Supporting Information for:

Ring Opening Polymerization of Macrolactones: High Conversions and Activities Using an Yttrium Catalyst

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Experimental Section

Reagents and Methods:

All solvents and reagents were purchased from commercial sources (Sigma-Aldrich, VWR, Strem) unless stated otherwise. ω-Pentadecalactone (PDL) was freshly distilled from CaH_2 under argon prior to use. Nonadecalactone (NDL) and tricosalactone (TCL) were synthesised using literature protocol.[1] The yttrium phosphasalen catalyst was prepared using literature protocol.[2] Toluene was dried by reflux over sodium/benzophenone and stored under nitrogen over 3 Å molecular sieves. Toluene was degassed three times by free-pump-thaw cycles before use. Deuterated solvents: chloroform-*d* and 1,1,2,2-tetrachloroethane-d_2 were purchased for Cambridge Isotope Laboratories, Inc. and used as received.

Silanisation procedure:

For Glass vials heated in an oven set to 403 K were rinsed several times in a solution of dichlorodimethylsilane in dichloromethane (0.8 M, 10 mL) before being left to dry in an oven prior to use.

Polymerisation procedure:

Aliquot polymerisations: For a typical run, in a glovebox the catalyst was either directly weighed out (6.3 mg, 6.24×10^{-3} mmol) or made up from a stock solution (10 mg in 2 mL) depending on scale. The monomer was then weighed into a separate vial (150 mg) and dissolved in toluene; when using a stock solution, the monomer was dissolved in ~ 0.7 mL of toluene. The monomer and catalyst were then combined in a small silanised vial and stirred vigorously. At regular intervals, a small amount of the polymerisation mixture was removed from the vial (approx. 0.05-0.1 mL) and quickly added to a vial of cold hexane. The vial was then immediately removed from the glovebox, prior to adding a few drops of chloroform and exposing to air. Each vial was then fully dissolved in either $CDCl_3$ or 1,1,2,2-tetrachloroethane-d_2 as appropriate and submitted for NMR spectroscopy in order to obtain crude polymer conversions.

Sealed polymerisations: For a typical run, in a glovebox the catalyst was made up from a stock solution (10 mg in 1 mL). The monomer was then weighed out (174.4 mg) and made up into a stock solution (1.1 mL) suitable for two polymerisations. A portion of the catalyst stock solution (0.25 mL) was then added to a silanised vial before subsequent addition of a portion of the monomer solution (0.55 mL). After this, the vial was capped and removed from the glovebox and quickly suspended into a 373 K preheated oil bath stirring vigorously. After the appropriate allotted time, the polymerisation was quenched by removal from the oil bath and immediate suspension into a 0 °C ice bath to precipitate the polymer. To ensure deactivation of the catalyst, the mixture was exposed to air and a few drops of chloroform added.

NMR: ^1H NMR spectra of PDL polymers were recorded using an Av 400 MHz spectrometer at 25 °C using chloroform-*d* as the solvent. ^1H NMR spectra of NDL and TCL polymers were recorded using an Av 500 MHz spectrometer at 105 °C using 1,1,2,2-tetrachloroethane-d_2 as the solvent.

SEC: Analysis was performed with a Polymer-Laboratories GPC220 instrument equipped with PLgel Olexis columns using the refractive index detector. Molecular weights were determined by calibration with PE standards at 160 °C in 1,2,4-trichlorobenzene (Flow rate: 1.0 mL min^{-1}).

DSC: DSC analysis was performed on a Netzsch DSC 204 F1 at a heating rate of 10 °C per minute in a temperature range from 50 °C to 160 °C

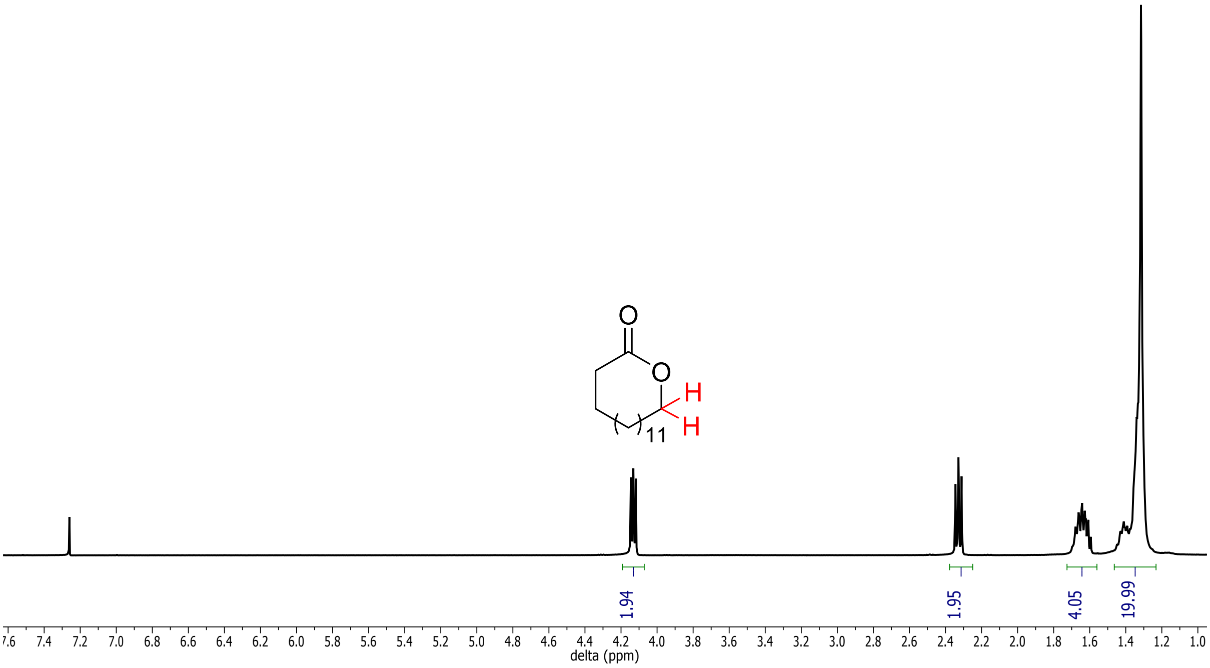


Figure S1. ^{1}H NMR spectrum of PDL ($CDCl_3$, 298 K).

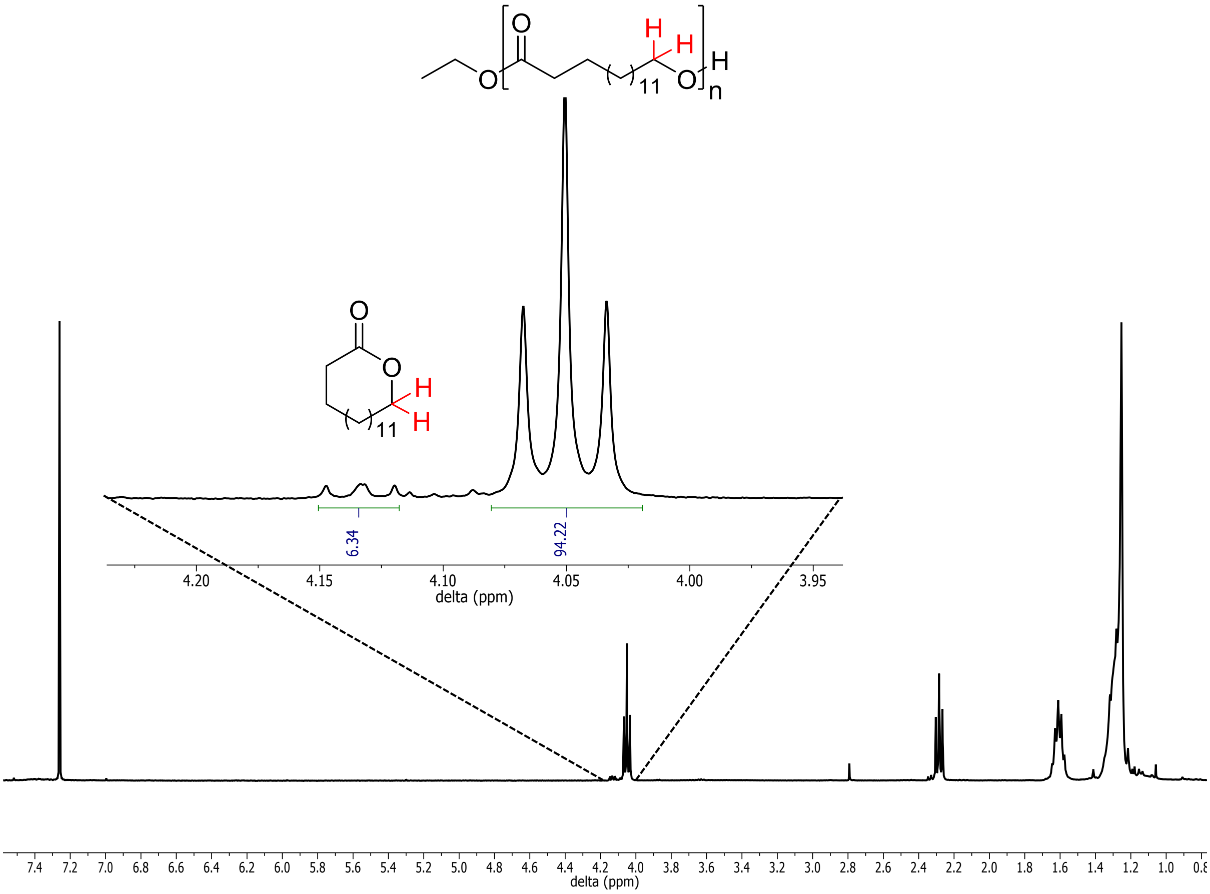


Figure S2. ^{1}H NMR of a crude PPDL polymer/monomer mixture; **Table 1,** entry 1 ($CDCl_3$, 298 K).

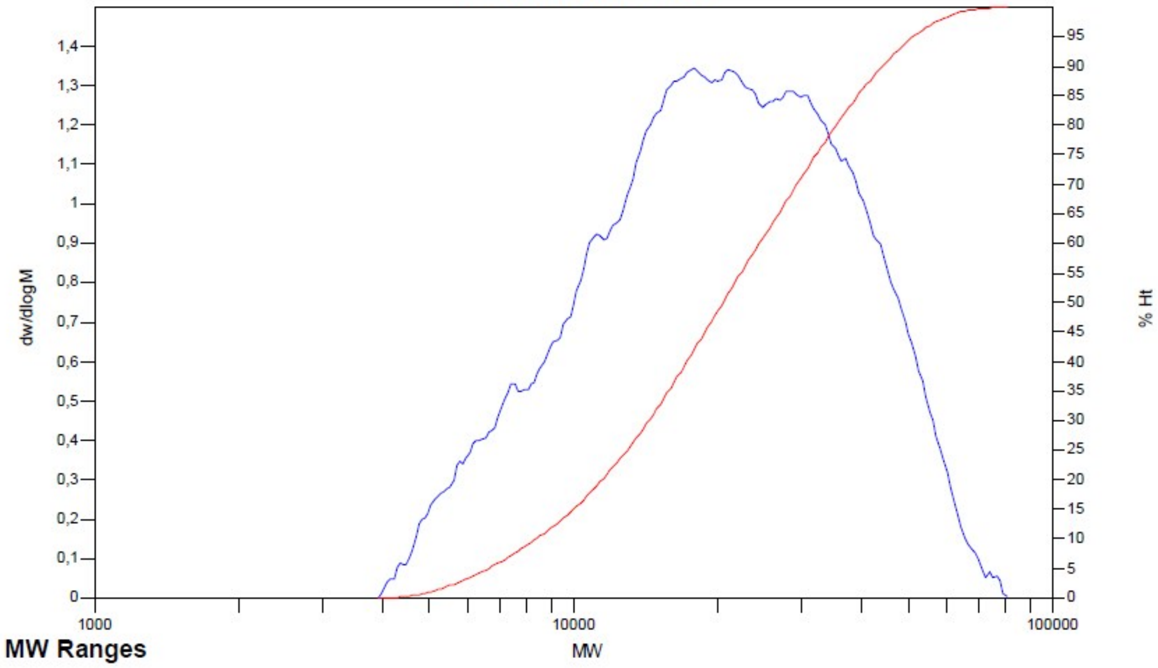


Figure S3. SEC trace of a PPDL polymer/monomer mixture; **Table 1,** entry 1.

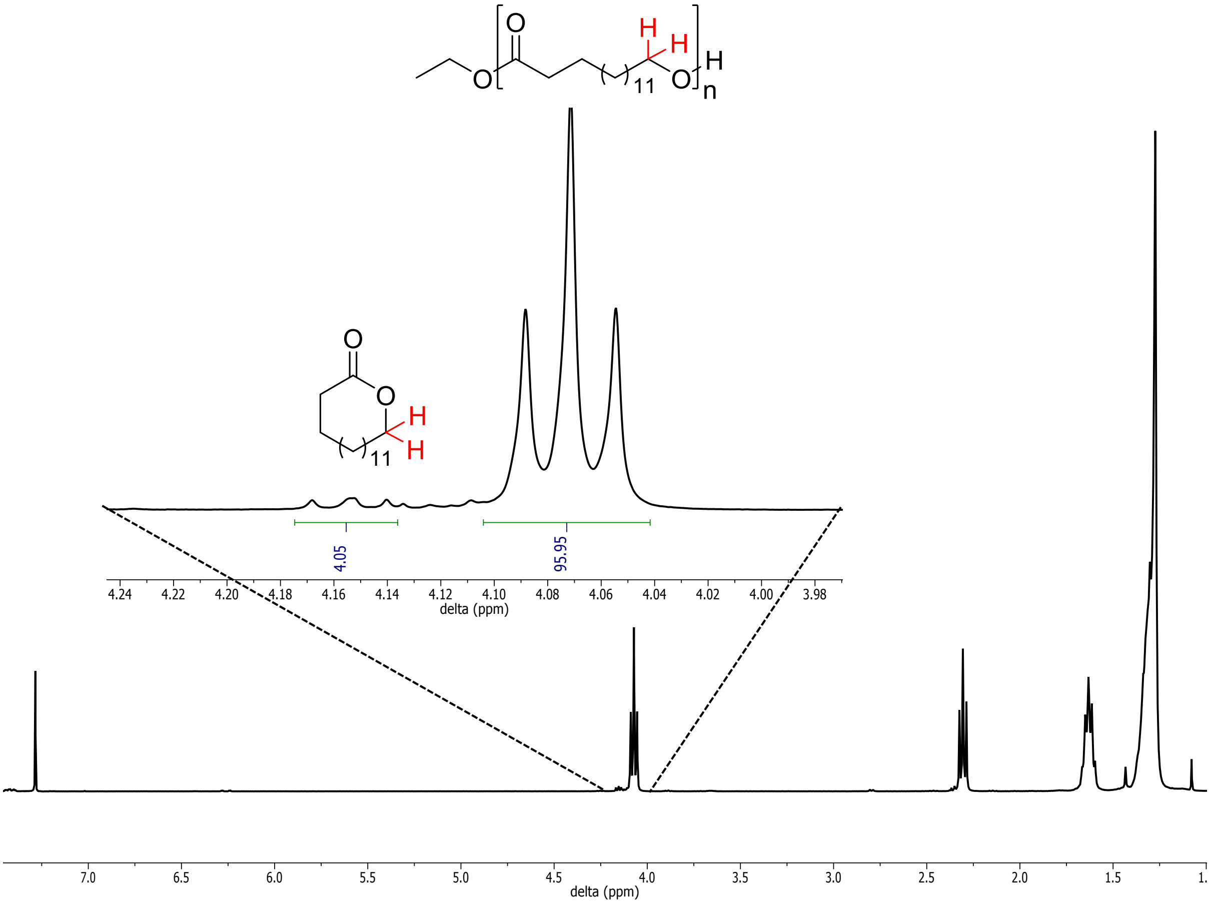


Figure S4. ^{1}H NMR spectrum of a PPDL polymer/monomer mixture; **Table 1,** entry 2 ($CDCl_3$, 298 K).

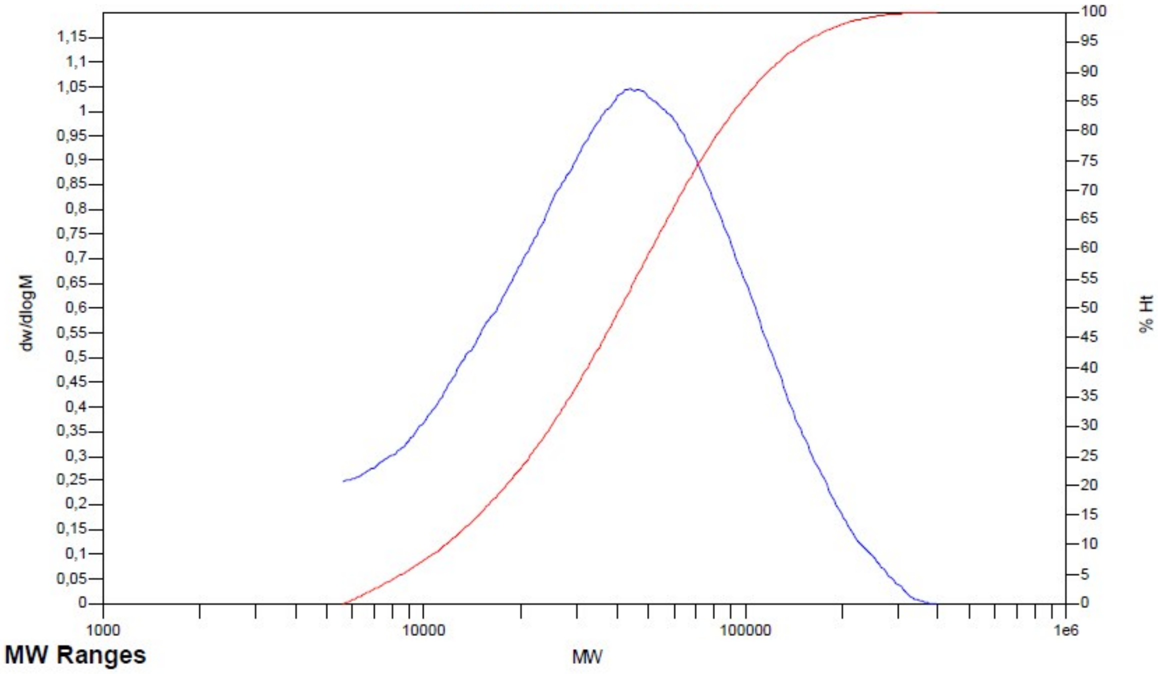


Figure S5. SEC trace of a PPDL polymer/monomer mixture; **Table 1,** entry 2.

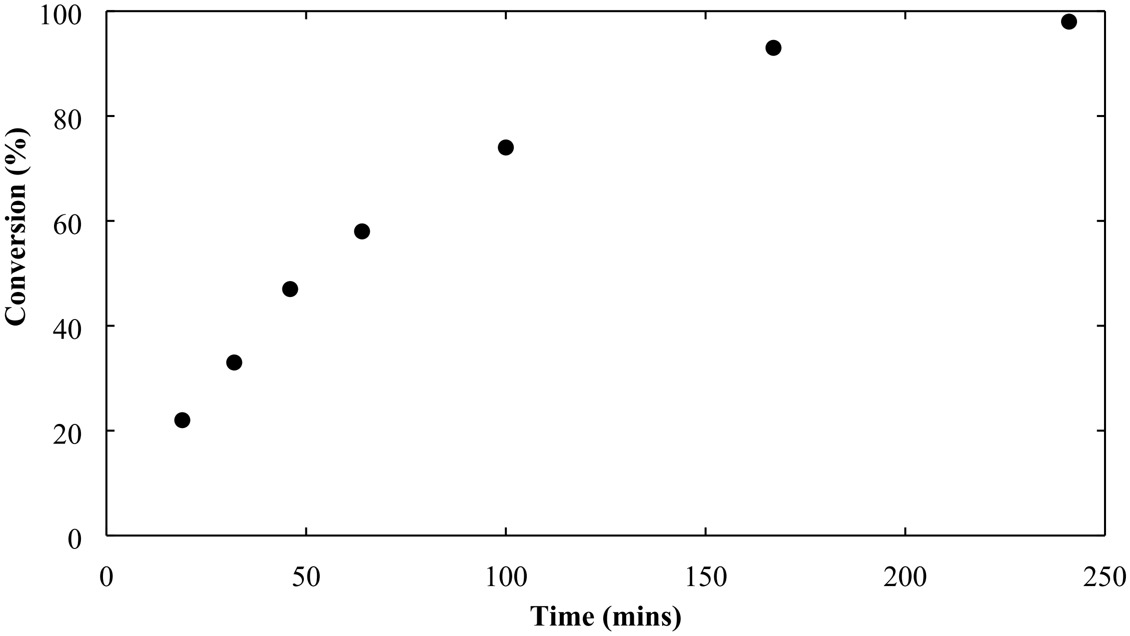


Figure S6. Plot of the conversion vs time data for the polymerisation of PDL. Conditions: $[PDL]_0$ = 1.0 M, toluene, 298 K.

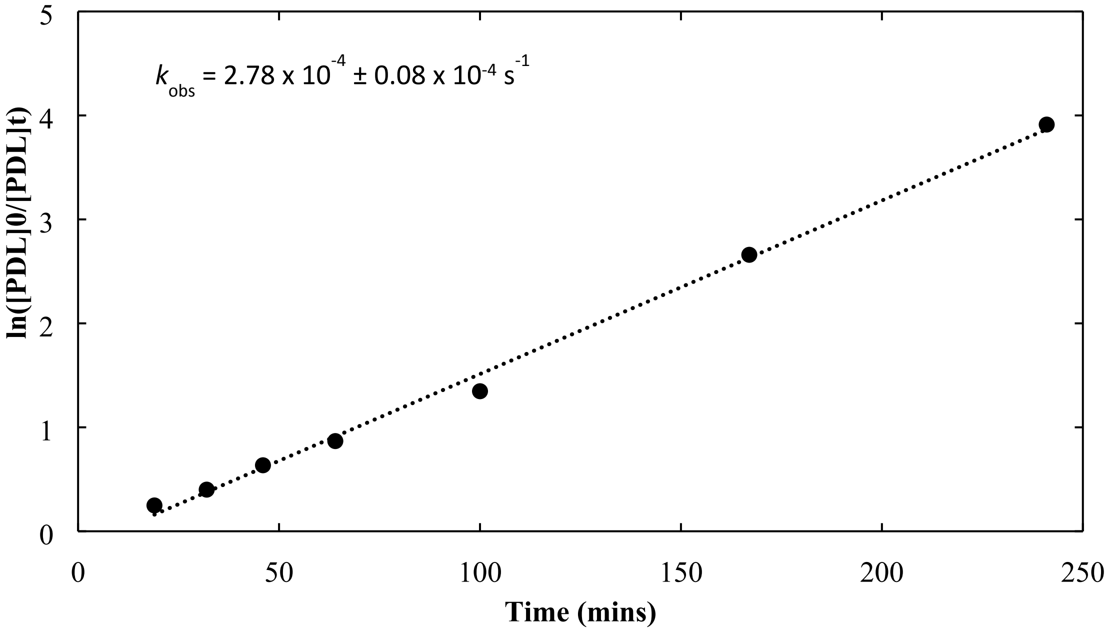


Figure S7. Semi-logarithmic pseudo first-order rate plot for the polymerisation of PDL. Conditions: [PDL]/[**1**] = 100, $[PDL]_0$ = 1.0 M, toluene, 298 K.

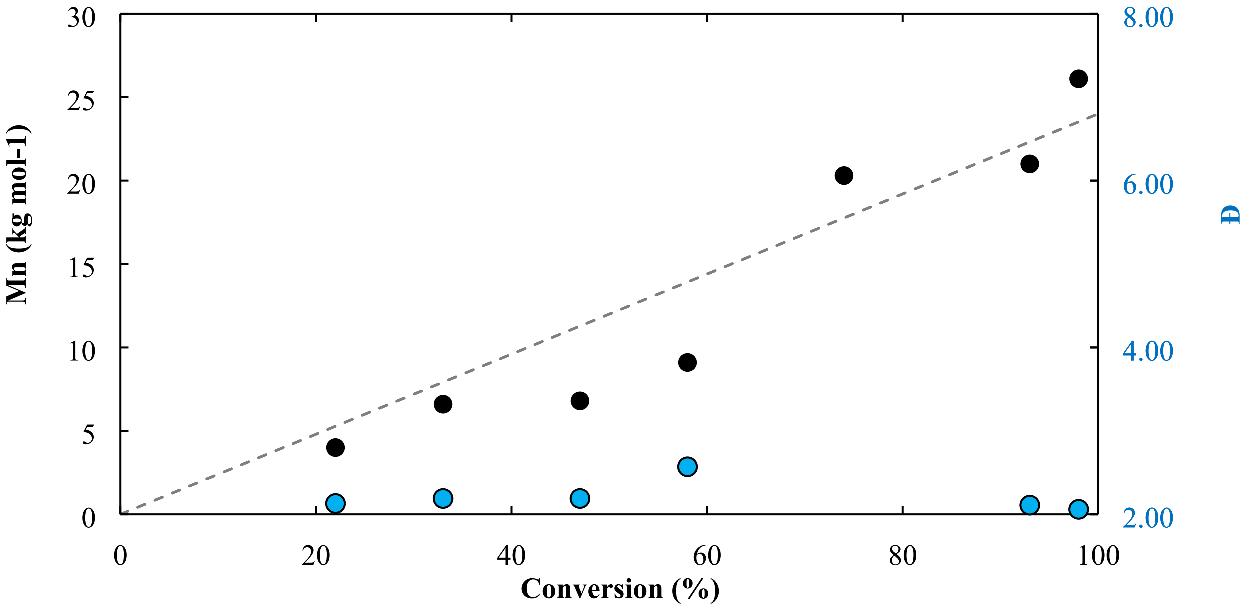


Figure S8. Plot of the molecular weight (black circles) and Đ (blue circles) determined by SEC vs conversion, concurrent with the theoretical molecular weight (black dotted line) for the polymerisation of PDL. Conditions: [PDL]/[**1**] = 100, $[PDL]_0$ = 1.0 M, toluene, 298 K.

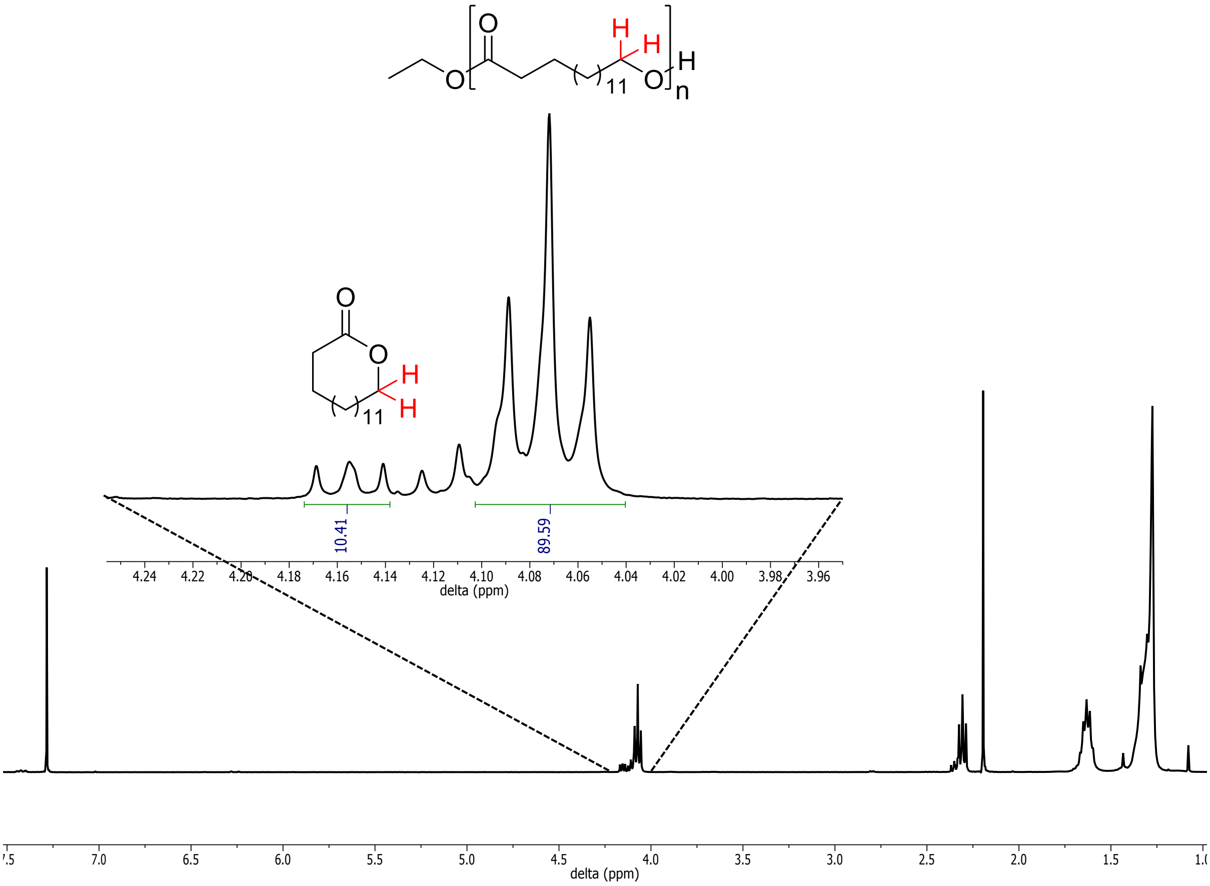


Figure S9. ^{1}H NMR spectrum of a PPDL polymer/monomer mixture; **Table 1,** entry 3 ($CDCl_3$, 298 K).

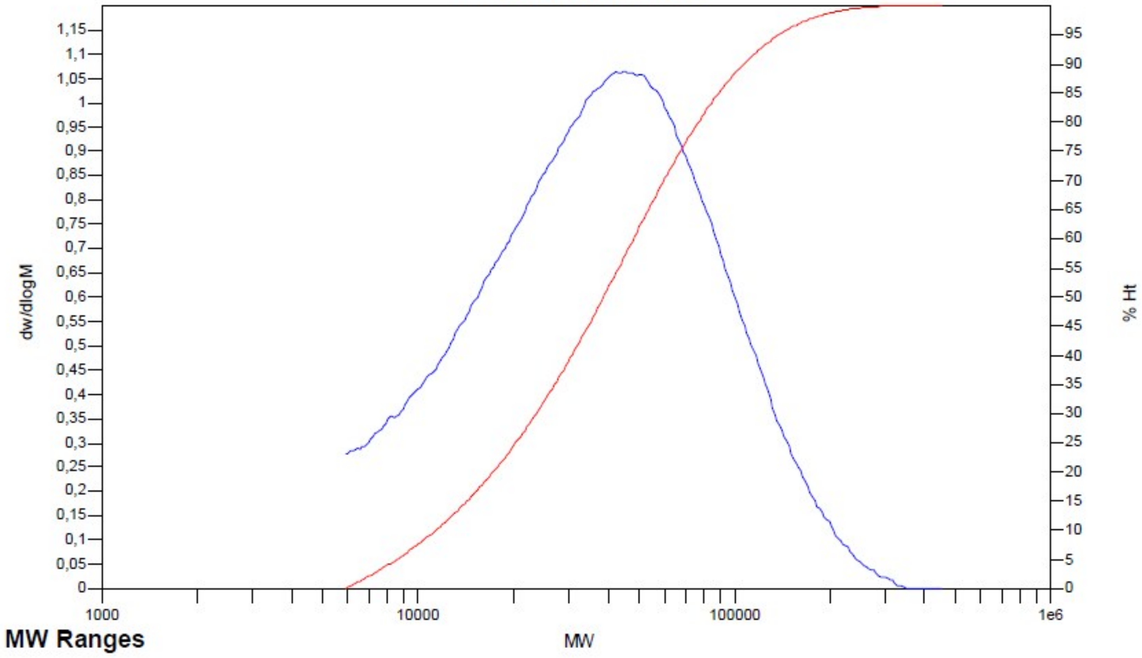


Figure S10. SEC trace of a PPDL polymer/monomer mixture; **Table 1,** entry 3.

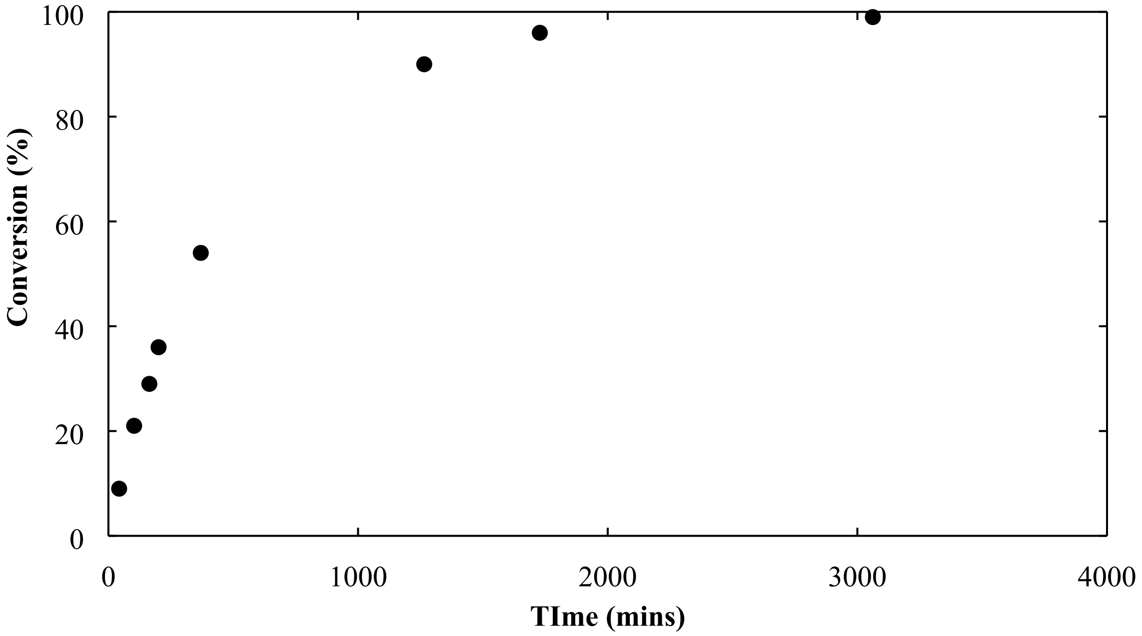


Figure S11. Plot of the conversion vs time data for the polymerisation of PDL. Conditions: $[PDL]_0$ = 0.25 M, toluene, 298 K.

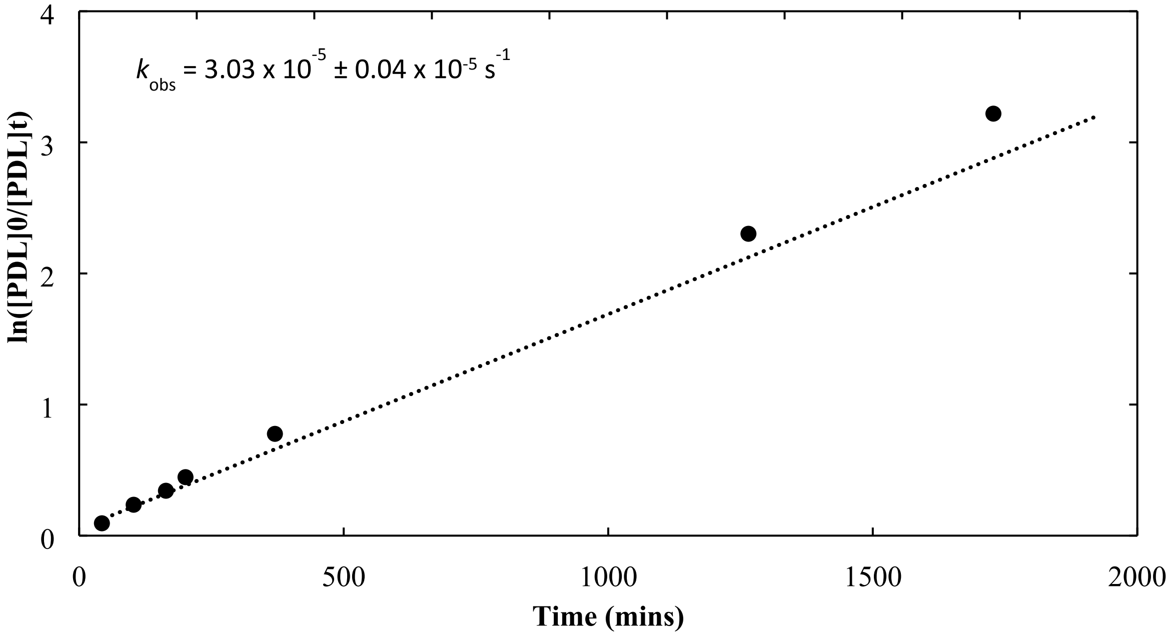


Figure S12. Semi-logarithmic pseudo first-order rate plot for the polymerisation of PDL. Conditions: [PDL]/[**1**] = 100, $[PDL]_0$ = 0.25 M, toluene, 298 K.

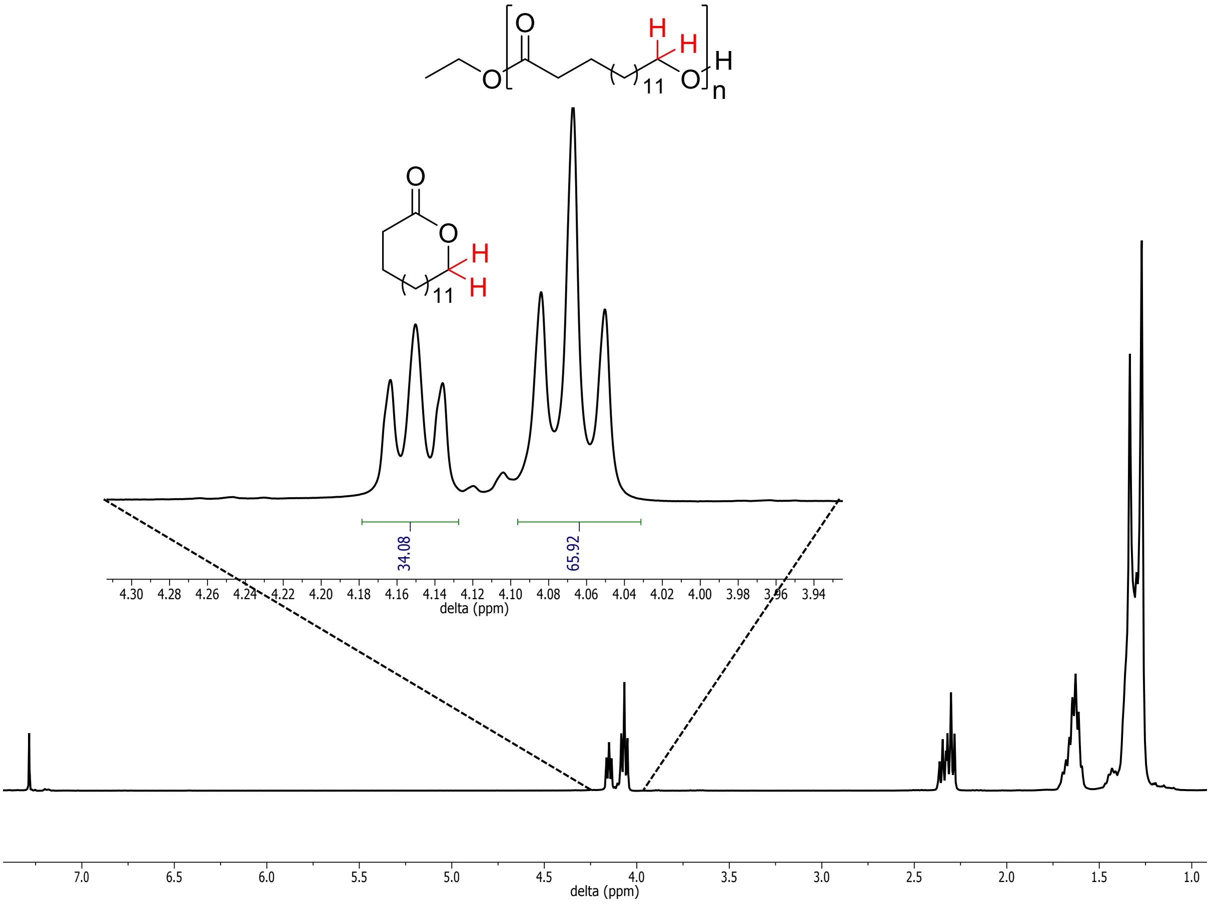


Figure S13. ^{1}H NMR spectrum of a PPDL polymer/monomer mixture; **Table 1,** entry 4 ($CDCl_3$, 298 K).

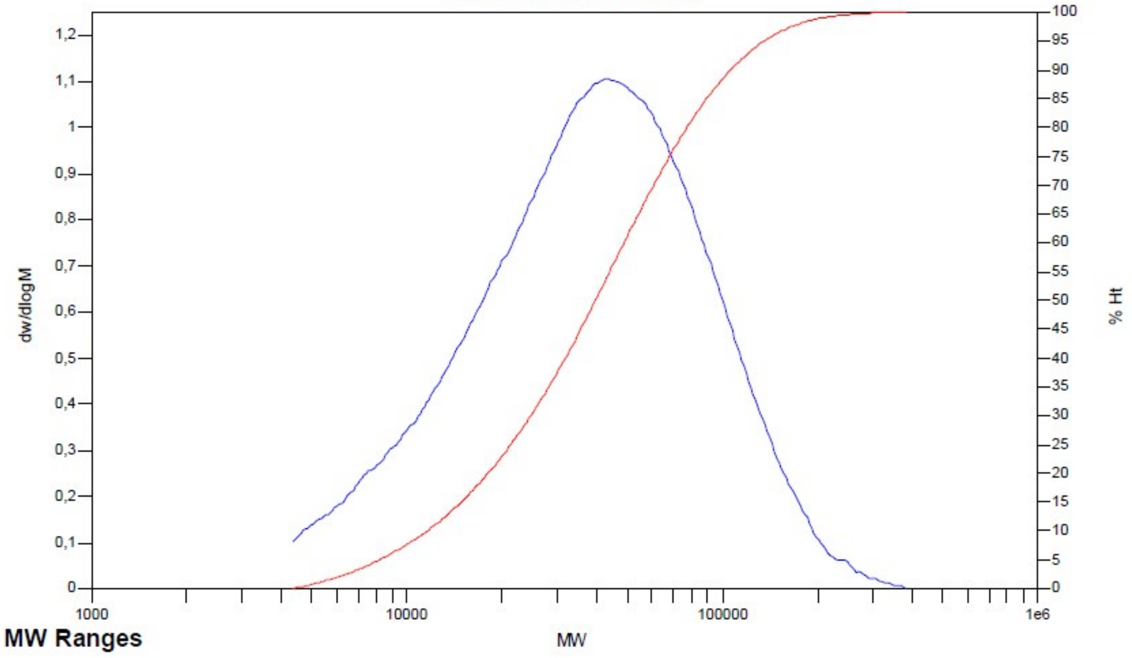


Figure S14. SEC trace of a PPDL polymer/monomer mixture; **Table 1,** entry 4.

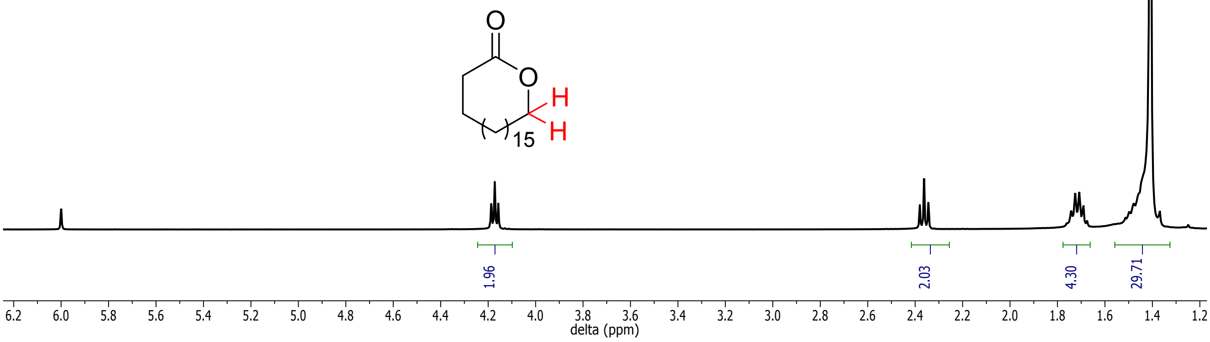


Figure S15. ^{1}H NMR spectrum of NDL (TCE-d_2, 403 K).

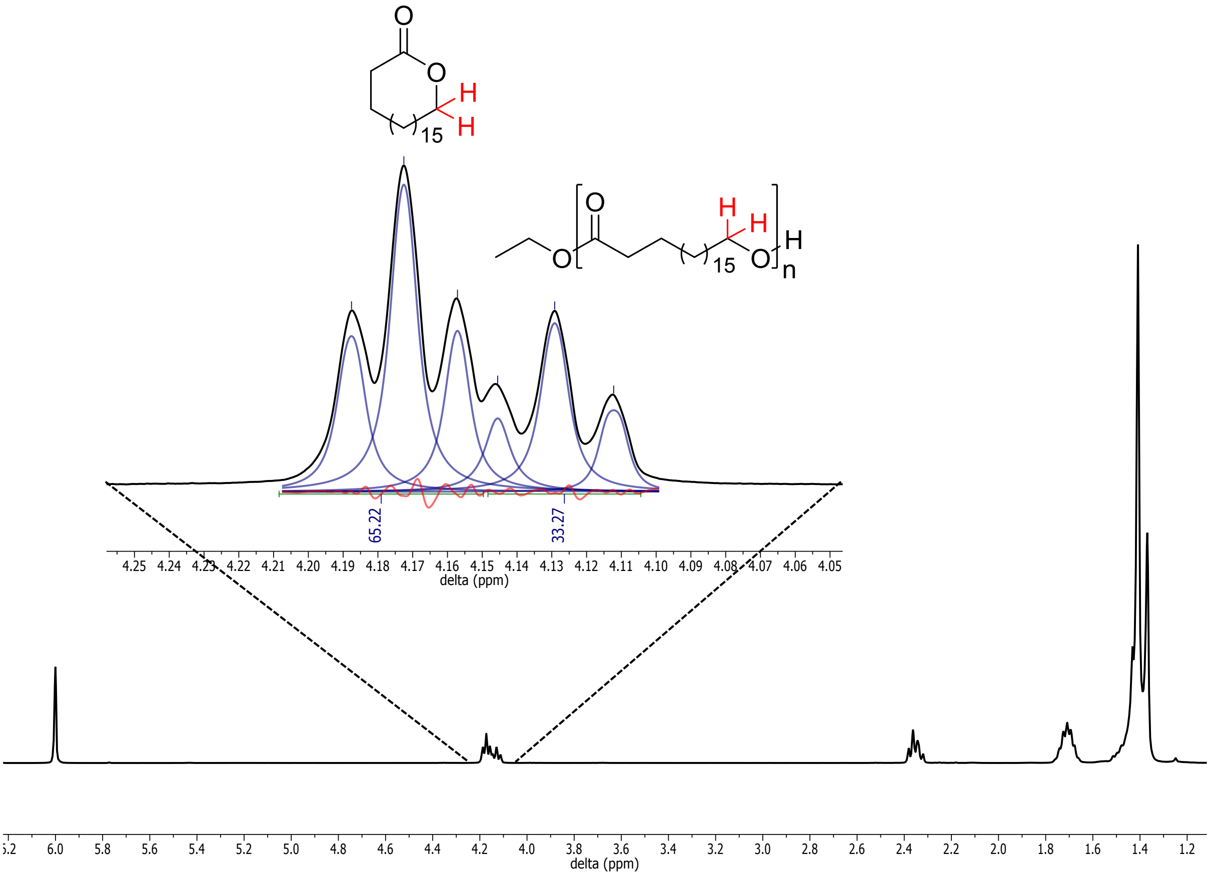


Figure S16. ^{1}H NMR spectrum of a PNDL polymer/monomer mixture; **Table 1,** entry 5 (TCE-d_2, 403 K). Peak deconvolution was used to determine conversion.

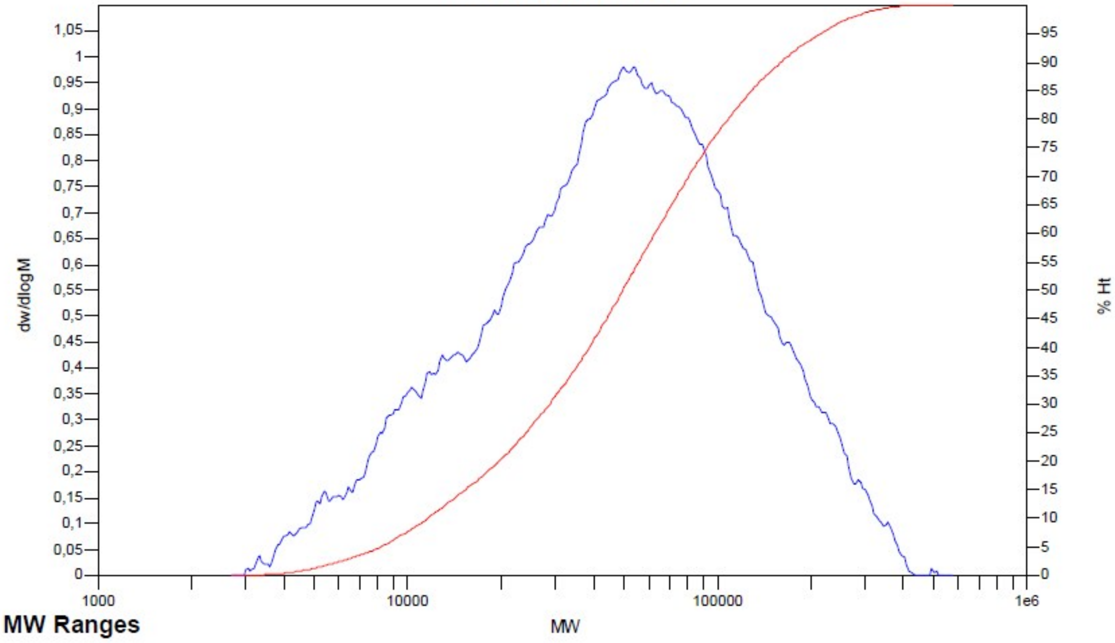


Figure S17. SEC trace of a PNDL polymer/monomer mixture; **Table 1,** entry 5.

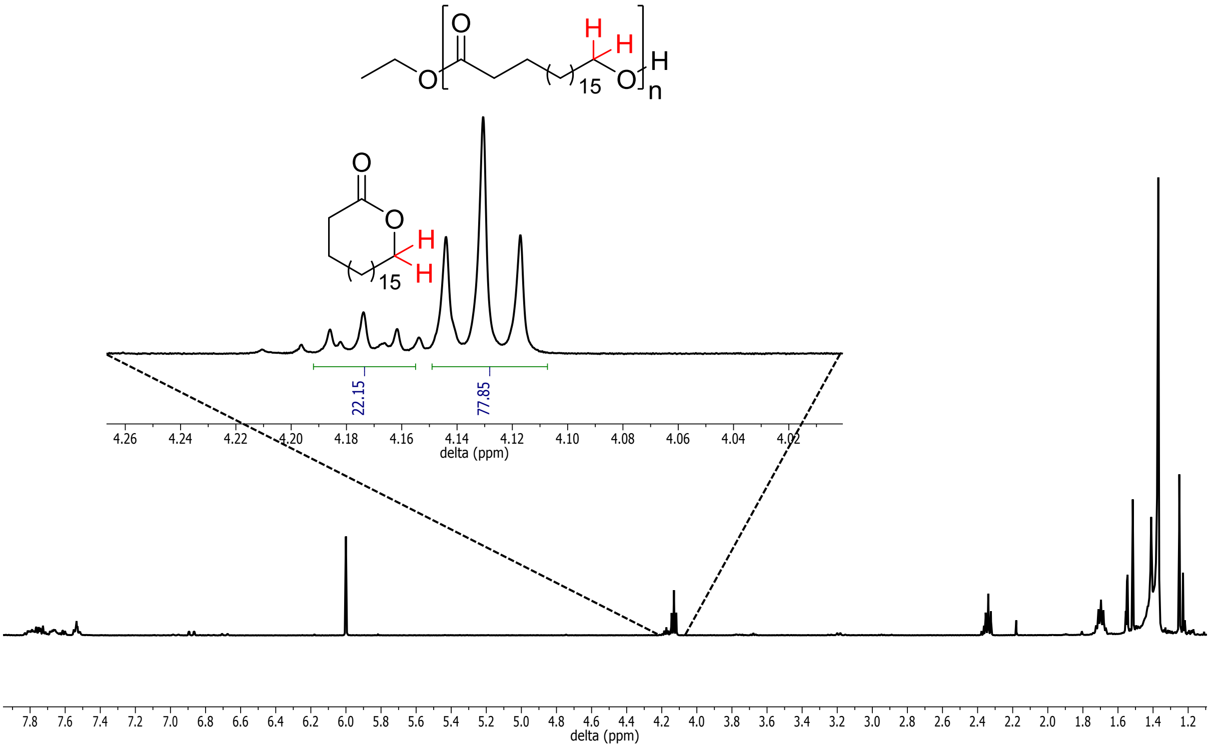


Figure S18. ^{1}H NMR spectrum of a PNDL polymer/monomer mixture; **Table 1,** entry 6 (TCE-d_2, 403 K).

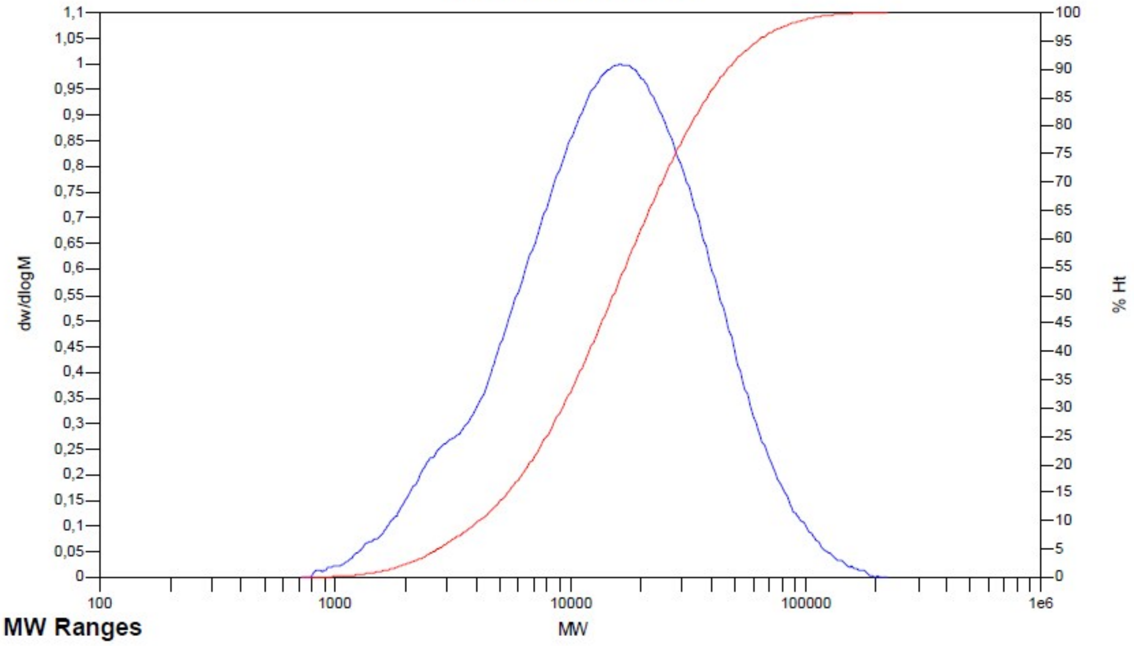


Figure S19. SEC trace of a PNDL polymer/monomer mixture; **Table 1,** entry 6.

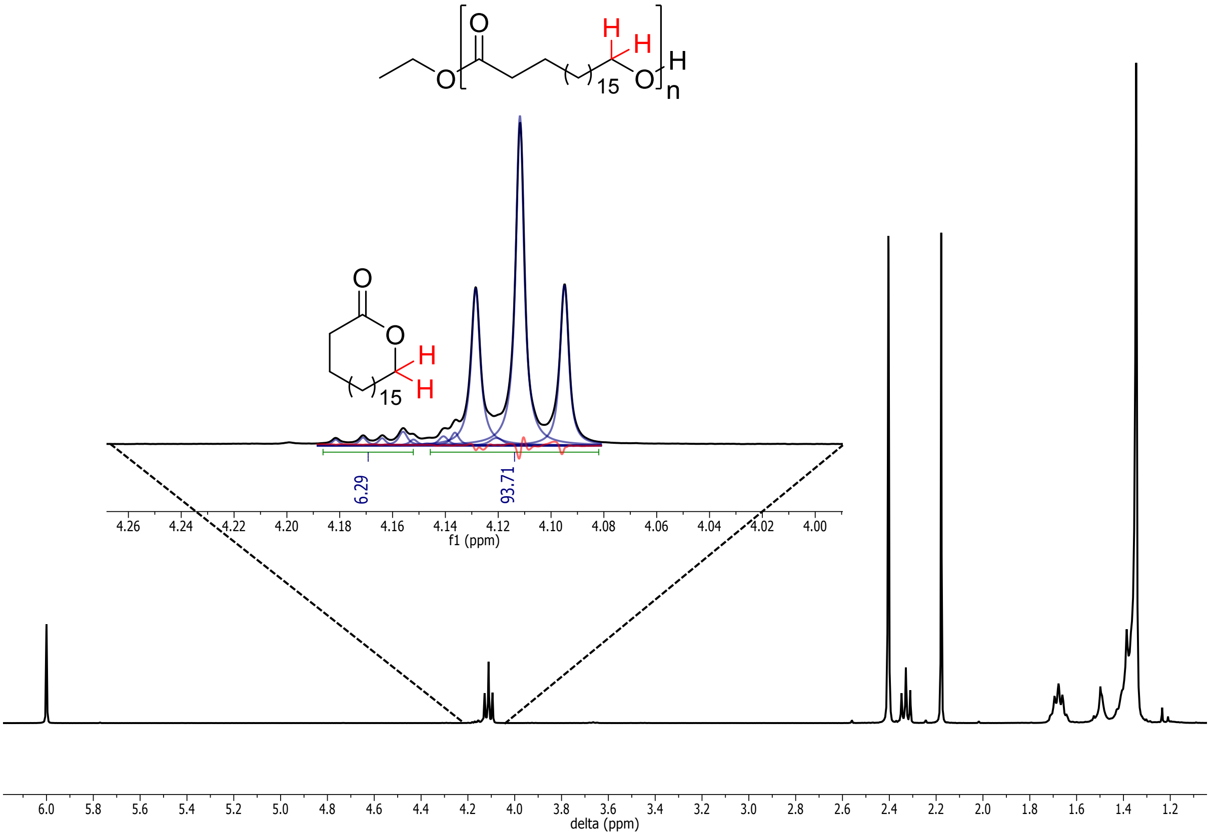


Figure S20. ^{1}H NMR spectrum of a PNDL polymer/monomer mixture; [NDL]$_0$ = 0.75 M, [NDL]/[**1**] = 100, conv. = 94 %, time = 1055 mins (TCE-d$_2$, 403 K). Peak deconvolution was used to determine conversion.

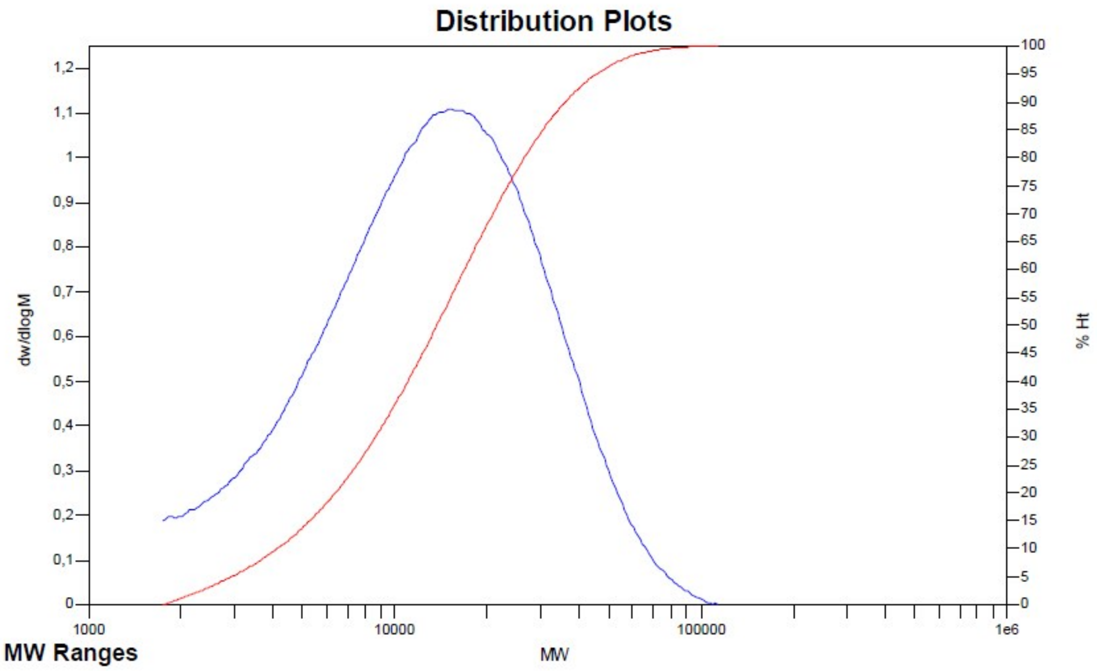


Figure S21. SEC trace of a PNDL polymer/monomer mixture; $[NDL]_0$ = 0.75 M, [NDL]/[**1**] = 100, conv. = 94 %, time = 1055 mins (TCE-d_2, 403 K).

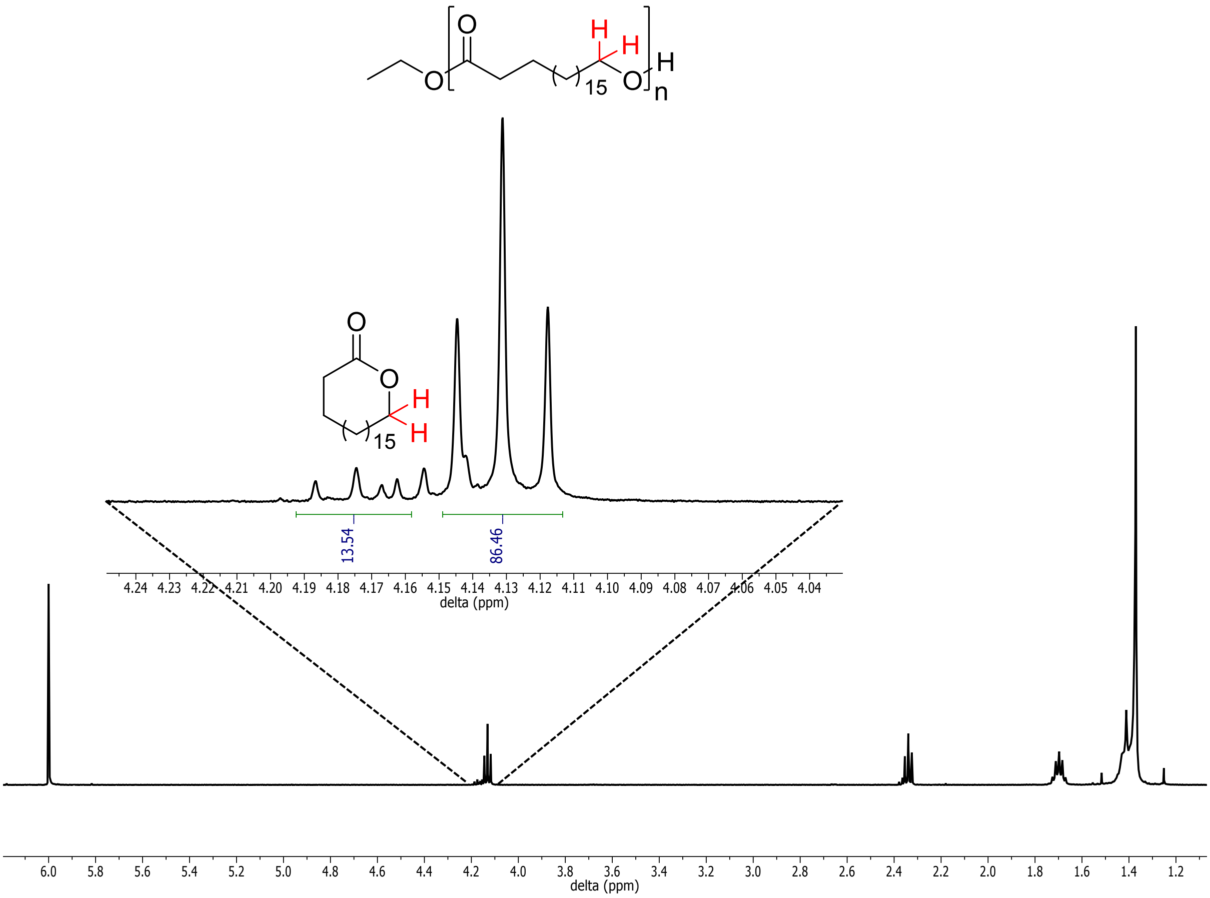


Figure S22. ^{1}H NMR spectrum of a PNDL polymer/monomer mixture; **Table 1,** entry 7 (TCE-d_2, 403 K).

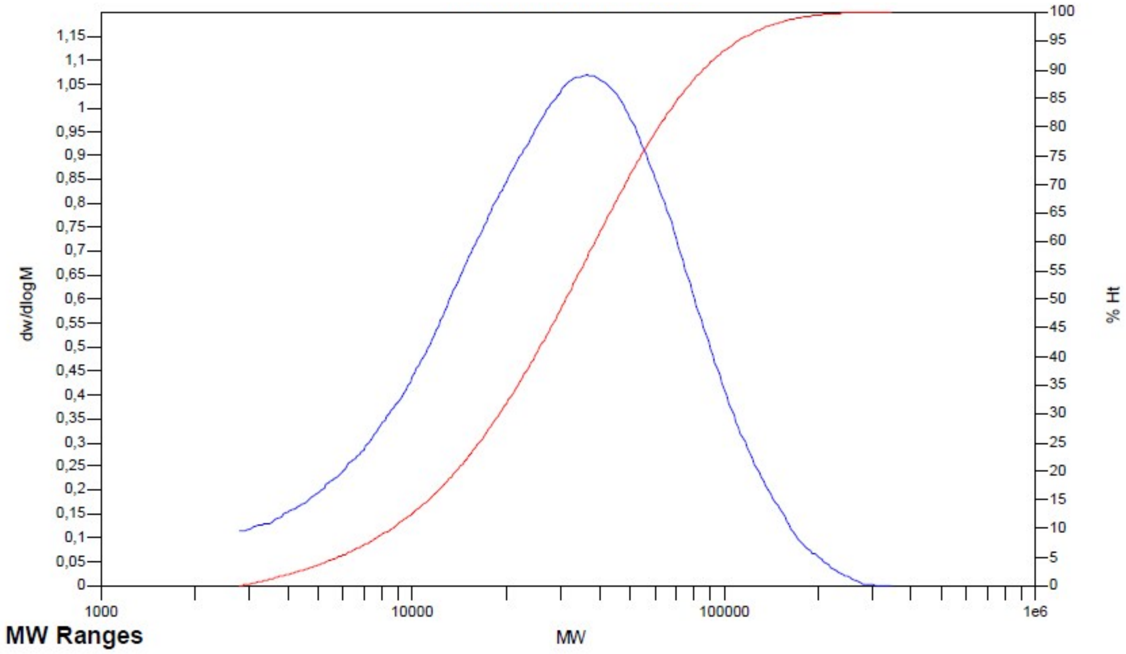


Figure S23. SEC trace of a PNDL polymer/monomer mixture; **Table 1,** entry 7.

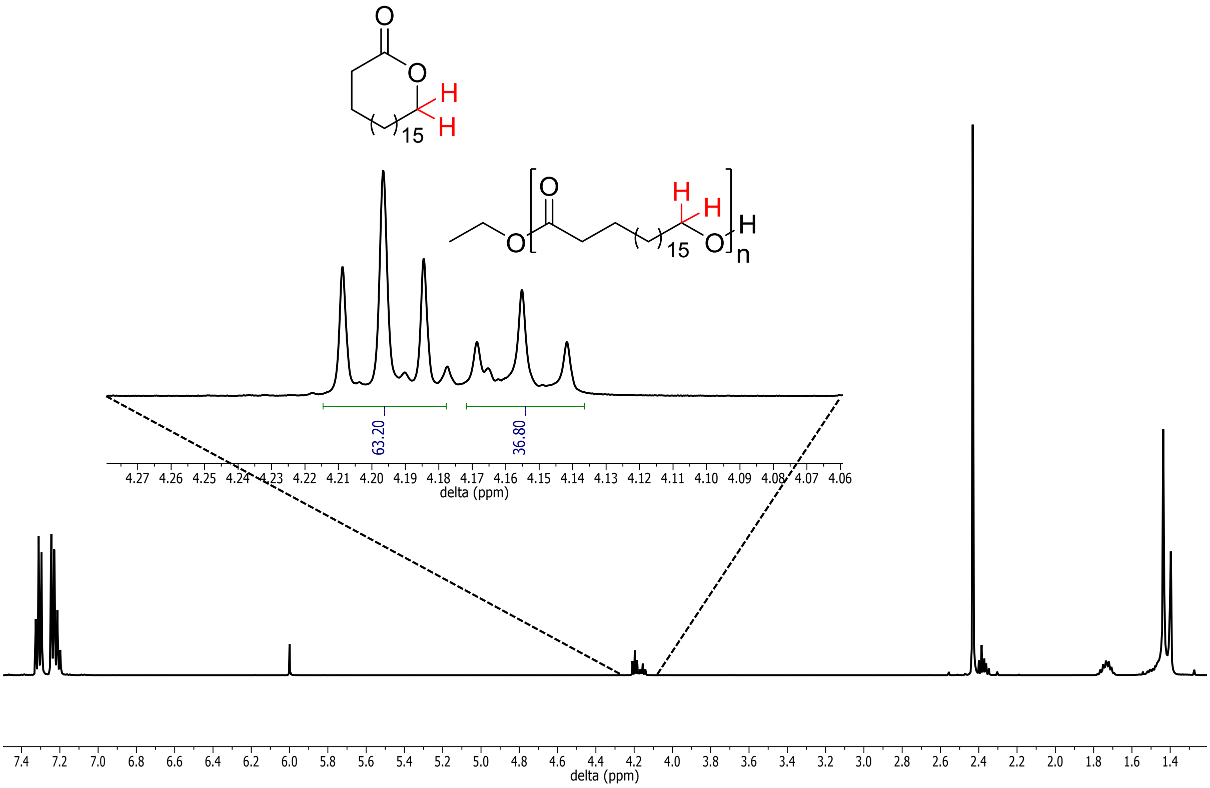


Figure S24. ^{1}H NMR spectrum of a PNDL polymer/monomer mixture; **Table 1,** entry 8 (TCE-d_2, 403 K).

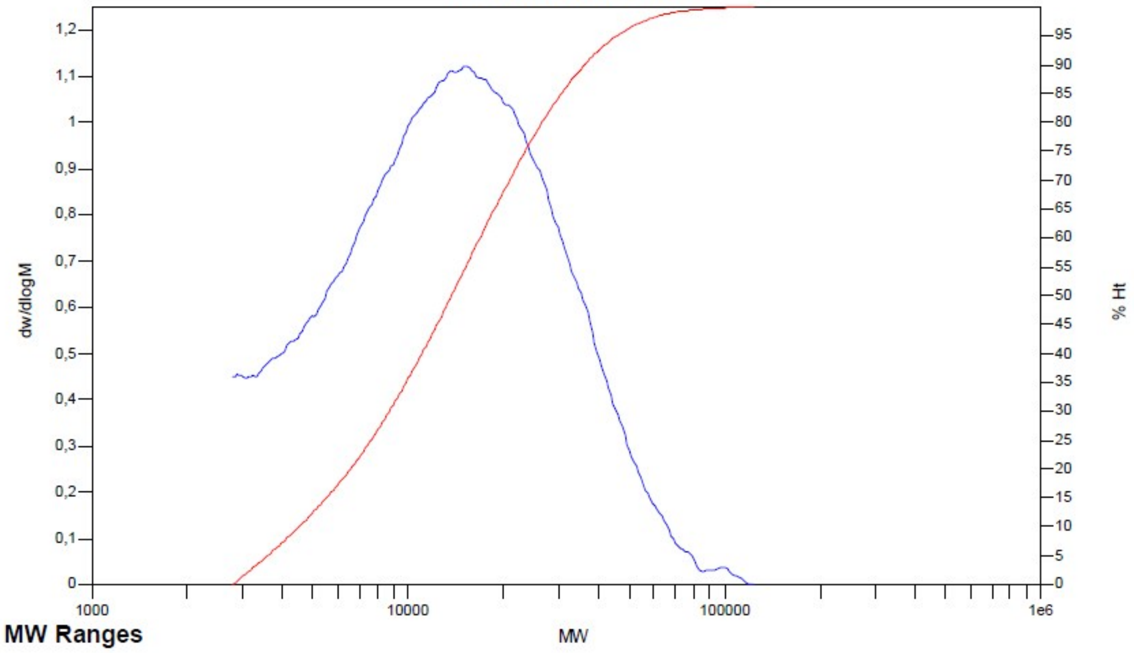


Figure S25. SEC trace of a PNDL polymer/monomer mixture; **Table 1,** entry 8.

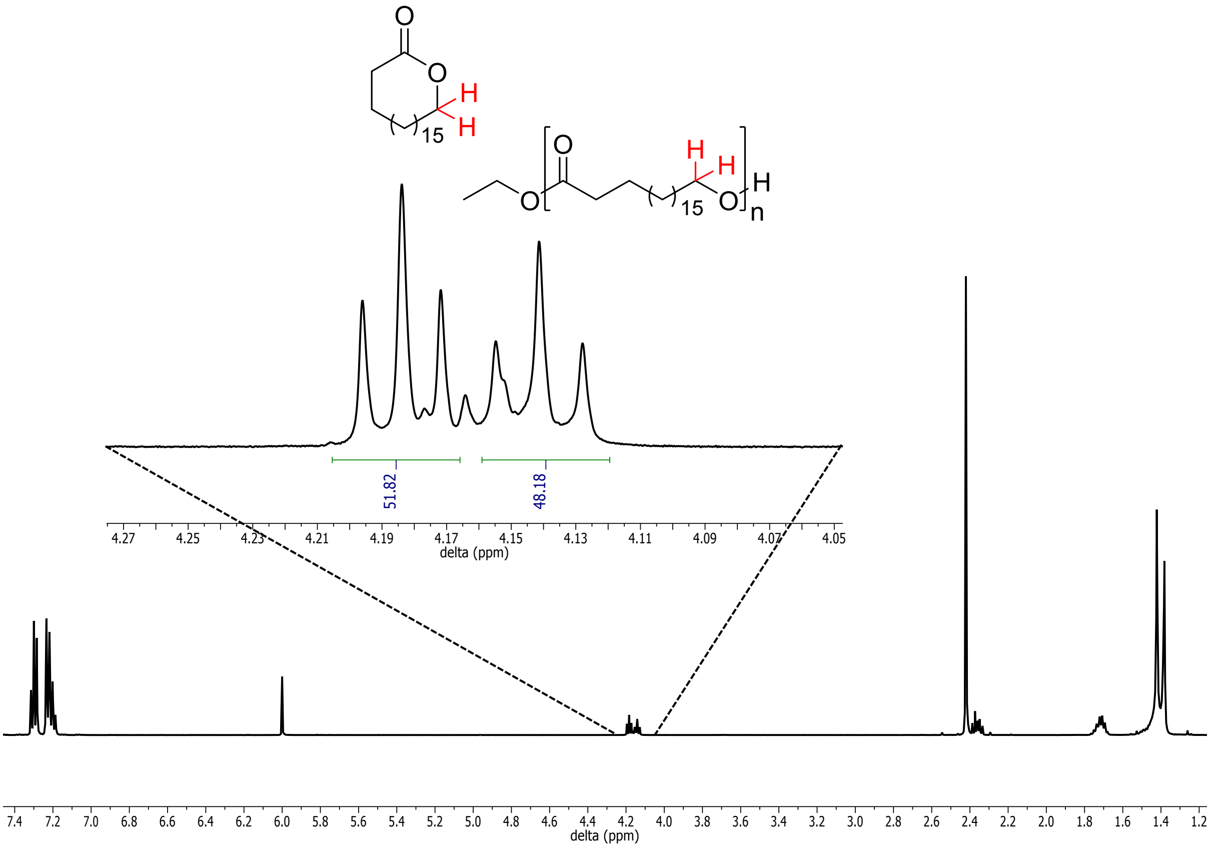


Figure S26. ^{1}H NMR spectrum of a PNDL polymer/monomer mixture; **Table 1,** entry 9 (TCE-d_2, 403 K).

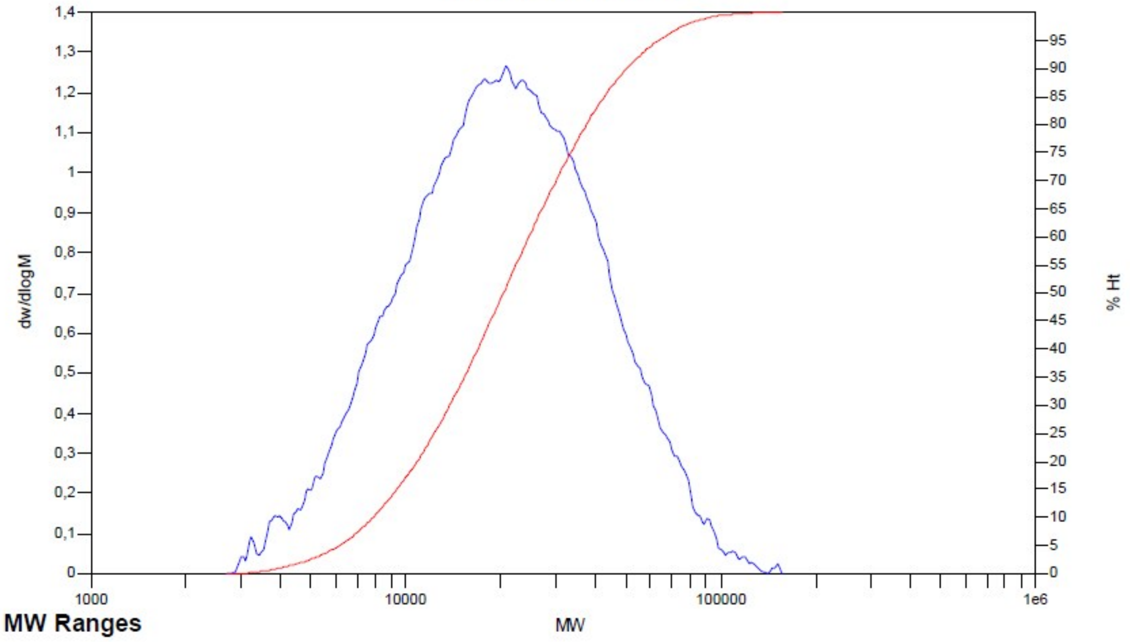


Figure S27. SEC trace of a PNDL polymer/monomer mixture; **Table 1,** entry 9.

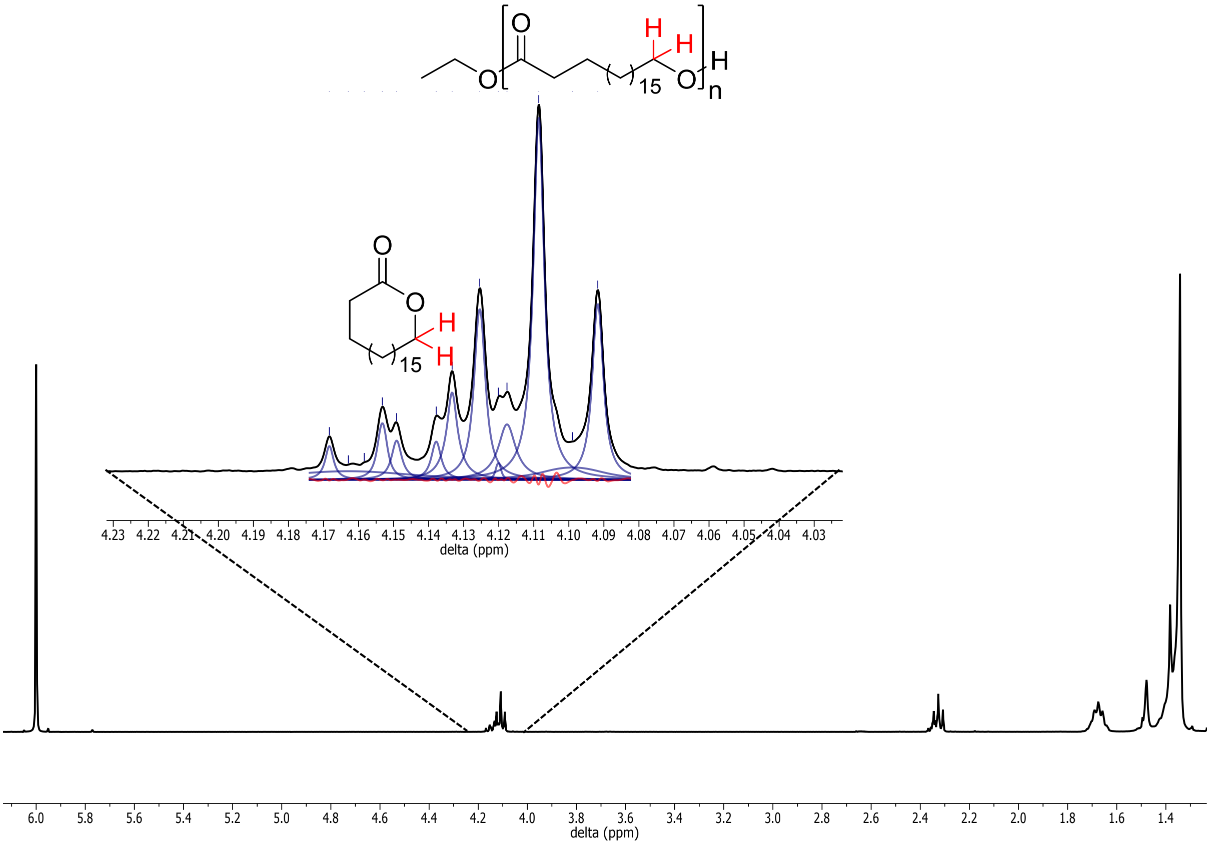


Figure S28. ^{1}H NMR spectrum of a PNDL polymer/monomer mixture; **Table 1,** entry 10 (TCE-d_2, 373 K). Peak deconvolution was used to determine conversion.

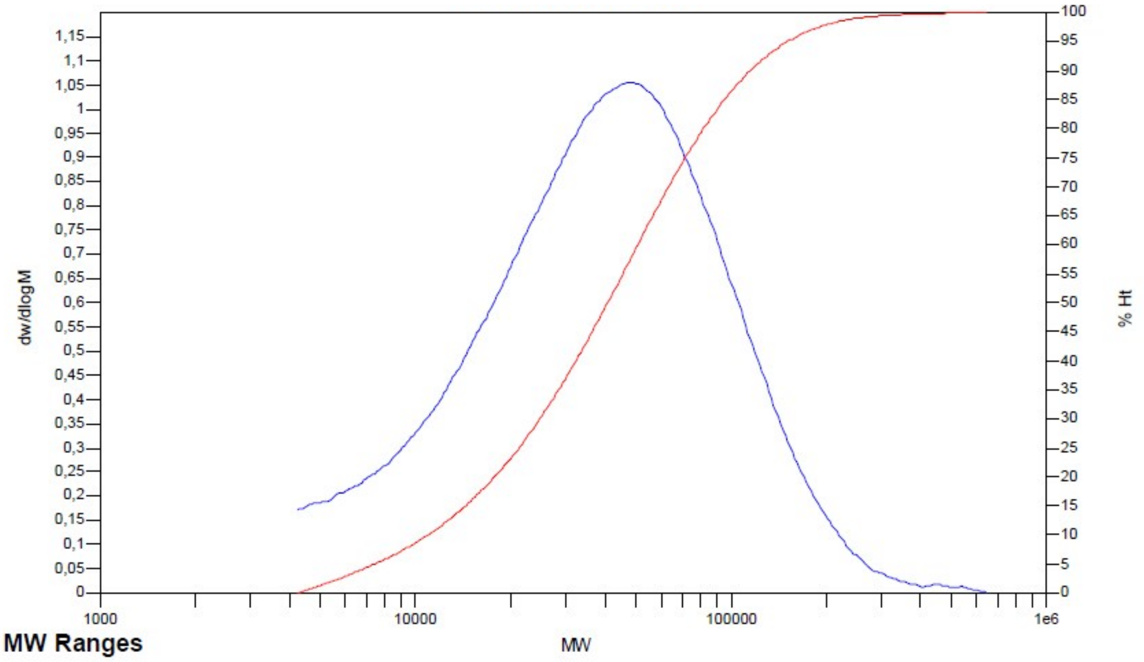


Figure S29. SEC trace of a PNDL polymer/monomer mixture; **Table 1,** entry 10.

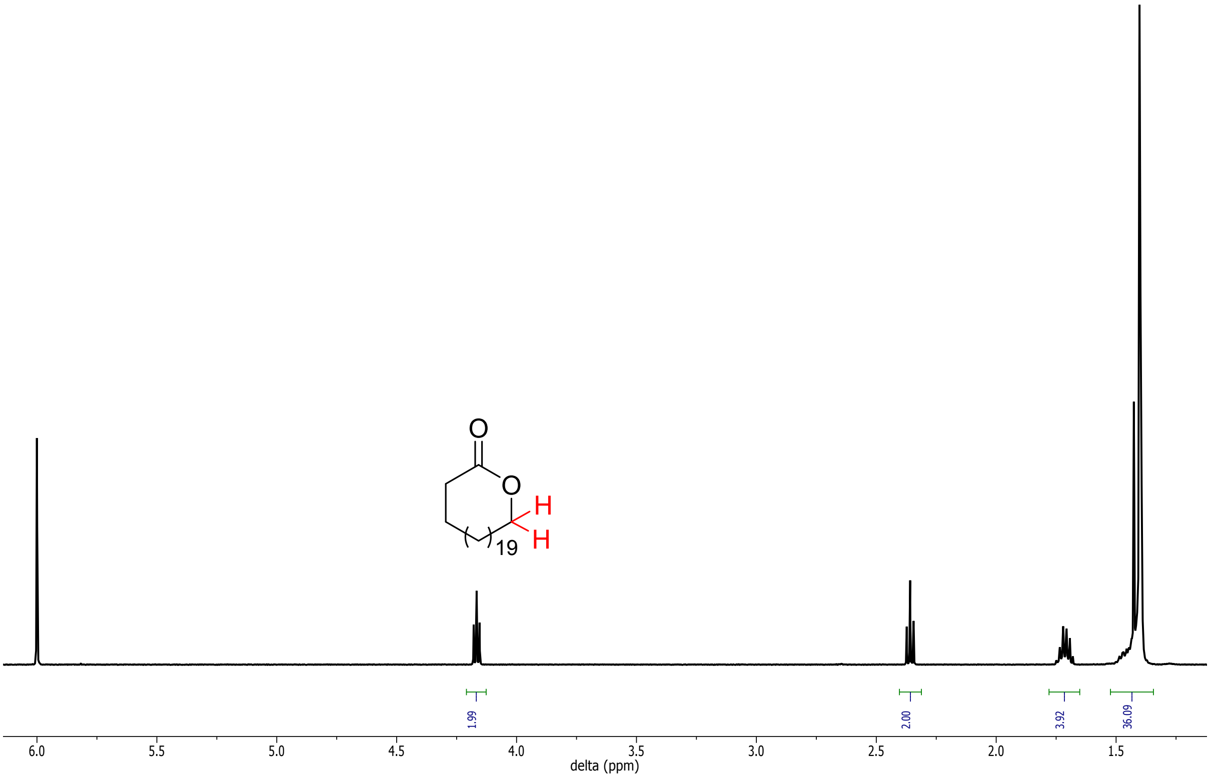


Figure S30. ^{1}H NMR spectrum of TCL (TCE-d_2, 403 K).

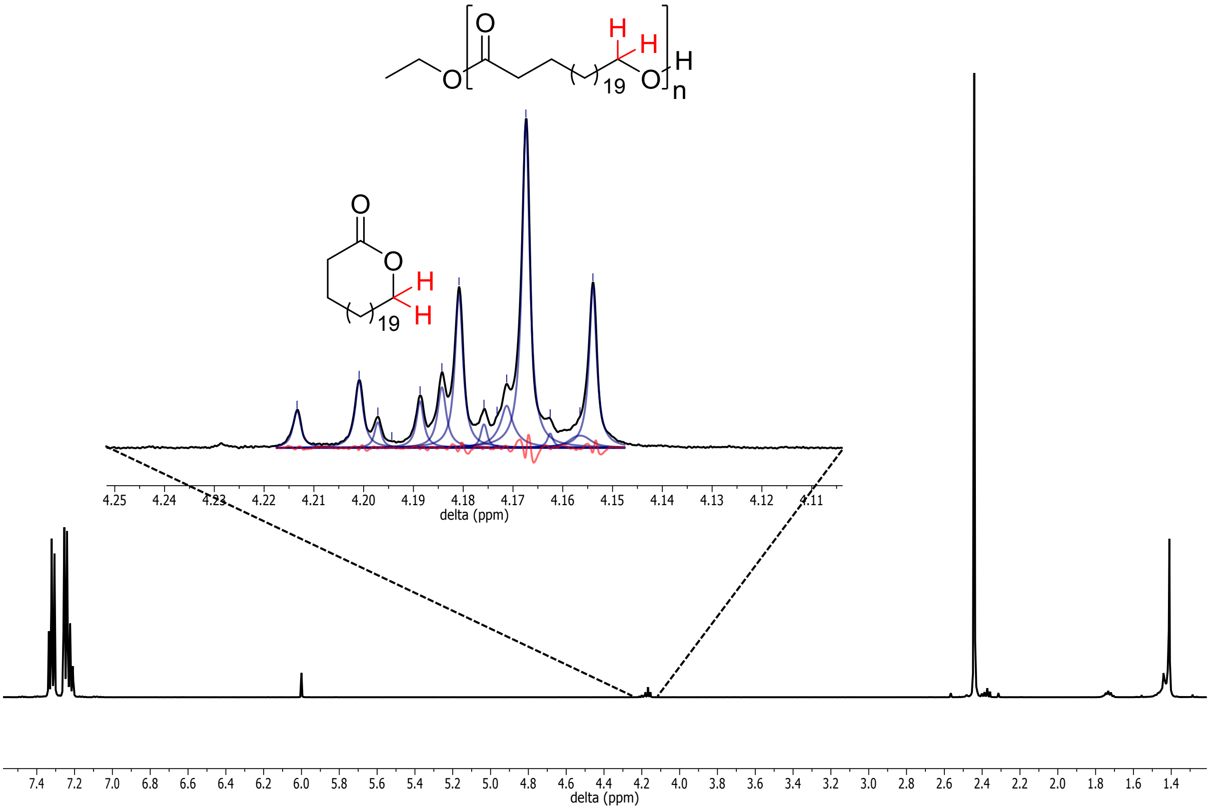


Figure S31. ^{1}H NMR spectrum of a PTCL polymer/monomer mixture; **Table 1,** entry 11 (TCE-d$_2$, 403 K). Peak deconvolution was used to determine conversion.

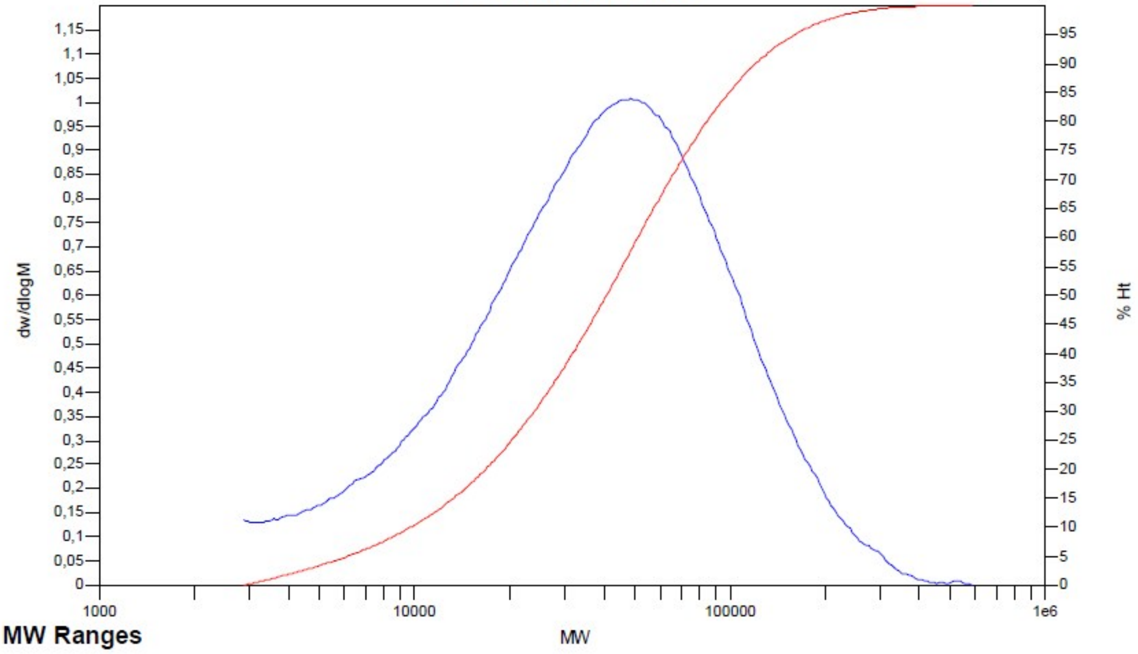


Figure S32. SEC trace of a PTCL polymer/monomer mixture; **Table 1,** entry 11.

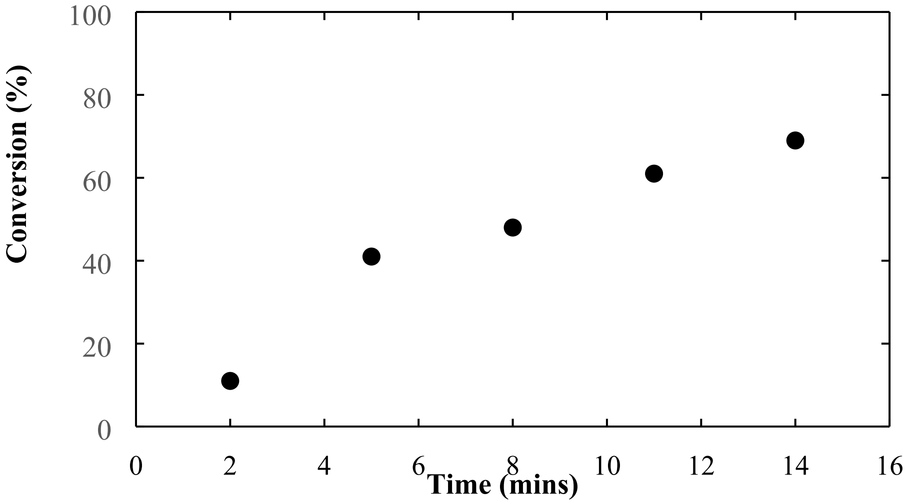


Figure S33. Conversion vs time data for the polymerisation for PDL. Conditions: $[PDL]_0$ = 0.3 M, [PDL]/[**1**] = 100, toluene, 373 K.

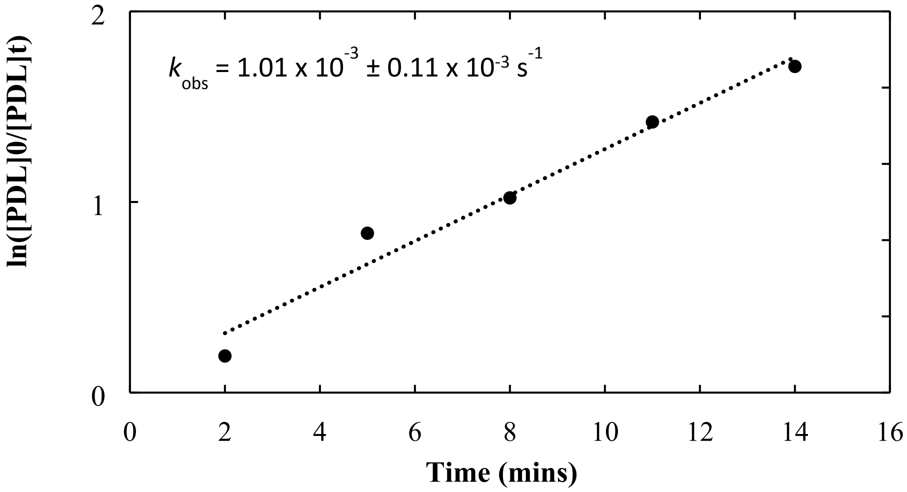


Figure S34. Semi-logarithmic pseudo first-order rate plot for the polymerisation of PDL. Conditions: $[PDL]_0$ = 0.3 M, [PDL]/[**1**] = 100, toluene, 373 K.

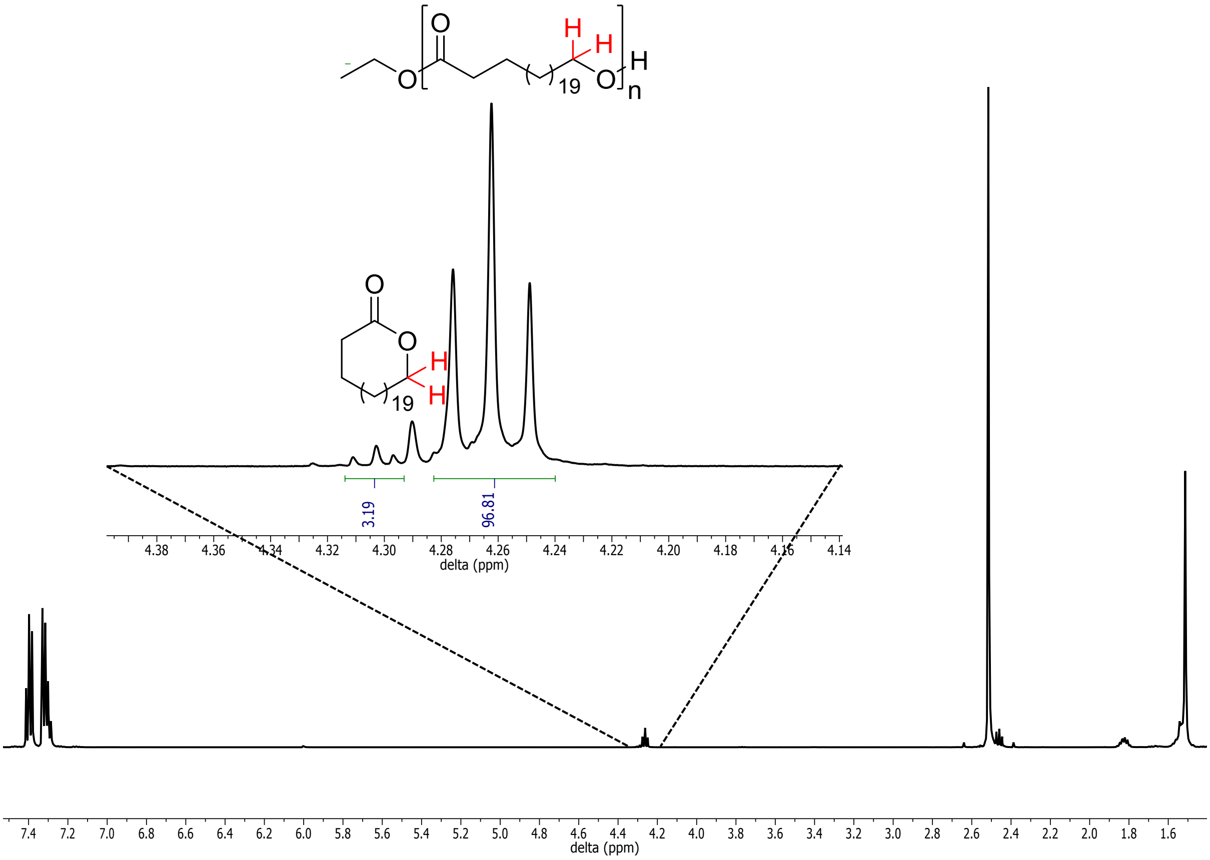


Figure S35. ^{1}H NMR spectrum of a PTCL polymer/monomer mixture; **Table 1,** entry 12 (TCE-d_2, 403 K).

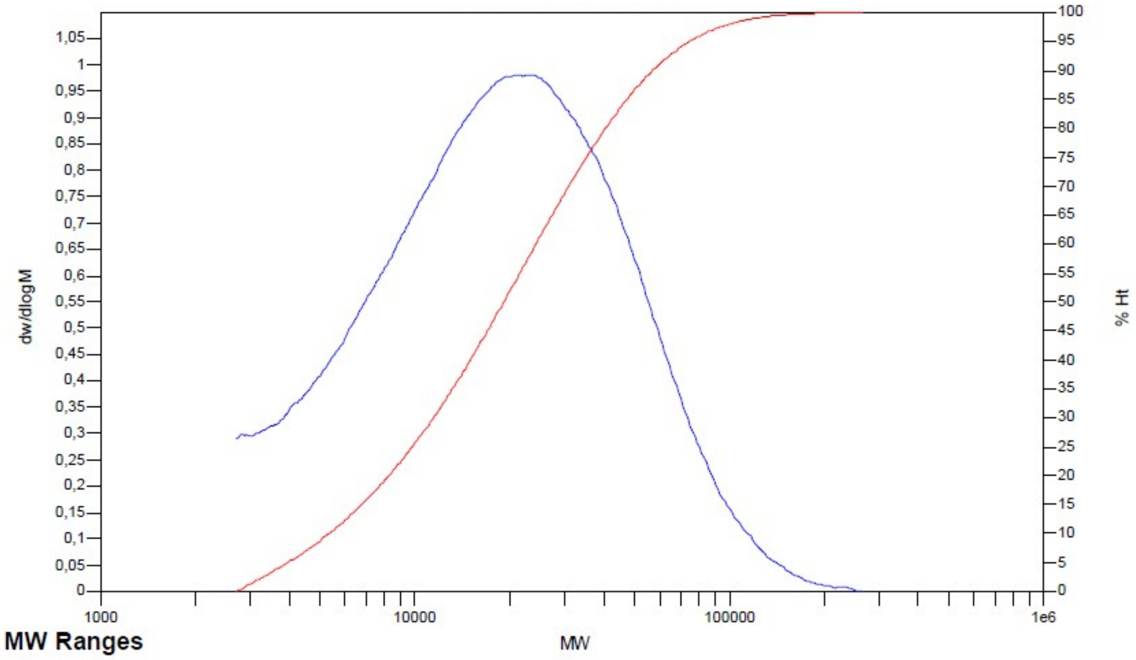


Figure S36. SEC trace of a PTCL polymer/monomer mixture; **Table 1,** entry 12.

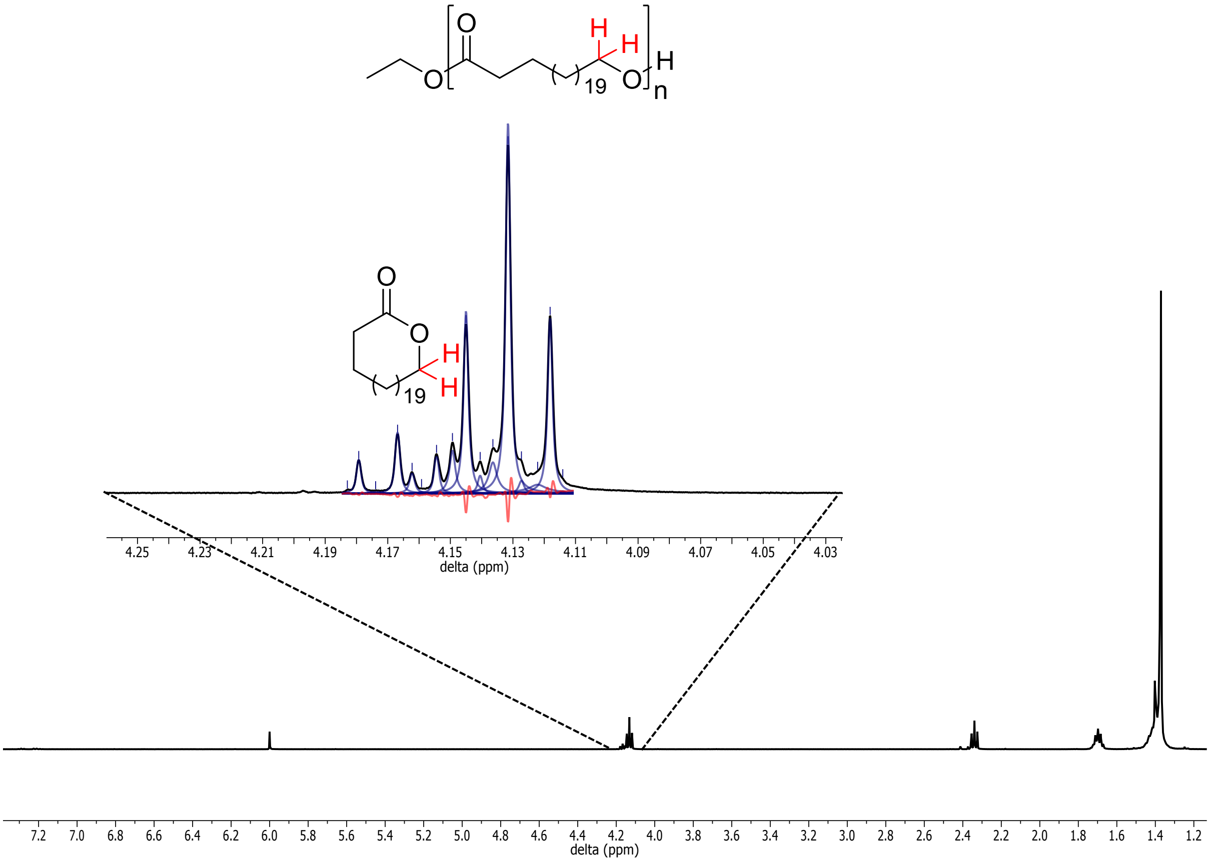


Figure S37. ^{1}H NMR spectrum of a PTCL polymer/monomer mixture; **Table 1,** entry 13 (TCE-d_2, 403 K). Peak deconvolution was used to determine conversion.

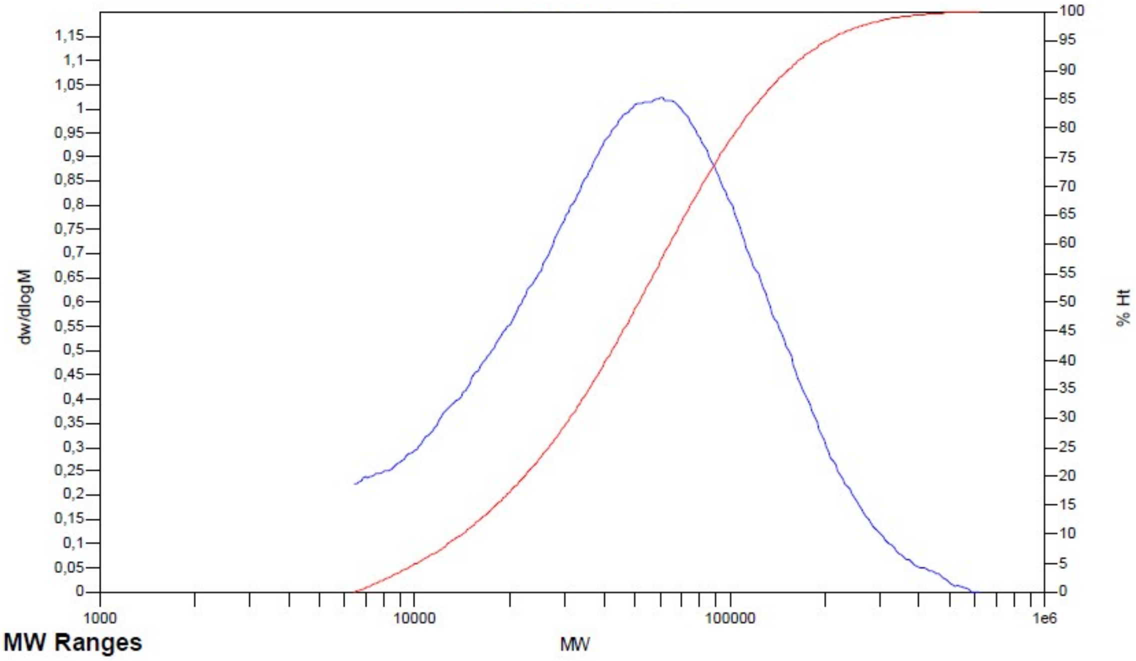


Figure S38. SEC trace of a PTCL polymer/monomer mixture; **Table 1,** entry 13.

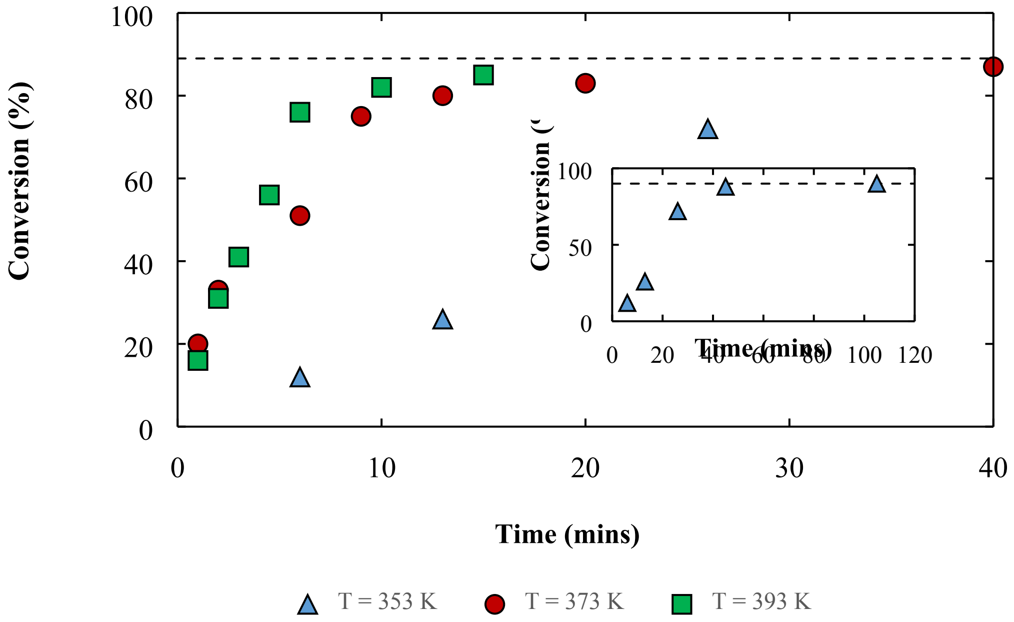
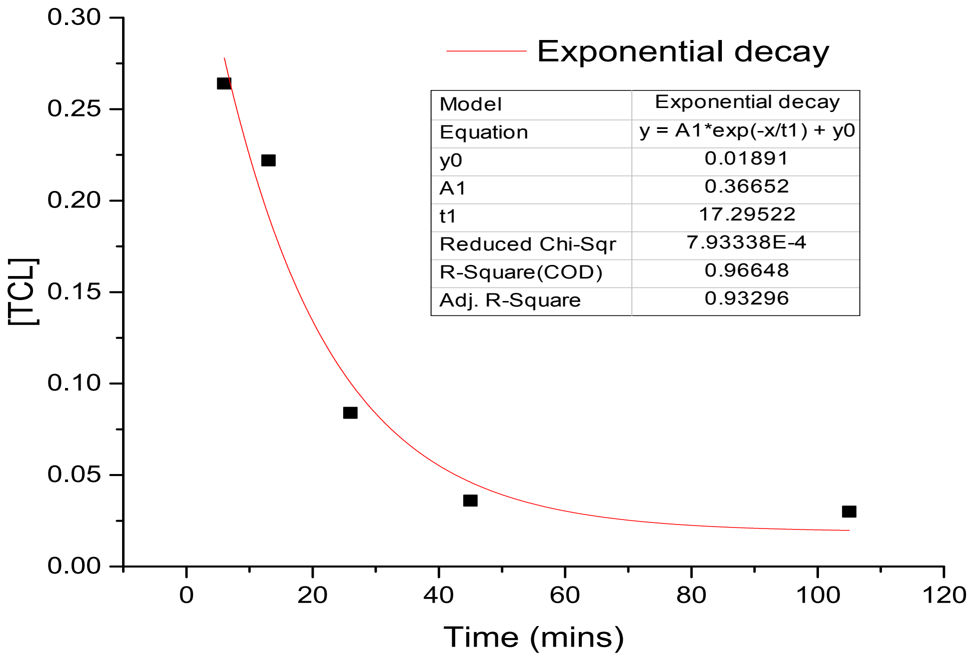


Figure S39. Conversion vs time data at different temperatures for the polymerisation of TCL. Conditions: $[TCL]_0$ = 0.3 M, [TCL]/[**1**] = 100, toluene.



Model	Exponential decay
Equation	y = A1*exp(-x/t1) + y0
y0	0.01891
A1	0.36652
t1	17.29522
Reduced Chi-Sqr	7.93338E-4
R-Square(COD)	0.96648
Adj. R-Square	0.93296

Figure S40. Exponential fit of the concentration vs time data for the polymerisation of TCL. Conditions: $[TCL]_0$ = 0.3 M, [TCL]/[**1**] = 100, toluene, 353 K.

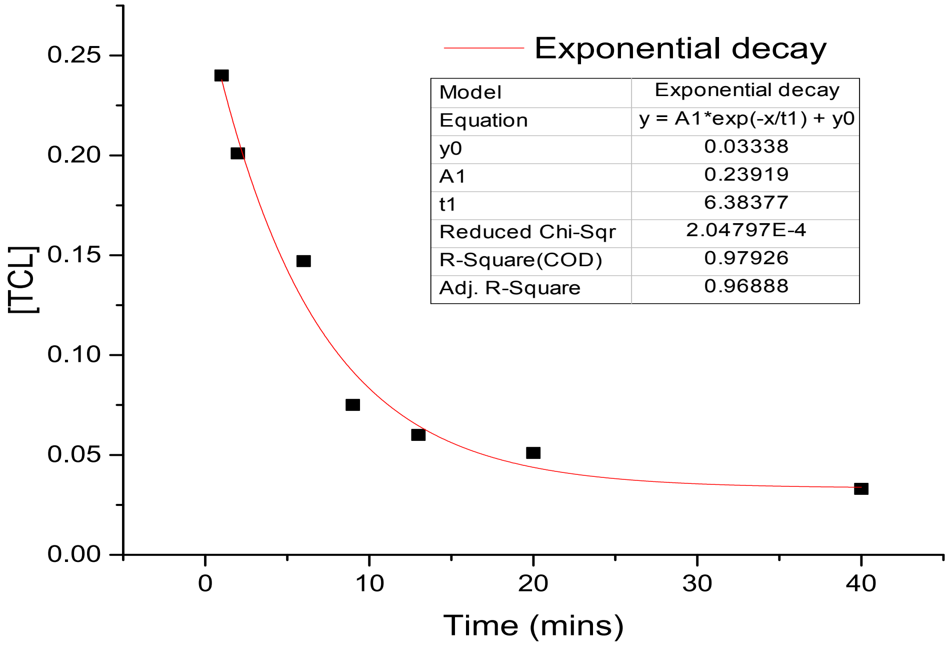


Figure S41. Exponential fit of the concentration vs time data for the polymerisation of TCL. Conditions: $[TCL]_0$ = 0.3 M, [TCL]/[**1**] = 100, toluene, 373 K.

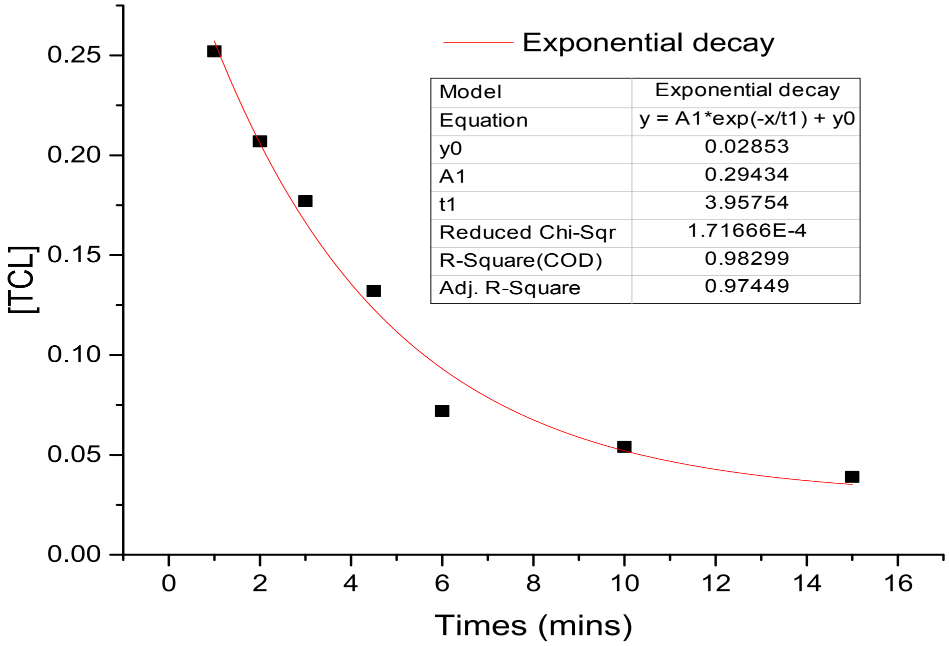


Figure S42. Exponential fit of the concentration vs time data for the polymerisation of TCL. Conditions: $[TCL]_0$ = 0.3 M, [TCL]/[**1**] = 100, toluene, 393 K.

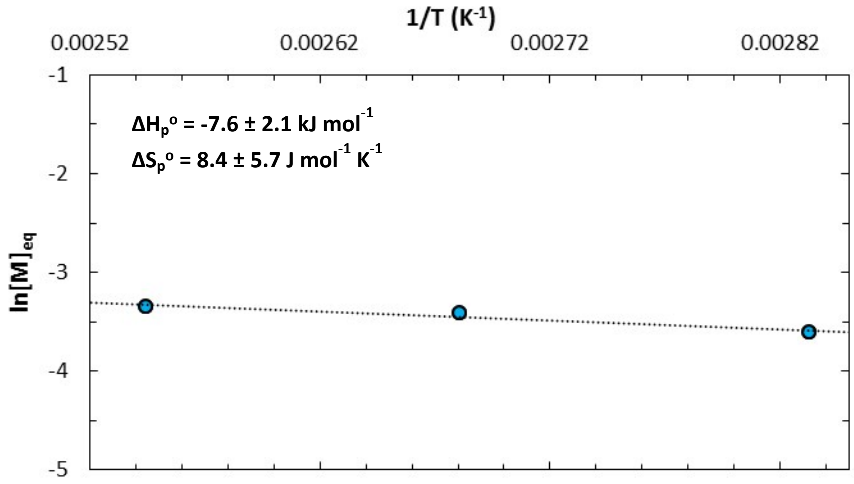


Figure S43. Semi-quantitative Van 'T Hoff plot for the polymerisation of TCL. Conditions: $[TCL]_0$ = 0.3 M, [TCL]/[**1**] = 100, toluene.

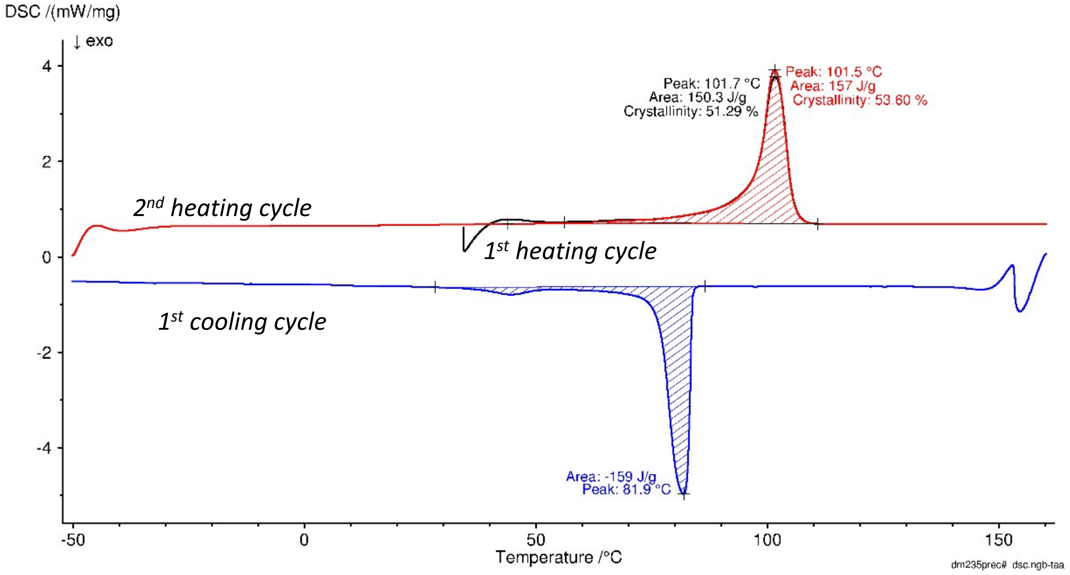


Figure S44. Heat flow vs temperature curve for a PNDL sample (**Table 1**, entry 10). First heating cycle (black curve), second heating cycle (red curve) and first cooling cycle (blue curve).

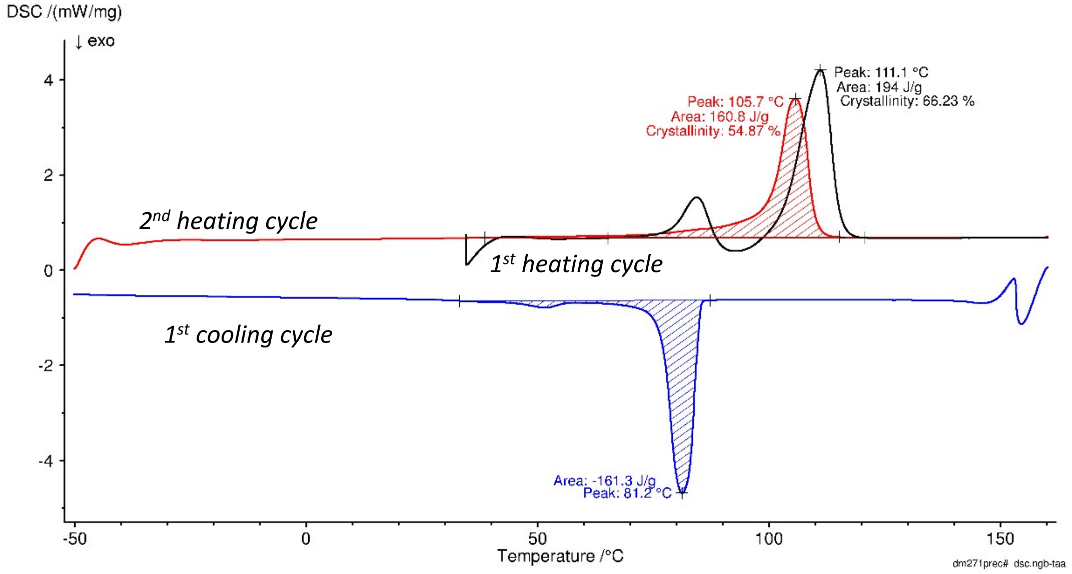


Figure S45. Heat flow vs temperature curve for a PNDL sample (**Table 1**, entry 13). First heating cycle (black curve), second heating cycle (red curve) and first cooling cycle (blue curve).

References

1. T. Witt, M. Haussler and S. Mecking, *Macromol. Rapid Commun.*, 2017, **38**, 5.
2. C. Bakewell, T.-P.-A. Cao, N. Long, X. F. Le Goff, A. Auffrant and C. K. Williams, *J. Am. Chem. Soc.*, 2012, **134**, 20577-20580.