

## SUPPORTING INFORMATION

### "Oxidative esterification of aliphatic $\alpha,\omega$ -diols, an alternative route to polyester precursors for the synthesis of polyurethanes."

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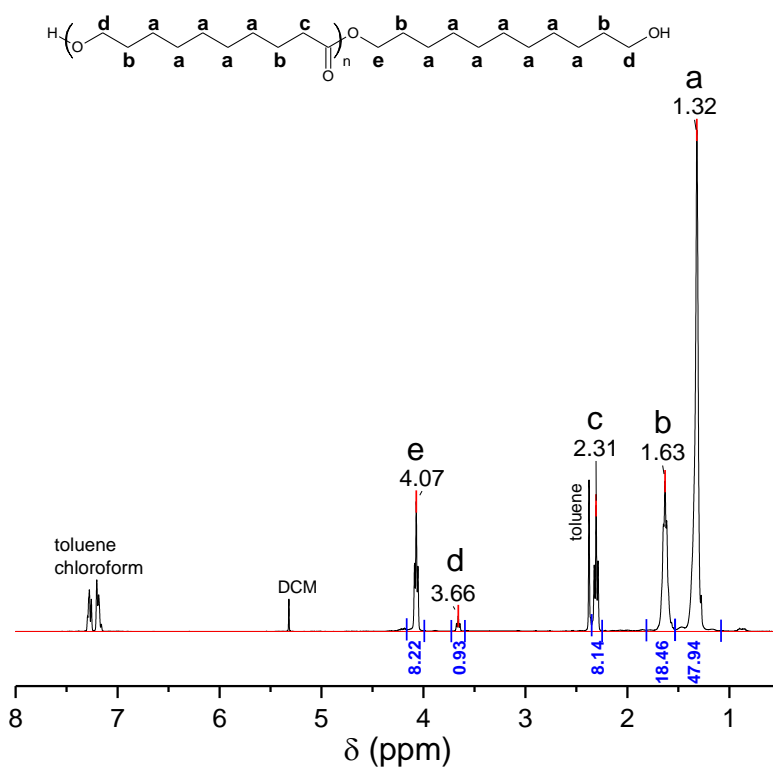


Figure S1. <sup>1</sup>H NMR spectrum of poly(decane sebacate) (CDCl<sub>3</sub>, 400 MHz).

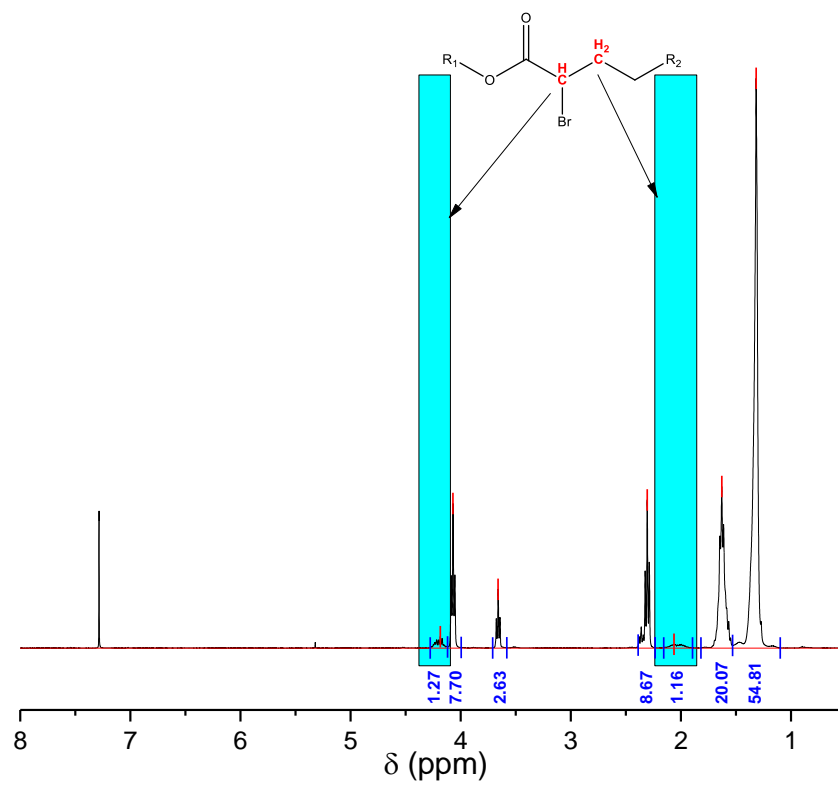


Figure S2. <sup>1</sup>H NMR spectrum of poly(decane sebacate) synthesized at 80°C (CDCl<sub>3</sub>, 400 MHz).

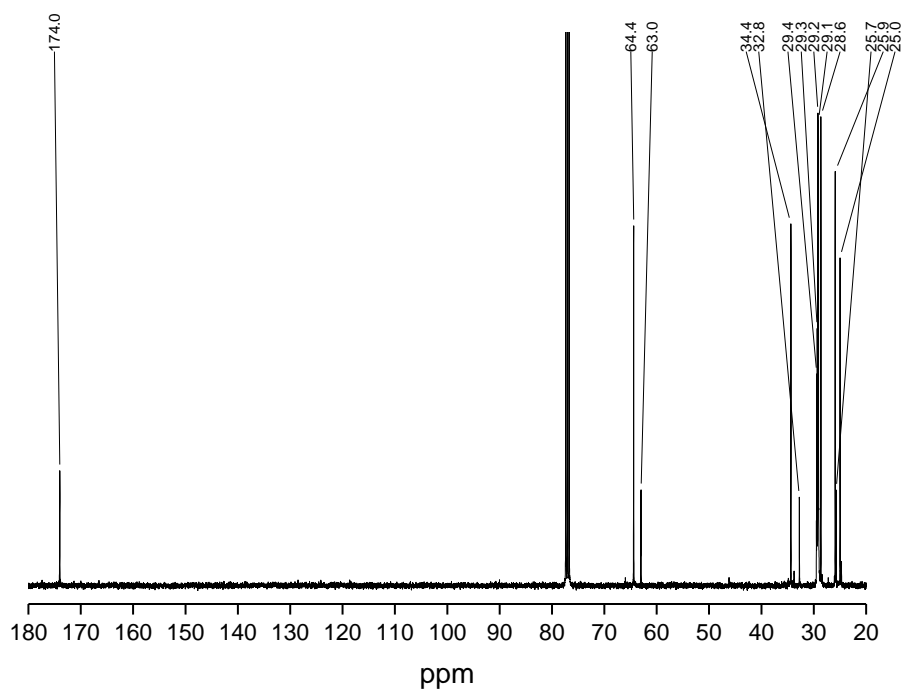


Figure S3. <sup>13</sup>C NMR spectrum of poly(decane sebacate) CDCl<sub>3</sub>. (CDCl<sub>3</sub>, 100 MHz).

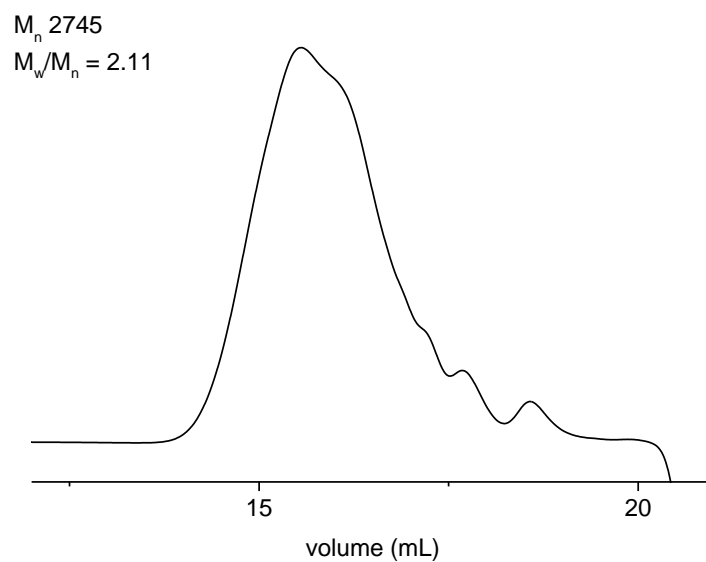


Figure S4. GPC chromatogram of poly(decane sebacate).

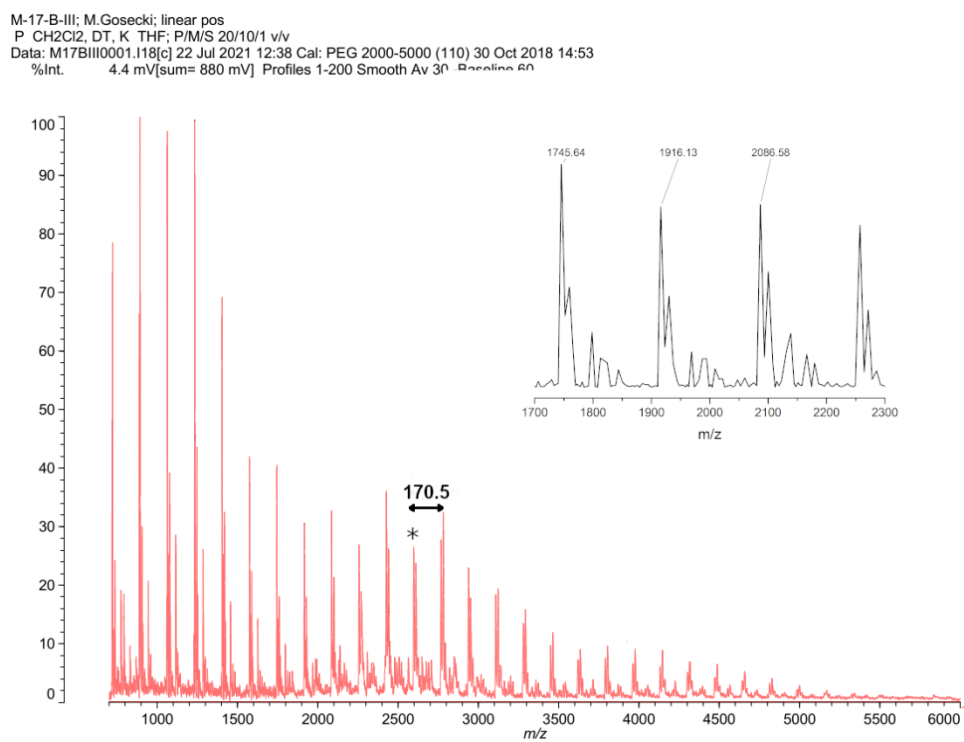


Figure S5 MALDI TOF mass spectrum of poly(decane sebacate); \*denotes population of signals ascribed to  $\text{HO}(\text{CH}_2)_{10}\text{O}[(\text{O})\text{C}(\text{CH}_2)_9\text{O}]_n\text{-H} + \text{K}^+$ .

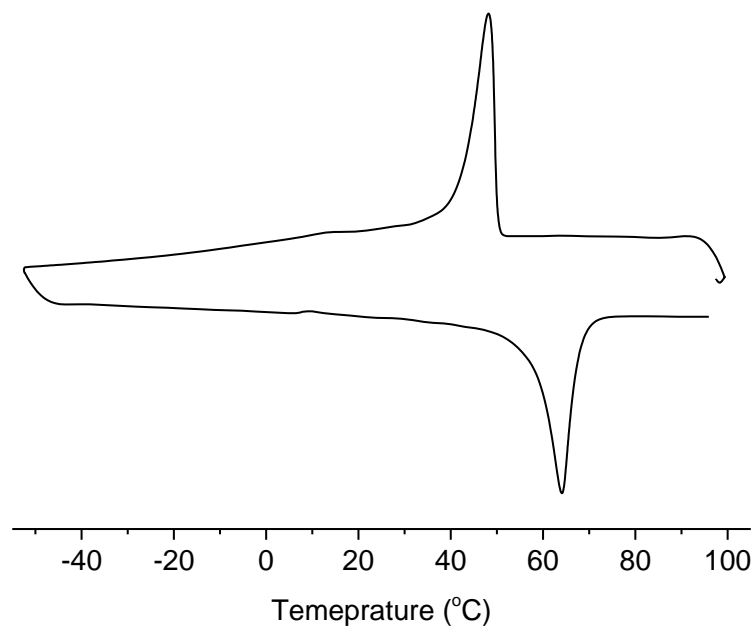


Figure S6. DSC of poly(decane sebacate).

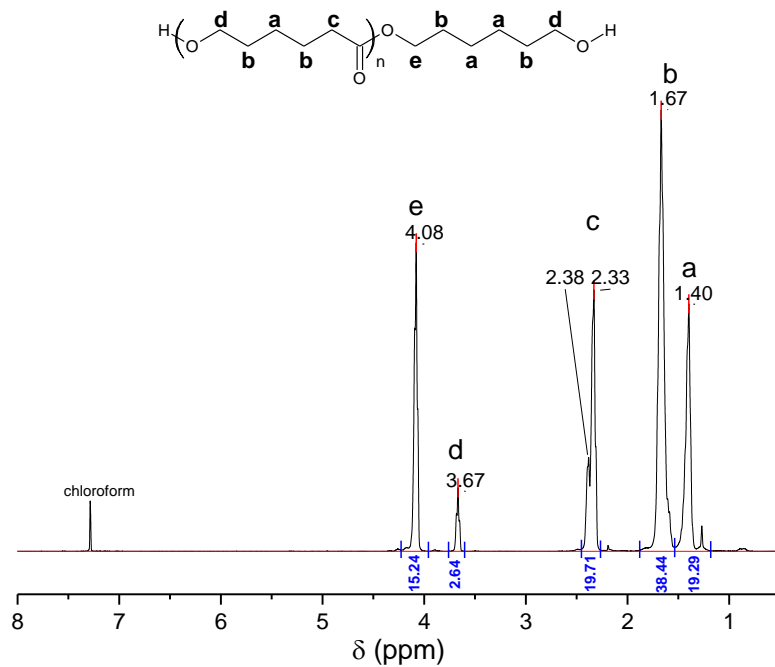


Figure S7. <sup>1</sup>H NMR spectrum of poly(hexane adipate) (CDCl<sub>3</sub>, 400 MHz).

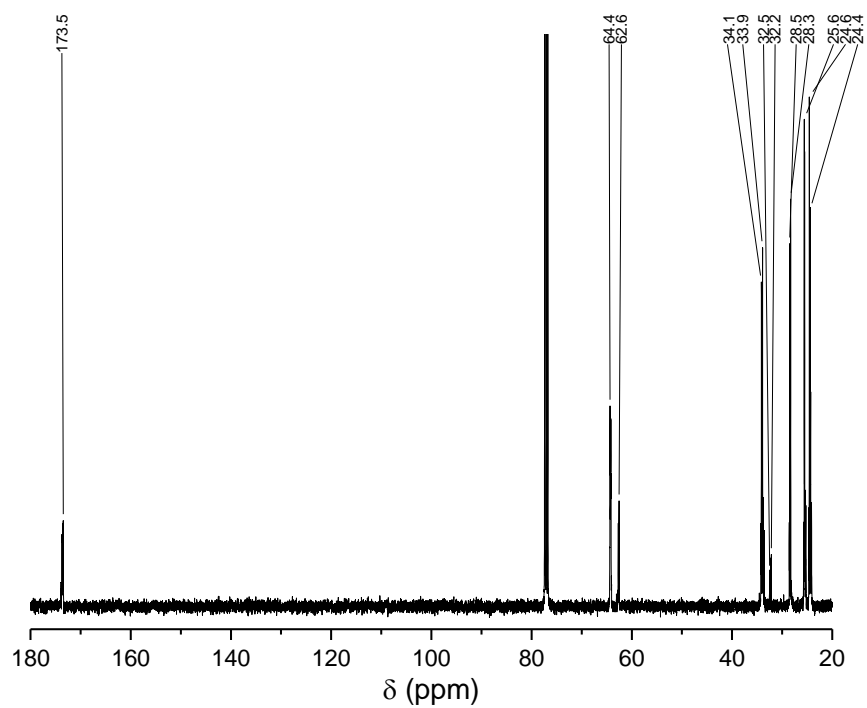


Figure S8.  $^{13}\text{C}$  NMR spectrum of poly(hexane adipate) ( $\text{CDCl}_3$ , 100 MHz).

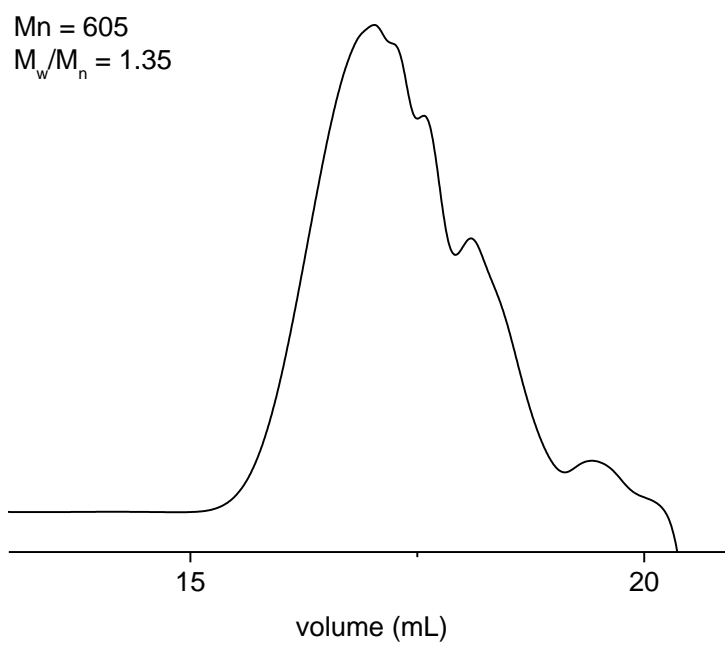


Figure S9. GPC chromatogram of poly(hexane adipate).

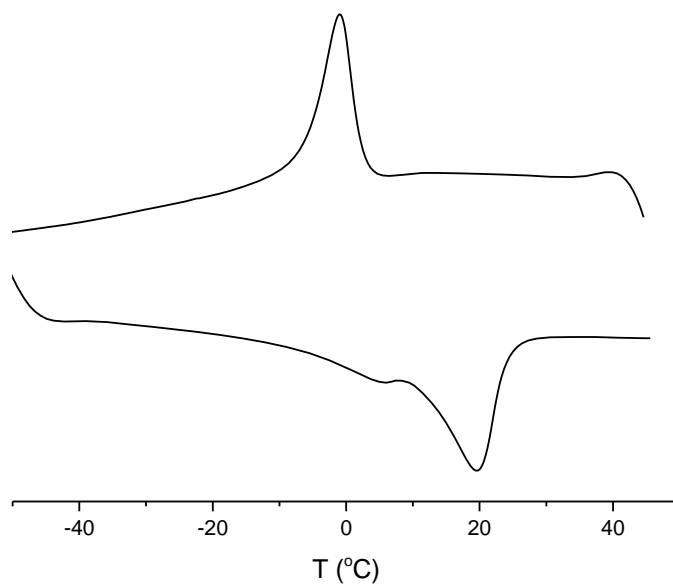


Figure S10. DSC of poly(hexane adipate).

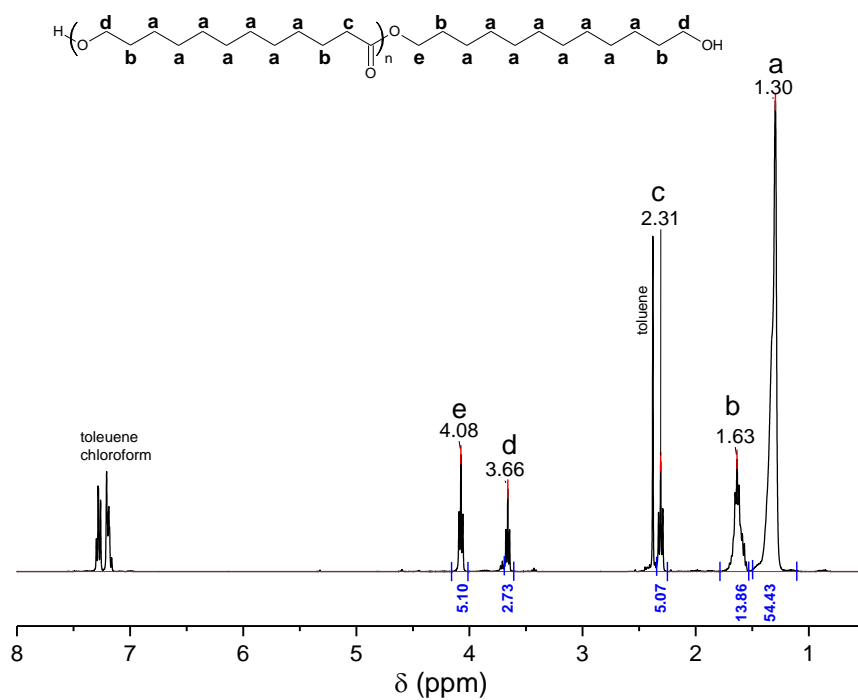


Figure S11. <sup>1</sup>H NMR spectrum of poly(dodecane dodecanedioate) (CDCl<sub>3</sub>, 400 MHz).

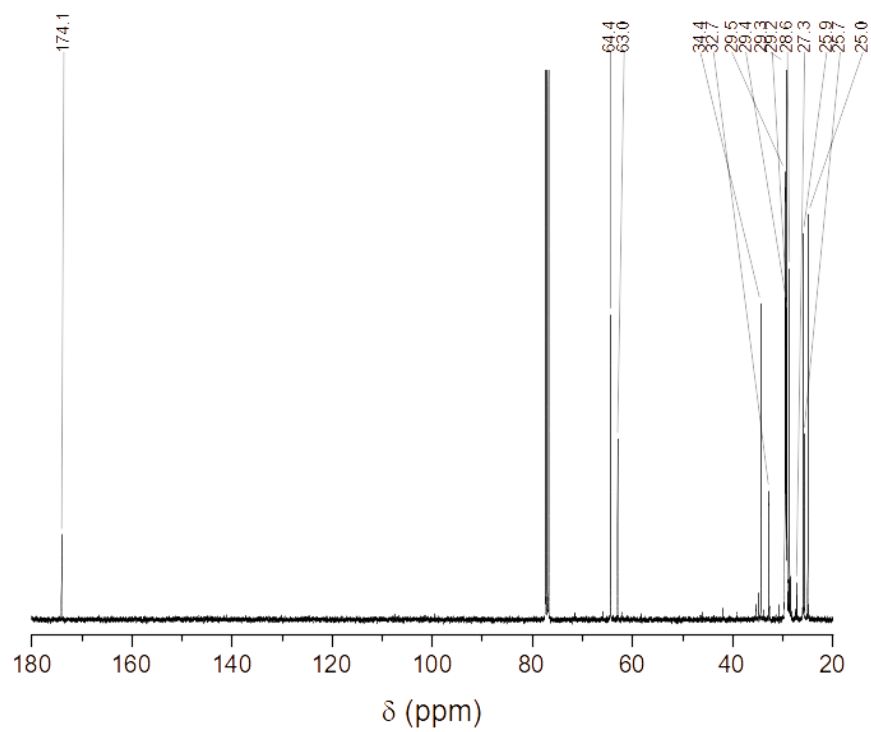


Figure S12.  $^{13}\text{C}$  NMR spectrum of poly(dodecane dodecanedioate) ( $\text{CDCl}_3$ , 100 MHz).

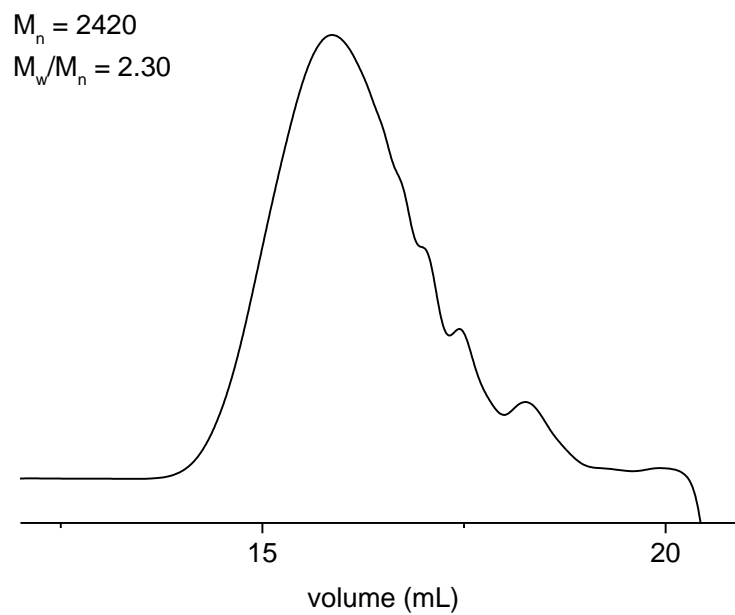


Figure S13. GPC chromatogram of poly(dodecane dodecanedioate).

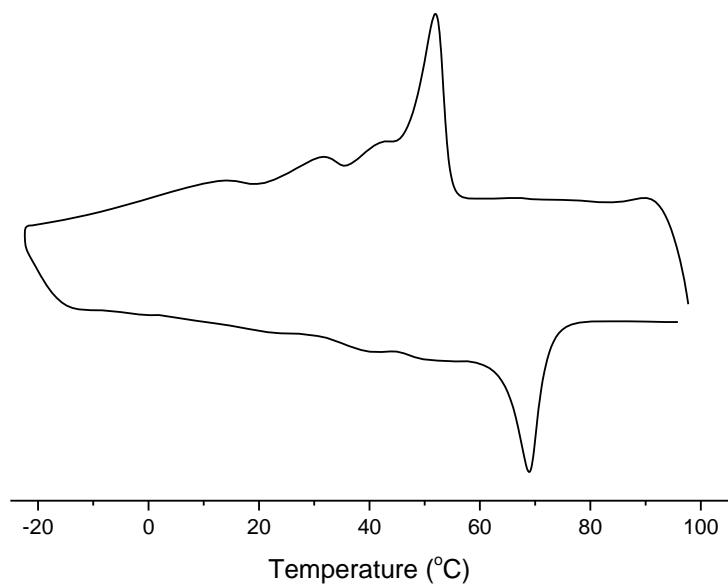


Figure S14. DSC of poly(dodecane dodecanediote).

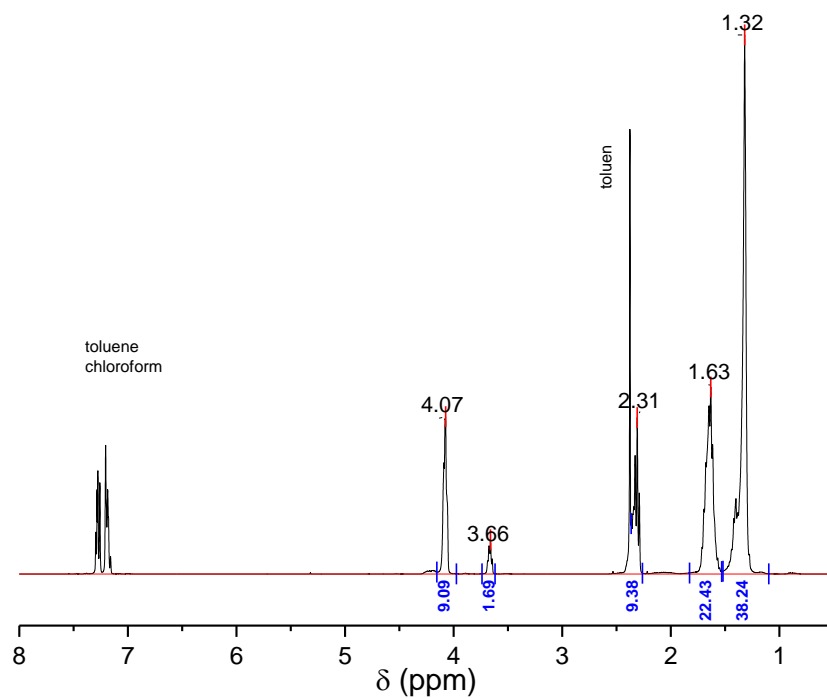


Figure S15. <sup>1</sup>H NMR spectrum of 1,6 hexanediol and 1,10-decanediol copolymer (CDCl<sub>3</sub>, 400 MHz).



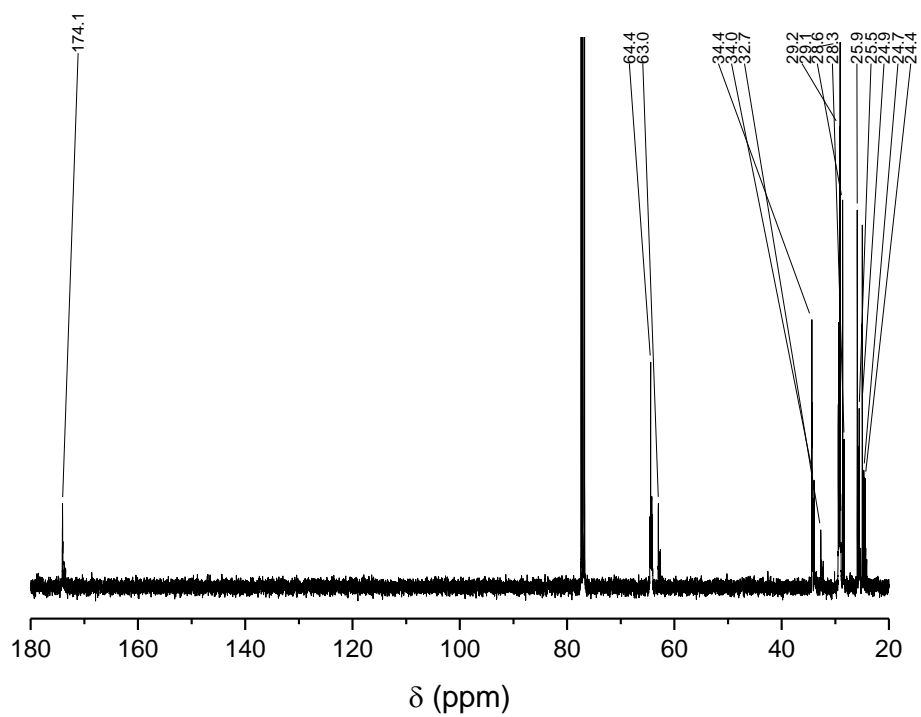


Figure S16.  $^{13}\text{C}$  NMR spectrum of 1,6 hexanediol and 1,10-decanediol copolymer ( $\text{CDCl}_3$ , 100 MHz).

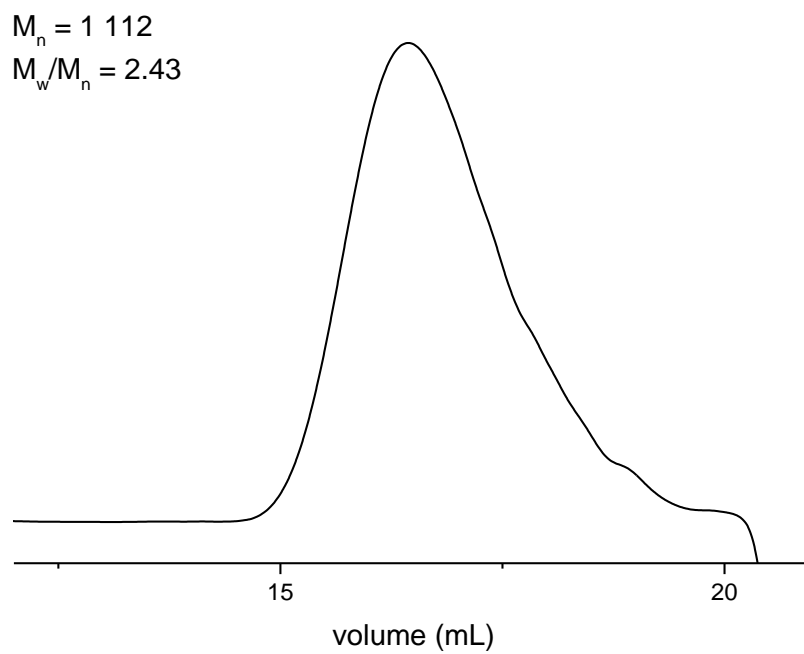


Figure S17. GPC chromatogram of 1,6 hexanediol and 1,10-decanediol copolymer.

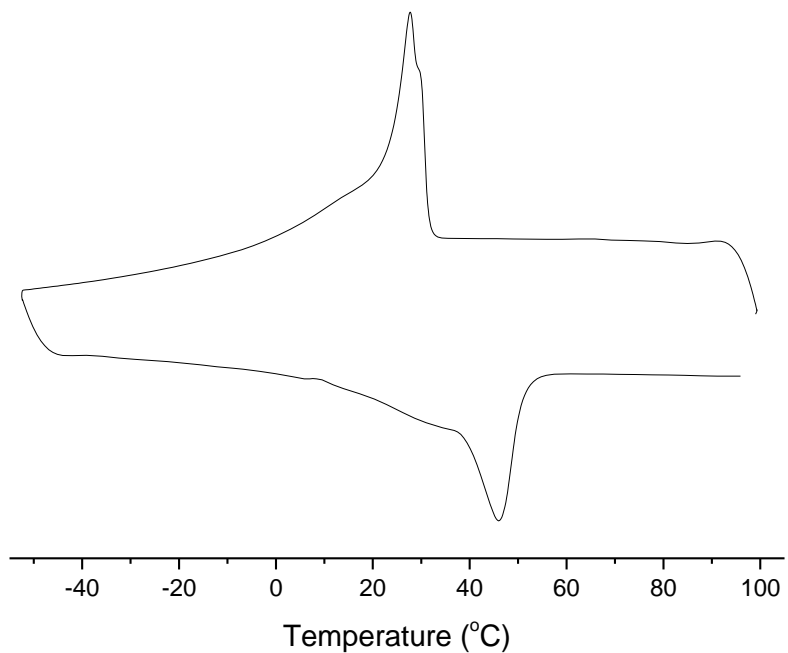


Figure S18. DSC of 1,6 hexanediol and 1,10-decanediol copolymer.

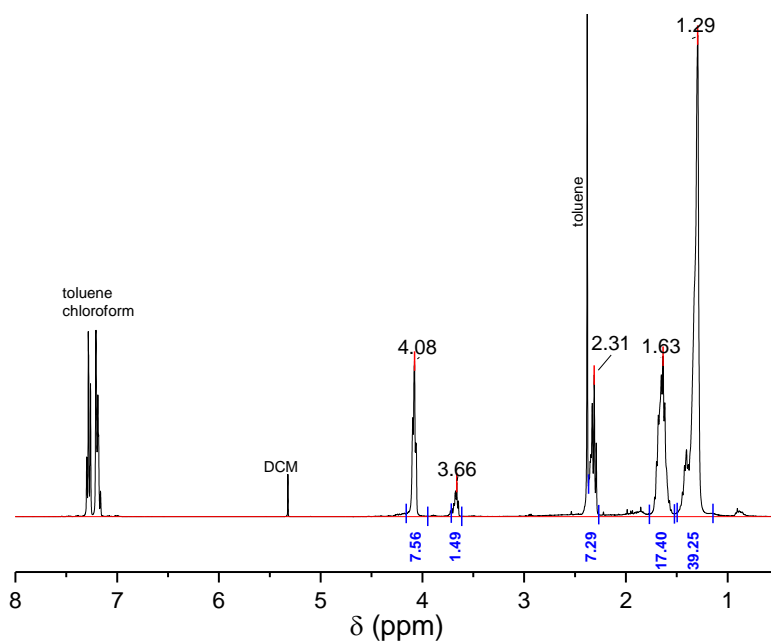


Figure S19.  $^1\text{H}$  NMR spectrum of 1,6-hexanediol and 1,12-dodecanediol copolymer ( $\text{CDCl}_3$ , 400 MHz).

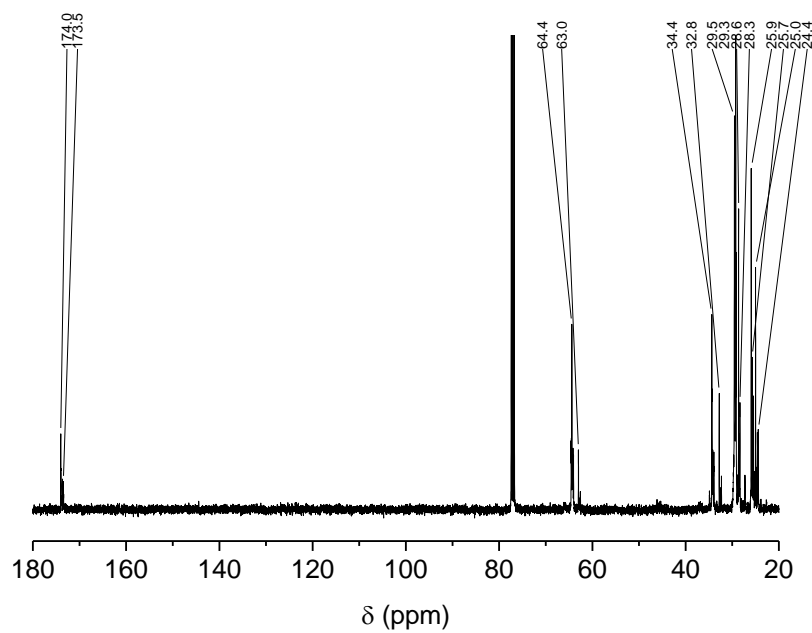


Figure S20.  $^{13}\text{C}$  NMR spectrum of 1,6-hexanediol and 1,12-dodecanediol copolymer ( $\text{CDCl}_3$ , 100 MHz).

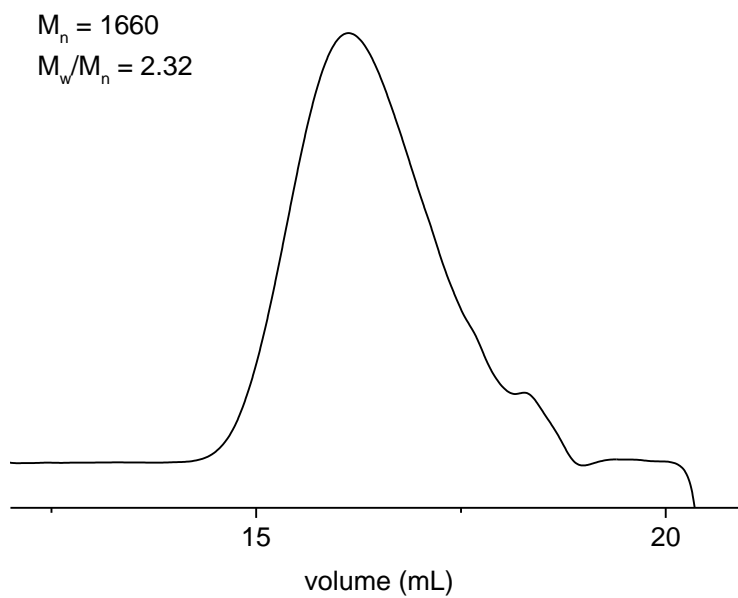


Figure S21. GPC chromatogram of 1,6-hexanediol and 1,12-dodecanediol copolymer.

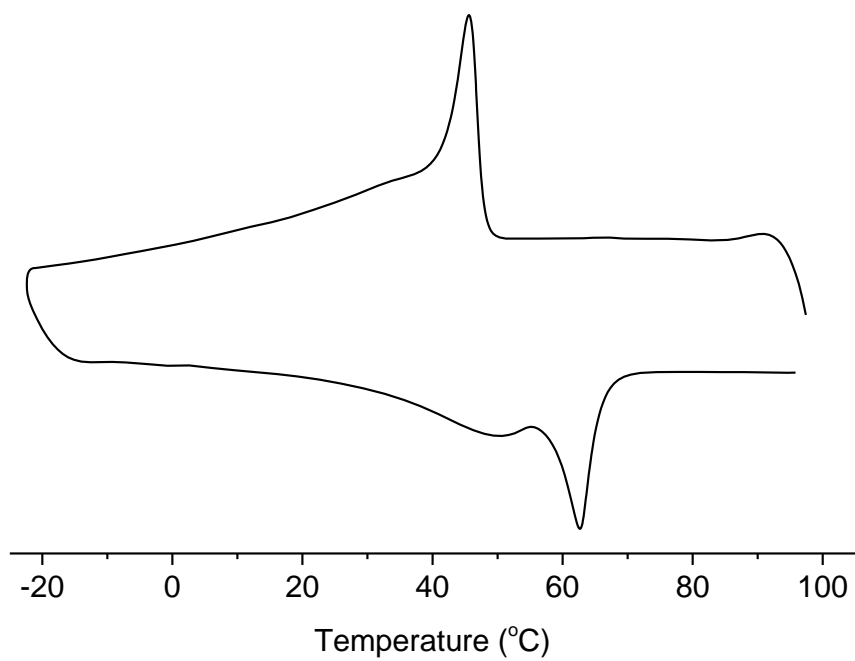


Figure S22. DSC of 1,6-hexanediol and 1,12-dodecanediol copolymer.

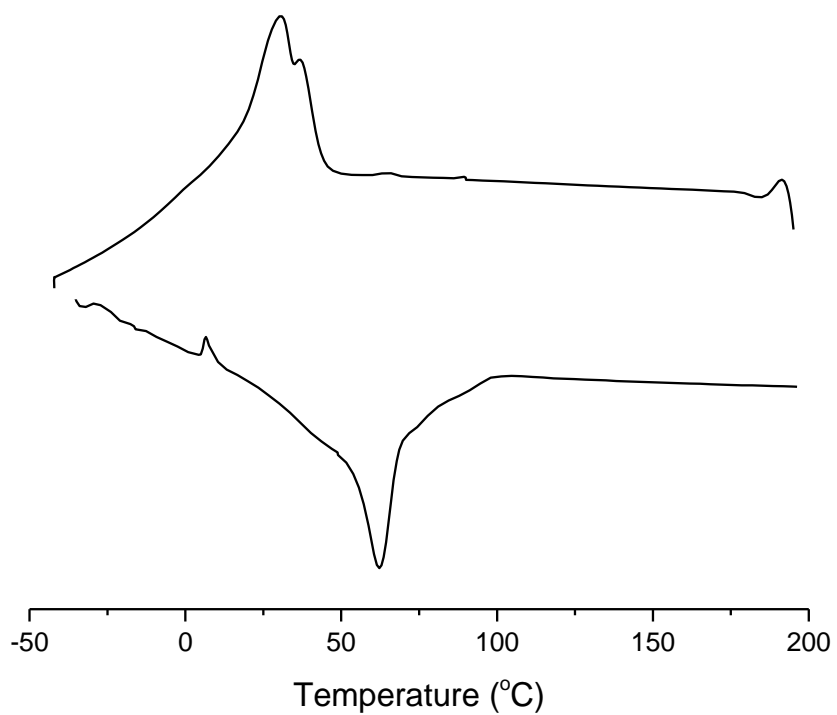


Figure S23. DSC of a polyurethane prepared from poly(decane sebacate) and hexamethylene diisocyanate.

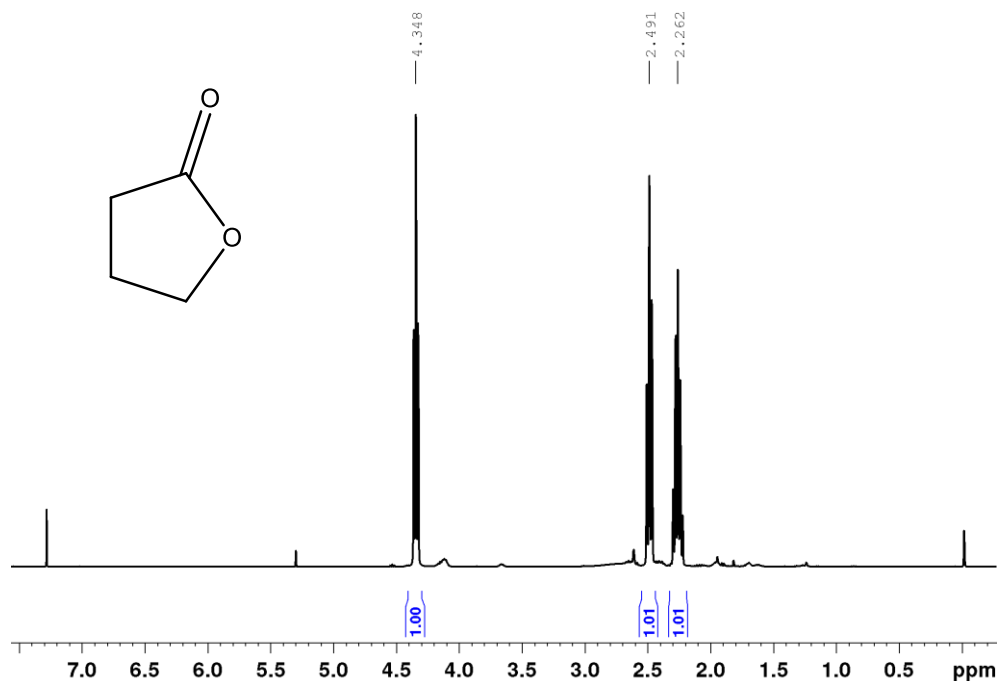


Figure S24.  $^1\text{H}$  NMR spectrum of the product of oxidative self-esterification of 1,4-butanediol ( $\text{CDCl}_3$ , 400 MHz).  $\delta_{\text{H}}$ : 4.35 (2H t,  $\text{CH}_2\text{O}$ ); 2.49 (2H, t,  $\text{CH}_2\text{C}(\text{O})$ ); 2.26 (2H, m,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ). The product has been identified as  $\gamma$ -butyrolactone.

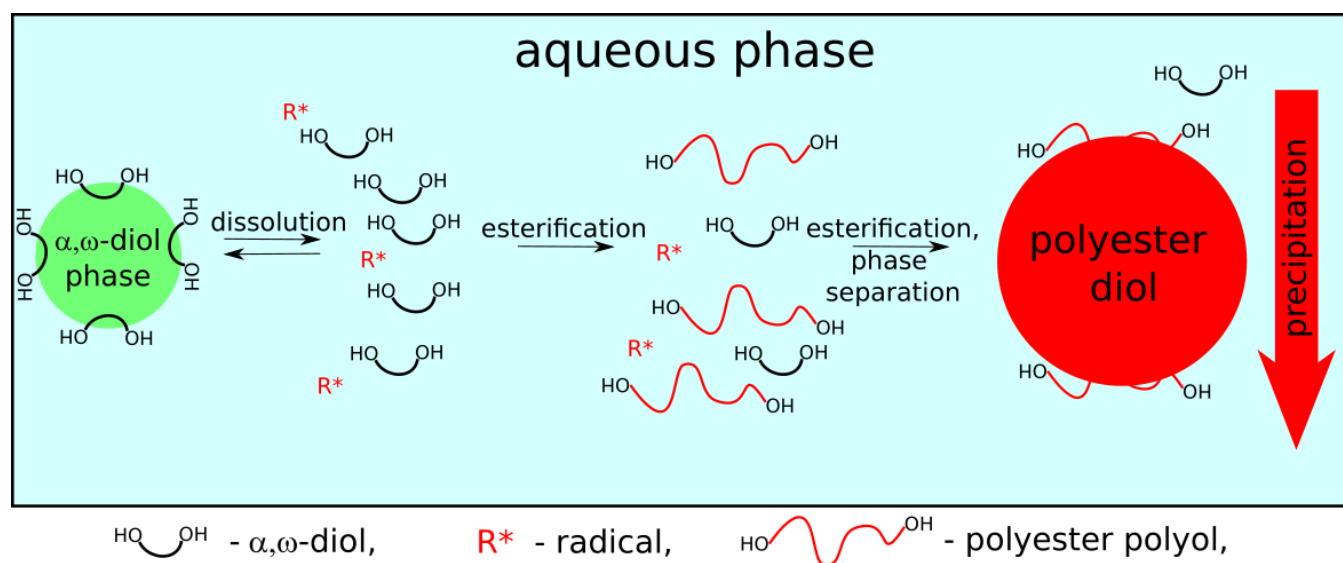


Figure S25. The cartoon shows a proposed sequence of processes that lead from a  $\alpha,\omega$ -aliphatic diol to a polyester polyol via radical oxidative self-esterification carried out in an aqueous solution. A diol, which is fully or partially dissolved in water, reacts with generated in the solution radicals and forms oligomers. With the increase of the molecular weight, molecules reach a critical size at which they collapse and phase out from the solution, which prevents them from growing further.