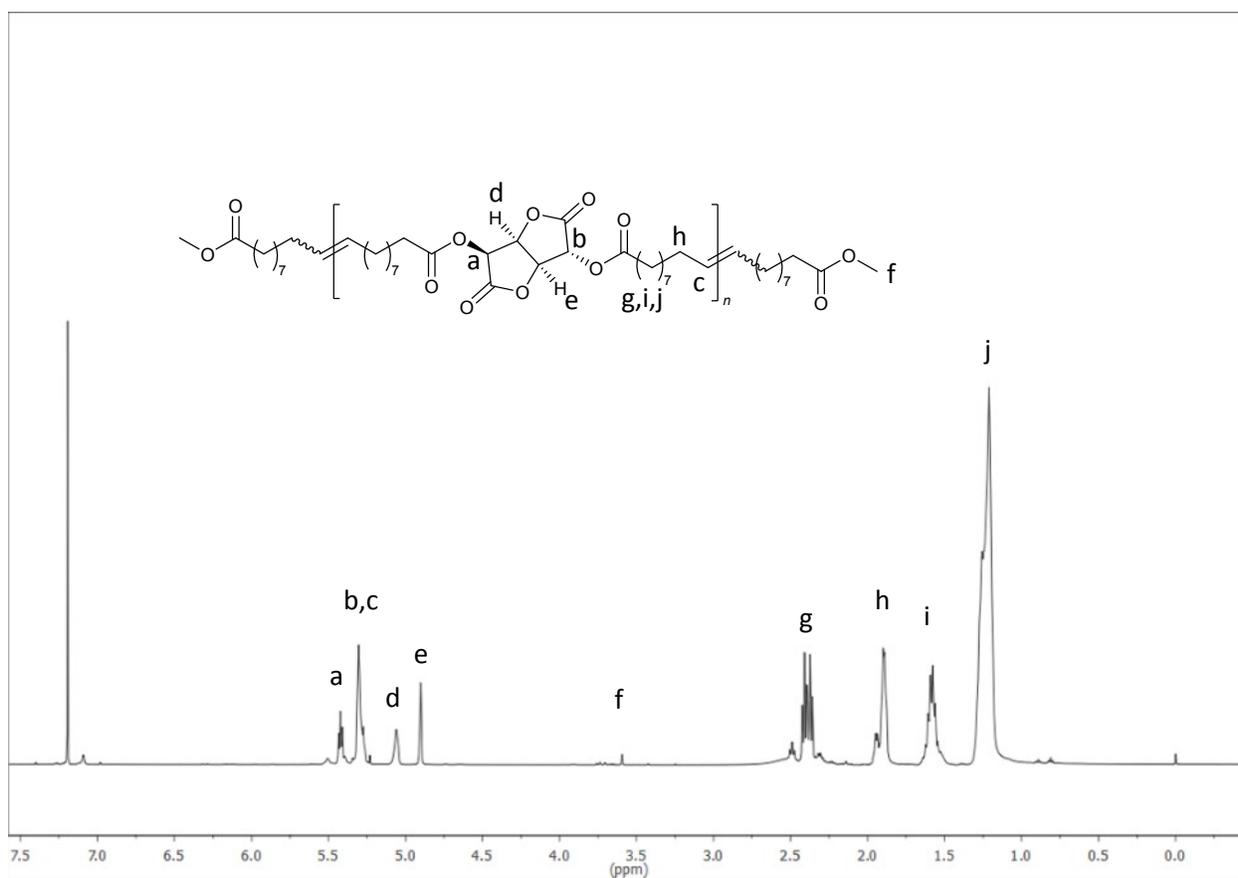


Figure S5. ¹H-NMR spectrum of **P(GDLU)** (CDCl₃, 500 MHz).

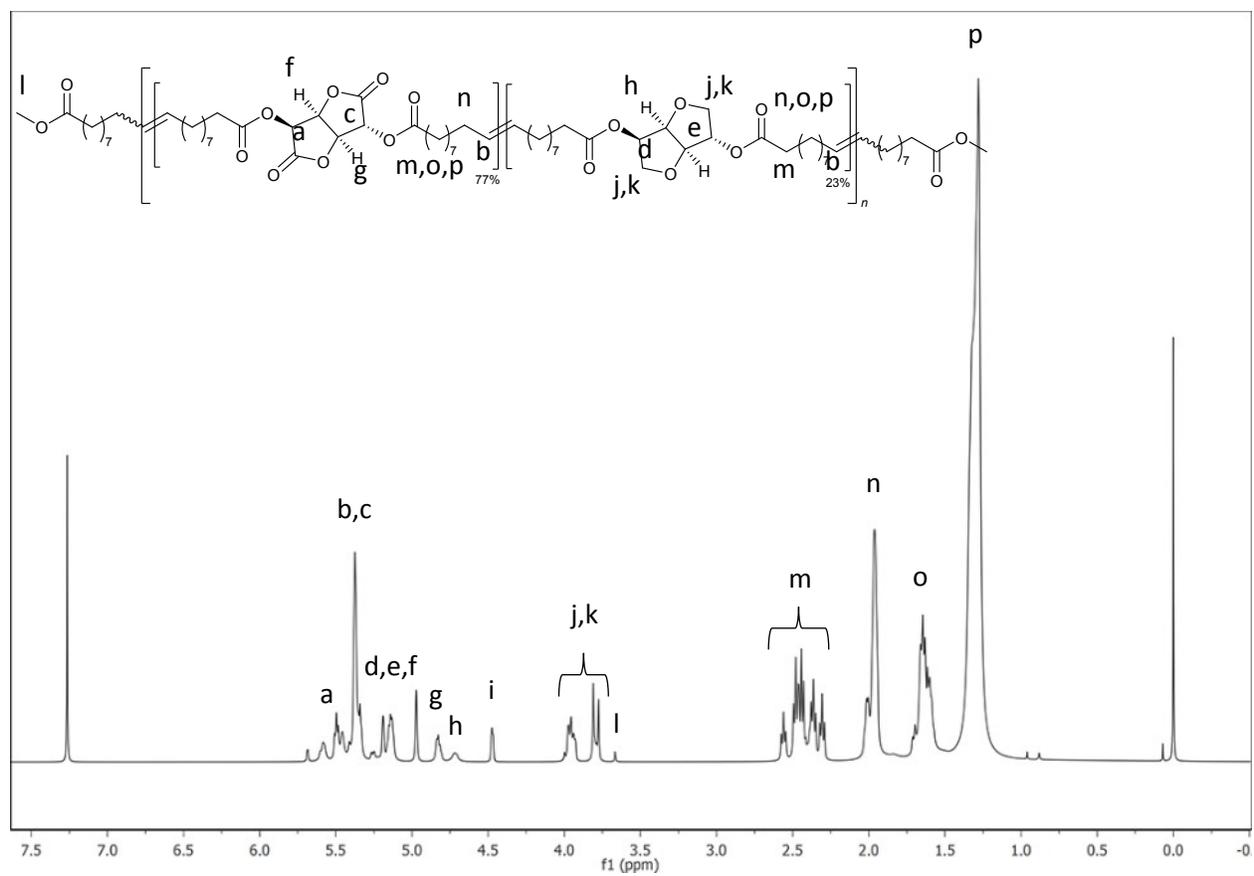


Figure S6. ¹H-NMR spectrum of P(GDLU₇₇-co-IU₂₃) (CDCl₃, 500 MHz).

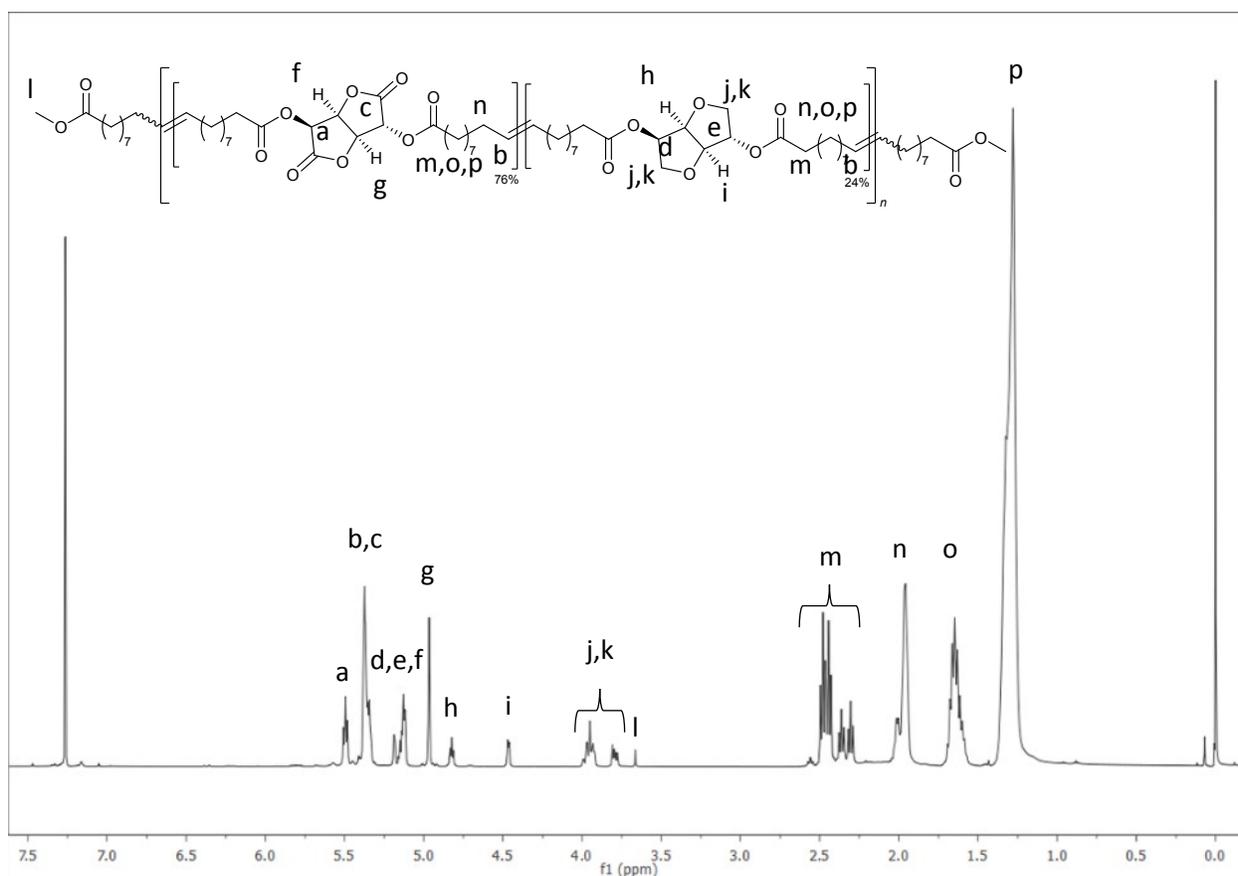


Figure S7. ¹H-NMR spectrum of P(GDLU₇₆-co-IU₂₄) (CDCl₃, 500 MHz).

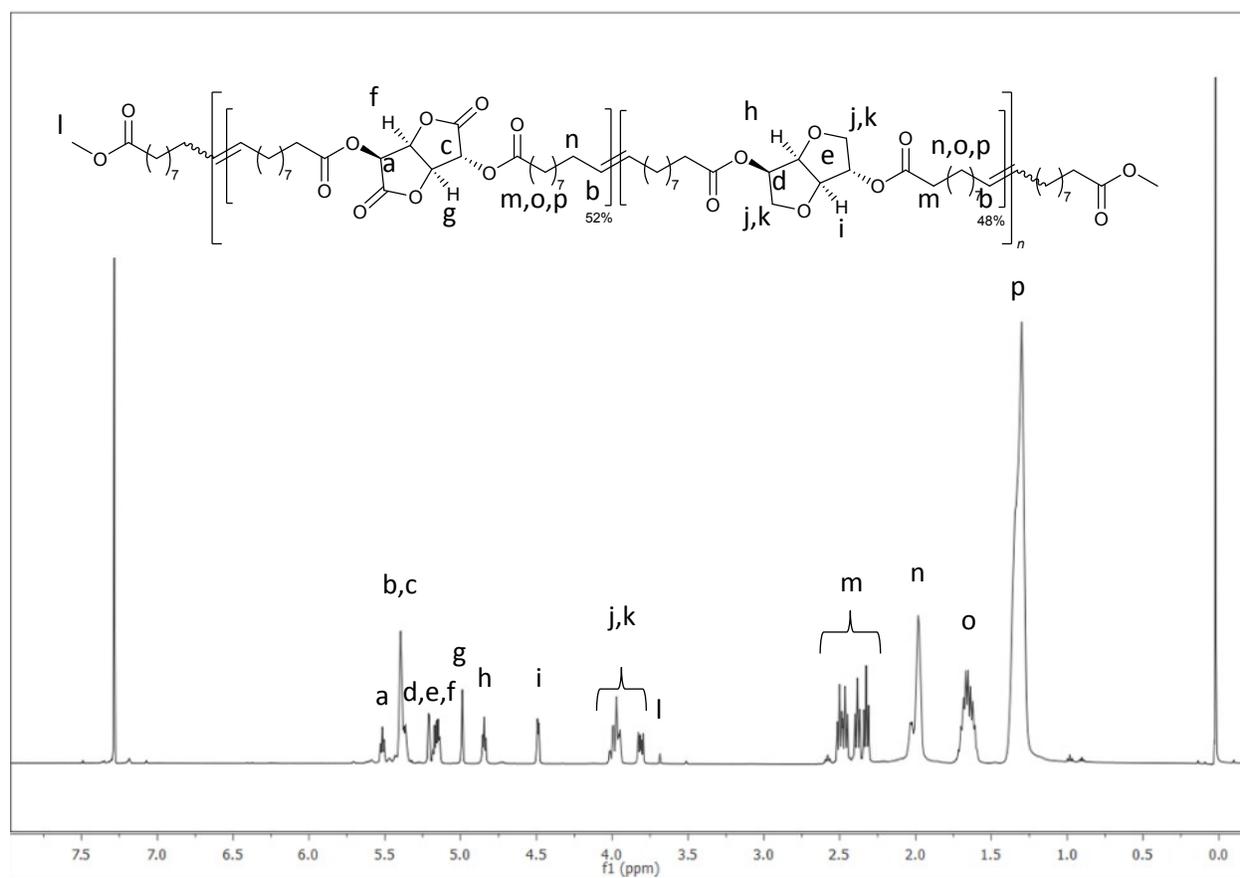


Figure S8. $^1\text{H-NMR}$ spectrum of $P(\text{GDLU}_{52}\text{-co-IU}_{48})$ (CDCl_3 , 500 MHz).

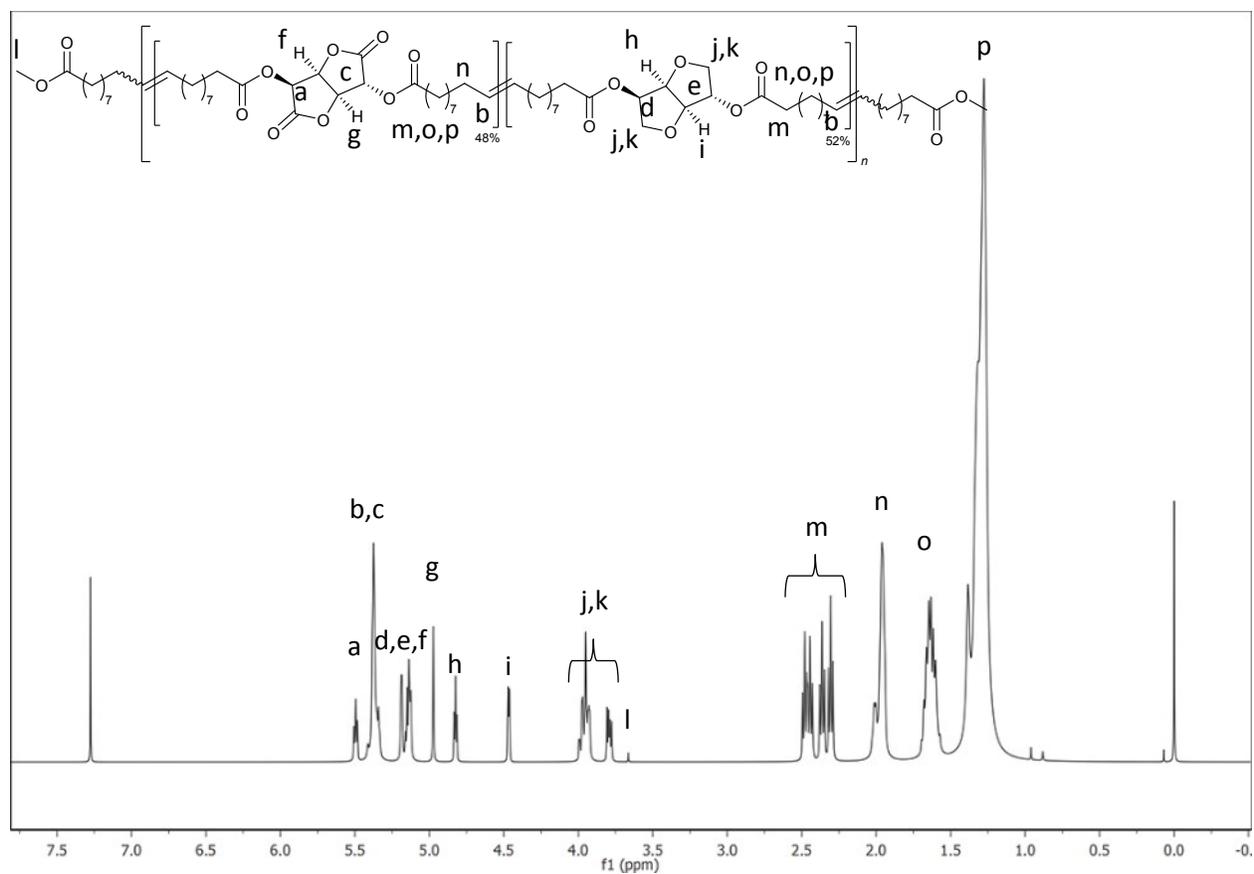


Figure S9. $^1\text{H-NMR}$ spectrum of $P(\text{GDLU}_{48}\text{-co-IU}_{52})$ (CDCl_3 , 500 MHz).

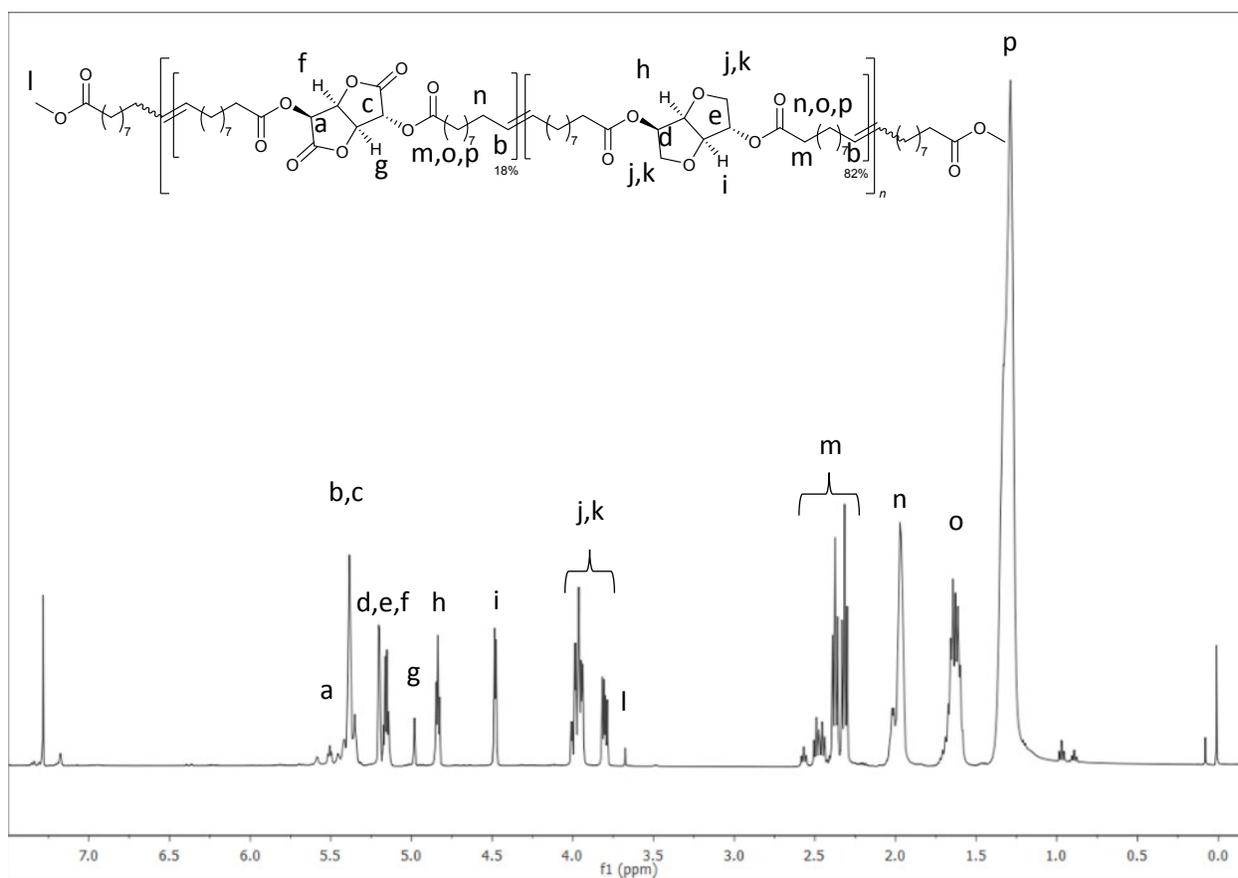


Figure S10. ¹H-NMR spectrum of P(GDLU₁₈-co-IU₈₂) (CDCl₃, 500 MHz).

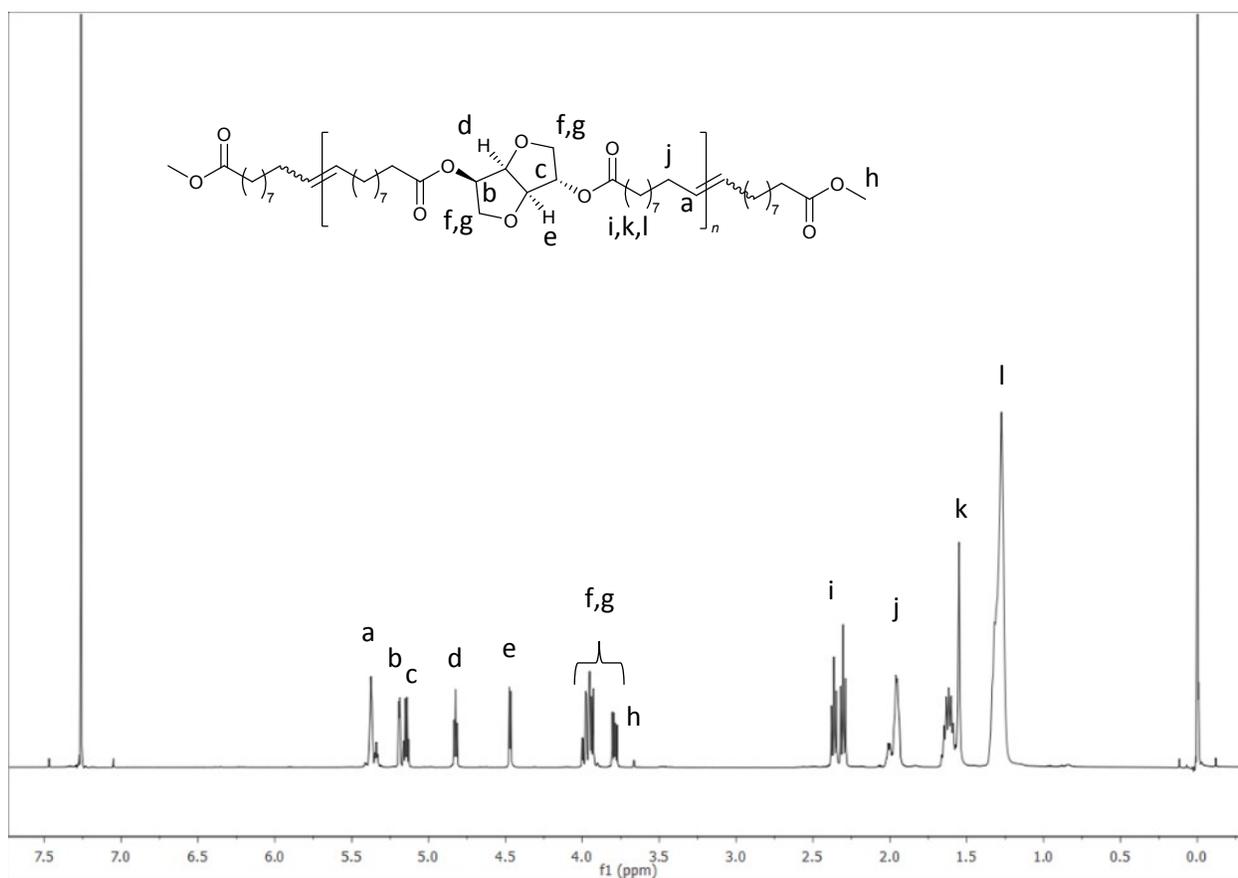


Figure S11. ¹H-NMR spectrum of **P(IU)** (CDCl₃, 500 MHz).

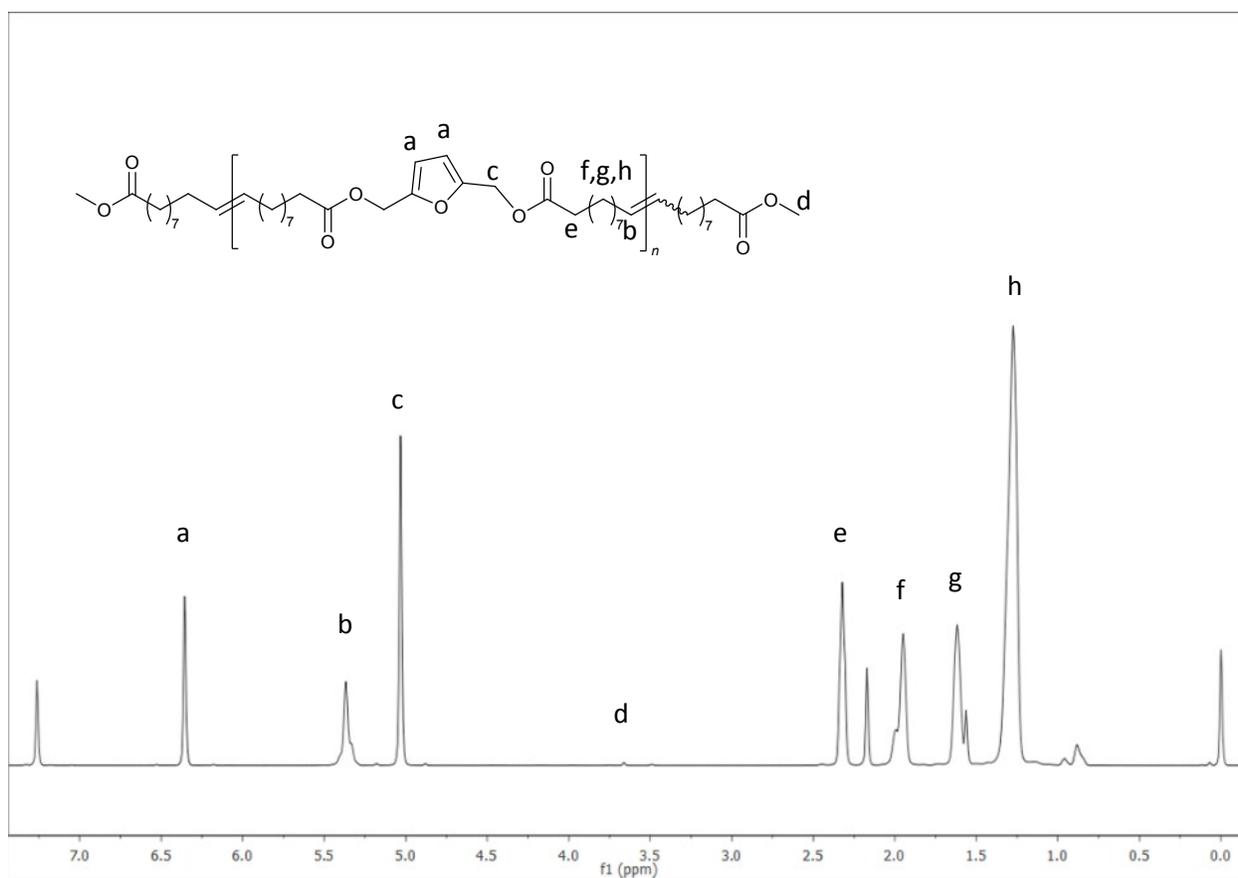


Figure S12. ¹H-NMR spectrum of P(BHMFU) (CDCl₃, 500 MHz).

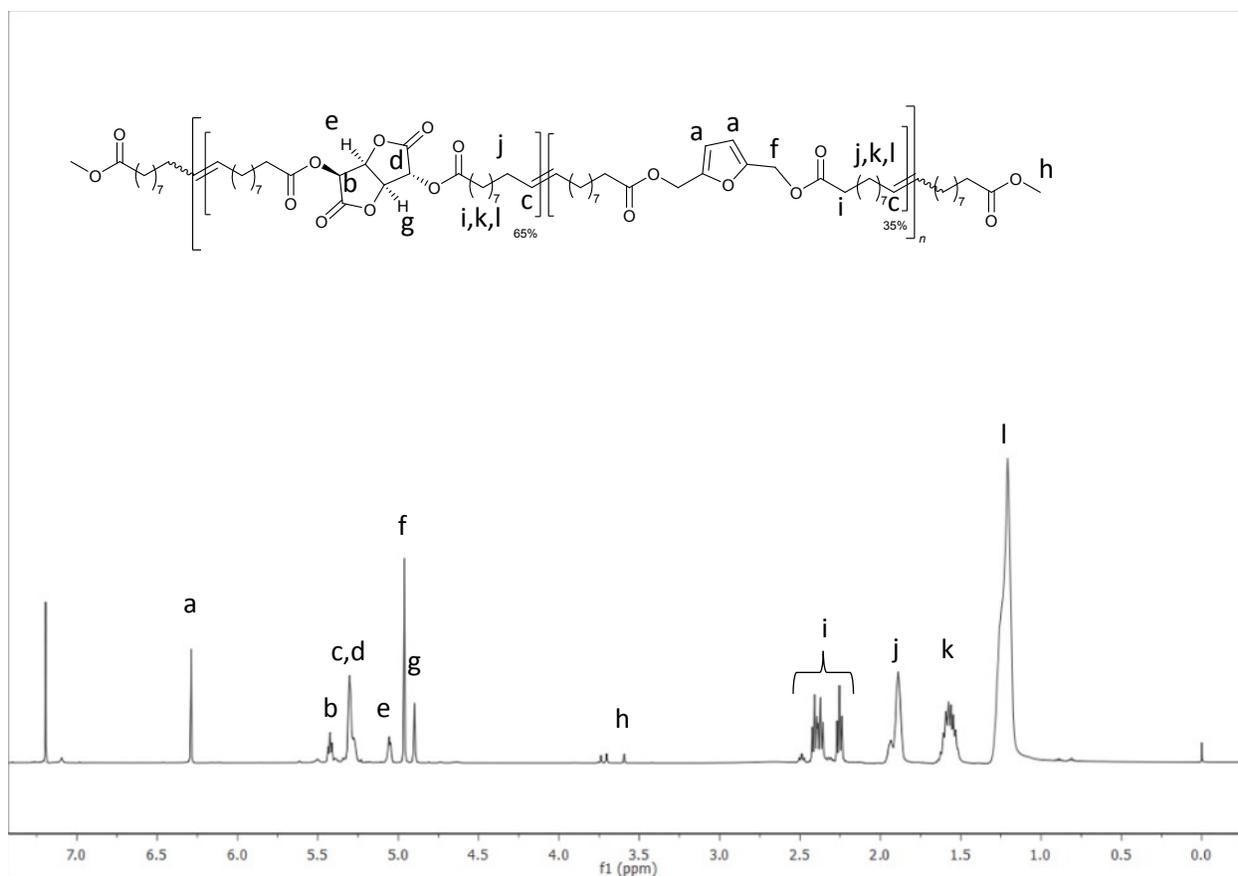


Figure S13. $^1\text{H-NMR}$ spectrum of $P(\text{BHMFU}_{35}\text{-co-GDLU}_{65})$ (CDCl_3 , 500 MHz).

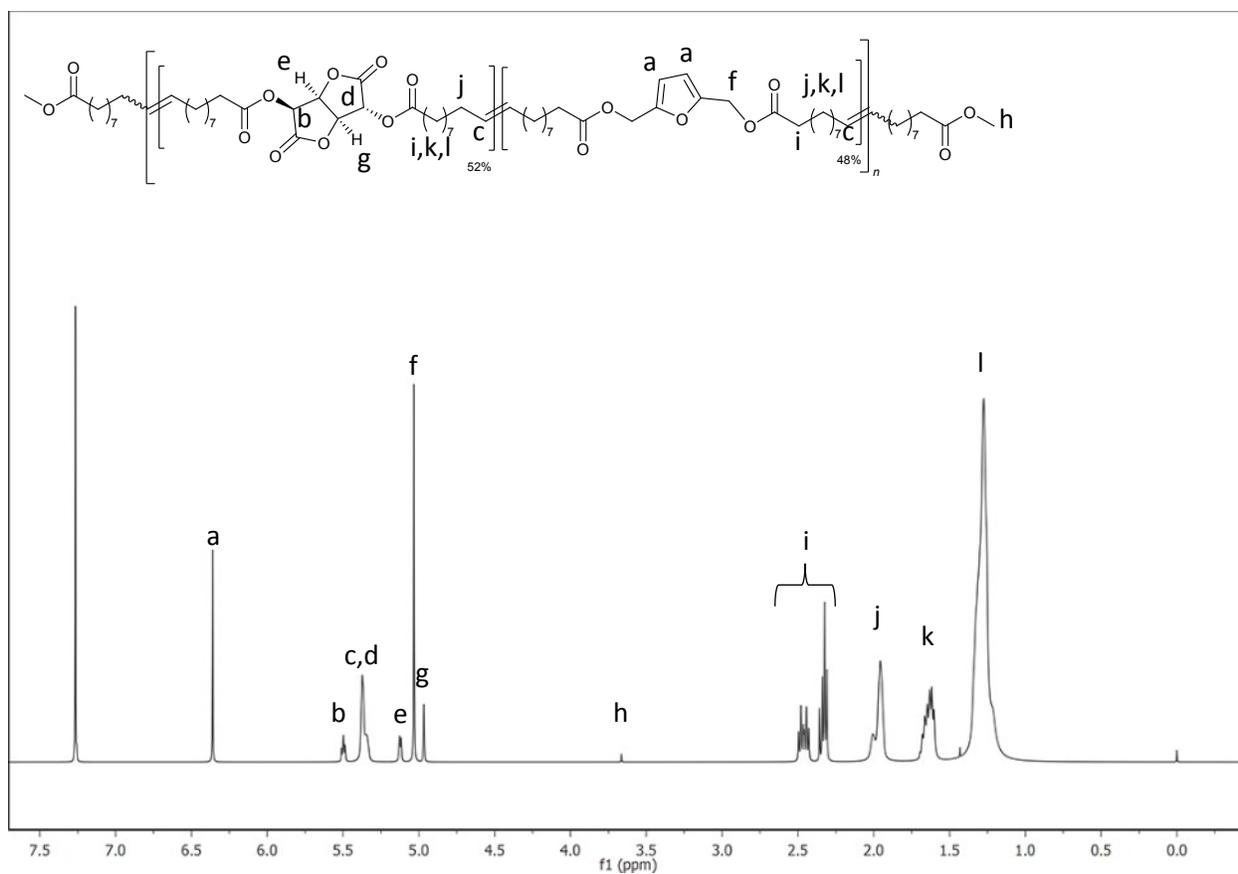


Figure S 14. ¹H-NMR spectrum of P(BHMFU₄₈-co-GDLU₅₂) (CDCl₃, 500 MHz).

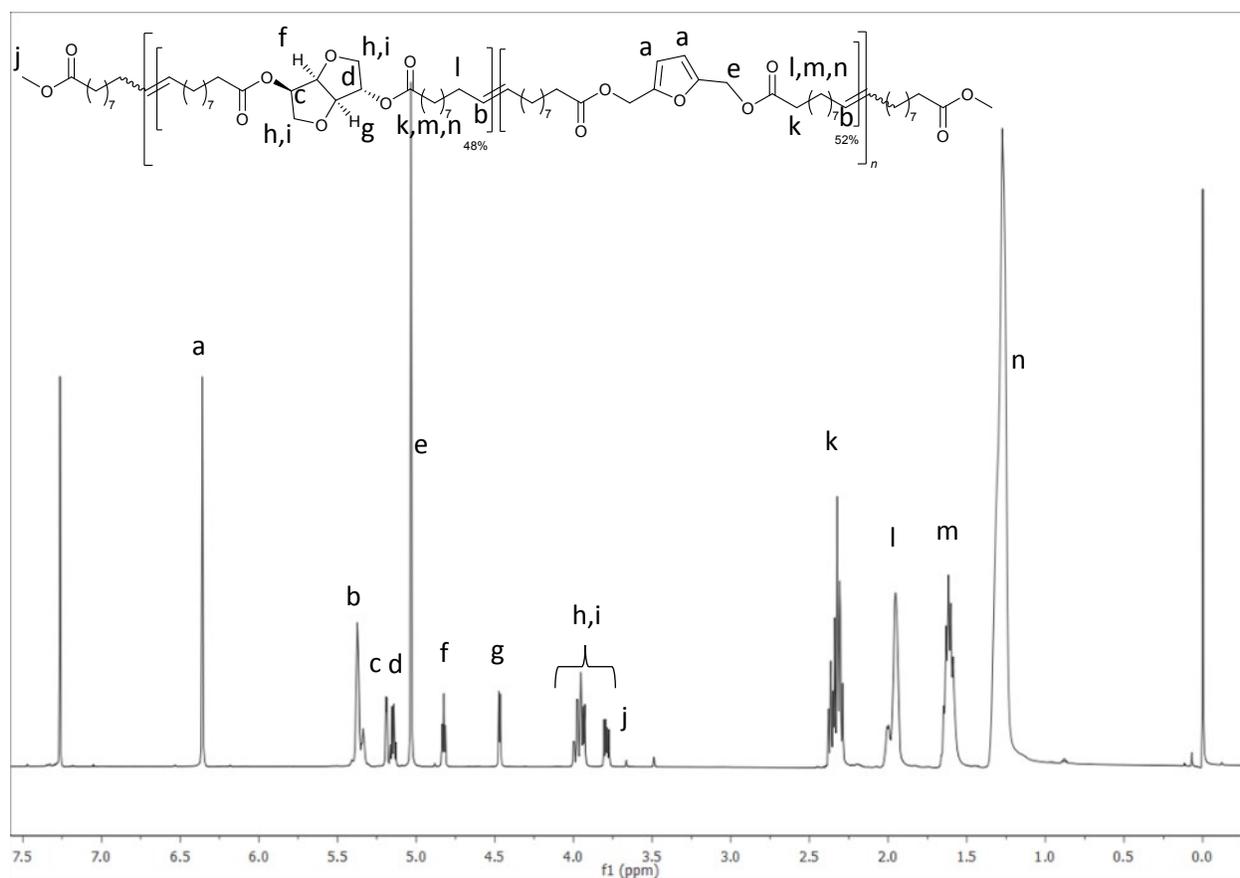


Figure S15. ¹H-NMR spectrum of P(BHMFU₅₂-co-IU₄₈) (CDCl₃, 500 MHz).

Table S1. Comparison of feed ratio of GDLU to the GDLU content of the P(GDLU_x-co-IU_y) copolymers, determined by ¹H NMR.

Copolymer	Feed Ratio GDLU (%)	Polymer Ratio (¹H NMR, %)	Percent Difference (%)
P(GDLU ₇₇ -co-IU ₂₃)	74.7	77	3.0
P(GDLU ₇₆ -co-IU ₂₄)	75.0	76	1.3
P(GDLU ₅₂ -co-IU ₄₈)	50.0	52	3.9
P(GDLU ₄₈ -co-IU ₅₂)	49.6	48	3.2
P(GDLU ₁₈ -co-IU ₈₂)	25.2	18	33

Table S2. Backbone olefin stereoregularity of the P(GDLU_x-co-IU_y) copolymer system, determined by ¹H NMR.

Polymer	E/Z Ratio (%:%)
P(GDLU)	81:19
PGDLU ₇₇ -co-IU ₂₃	83:17
PGDLU ₇₆ -co-IU ₂₄	81:19
PGDLU ₅₂ -co-IU ₄₈	81:19
PGDLU ₄₈ -co-IU ₅₂	81:19
PGDLU ₁₈ -co-IU ₈₂	82:18
P(IU)	80:20

¹³C NMR Spectra

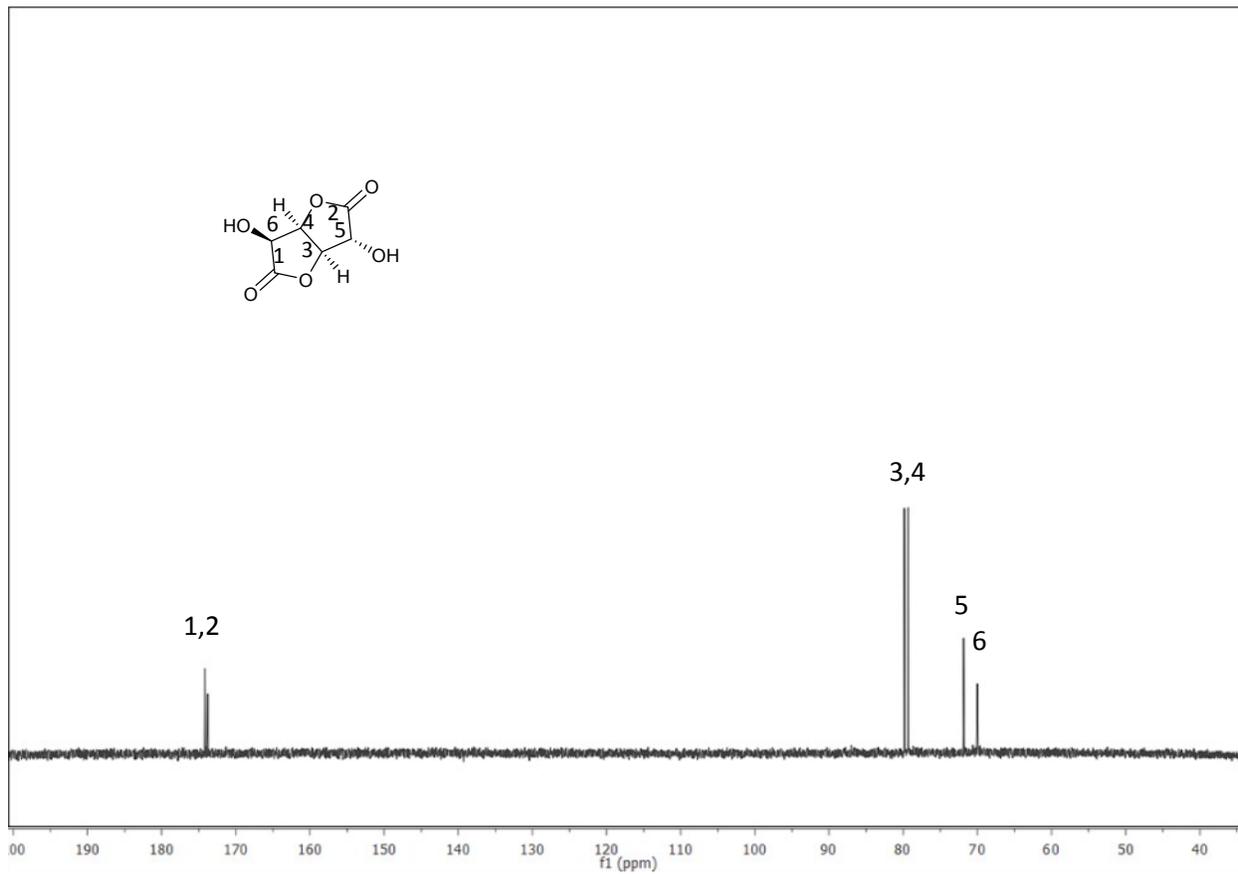


Figure S16. ¹³C-NMR spectrum of D-glucaro-1,4:6,3-dilactone (GDL) ((CD₃)₂CO, 125 MHz).

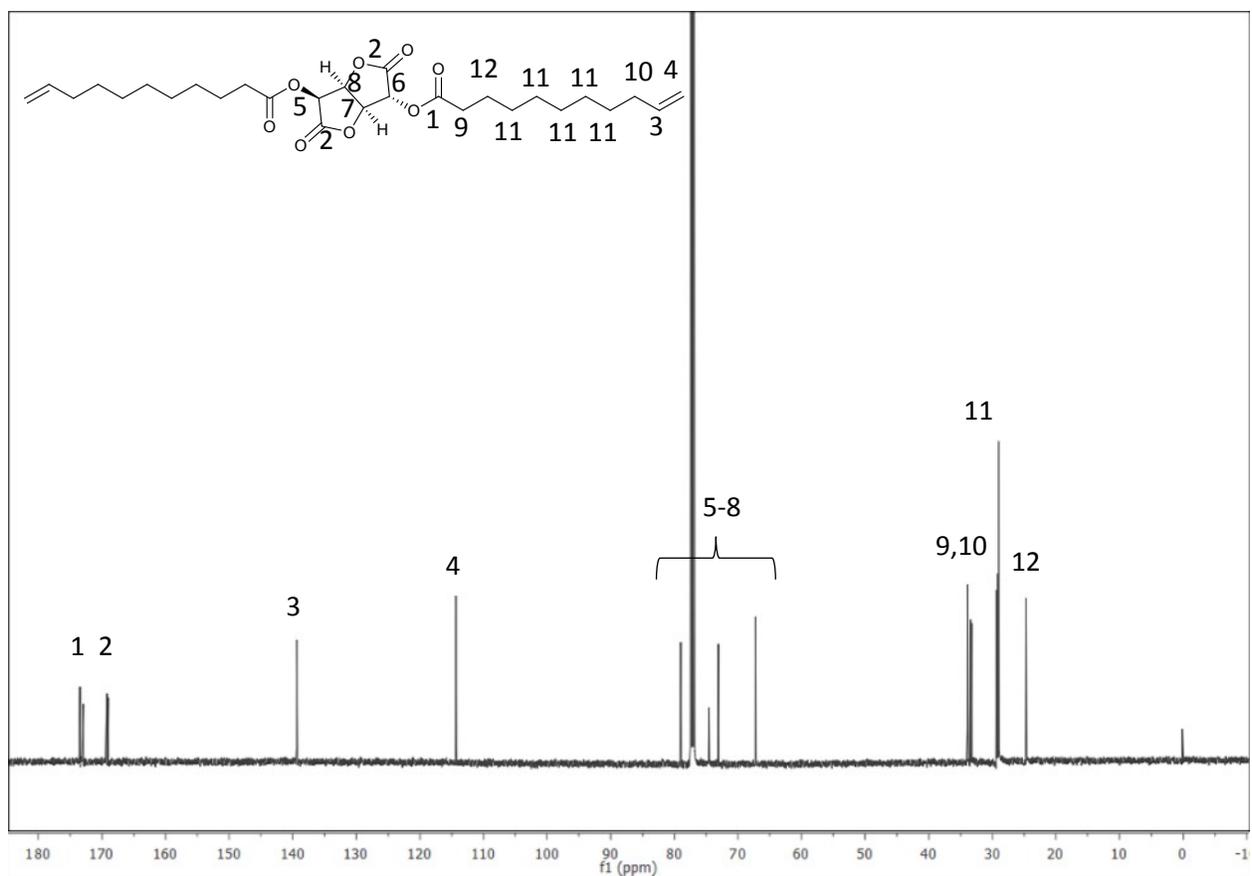


Figure S17. ¹³C-NMR spectrum of glucarodilactone undecenoate (**GDLU**) (CDCl₃, 125 MHz).

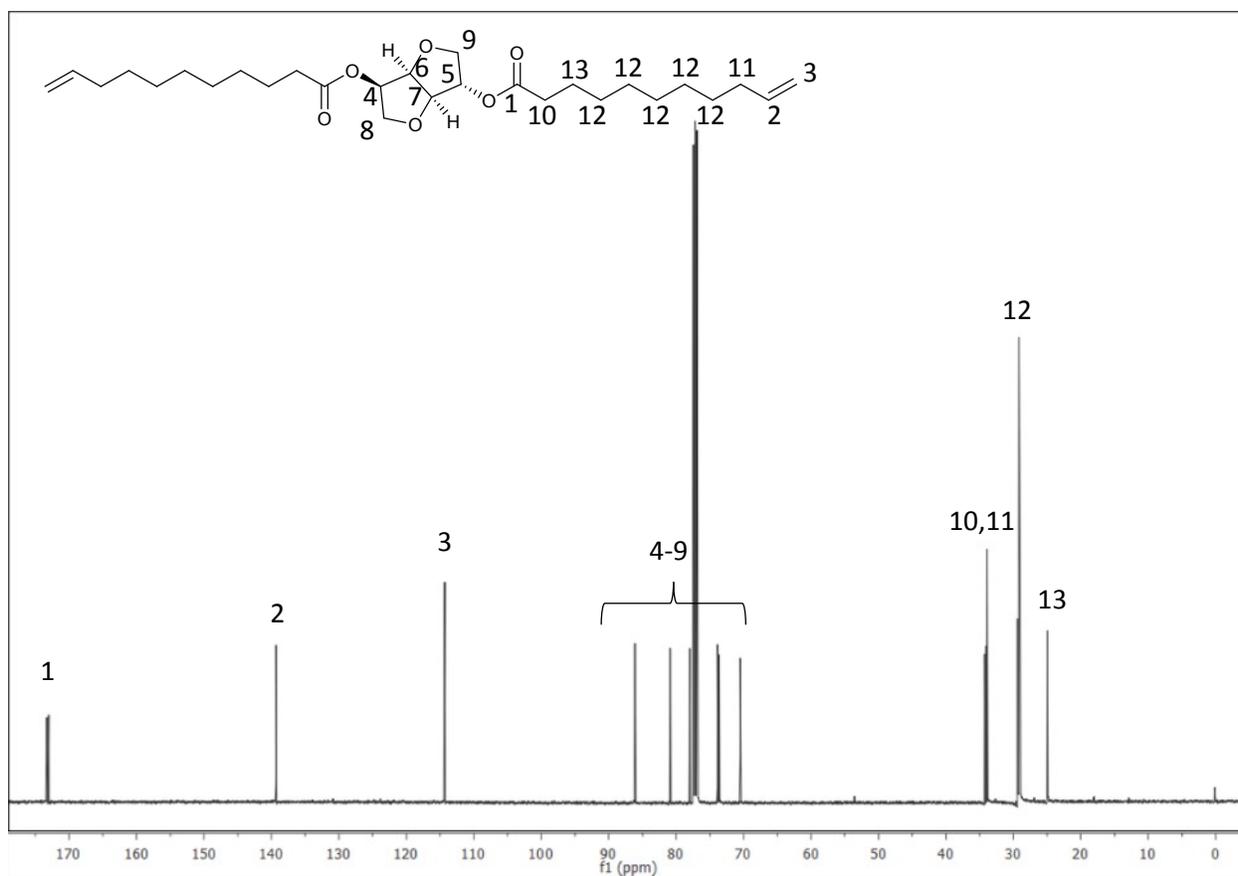


Figure S18. ^{13}C -NMR spectrum of isororbide undecenoate (IU) (CDCl_3 , 125 MHz).

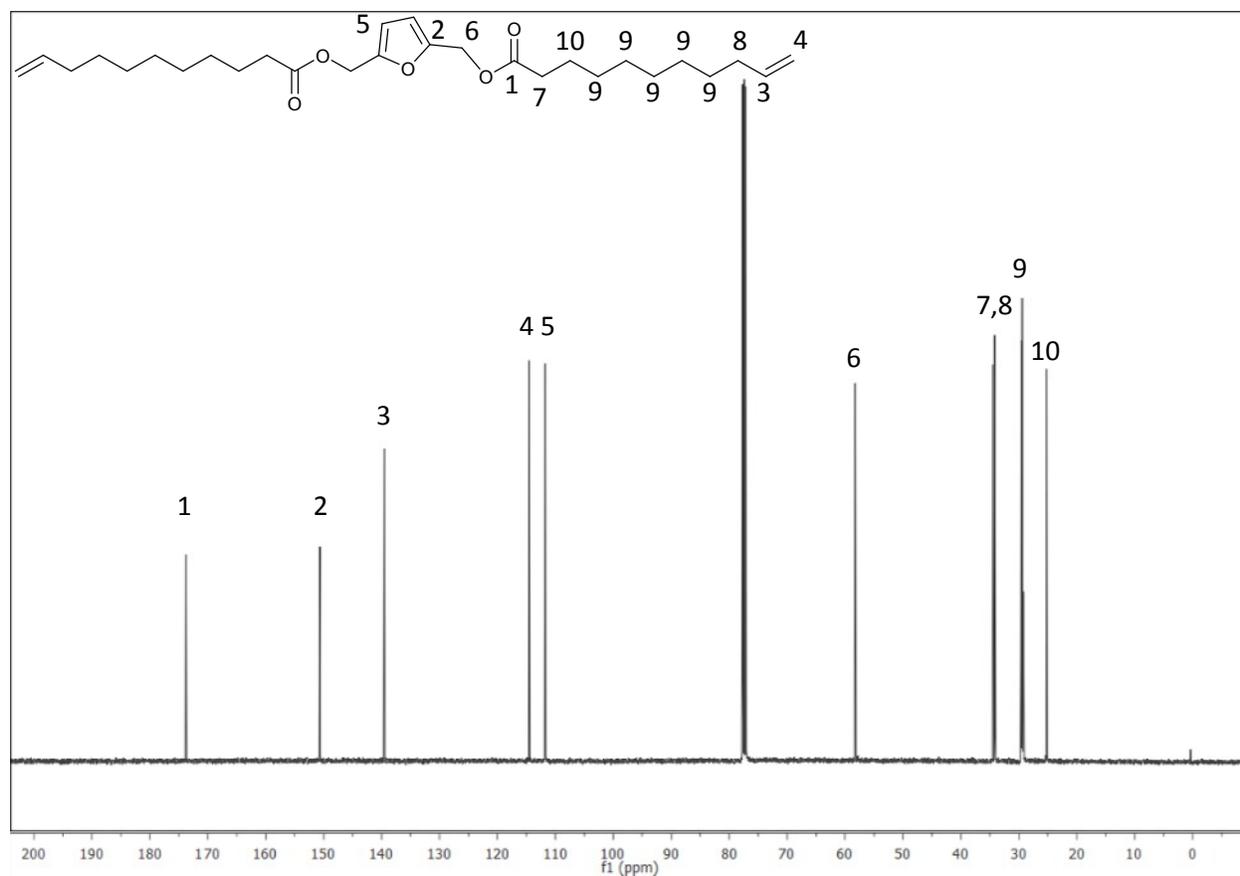


Figure S19. ¹³C-NMR spectrum of 2,5-bis(hydroxymethyl)furan undecenoate (**BHMFU**) (CDCl₃, 125 MHz).

ATR-IR Spectra

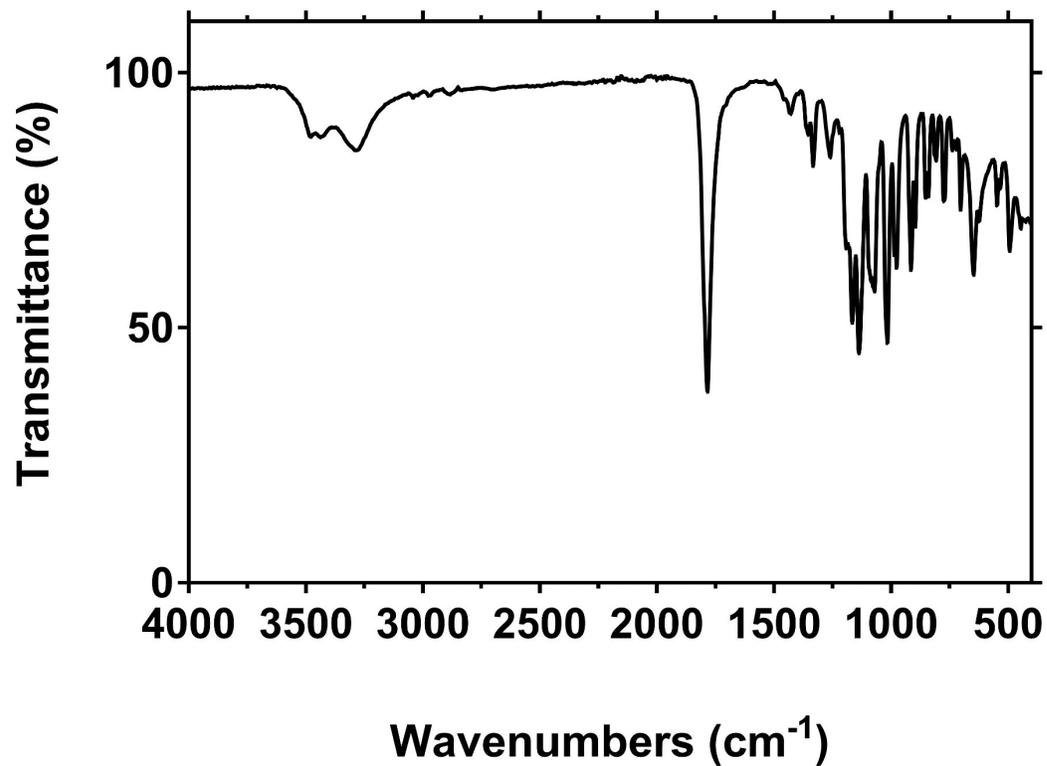


Figure S20. ATR-FTIR spectra of D-glucaro-1,4:6,3-dilactone.

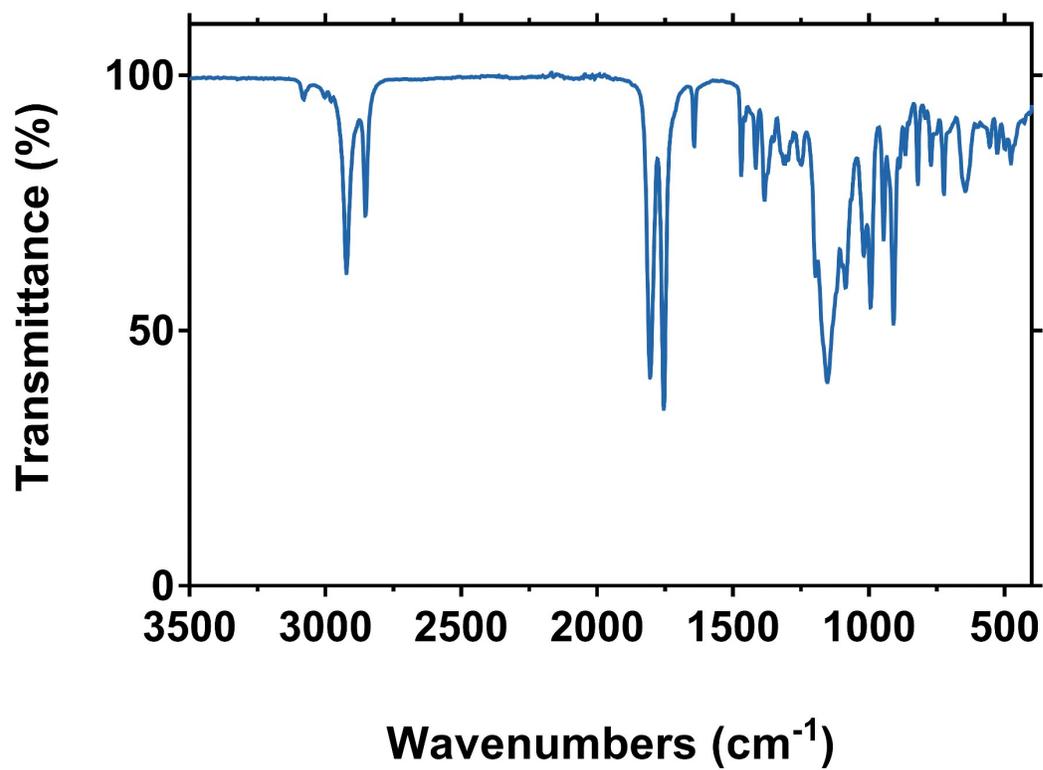


Figure S21. ATR-FTIR spectra of glucarodilactone undecenoate.

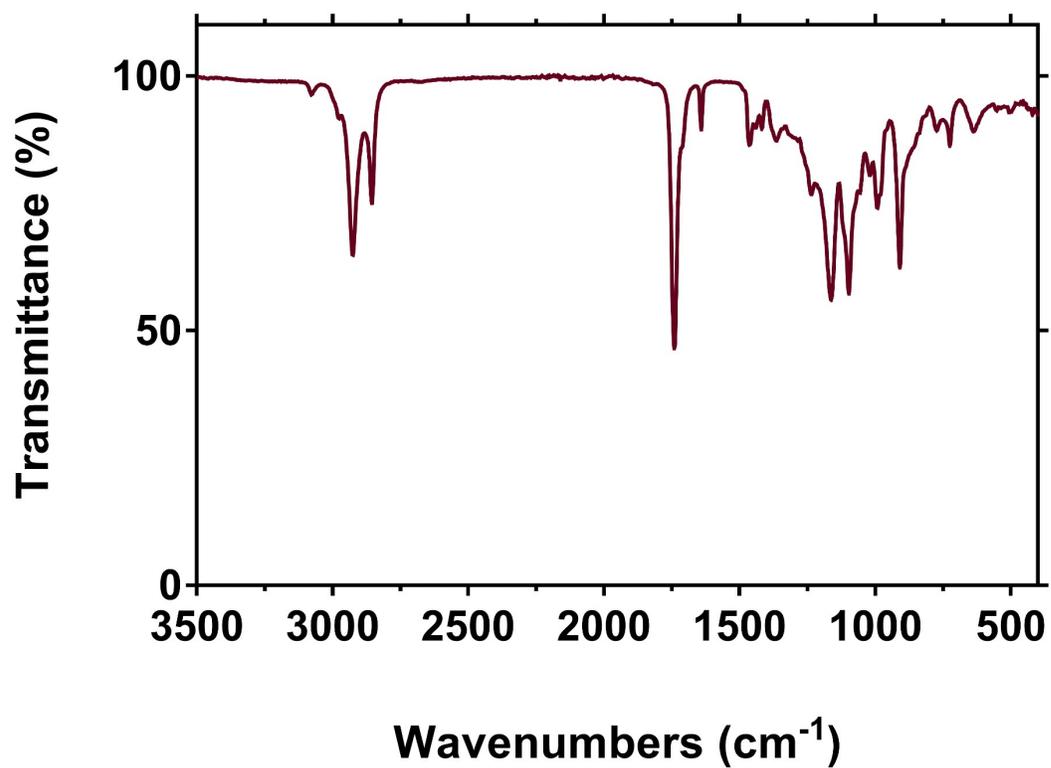


Figure S22. ATR-FTIR spectra of isosorbide undecenoate.

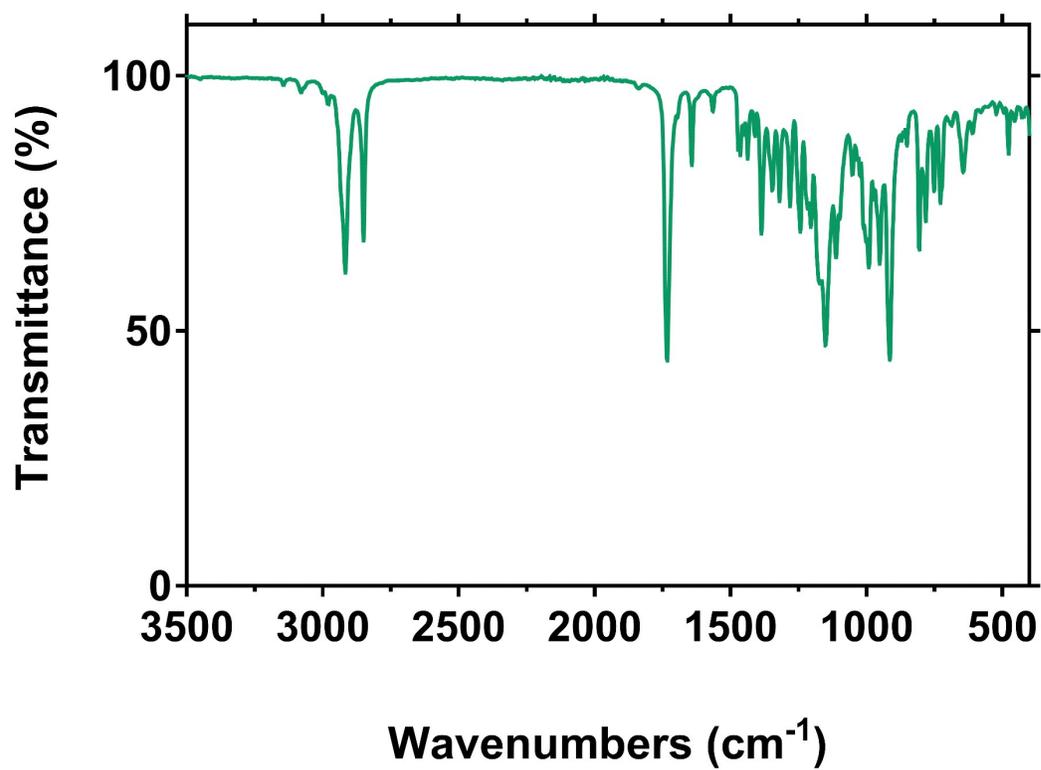


Figure S23. ATR-FTIR spectra of 2,5-bis(hydroxymethyl)furan undecenoate.

Differential Scanning Calorimetry

A singular T_g , following the Fox relationship was observed for each sample, indicating uniform copolymerization between the two monomers.¹ For each composition, except for P(GDLU₁₈-co-IU₈₂), there is a singular melting event as seen in Figure 2 with close proximity to the T_g . A commonly observed feature in polymeric materials is the ratio of glass transition temperature to melting point, expressed in Kelvin and can be estimated to be $T_g/T_m \approx 2/3$ for an unsymmetrical polymer.^{2,3} In this case unsymmetrical polymers are defined as containing backbone atoms which do not have two identical substituents.² Interestingly, our system significantly deviates from the traditional 2/3 ratio with $T_g/T_m \approx 0.85$ -0.94. While high T_g/T_m ratios are common in copolymers due to the depression of the melting temperature, the homopolymers P(GDLU) ($T_g/T_m \approx 0.92$) and P(IU) ($T_g/T_m \approx 0.84$) still deviate significantly from the empirical ratio. The high T_g/T_m ratio is indicative of the highly unsymmetrical nature of our homopolymers, due to the incompatibility between the rigid sugar-derivatives and the respective olefin linker. Annealing of the low-crystallinity P(GDLU₅₂-co-IU₄₈) copolymer at 40 °C, 80 °C, 100 °C, and 120 °C was attempted to induce higher melting temperatures in P(GDLU₅₂-co-IU₄₈) but post-annealing characterization by DSC showed failure to induce higher melting temperatures in this material. Thus, the T_g/T_m relationship in our material indicates the crystallinity in our materials is limited to the formation of small crystallites.

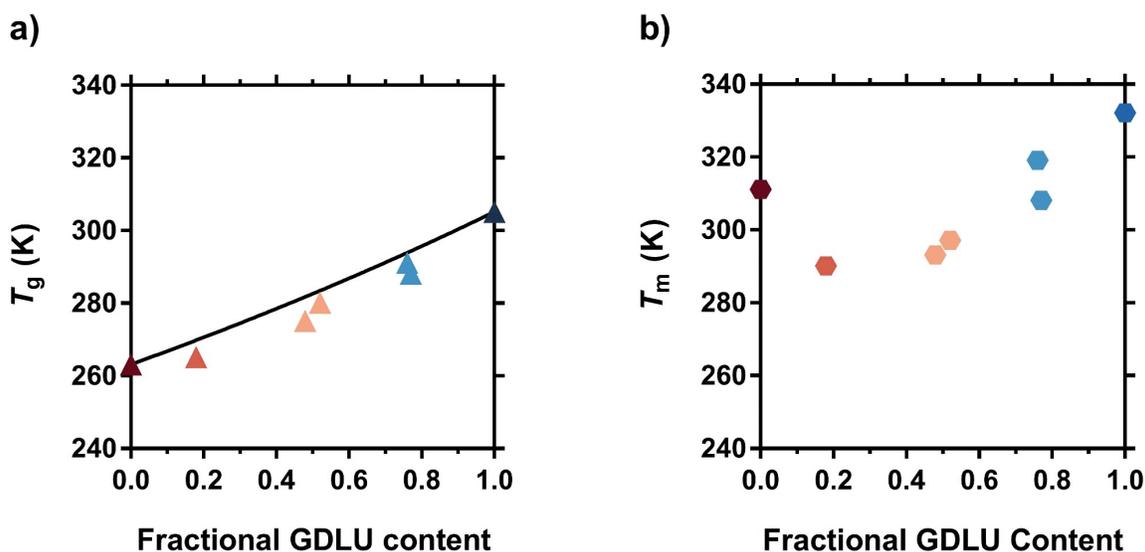


Figure S24. Differential scanning calorimetry data for P(GDLU), P(GDLU₇₇-co-IU₂₃), P(GDLU₇₆-co-IU₂₄), P(GDLU₅₂-co-IU₄₈), P(GDLU₄₈-co-IU₅₂), P(GDLU₁₈-co-IU₈₂), P(IU). **a)** IU Fox relationship comparison to the GDLU:IU copolymer family. Black line shows the expected empirical relationship between copolymers of with similar T_g 's as P(GDLU) and P(IU). **b)** Describes melting point suppression as function of GDLU content.

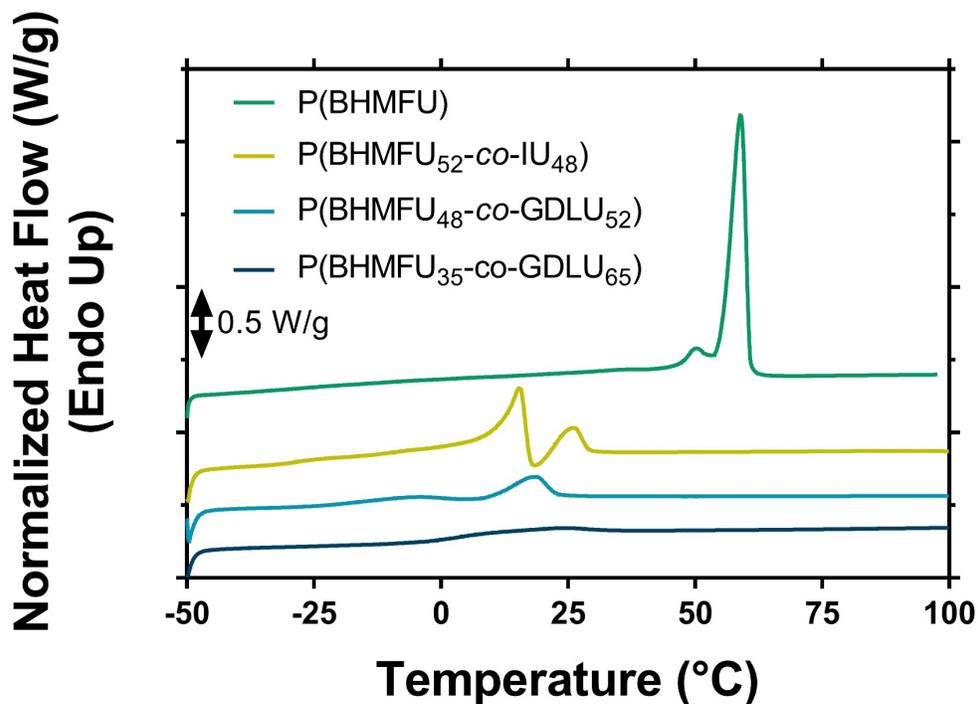


Figure S25. Differential scanning calorimetry (DSC) of the BHMFCU-containing polyesters. Polymer samples were heated and cooled at $10\text{ }^{\circ}\text{C min}^{-1}$ from $-50\text{ }^{\circ}\text{C}$ to $200\text{ }^{\circ}\text{C}$. Second heating was using for melting point analysis.

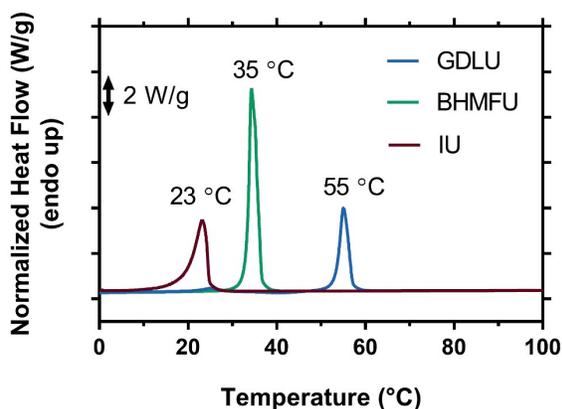


Figure S26. Differential scanning calorimetry (DSC) of GDLU, BHMFCU, and IU. Polymer samples were heated and cooled at $10\text{ }^{\circ}\text{C min}^{-1}$ from $-50\text{ }^{\circ}\text{C}$ to $200\text{ }^{\circ}\text{C}$. Second heating was using for melting point analysis.

Size Exclusion Chromatography (SEC) Traces

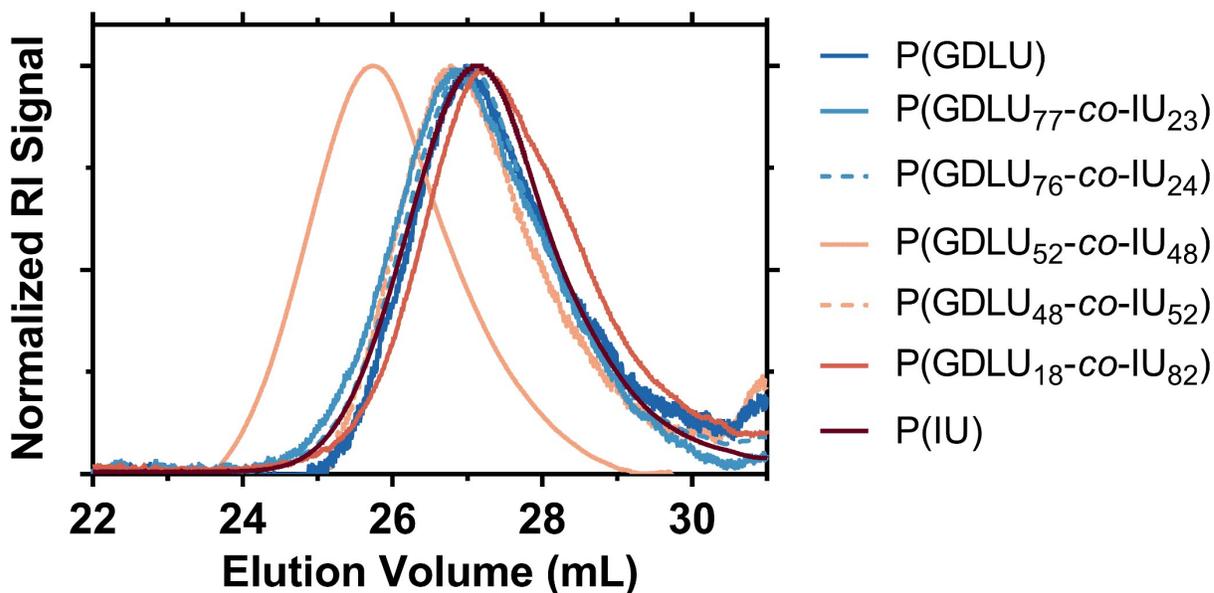


Figure S27. SEC profiles of the P(GDLU_x-co-IU_y) copolymers. The mobile phase was THF with a flow rate of 1 mL/min. The RI signal from each sample was normalized for comparison between samples.

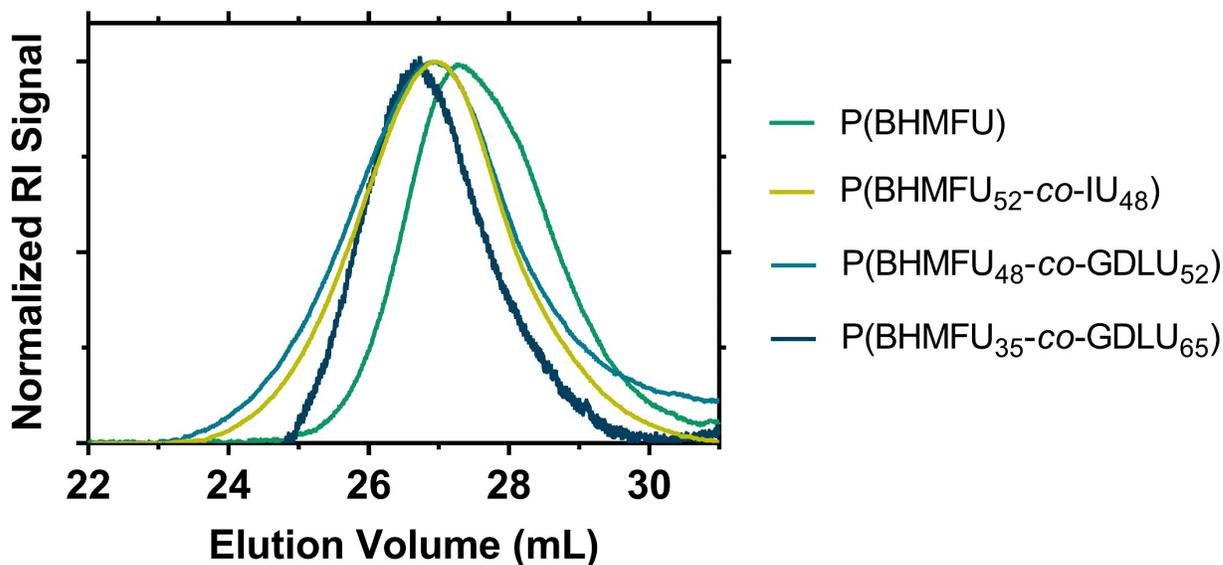


Figure S28. SEC profile of P(BHMFU) and BHMFU-containing copolymers. The mobile phase was THF with a flow rate of 1 mL/min. The RI signal from each sample was normalized for comparison between samples.

Rheology

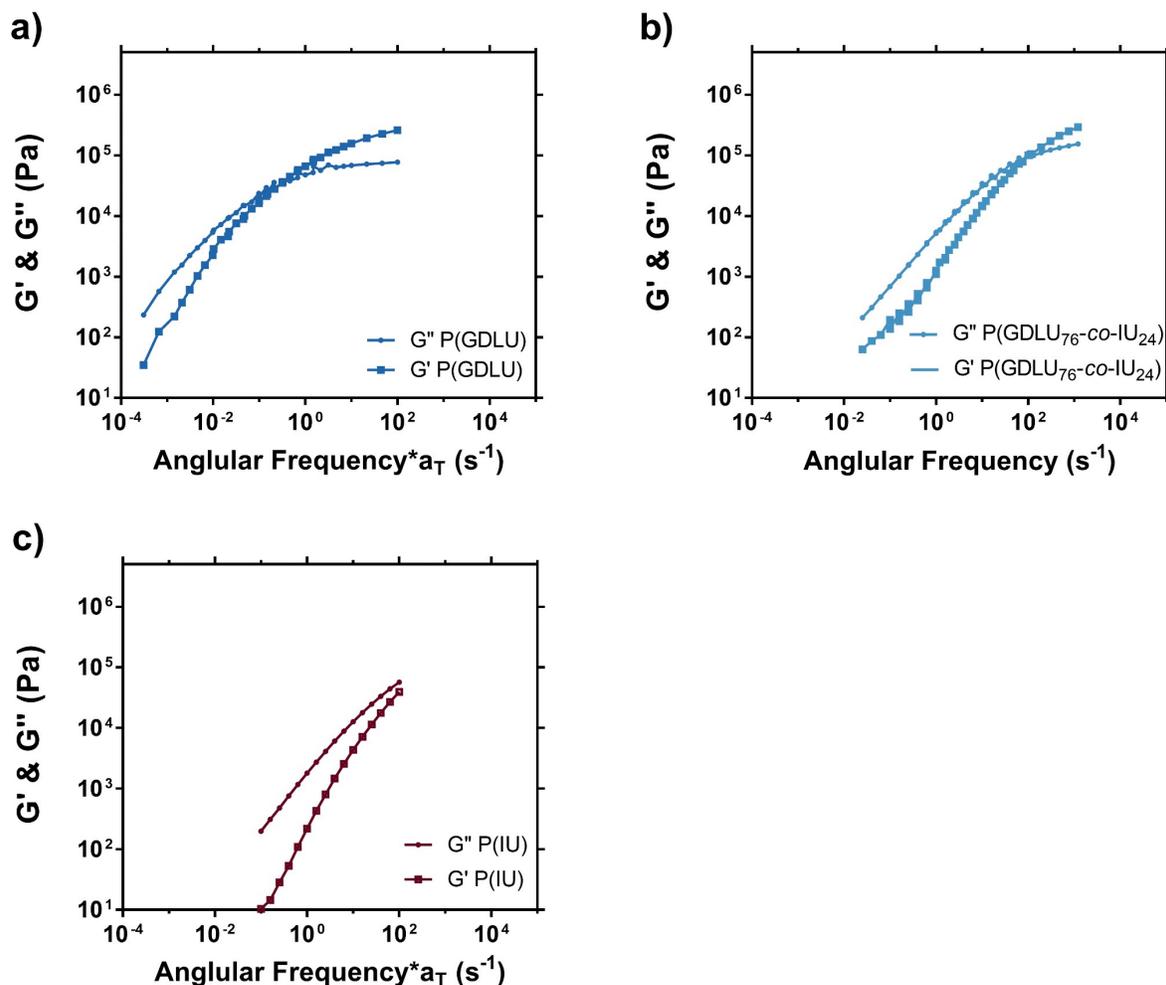


Figure S29. Linear viscoelasticity of select P(GDLU_x-co-IU_y) compositions. Small-amplitude oscillatory shear measurements were obtained at 1 rad/s from 1-10% strain to ensure the sample remained in the linear viscoelastic regime of the materials. a) TTS for P(GDLU) used 80 °C as the reference temperature to generate this master curve, b) TTS for P(GDLU₇₆-co-IU₂₄) used 80 °C as the reference temperature to generate this master curve, c) P(IU)'s results are shown as a singular frequency sweep experiment performed at 80 °C for comparison.

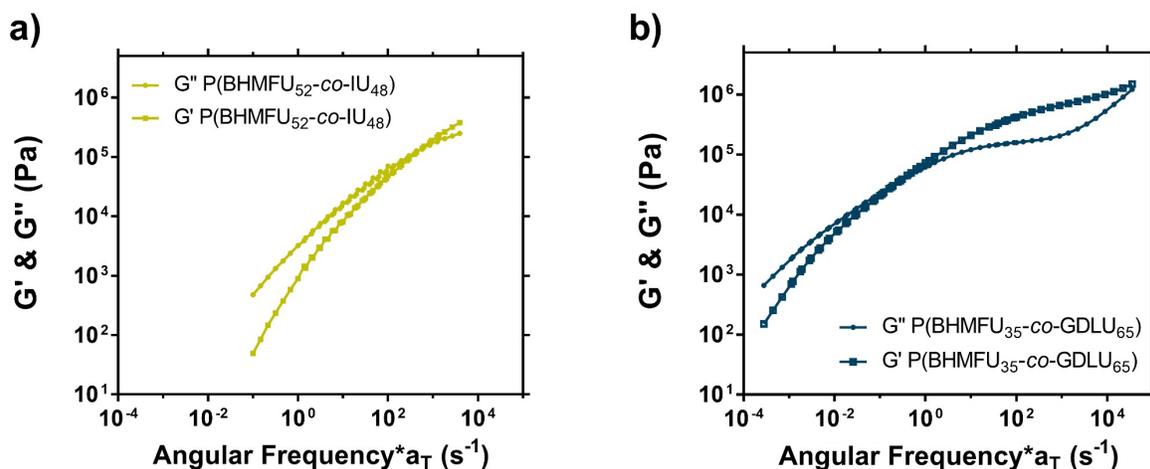


Figure S30. Linear Viscoelasticity of select P(BHMFU-co-IU or GDLU) compositions: a) P(BHMFU₅₂-co-IU₄₈) and b) P(BHMFU₃₅-co-GDLU₆₅). Small-amplitude oscillatory shear measurements were obtained at 1 rad/s from 1-10% strain to ensure the sample remained in the linear viscoelastic regime of the materials.

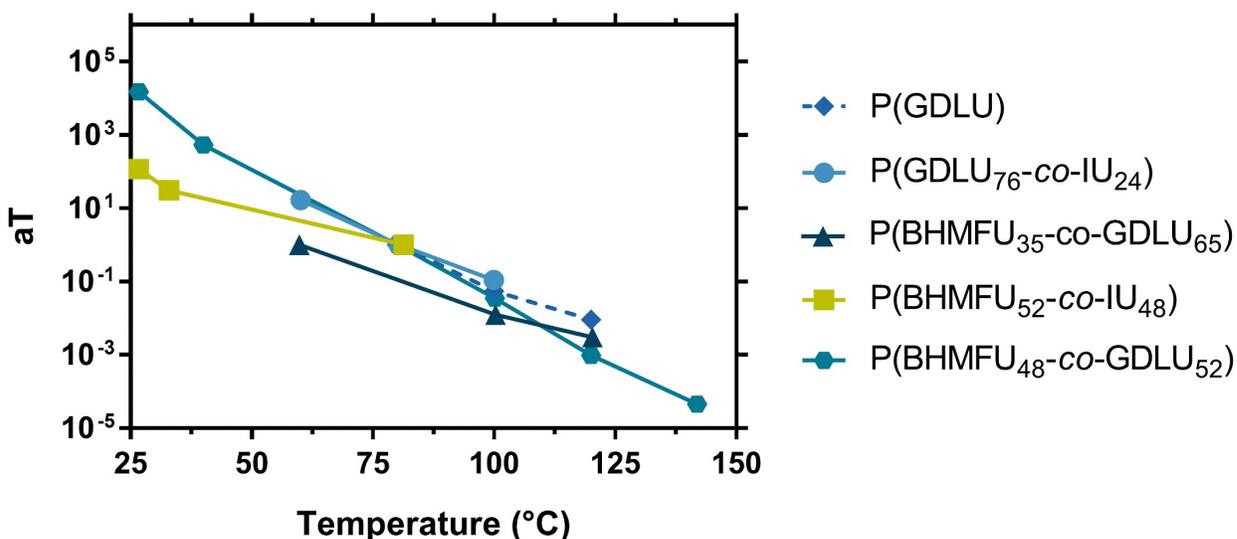


Figure S31. Time-temperature superposition (TTS) shift factors for reported polymers. Polymers were shifted in reference to 80 °C, except for P(BHMFU₃₅-co-GDLU₆₅) which was shifted in reference to 60 °C.

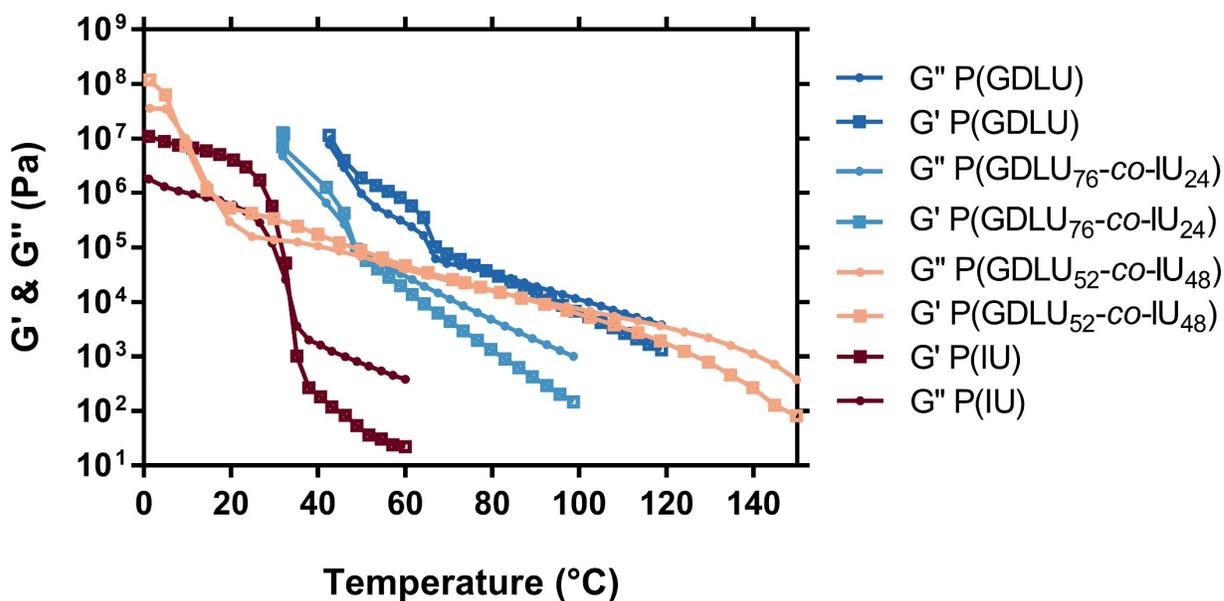


Figure S32. Temperature sweep rheology curves for the P(GDLU_x-co-IU_y) copolymers. Temperature sweeps were performed at 3 °C/min at a frequency of 1 rad/s from 5-10 °C above the T_g to where the minimum torque limit was observed for the instrument (0.02 N).

Hydrolytic Degradation Testing

Samples from the P(GDLU_x-co-IU_y) copolymer matrix were exposed to basic (0.25 M NaOH), neutral, and acidic (0.25 M HCl) aqueous conditions over the course of six days and the insoluble mass was monitored over this period (data is shown in Figure 4 in the main manuscript). All samples containing GDL were found to degrade rapidly under basic (0.25M NaOH) conditions. These polyesters are relatively stable under neutral aqueous conditions, with only minor mass loss during the six-day period. Minor mass loss is observed in most compositions exposed to acidic conditions. P(GDLU₄₈-co-IU₅₂) does show a rapid 15% mass loss after the first day of hydrolytic insult, but further degradation of the materials was not observed.

After the six-day hydrolytic degradation experiment, the remaining insoluble mass was characterized by NMR and SEC. NMR showed a slight (1-7%) reduction in GDL content compared to isosorbide for all testing conditions with remaining insoluble mass. More drastically, SEC of the neutral and acid conditions shows a reduction on the order of half in molecular weight. We hypothesize that the hydrolytic ring opening of GDL leads to a change in the polarity of the material, allowing for an influx of aqueous solution into the material leading to bulk erosion of the polymer.^{4,5} This process would explain the significant discrepancies in the hydrolytic degradation behavior observed for P(IU) vs the GDL-containing polyesters.

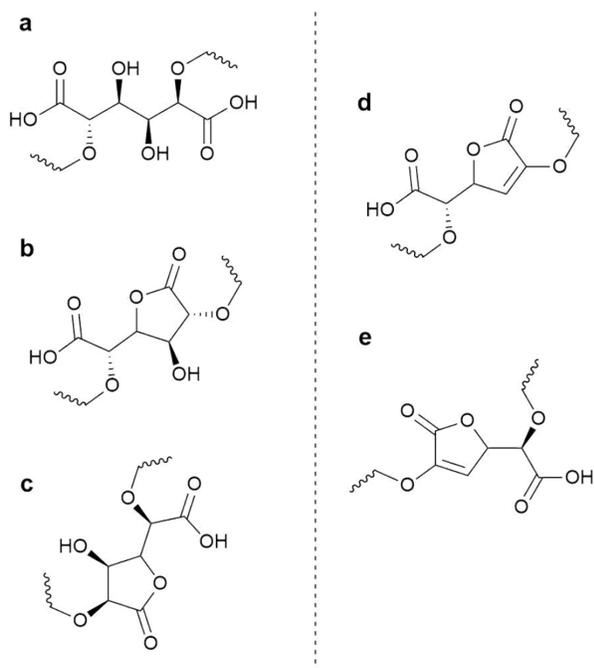


Figure S33. Proposed hydrolytic and thermal routes of degradation of GDL within the polymeric backbone. GDL is known to decompose by either hydrolytic (a-c) and thermal (d,e) routes and the analogous chemical name for decomposed non-functionalized GDL is as follows: **a** – D-glucaric acid; **b** – D-glucaro-1,4-lactone; **c** – D-glucaro-6,3-lactone; **d** – 4-deoxy-L-erythro-hex-4-enaro-6,3-lactone; **e** – L-threo-4-deoxy-hex-4-enaro-6,3-lactone.

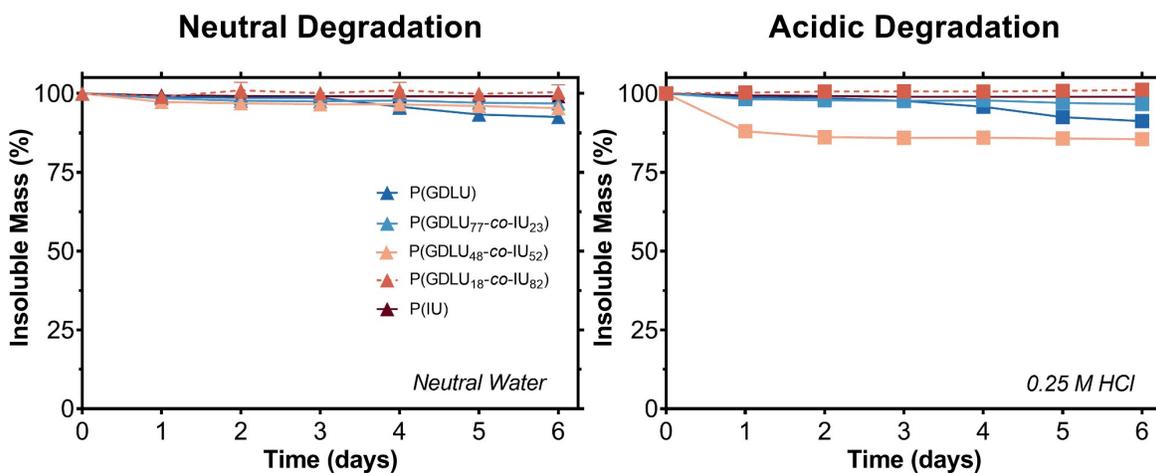


Figure S34. Hydrolytic stability testing of P(GDLU_x-co-IU_y) copolymer system in basic (0.25 M NaOH), neutral, and acidic (0.25 M HCl) aqueous conditions. Samples were characterized in triplicate and each sample was exposed to 0.25 M NaOH for 24 hour periods, dried and insoluble mass was massed. Then samples were exposed to new aqueous solution for the next 24-hour period. This process was repeated over the course of 6 days.

Table S3. Hydrolytic degradation testing of P(GDLU₇₇-co-IU₂₃). Individual polymer samples were run in triplicate.

Time (Days)	Insoluble Sample Mass (g)								
	P(GDLU ₇₇ -co-IU ₂₃) 0.25 M NaOH			P(GDLU ₇₇ -co-IU ₂₃) Neutral Water			P(GDLU ₇₇ -co-IU ₂₃) 0.25 M HCl		
	1	2	3	1	2	3	1	2	3
0	0.20	0.19	0.19	0.18	0.20	0.19	0.18	0.19	0.19
1	0.04	0.03	0.04	0.18	0.20	0.19	0.18	0.18	0.18
2	0.00	0.00	0.00	0.18	0.19	0.19	0.18	0.18	0.18
3				0.18	0.19	0.19	0.18	0.18	0.18
4				0.18	0.20	0.19	0.18	0.18	0.18
5				0.18	0.19	0.19	0.18	0.18	0.18
6				0.18	0.19	0.19	0.18	0.18	0.18

Table S4. Hydrolytic degradation testing of P(GDLU_{18-co}-IU₈₂). Individual polymer samples were run in triplicate.

Time (Days)	Insoluble Sample Mass (g)								
	P(GDLU _{18-co} -IU ₈₂) 0.25 M NaOH			P(GDLU _{18-co} -IU ₈₂) Neutral Water			P(GDLU _{18-co} -IU ₈₂) 0.25 M NaOH		
	1	2	3	1	2	3	1	2	3
0	0.17	0.10	0.17	0.13	0.13	0.13	0.17	0.15	0.17
1	0.00	0.00	0.00	0.13	0.12	0.13	0.17	0.15	0.17
2				0.13	0.12	0.13	0.17	0.15	0.17
3				0.13	0.12	0.13	0.17	0.15	0.17
4				0.13	0.12	0.13	0.17	0.15	0.17
5				0.13	0.12	0.13	0.17	0.15	0.17
6				0.13	0.12	0.13	0.17	0.15	0.17

Table S5. Hydrolytic degradation testing of P(GDLU_{48-co}-IU₅₂). Individual polymer samples were run in triplicate.

Time (Days)	Insoluble Sample Mass (g)					
	P(GDLU _{48-co} -IU ₅₂) Neutral Water			P(GDLU _{48-co} -IU ₅₂) 0.25 M HCl		
	1	2	3	1	2	3
0	0.083	0.098	0.109	0.279	0.264	0.275
1	0.080	0.096	0.106	0.242	0.237	0.240
2	0.080	0.095	0.106	0.239	0.231	0.234
3	0.080	0.095	0.106	0.238	0.231	0.233
4	0.080	0.095	0.106	0.238	0.231	0.233
5	0.079	0.094	0.105	0.237	0.231	0.232
6	0.078	0.094	0.0143	0.236	0.230	0.233

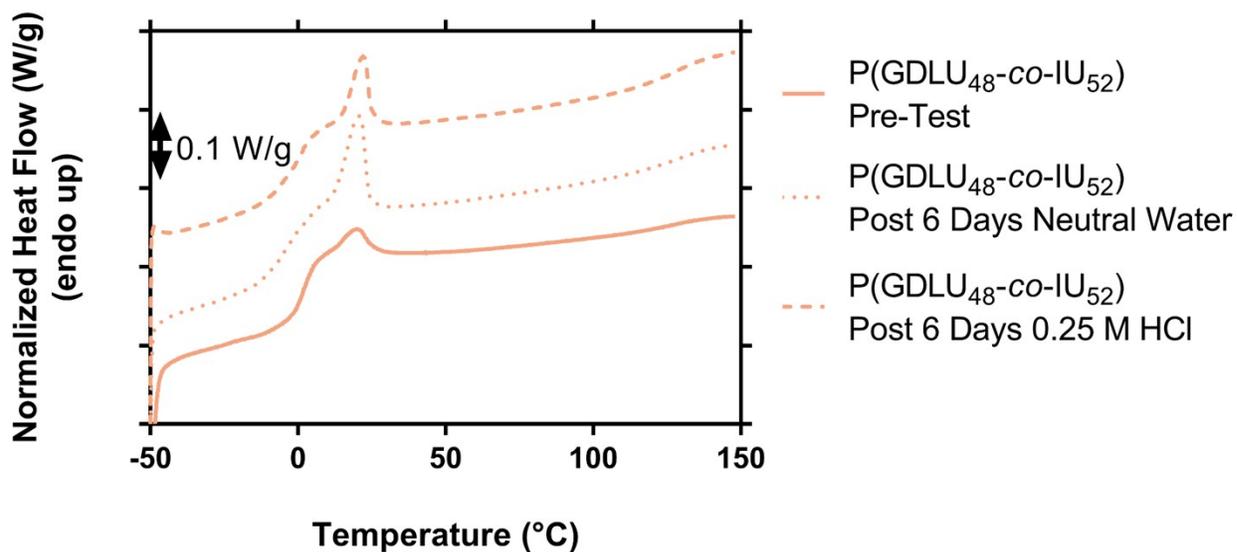


Figure S35. DSC of the P(GDLU₄₈-co-IU₅₂) before and after 6-day exposure to hydrolytic degradation conditions. Polymer samples were heated and cooled at 10 °C min⁻¹ from -50 °C to 200 °C. Second heating was using for melting point analysis.

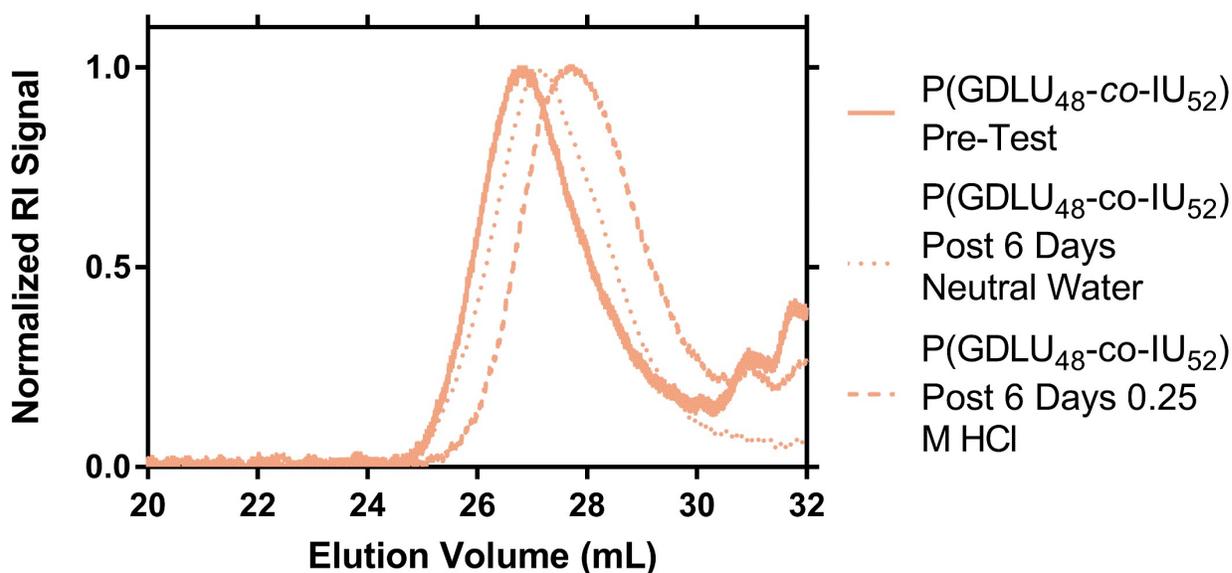


Figure S36. SEC data for the hydrolytic degradation of P(GDLU₄₈-co-IU₅₂). Insoluble mass of the neutral and acidic conditions were dissolved in THF and filtered prior to injection.

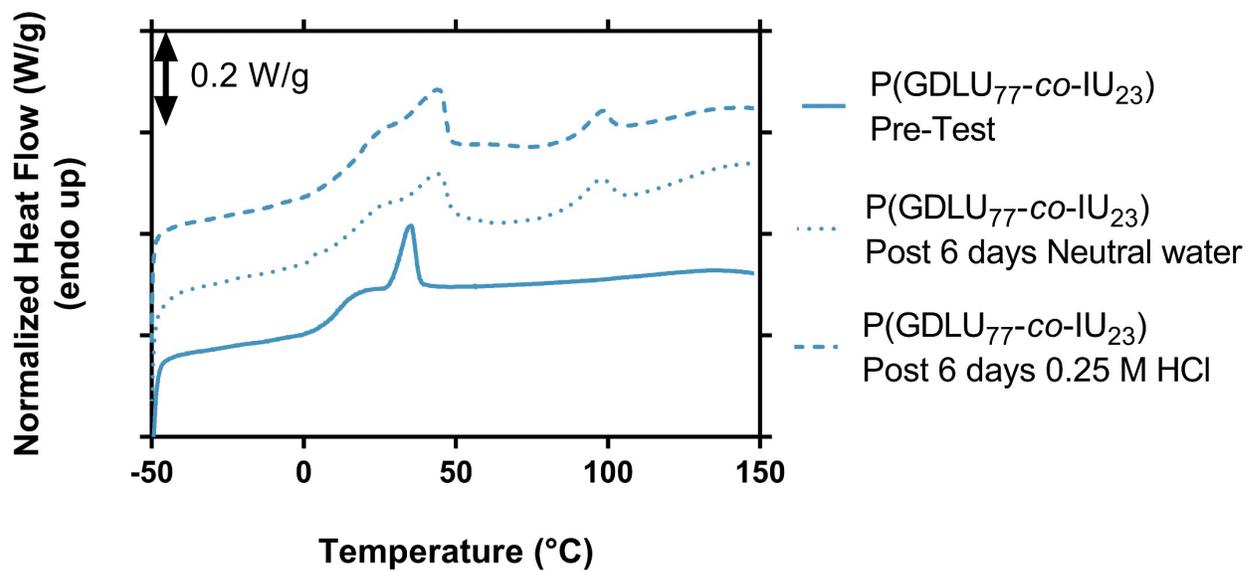


Figure S37. DSC of the P(GDLU₇₇-co-IU₂₃) before and after 6-day exposure to hydrolytic degradation conditions. Polymer samples were heated and cooled at 10 °C min⁻¹ from -50 °C to 200 °C. Second heating was using for melting point analysis.

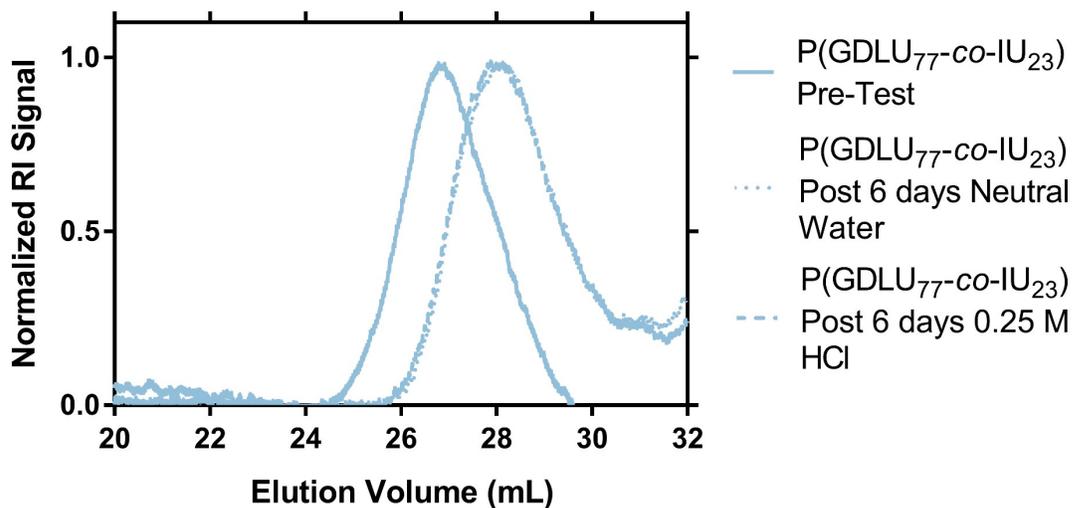


Figure S38. SEC data for the hydrolytic degradation of P(GDLU₇₇-co-IU₂₃). Insoluble mass of the neutral and acidic conditions were dissolved in THF and filtered prior to injection.

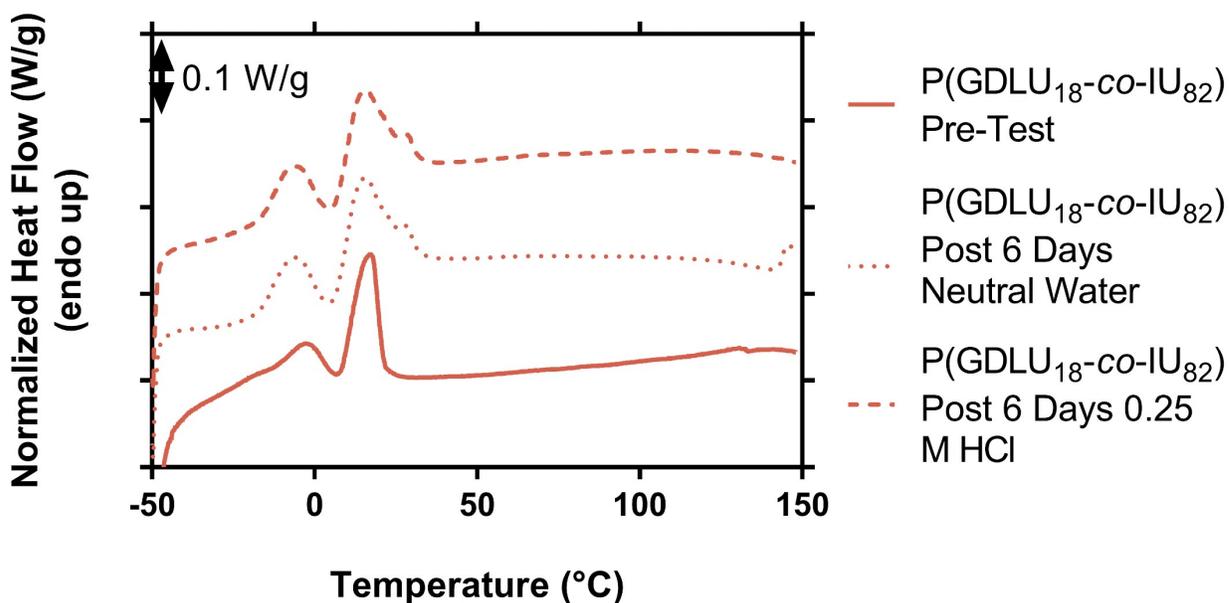


Figure S39. DSC of the P(GDLU₁₈-co-IU₈₂) before and after 6-day exposure to hydrolytic degradation conditions. Polymer samples were heated and cooled at 10 °C min⁻¹ from -50 °C to 200 °C. Second heating was using for melting point analysis.

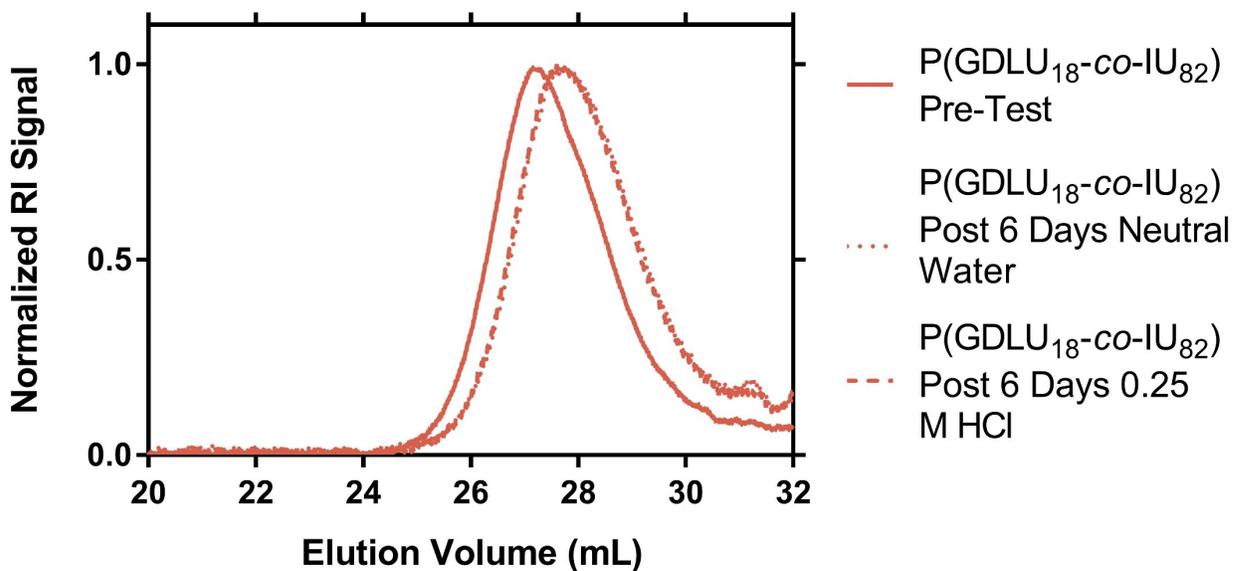


Figure S40. SEC data for the hydrolytic degradation of P(GDLU₁₈-co-IU₈₂). Insoluble mass of the neutral and acidic conditions were dissolved in THF and filtered prior to injection.

Thermogravimetric Analysis (TGA)

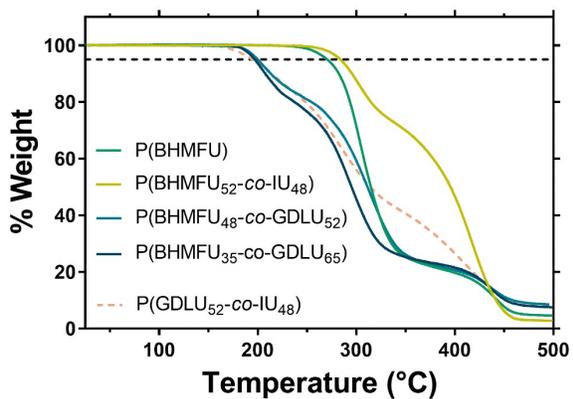


Figure S41. TGA of the PBHMFU and BHMFU-containing copolymers. Degradation temperatures are recorded at 5% weight loss denoted by the black dashed line. P(GDLU₅₂-co-IU₄₈) is shown for comparison to the P(GDLU_x-co-IU_y) system.

X-Ray Scattering

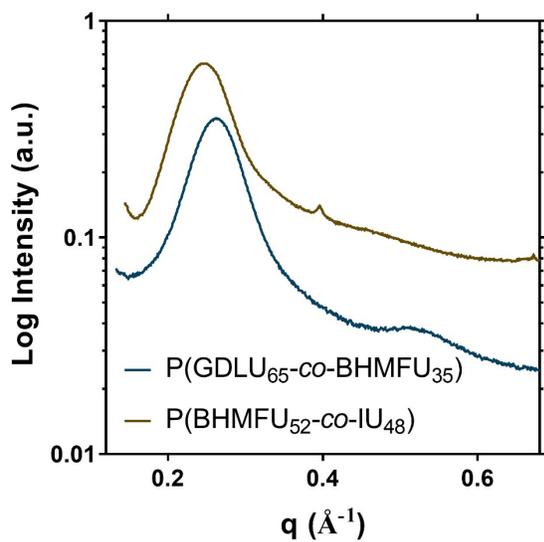
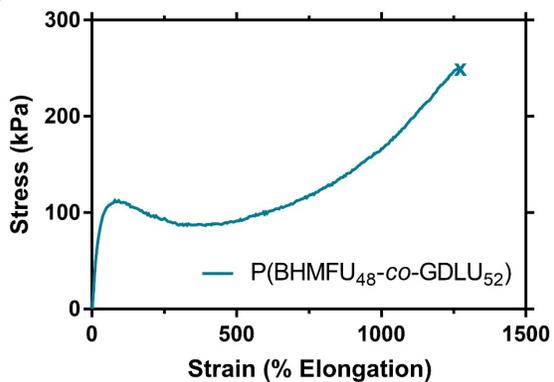


Figure S42. Experimental 1D medium-angle X-ray scattering of the BHMFU copolymer matrix at 25 °C. These samples have been background subtracted. Plots are vertically shifted for clarity.

Tensile Testing

a)



b)

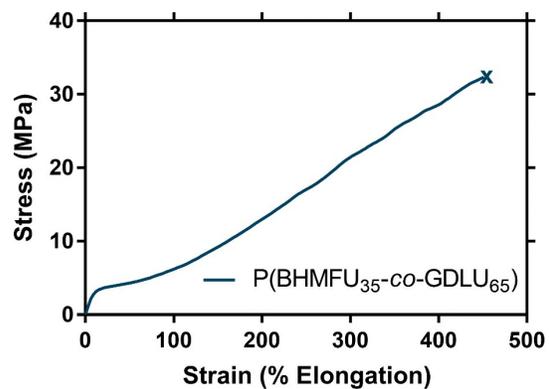


Figure S43. Tensile testing of P(BHMFU₄₈-co-GDLU₅₂) and P(BHMFU₃₅-co-GDLU₆₅). Curve shown is a representative run from the five replicates. Tensile testing was performed at 50 mm/min and samples were deformed until break.

Hysteresis Testing

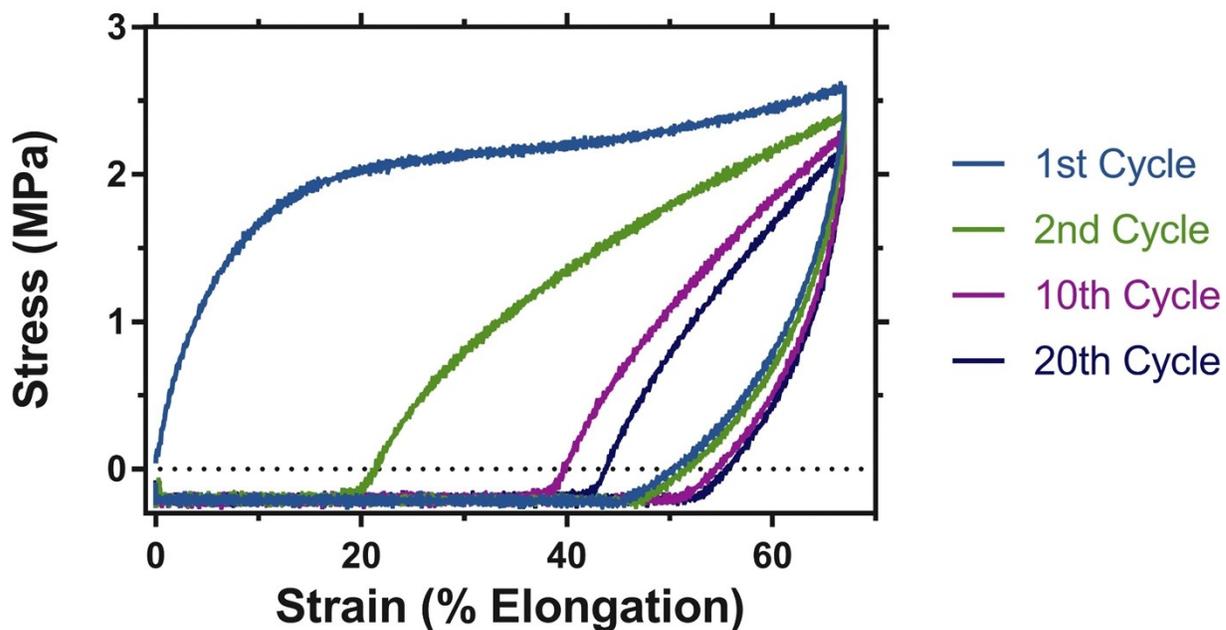


Figure S44. Hysteresis testing of P(GDLU₅₂-co-IU₄₈). Sample was elongated to 66 % strain at a rate of 50 mm/min, then grips were returned to 0 % strain at 50 mm/min. This cycle was repeated 20 times for this sample.

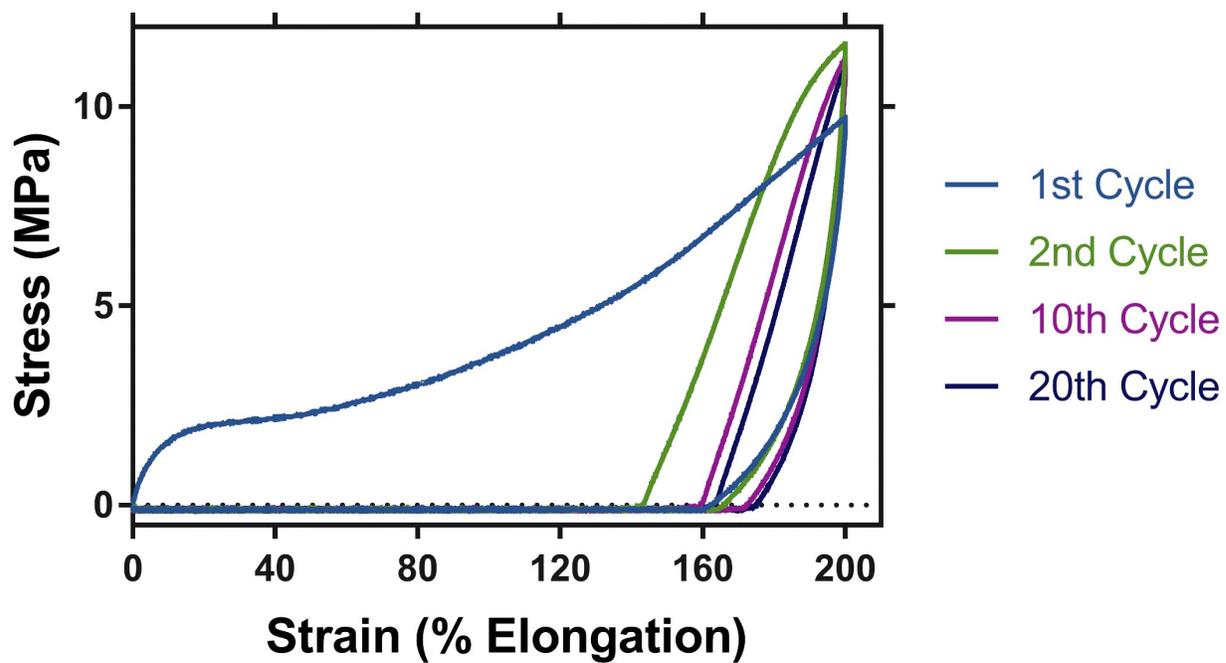


Figure S45. Hysteresis testing of P(GDLU₅₂-co-IU₄₈). Sample was elongated to 200 % strain at a rate of 50 mm/min, then grips were returned to 0 % strain at 50 mm/min. This cycle was repeated 20 times for this sample

References:

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