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Supporting Information for

High activity of an indium alkoxide complex toward the ring opening polymerization of cyclic esters

*Stephanie M. Quan and Paula L. Diaconescu**

Department of Chemistry & Biochemistry, University of California, Los Angeles, 607 Charles E. Young Drive East, Los Angeles, CA 90095

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Experimental Details

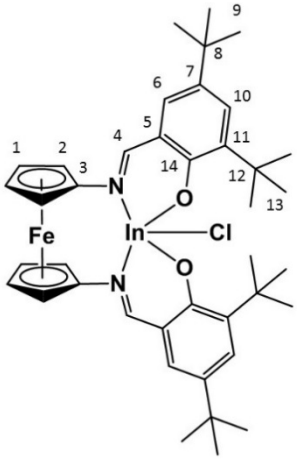
General Considerations

All experiments were performed under a dry nitrogen atmosphere using standard Schlenk techniques or an MBraun inert-gas glovebox. Solvents were purified using a two-column solid-state purification system by the method of Grubbs[1] and transferred to the glove box without exposure to air. Liquid monomers were distilled over CaH_2 and brought into the glove box without exposure to air. Solid monomers and 1,3,5-trimethylbenzene were recrystallized from toluene at least twice before use. 2,4-di-*tert*-butylphenol, *n*-BuLi were purchased from Sigma Aldrich and used as received. $InCl_3$ was purchased from Alfa Aesar and used as received. H_2(salfen)[2] was synthesized following previously published procedures. NMR solvents were obtained from Cambridge Isotope Laboratories, degassed and stored over activated molecular sieves prior to use. ^{1}H NMR spectra were recorded on Bruker 300, Bruker 400 or Bruker 500 spectrometers at room temperature in C_6D_6 or $CDCl_3$. Chemical shifts are reported with respect to internal solvent, 7.16 ppm (C_6D_6) and 7.26 ppm ($CDCl_3$) for ^{1}H NMR spectra. CHN analyses were performed on an Exeter Analytical, Inc. CE-440 Elemental Analyzer. Cyclic voltammetric studies were carried out in a 25 mL three neck round bottom flask with electrodes fixed in position by rubber stoppers, in a 0.10M [^{n}Pr$_4$N][BAr$^F_4$] (Ar^F = 3,5-(CF$_3$)$_2$C$_6$H$_3$) solution in tetrahydrofuran. A glassy carbon working electrode (planar circular area = 0.071 cm^2), a platinum reference electrode (planar circular area = 0.031 cm^2), and a silver-wire pseudo-reference electrode were purchased from CH Instruments. Cyclic voltammograms were acquired with a CH Instruments CHI630D potentiostat and recorded with CH Instruments software (version 13.04) with data processing on Origin 9.1. All potentials are given with respect to the ferrocene-ferrocenium couple. Molecular weights of the polymers were determined by GPC-LLS (Gel Permeation Chromatography, Laser Light Scattering). GPC-LLS uses an Agilant liquid chromatograph equipped with an Agilant 1200 series pump and autosampler, three Phenogel 5 µm Narrow Bore columns, a Wyatt Optilab differential refractometer, Wyatt Tristar miniDAWN and a Wyatt Viscostar viscometer. A flow rate of 1.0 mL/min was used and samples were dissolved in chloroform with 0.25% triethylamine. Results were calibrated to a narrow molecular weight polystyrene standards.

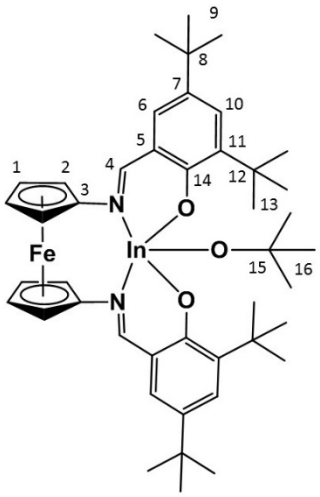
Synthesis of K_2(salfen). A saturated THF solution of H_2(salfen)[2] (1.00 g, 1.54 mmol) was added dropwise to a THF slurry of KH (132 mg, 3.18 mmol) (2 equiv, 57% oil dispersion). Some bubbles were formed indicating the release of hydrogen gas. The solution was stirred for 2 h and then filtered through Celite. The volatiles were removed under reduced pressure. The obtained red solid was washed with hexanes over a medium frit until the resulting liquid was clear. Yield: 1.02 g, 89%. ^{1}H NMR (300 MHz, 25 ºC, C_6D_6), δ (ppm): 8.58 (s, 2H, Ph*H*), 7.70 (s, 2H, Ph*H*), 4.09 (t, 4H, Cp*H*), 3.97 (t, 4H, Cp*H*), 3.42 (s, 2H, Cp*H*), 1.79 (s, 18H, C*H*$_3$), 1.48 (s, 18H, C*H*$_3$). A ^{13}C NMR spectrum could not be obtained due to solubility issues.

Synthesis of (salfen)InCl. A THF solution of K_2(salfen) (117 mg, 0.161 mmol) was added dropwise to a THF solution of $InCl_3$ (35.7 mg, 0.161 mmol). The solution was stirred for one hour. Volatiles were removed under reduced pressure. The crude product was dissolved in diethyl ether, the resulting solution filtered through Celite and cooled to -36 °C overnight. An orange solid precipitate was collected over a medium frit, washed with hexanes (2 x 2.5 mL) and then dried. The solid was dissolved in diethyl ether and

recrystallized at -36 °C before further use. Additional product can be precipitated by concentrating the mother liquor and placing in the freezer. Yield: 97.5 mg, 79.5%. ^{1}H NMR (300 MHz, 25 °C, C_6D_6), δ (ppm): 7.80 (s, 2H, Ph*H*), 7.77 (s, 2H, Ph*H*), 6.75 (s, 2H, Ph*H*), 4.71 (t, 4H, Cp*H*), 3.97 (t, 4H, Cp*H*), 3.64 (s, 2H, Cp*H*), 1.85 (s, 18H, C*H*$_3$), 1.34 (s, 18H, C*H*$_3$). ^{13}C NMR (500 MHz, 25 °C, C_6D_6), δ (ppm): *see figure below* 173.52 (4), 171.00 (14), 143.24, 130.04, 117.91, 106.28 (3, 5, 7, or 11), 137.95 (6), 131.88 (10), 69.75, 67.99, 65.86, 64.99 (1, 2), 36.20 (12), 34.13 (8), 30.32 (13), 25.76 (9). Analysis for $C_{40}H_{50}N_2O_2FeInCl$: Calcd.: C, 60.28%; H, 6.32%; N, 3.52%. Found: C, 60.78%; H, 6.72 %; N, 3.06 %.



Synthesis of (salfen)In(O^{t}Bu). A THF solution of freshly sublimed KO^{t}Bu (137.6 mg, 1.11 mmol) was added dropwise to a THF solution of (salfen)InCl (787 mg, 0.99 mmol). The solution was stirred for 1 hour. Volatiles were removed under reduced pressure. The crude product was dissolved in hexanes, filtered through Celite, and dried. The compound was recrystallized from hexanes twice before polymerization studies. Yield: 560 mg, 68%. ^{1}H NMR (300 MHz, 25 °C, C_6D_6), δ (ppm): 7.84 (s, 2H, Ph*H*), 7.66 (s, 2H, Ph*H*), 6.70 (s, 2H, Ph*H*), 5.35 (t, 4H, Cp*H*), 3.86 (t, 4H, Cp*H*), 3.75 (s, 2H, Cp*H*), 1.74 (s, 9H, OC*H*$_3$), 1.69 (s, 18H, C*H*$_3$) 1.27 (s, 18H, C*H*$_3$). ^{13}C NMR (500 MHz, 25 °C, C_6D_6), δ (ppm): 173.30 (4), 170.77 (14), 142.52, 137.12, 118.12, 105.72 (3, 5, 7, 11), 130.99 (6), 129.72 (10), 69.26, 68.74, 67.91, (1, 2), 62.37 (15), 36.08 (12), 34.00 (8), 35.07 (16), 31.46 (13), 30.36 (9). Analysis for $C_{44}H_{59}N_2O_3FeIn$: Calcd.: C, 63.32%; H, 7.13%; N, 3.36%. Found: C, 63.60%; H, 7.21 %; N, 3.06%.



General Polymerization Procedure. In the glovebox, 1.5 mL of a 0.033 M monomer solution and 1.0 mL of a 0.010 M standard solution were added to a 20 mL scintillation vial. 1.0 mL of a 0.010 M catalyst solution was added to the stirring solution. To monitor the polymerizations, 0.05 mL aliquots were taken and quenched with 2 drops of wet hexanes. Volatiles were removed under reduced pressure. Progress was monitored by ^{1}H NMR spectroscopy until conversion reached 95%. The polymerization was quenched with cold MeOH outside the box. The solution was stirred for 10 min and filtered over a medium frit to collect solid polymer. The crude polymer was then dissolved in a minimum amount of CH_2Cl_2 and precipitated with cold MeOH until a pure white solid was obtained.

To increase [M]:[I], larger amounts of monomer were used while maintaining a 1.0 mL volume of a 0.010 M standard solution and a 1.0 mL volume of 0.010 M precatalyst solution. It should be noted that increasing the [M]:[I] ratio was also attempted by decreasing the amount of standard and precatalyst solution. However, issues with measuring small volumes accurately as well as rapidly decreasing activity were encountered.

Large Scale Polymerization (CL, VL, BBL). 1.0 mL of a 0.010 M standard solution, followed by the addition of 1.0 mL of a 0.010 M pre-catalyst solution was added to neat monomer in a 20 mL scintillation vial. The rest of the procedure follows the general procedure given above.

Notes of valerolactone work up. Valerolactone polymers were precipitated with cold hexanes instead of cold methanol.

Notes on β-butyrolactone work up. Polyhydroxybutyrate was quenched with 0.5 mL of 1.5 M HCl in diethyl ether. Volatiles were removed under reduced pressure. The polymer was precipitated by methanol as an oily substance. The vial was dipped in liquid nitrogen quickly to solidify the polymer before decanting the supernatant liquid and drying under vacuum.

Kinetic study of rac-LA polymerization. NMR scale polymerization was prepared on a 1/10th scale in a J-young tube with C_6D_6 as a solvent. The sample tube was inserted into the probe of a DRX500 Brucker spectrometer. The command "multi_zgvd" was applied to collect 1 scan automatically every 2 min. The data was processed with the Topspin 3.0 program. The product concentration was measured by ^{1}H NMR (comparing the methylene peak adjacent to oxygen of the monomer to methylene peak adjacent to the oxygen of the polymer). The polymerization was monitored to about 70% conversion.

NMR Spectroscopy

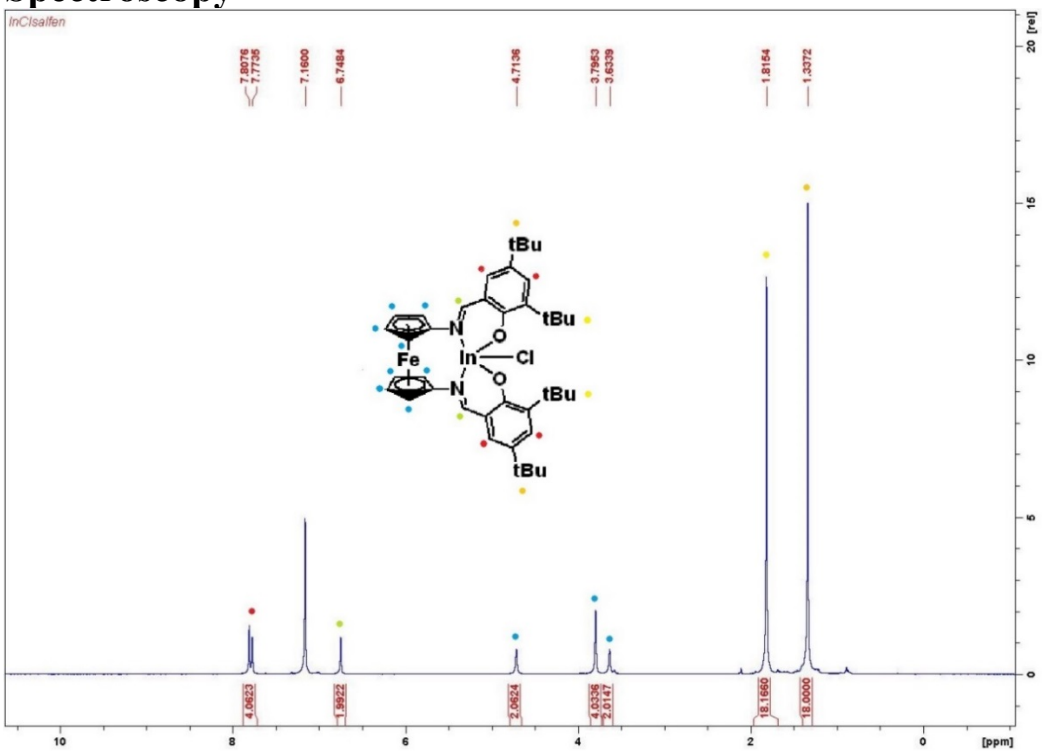


Figure S1. ^{1}H NMR (300 MHz, 25 °C, C_6D_6) spectrum of (salfen)InCl.

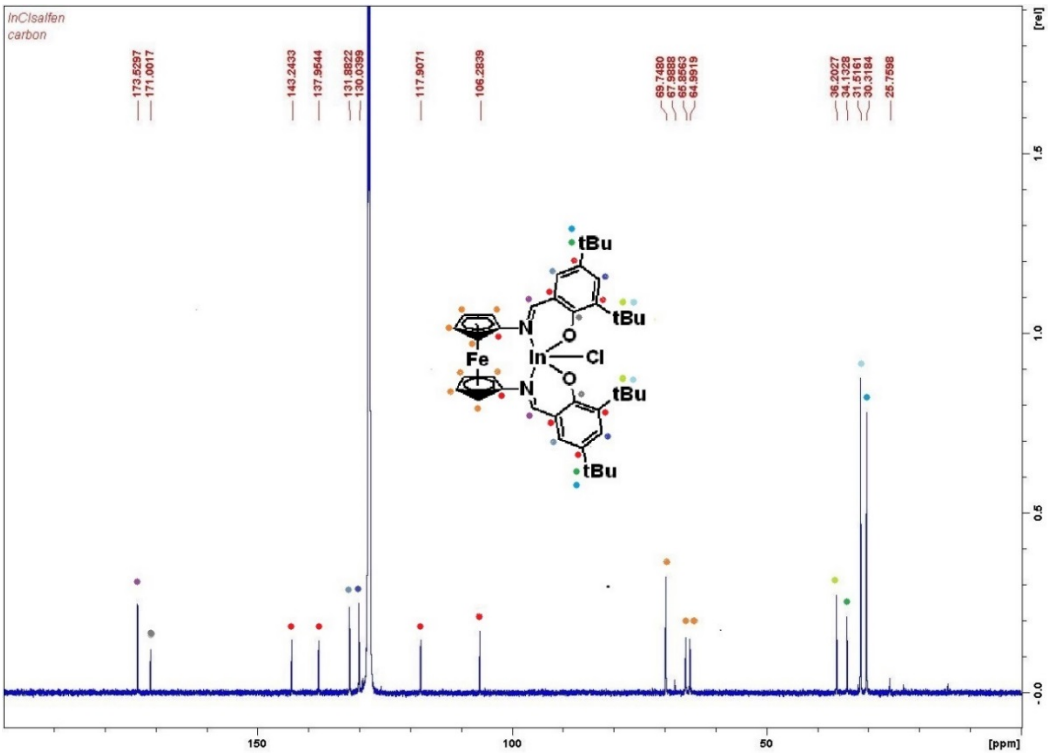


Figure S2. ^{13}C NMR (500 MHz, 25 °C, C_6D_6) spectrum of (salfen)InCl. Peak assignments were based on ^{13}C APT spectra below and previously published NMR spectra of similar compounds.[3]

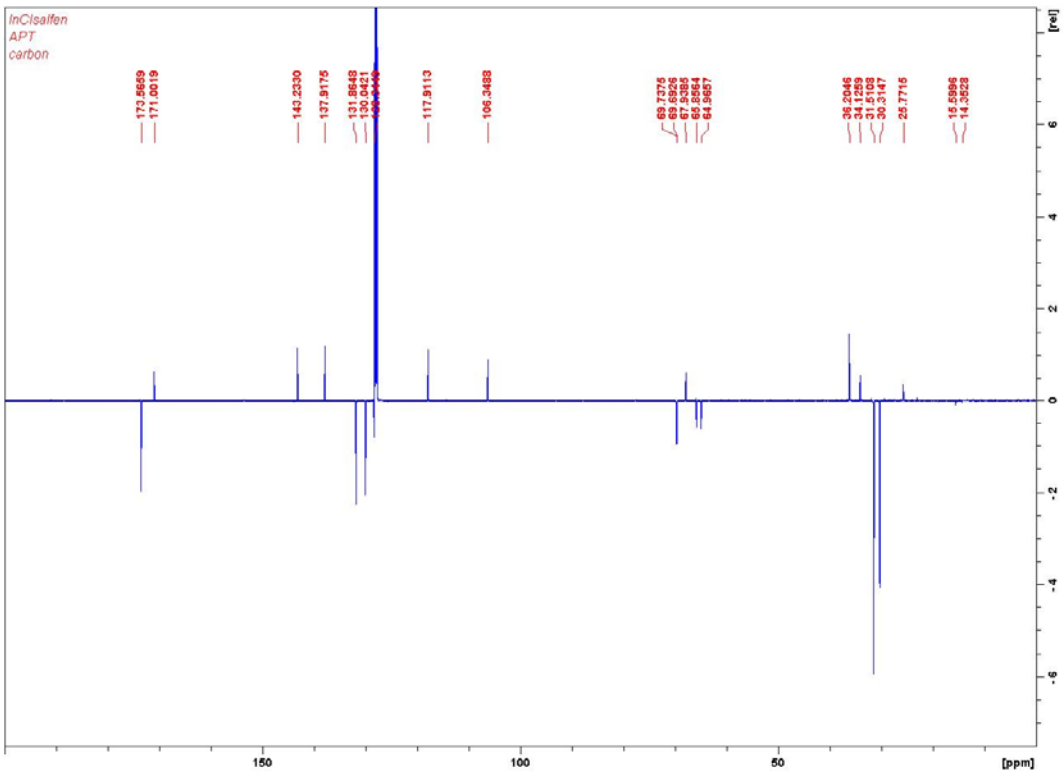


Figure S3. ^{13}C APT (attached proton test, 500 MHz, 25 °C, C_6D_6) spectrum of (salfen)InCl.

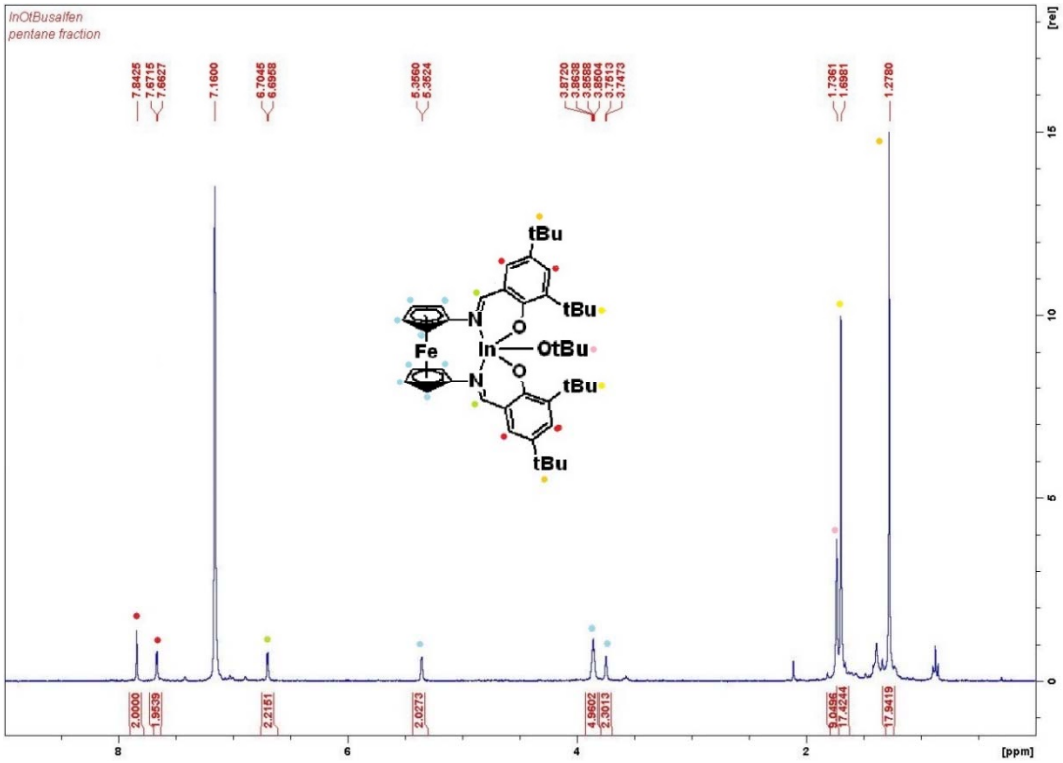


Figure S4. ^{1}H NMR (300 MHz, 25 °C, C_6D_6) spectrum of (salfen)In(O^{t}Bu).

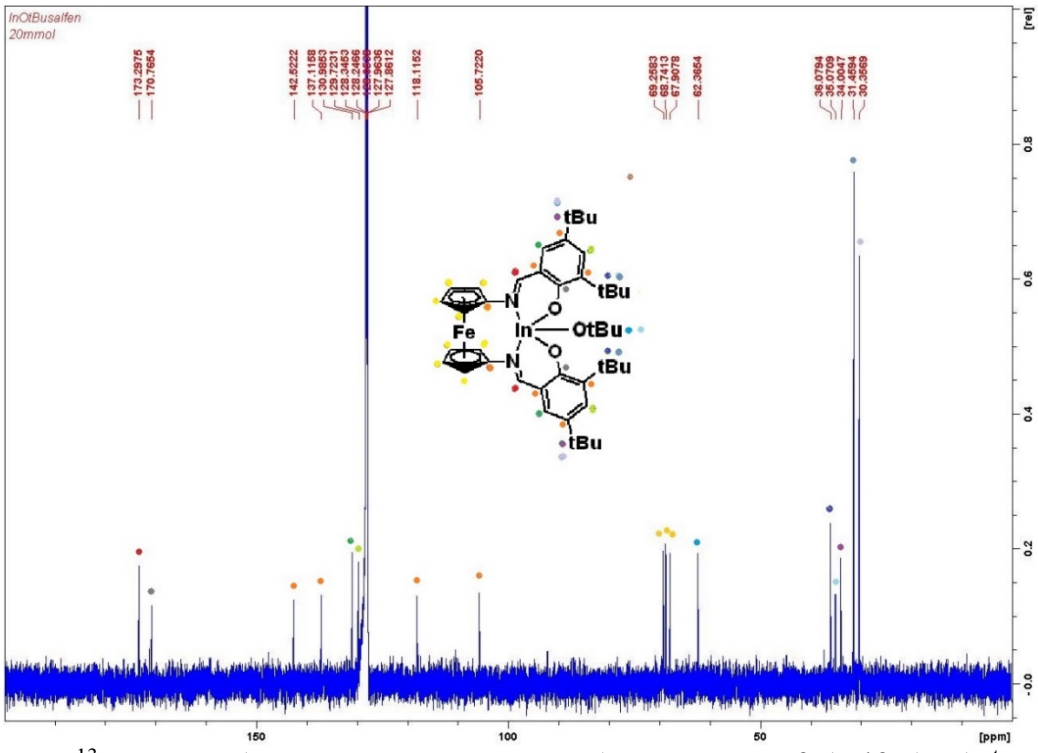


Figure S5. ^{13}C NMR (500 MHz, 25 °C, C_6D_6) spectrum of (salfen)In(O^{t}Bu). Peak assignments were based on ^{13}C APT spectra below and previously published NMR spectra of similar compounds.[3]

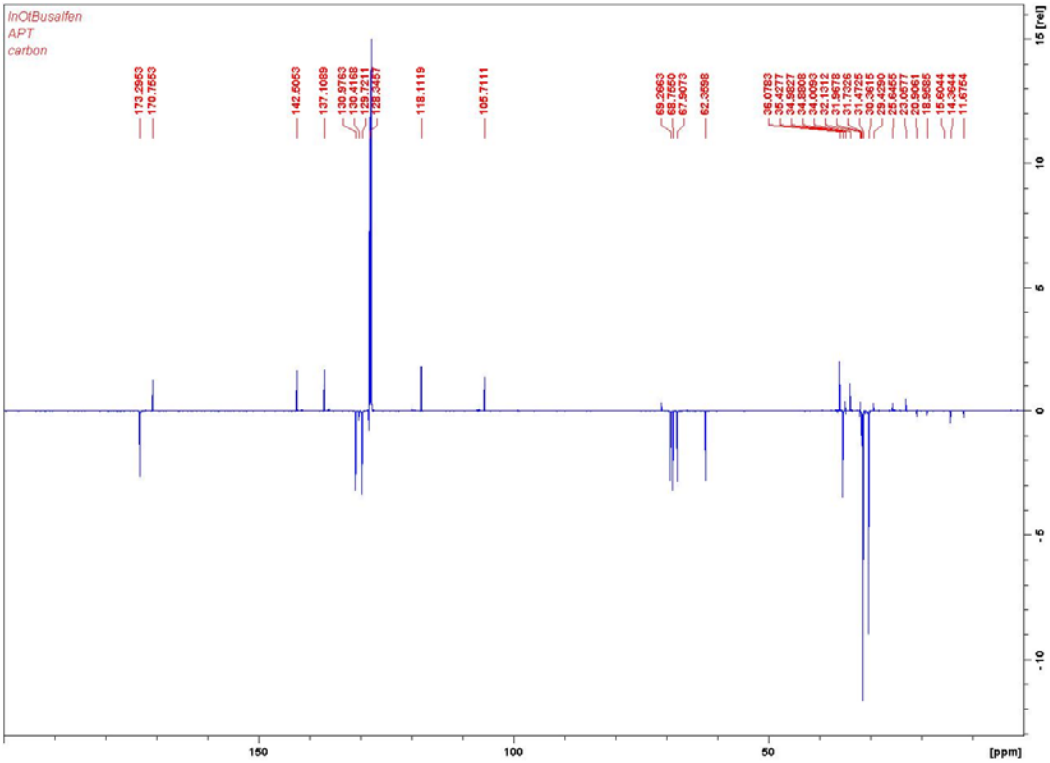


Figure S6. ^{13}C APT NMR (500 MHz, 25 °C, C_6D_6) spectrum of (salfen)In(O^{t}Bu).

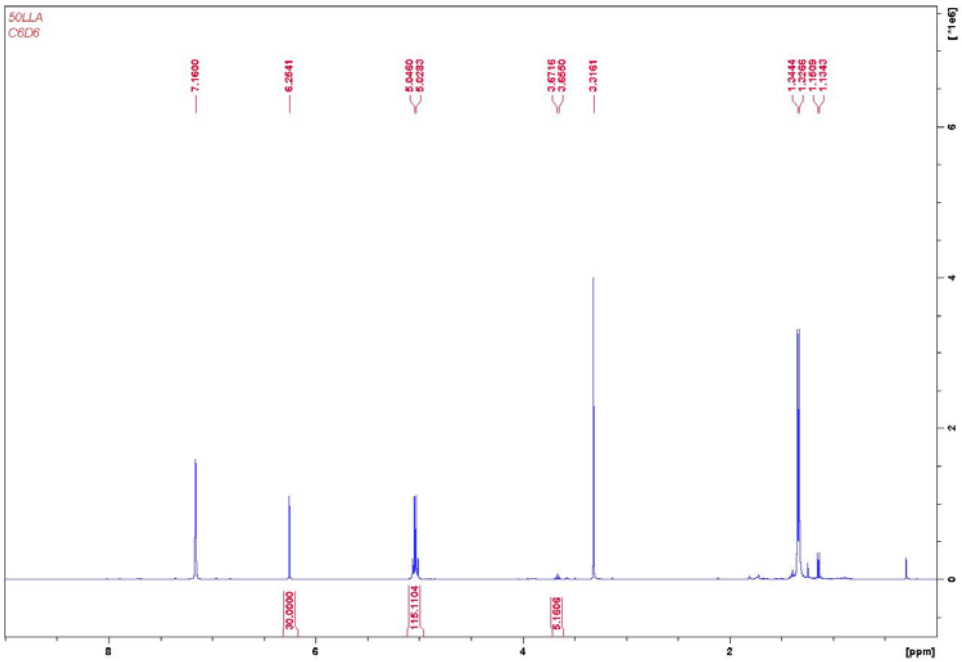


Figure S7. ^{1}H NMR (400 MHz, 25 °C, C_6D_6) spectrum of L-lactide polymerization. Standard is 1,3,5-trimethoxybenzene (TMB). Initiator: TMB: L-lactide ratio is 1: 10: 50. δ (ppm): 6.25 (s, 3H, Ph*H* TMB), 5.04 (q, 2H, C*H*CH$_3$ PLA), 3.60 (q, 2H, C*H*CH$_3$ L-lactide), 3.32 (s, 9H, C*H*$_3$ TMB), 1.34 (d, 6H, CHC*H*$_3$ PLA), 1.14 (d, 6H, CHC*H*$_3$ L-lactide).

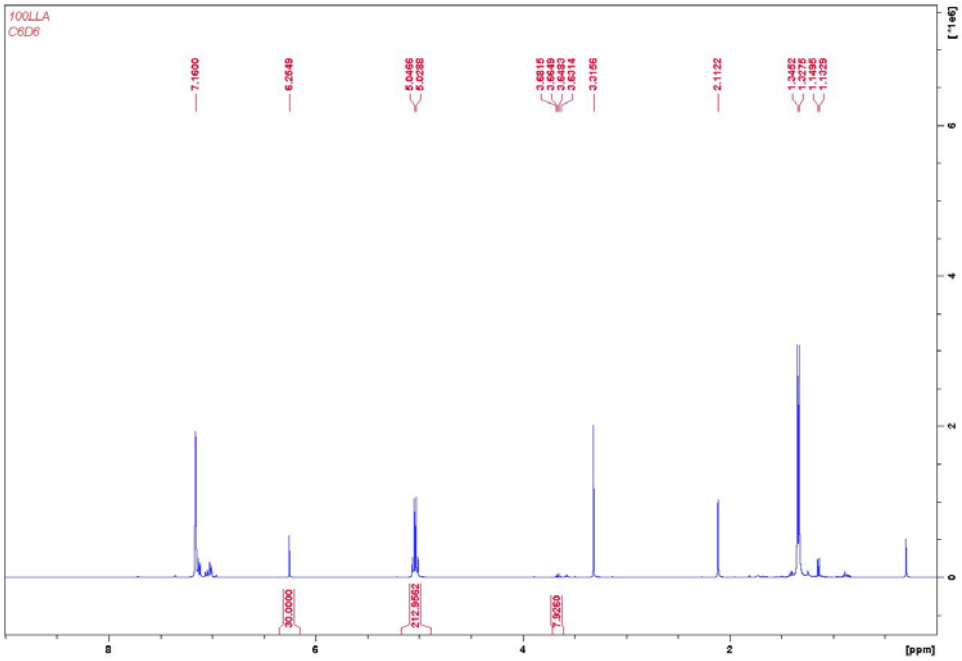


Figure S8. ^{1}H NMR (400 MHz, 25 °C, C_6D_6) spectrum of L-lactide polymerization. Standard is 1,3,5-trimethoxybenzene (TMB). Initiator: TMB: L-lactide ratio is 1:10:100. δ (ppm): 6.25 (s, 3H, Ph*H* TMB), 5.04 (q, 2H, C*H*CH$_3$ PLA), 3.60 (q, 2H, C*H*CH$_3$ L-lactide), 3.32 (s, 9H, C*H*$_3$ TMB), 1.34 (d, 6H, CHC*H*$_3$ PLA), 1.14 (d, 6H, CHC*H*$_3$ L-lactide).

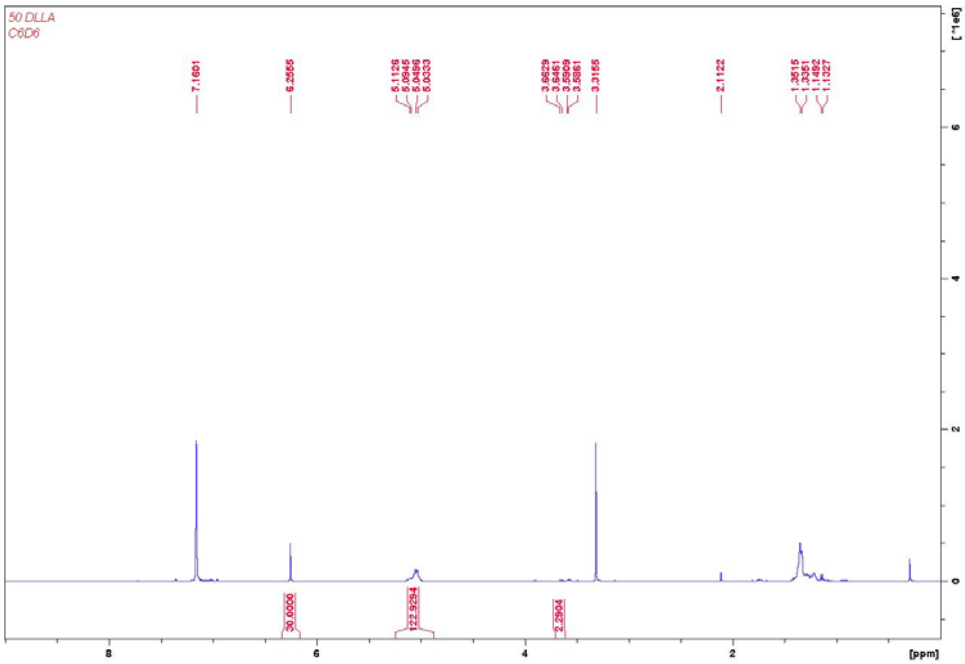


Figure S9. ^{1}H NMR (400 MHz, 25 °C, C_6D_6) spectrum of D,L-lactide polymerization. Standard is 1,3,5-trimethoxybenzene (TMB). Initiator: TMB: D,L-lactide ratio is 1:10:50. δ (ppm): 6.25 (s, 3H, Ph*H* TMB), 5.04 (m, 2H, C*H*CH$_3$ PLA), 3.60 (q, 2H, C*H*CH$_3$ D,L-lactide), 3.32 (s, 9H, C*H*$_3$ TMB), 1.34 (m, 6H, CHC*H*$_3$ PLA), 1.14 (d, 6H, CHC*H*$_3$ D,L-lactide).

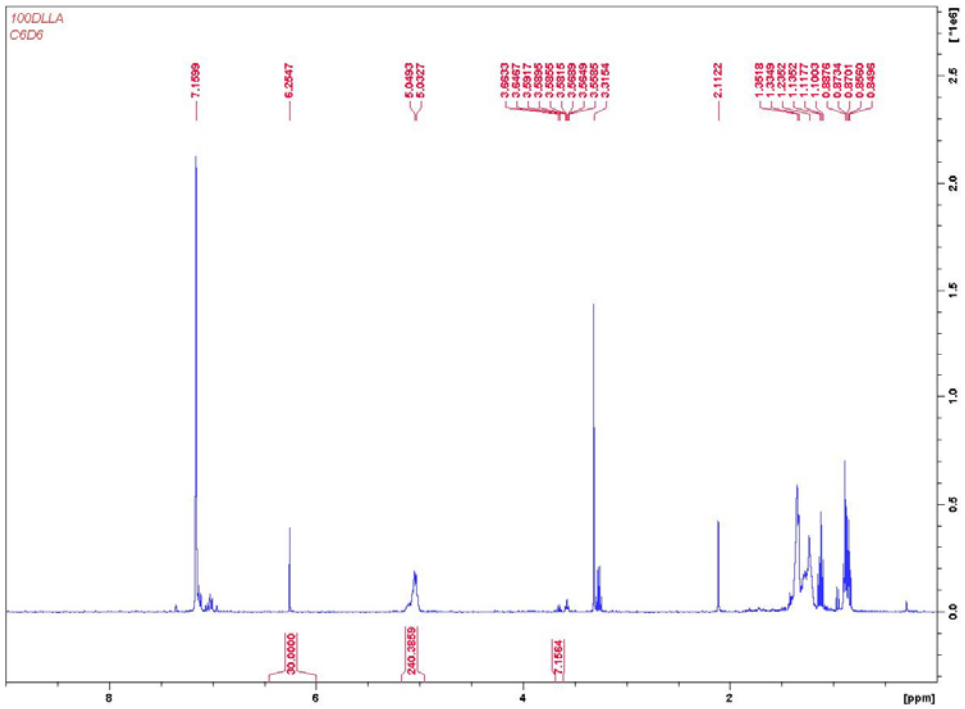


Figure S10. ^{1}H NMR (400 MHz, 25 °C, C_6D_6) spectrum of D,L-lactide polymerization. Standard is 1,3,5-trimethoxybenzene (TMB). Initiator: TMB: D,L-lactide ratio is 1:10:100. δ (ppm): 6.25 (s, 3H, Ph*H* TMB), 5.04 (m, 2H, C*H*CH$_3$ PLA), 3.60 (q, 2H, C*H*CH$_3$ D,L-lactide), 3.32 (s, 9H, C*H*$_3$ TMB), 1.34 (m, 6H, CHC*H*$_3$ PLA), 1.14 (d, 6H, CHC*H*$_3$ D,L-lactide).

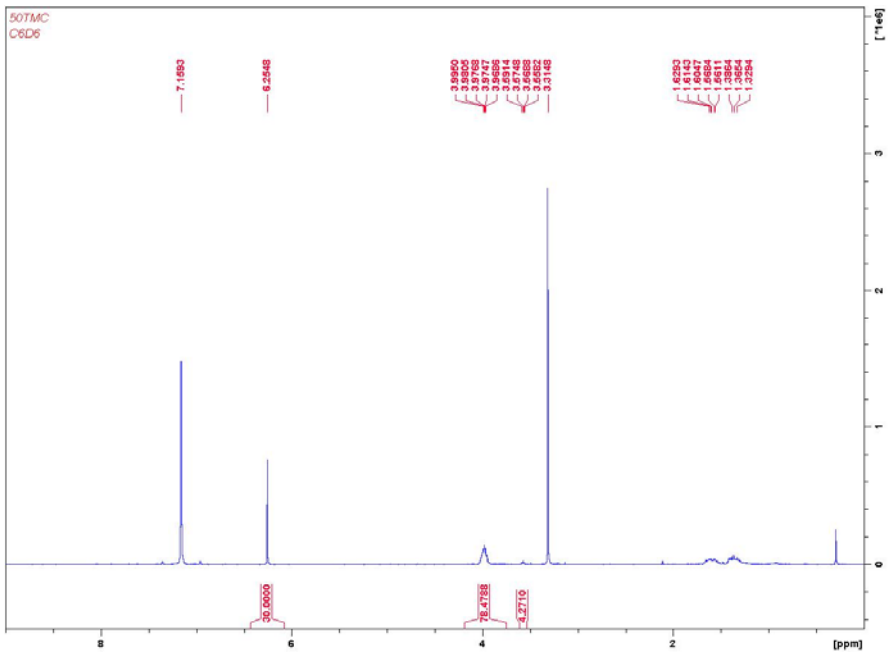


Figure S11. ^{1}H NMR (400 MHz, 25 °C, C_6D_6) spectrum of trimethylene carbonate (TMC) polymerization. Standard is 1,3,5-trimethoxybenzene (TMB). Initiator: TMB: TMC ratio is 1:10:50. δ (ppm): 6.25 (s, 3H, Ph*H* TMB), 3.98 (m, 4H, C*H*$_2$ PTMC), 3.57 (m, 4H, C*H*$_2$ TMC), 3.32 (s, 9H, C*H*$_3$ TMB), 1.34 (m, 2H, C*H*$_2$ PTMC), 1.14 (m, 2H, C*H*$_2$ TMC). *Note*: Aliquots were difficult to extract from the heterogeneous mixture of solid polymer and polymerization solution.

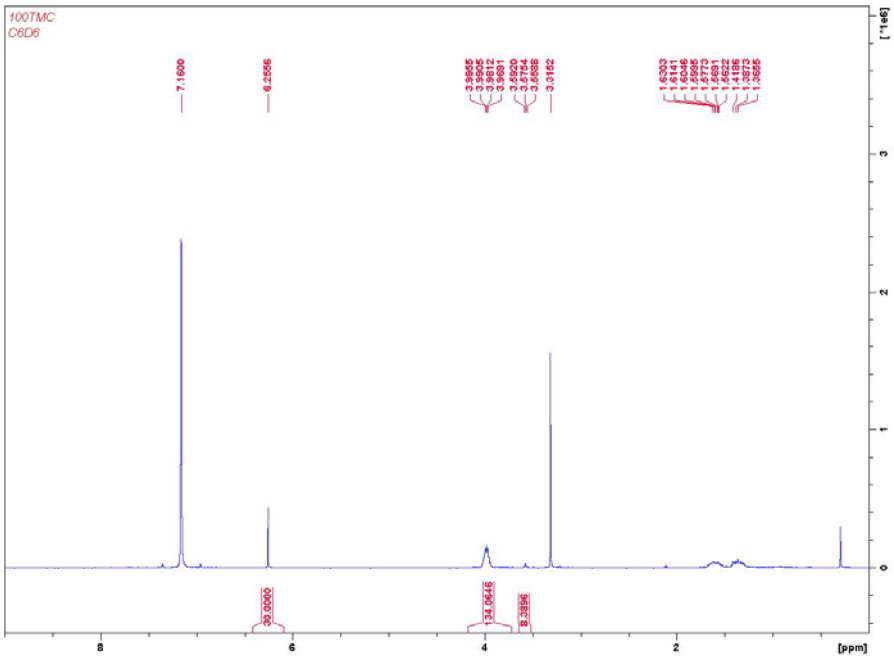


Figure S12. ^{1}H NMR (400 MHz, 25 °C, C_6D_6) spectrum of trimethylene carbonate (TMC) polymerization. Standard is 1,3,5-trimethoxybenzene (TMB). Initiator: TMB: TMC ratio is 1:10:100. δ (ppm): 6.25 (s, 3H, Ph*H* TMB), 3.98 (m, 4H, C*H*$_2$ PTMC), 3.57 (m, 4H, C*H*$_2$ TMC), 3.32 (s, 9H, C*H*$_3$ TMB), 1.34 (m, 2H, C*H*$_2$ PTMC), 1.14 (m, 2H, C*H*$_2$ TMC). Aliquots were difficult to extract from the heterogeneous mixture of solid polymer and polymerization solution.

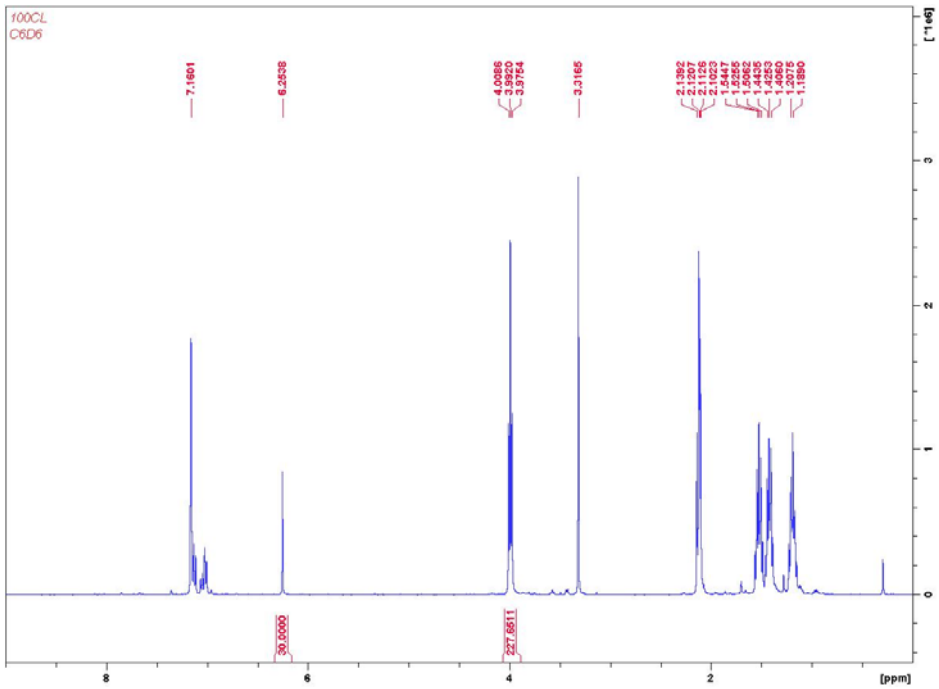


Figure S13. ^{1}H NMR (400 MHz, 25 °C, C_6D_6) spectrum of ε -caprolactone (CL) polymerization. Standard is 1,3,5-trimethoxybenzene (TMB). Initiator: TMB: CL ratio is 1:10:100. δ (ppm): 6.25 (s, 3H, Ph*H* TMB), 3.99 (t, 2H, OC*H*$_2$ PCL), 3.32 (s, 9H, C*H*$_3$ TMB), 2.12 (t, 2H, COC*H*$_2$, PCL), 1.53 (q, 2H, C*H*$_2$ PCL), 1.43 (q, 2H, C*H*$_2$ PCL), 1.19 (q, 2H, C*H*$_2$ PCL).

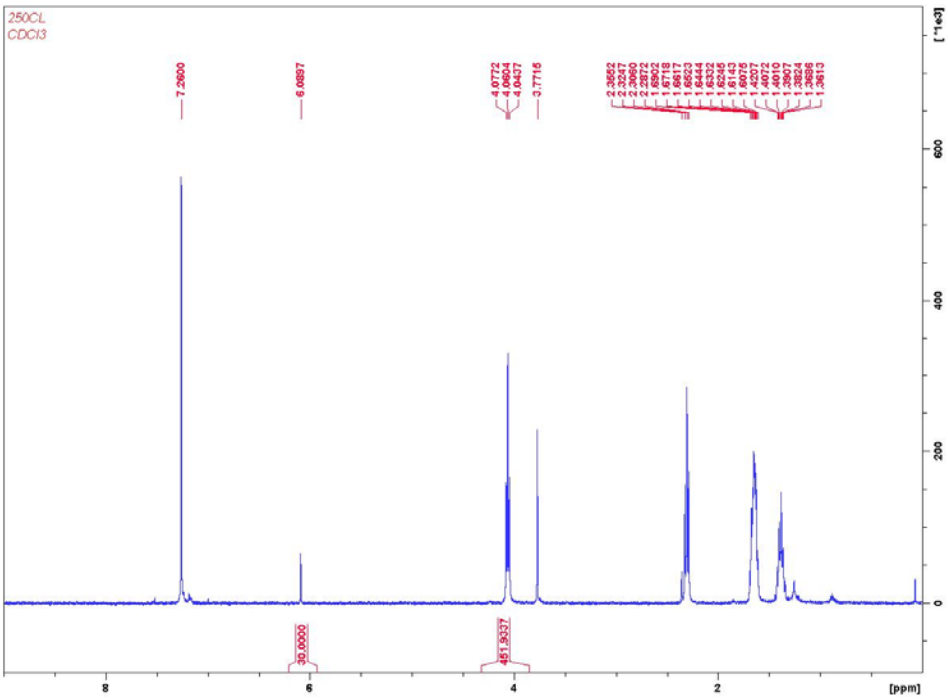


Figure S14. ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$) spectrum of ε -caprolactone (CL) polymerization. Standard is 1,3,5-trimethoxybenzene (TMB). Initiator: TMB: CL ratio is 1:10:250. δ (ppm): 6.09 (s, 3H, Ph*H* TMB), 4.06 (t, 2H, OC*H*$_2$ PCL), 3.77 (s, 9H, C*H*$_3$ TMB), 2.31 (t, 2H, COC*H*$_2$, PCL), 1.65 (m, 4H, C*H*$_2$CH$_2$C*H*$_2$ PCL), 1.39 (q, 2H, CH$_2$C*H*$_2$CH$_2$ PCL).

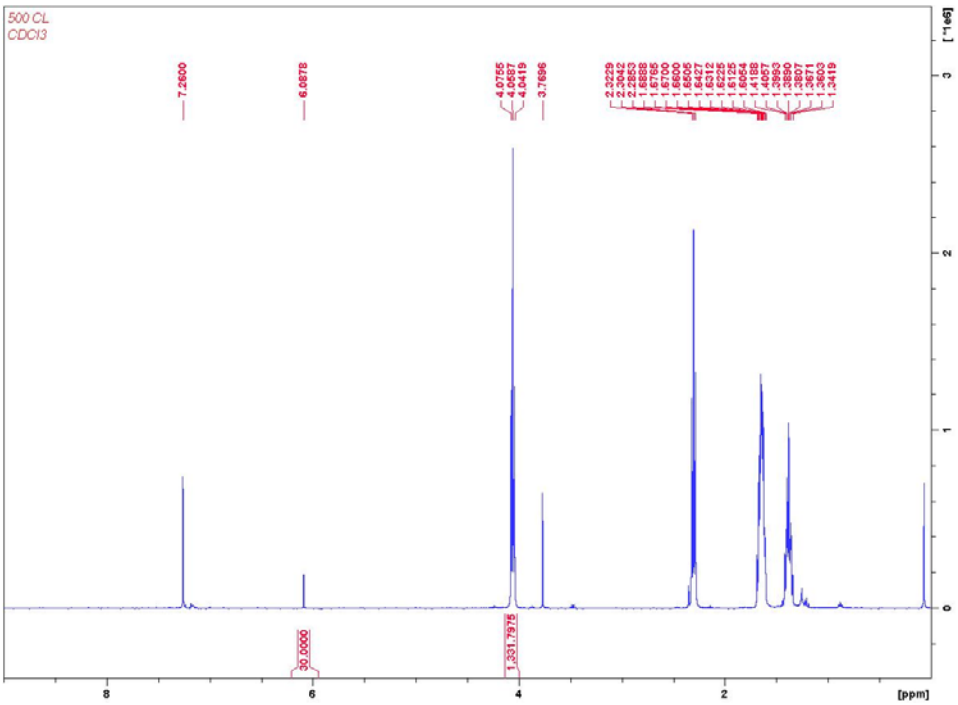


Figure S15. ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$) spectrum of ε -caprolactone (CL) polymerization. Standard is 1,3,5-trimethoxybenzene (TMB). Initiator: TMB: CL ratio is 1:10:500. δ (ppm): 6.09 (s, 3H, Ph*H* TMB), 4.06 (t, 2H, OCH_2 PCL), 3.77 (s, 9H, CH_3 TMB), 2.31 (t, 2H, COCH_2 PCL), 1.65 (m, 4H, CH_2CH$_2$CH_2 PCL), 1.39 (q, 2H, CH$_2$CH_2CH$_2$ PCL).

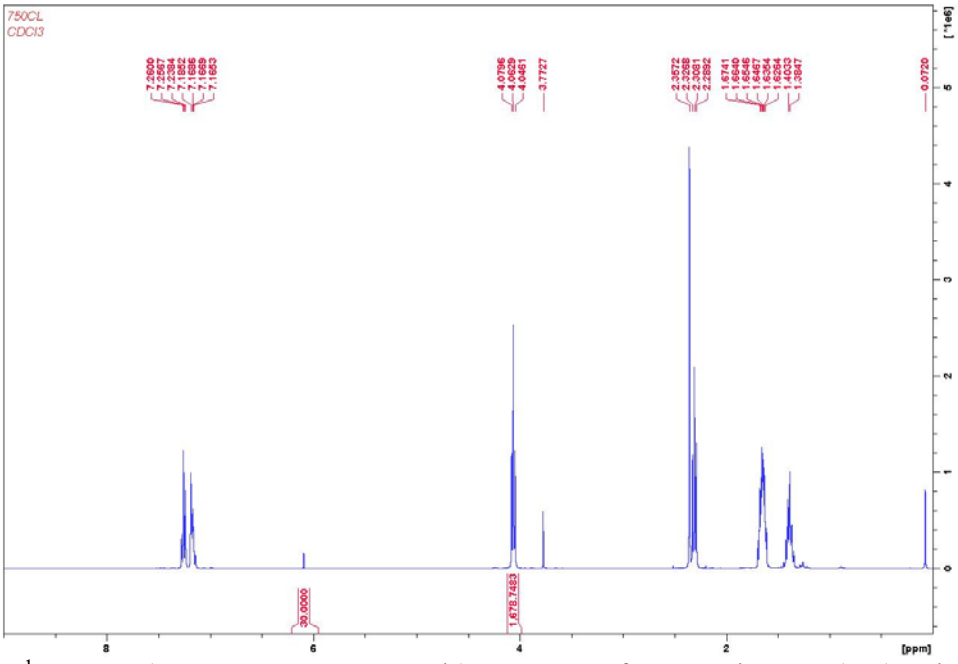


Figure S16. ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$) spectrum of ε -caprolactone (CL) polymerization. Standard is 1,3,5-trimethoxybenzene (TMB). Initiator: TMB: CL ratio is 1:10:750. δ (ppm): 6.09 (s, 3H, Ph*H* TMB), 4.06 (t, 2H, OCH_2 PCL), 3.77 (s, 9H, CH_3 TMB), 2.31 (t, 2H, COCH_2, PCL), 1.65 (m, 4H, CH_2CH$_2$CH_2 PCL), 1.39 (q, 2H, CH$_2$CH_2CH$_2$ PCL).

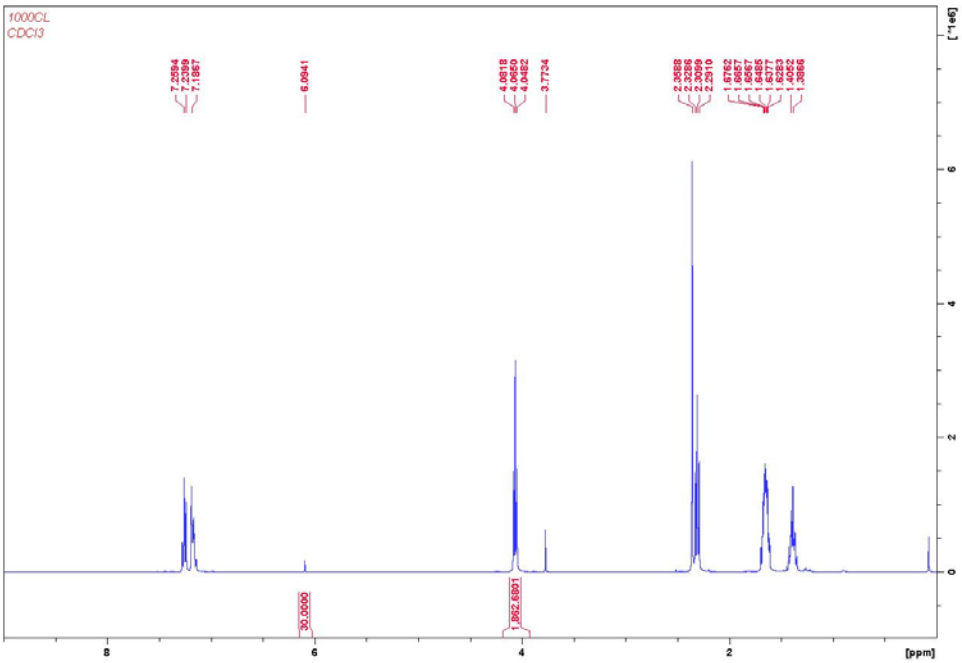


Figure S17. ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$) spectrum of ε -caprolactone (CL) polymerization. Standard is 1,3,5-trimethoxybenzene (TMB). Initiator: TMB: CL ratio is 1:10:1000. δ (ppm): 6.09 (s, 3H, Ph*H* TMB), 4.06 (t, 2H, OCH_2 PCL), 3.77 (s, 9H, CH_3 TMB), 2.31 (t, 2H, COCH_2, PCL), 1.65 (m, 4H, CH_2CH$_2$CH_2 PCL), 1.39 (q, 2H, CH$_2$CH_2CH$_2$ PCL).

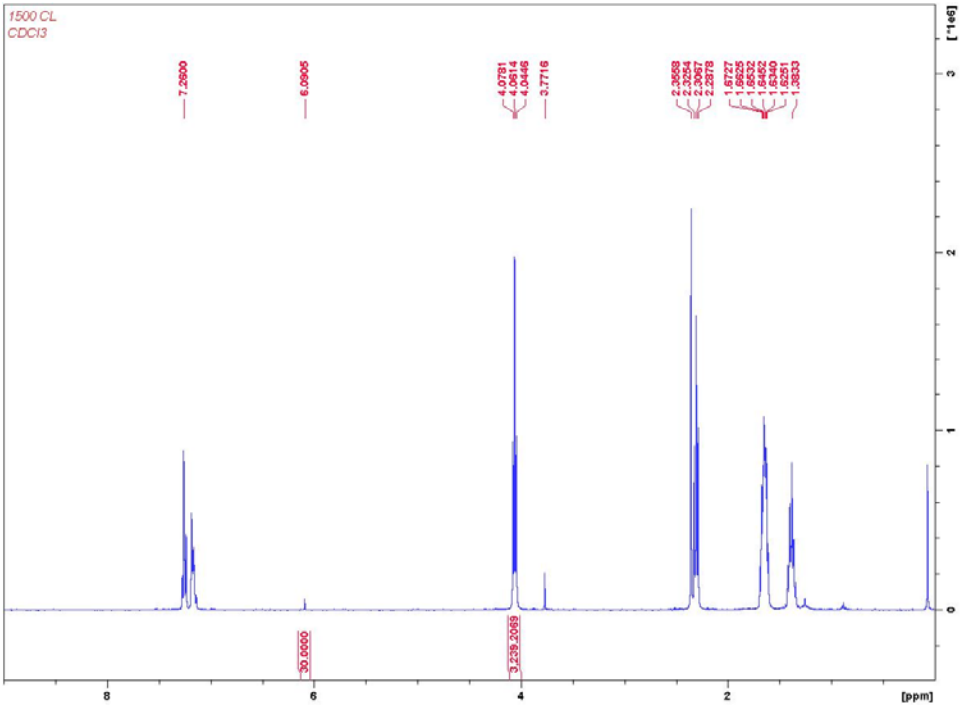


Figure S18. ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$) spectrum of ε -caprolactone (CL) polymerization. Standard is 1,3,5-trimethoxybenzene (TMB). Initiator: TMB: CL ratio is 1:10:1500. δ (ppm): 6.09 (s, 3H, Ph*H* TMB), 4.06 (t, 2H, OCH_2 PCL), 3.77 (s, 9H, CH_3 TMB), 2.31 (t, 2H, COCH_2, PCL), 1.65 (m, 4H, CH_2CH$_2$CH_2 PCL), 1.39 (q, 2H, CH$_2$CH_2CH$_2$ PCL).

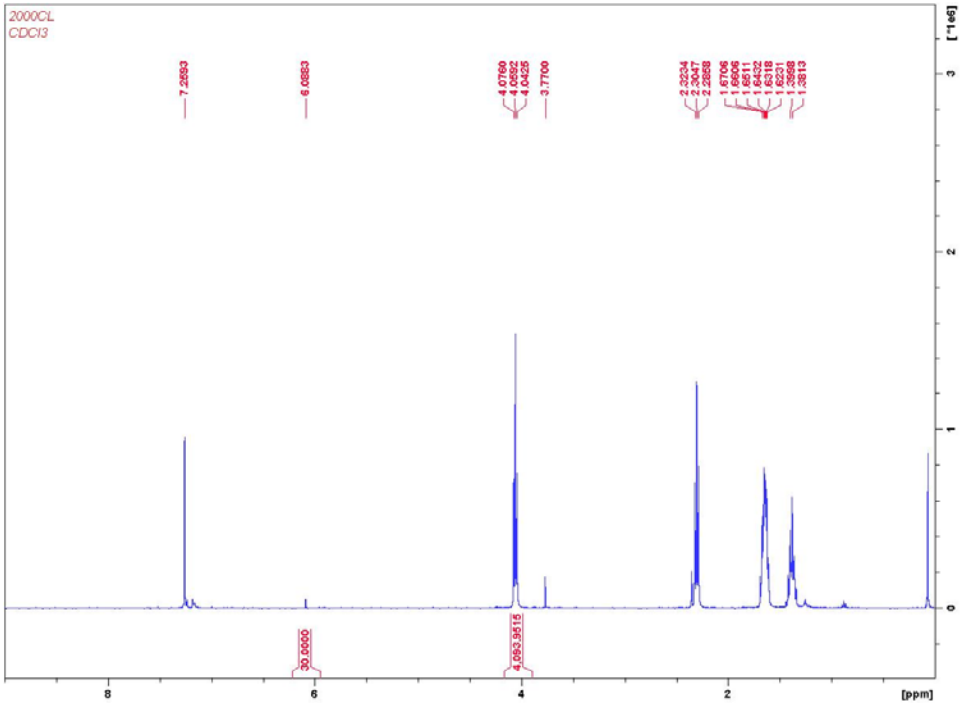


Figure S19. ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$) spectrum of ε-caprolactone (CL) polymerization. Standard is 1,3,5-trimethoxybenzene (TMB). Initiator: TMB: CL ratio is 1:10:2000. δ (ppm): 6.09 (s, 3H, Ph*H* TMB), 4.06 (t, 2H, OCH_2 PCL), 3.77 (s, 9H, CH_3 TMB), 2.31 (t, 2H, COCH_2 PCL), 1.65 (m, 4H, CH_2CH$_2$CH_2 PCL), 1.39 (q, 2H, CH$_2$CH_2CH$_2$ PCL).

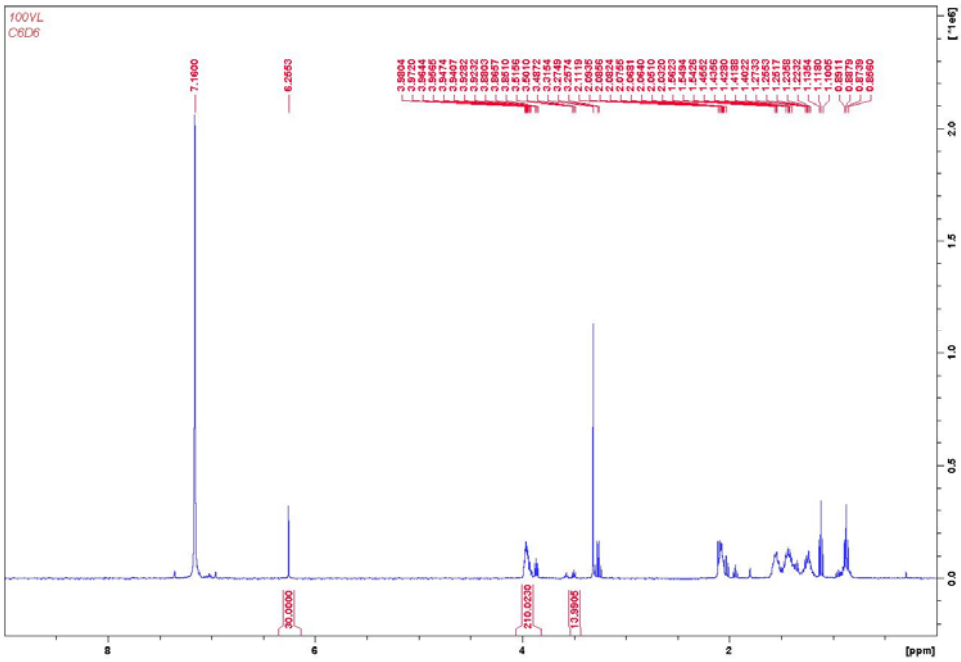


Figure S20. ^{1}H NMR (400 MHz, 25 °C, C_6D_6) spectrum of δ-valerolactone (VL) polymerization. Standard is 1,3,5-trimethoxybenzene (TMB). Initiator: TMB: VL ratio is 1:10:100. δ (ppm): 6.26 (s, 3H, Ph*H* TMB), 3.96 (m, 2H, OCH_2 PVL), 3.50 (t, 2H, OCH_2 VL), 3.32 (s, 9H, CH_3 TMB), 2.08 (m, 2H, COCH_2, PVL), 1.55 (m, 2H, CH_2 PVL), 1.43 (m, 2H, CH_2 PVL), 1.23 (m, 2H, CH_2 PVL).

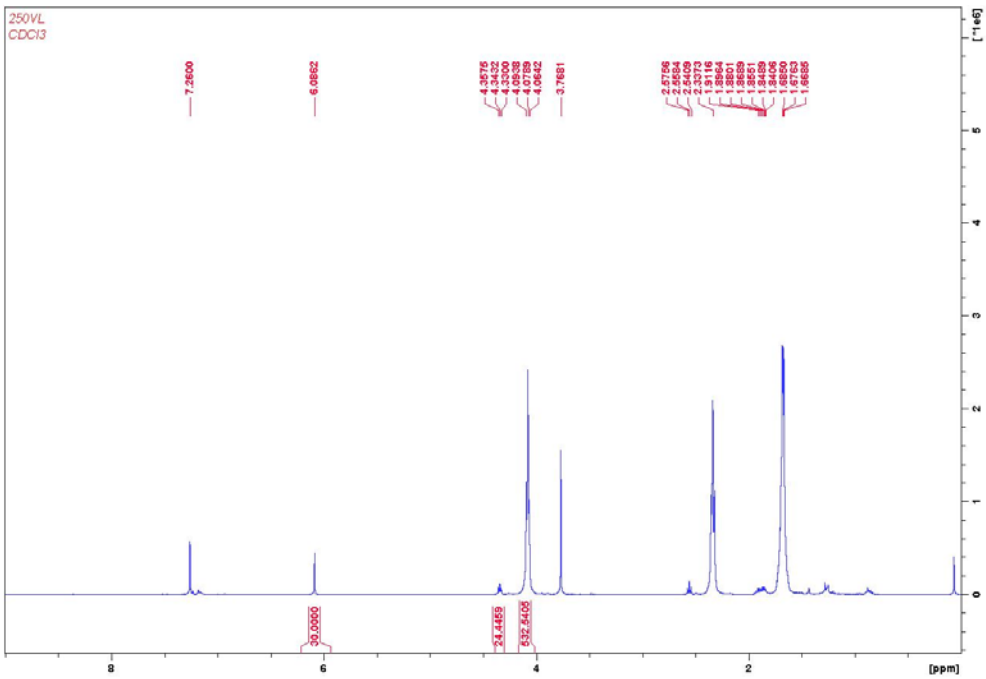


Figure S21. ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$) spectrum of δ-valerolactone (VL) polymerization. Standard is 1,3,5-trimethoxybenzene (TMB). Initiator: TMB: VL ratio is 1:10:250. δ (ppm): 6.09 (s, 3H, Ph*H* TMB), 4.34 (t, 2H, OC*H*$_2$ VL), 4.07 (t, 2H, OC*H*$_2$ PVL), 3.77 (s, 9H, C*H*$_3$ TMB), 2.56 (t, 2H, COC*H*$_2$, VL), 2.34 (t, 2H, COC*H*$_2$, PVL), 1.88 (m, 4H, C*H*$_2$ VL), 1.67 (m, 4H, C*H*$_2$ PVL).

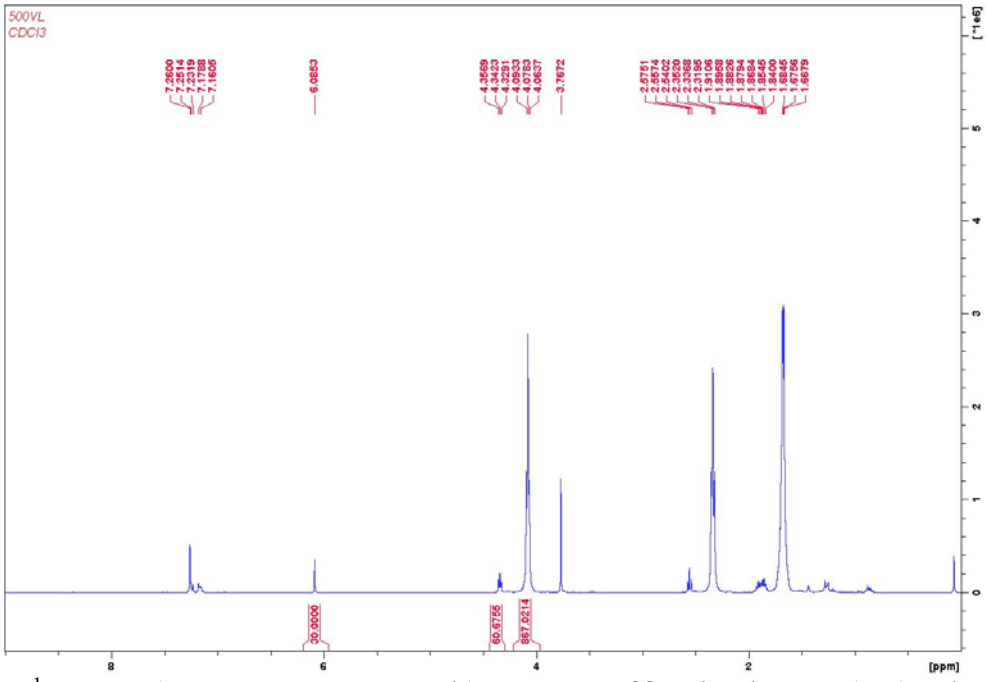


Figure S22. ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$) spectrum of δ-valerolactone (VL) polymerization. Standard is 1,3,5-trimethoxybenzene (TMB). Initiator: TMB: VL ratio is 1:10:500. δ (ppm): 6.09 (s, 3H, Ph*H* TMB), 4.34 (t, 2H, OC*H*$_2$ VL), 4.07 (t, 2H, OC*H*$_2$ PVL), 3.77 (s, 9H, C*H*$_3$ TMB), 2.56 (t, 2H, COC*H*$_2$, VL), 2.34 (t, 2H, COC*H*$_2$, PVL), 1.88 (m, 4H, C*H*$_2$ VL), 1.67 (m, 4H, C*H*$_2$ PVL).

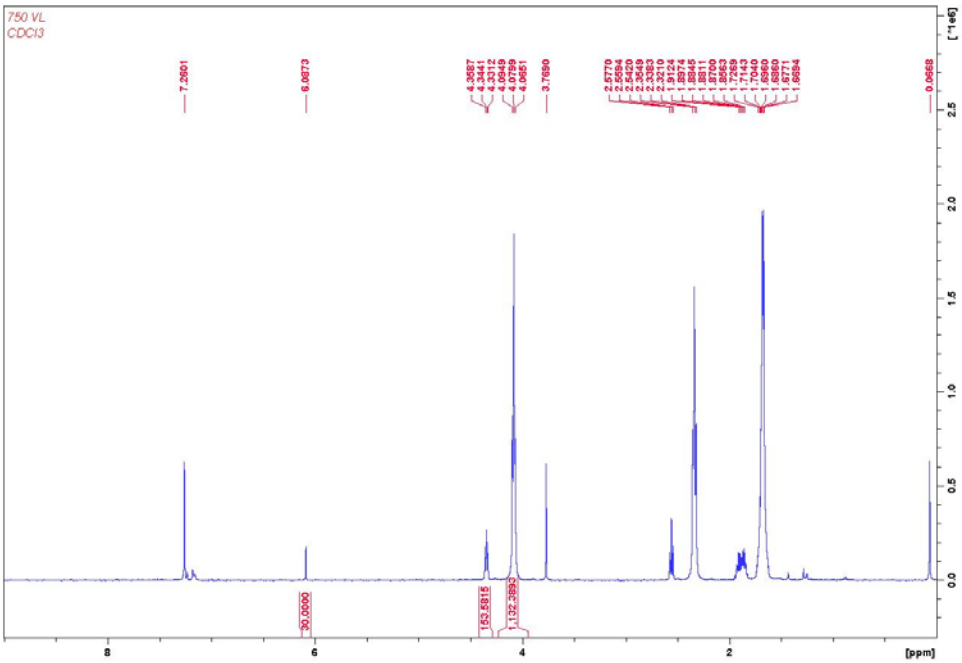


Figure S23. ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$) spectrum of δ-valerolactone (VL) polymerization. Standard is 1,3,5-trimethoxybenzene (TMB). Initiator: TMB: VL ratio is 1:10:750. δ (ppm): 6.09 (s, 3H, Ph*H* TMB), 4.34 (t, 2H, OC*H*$_2$ VL), 4.07 (t, 2H, OC*H*$_2$ PVL), 3.77 (s, 9H, C*H*$_3$ TMB), 2.56 (t, 2H, COC*H*$_2$, VL), 2.34 (t, 2H, COC*H*$_2$, PVL), 1.88 (m, 4H, C*H*$_2$ VL), 1.67 (m, 4H, C*H*$_2$ PVL).

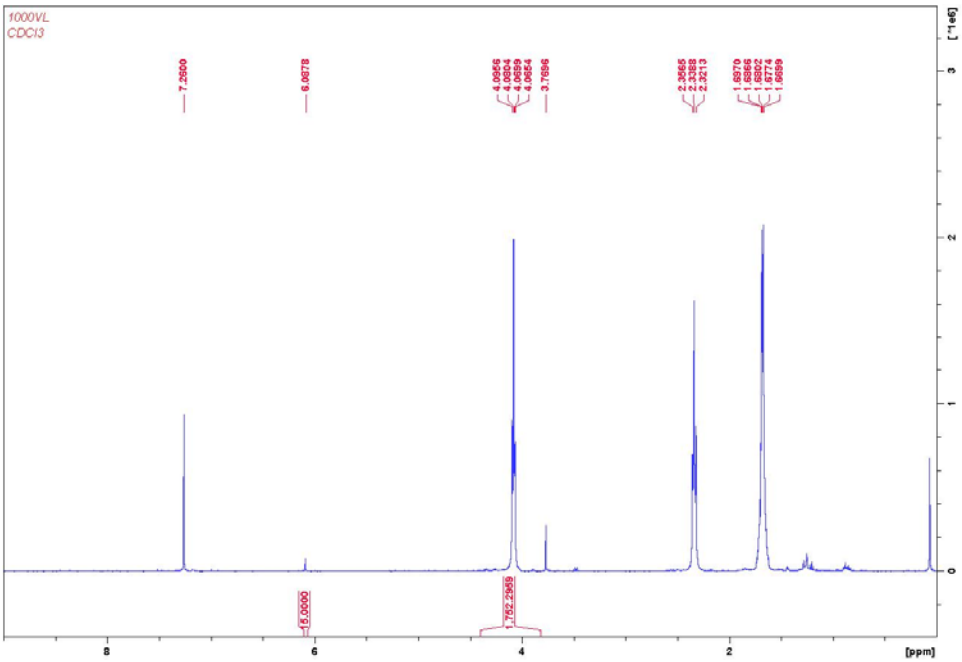


Figure S24. ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$) spectrum of δ-valerolactone (VL) polymerization. Standard is 1,3,5-trimethoxybenzene (TMB). Initiator: TMB: VL ratio is 1:10:1000. δ (ppm): 6.09 (s, 3H, Ph*H* TMB), 4.34 (t, 2H, OC*H*$_2$ VL), 4.07 (t, 2H, OC*H*$_2$ PVL), 3.77 (s, 9H, C*H*$_3$ TMB), 2.56 (t, 2H, COC*H*$_2$, VL), 2.34 (t, 2H, COC*H*$_2$, PVL), 1.88 (m, 4H, C*H*$_2$ VL), 1.67 (m, 4H, C*H*$_2$ PVL).

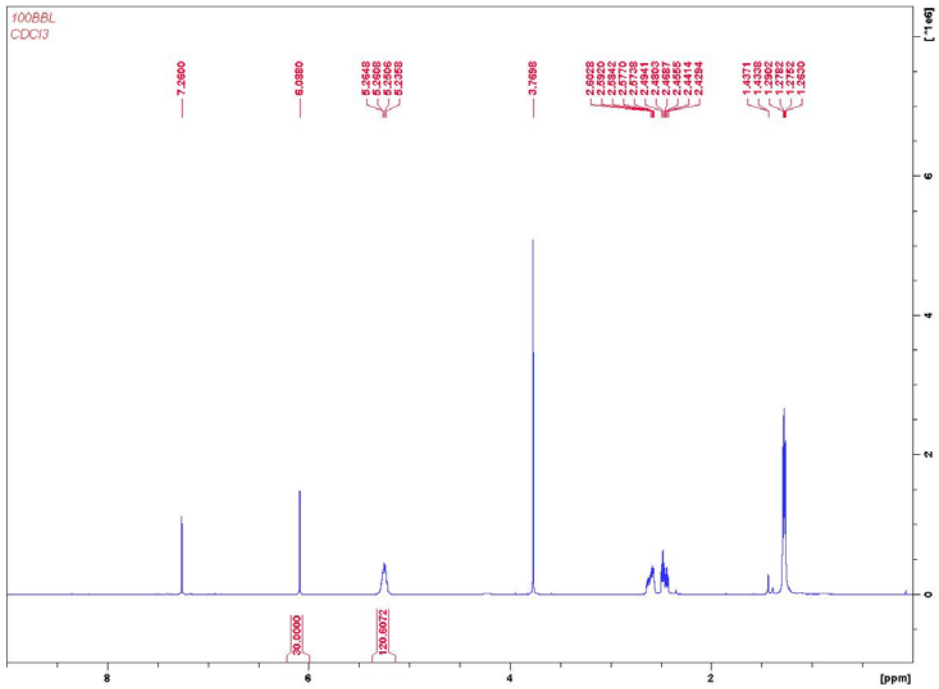


Figure S25. ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$) spectrum of β-butyrolactone (BBL) polymerization. Standard is 1,3,5-trimethoxybenzene (TMB). Initiator: TMB: BBL ratio is 1:10:100. δ (ppm): 6.09 (s, 3H, Ph*H* TMB), 5.26 (m, 1H, OC*H*CH_3 PHB), 3.77 (s, 9H, CH_3 TMB), 2.53 (m, 2H, COCH_2 PHB), 1.28 (t, 3H, OCHCH_3 PHB).

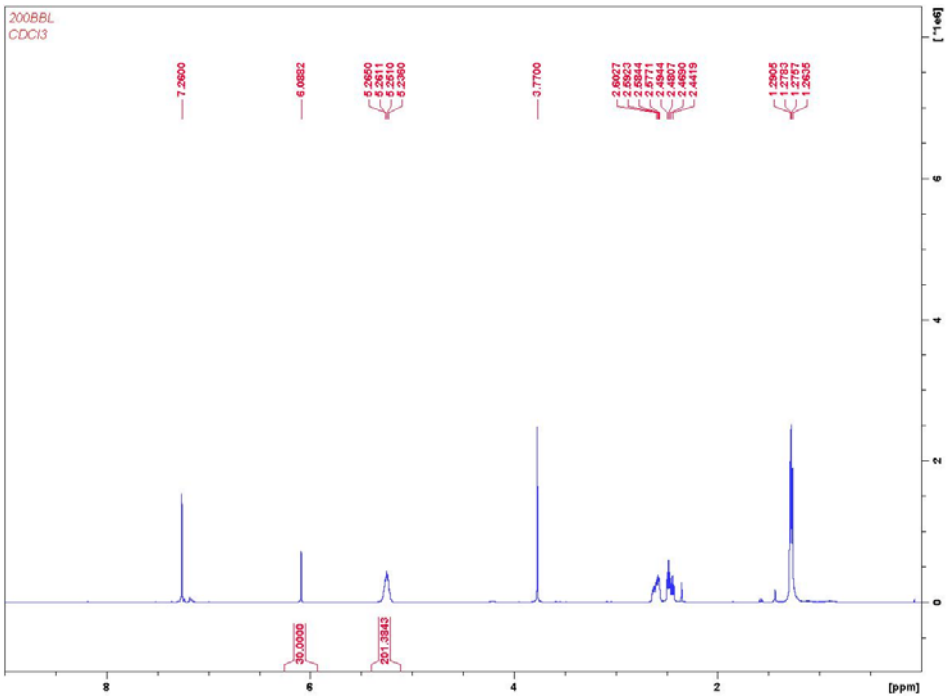


Figure S26. ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$) spectrum of β-butyrolactone (BBL) polymerization. Standard is 1,3,5-trimethoxybenzene (TMB). Initiator: TMB: BBL ratio is 1:10:200. δ (ppm): 6.09 (s, 3H, Ph*H* TMB), 5.26 (m, 1H, OC*H*CH_3 PHB), 3.77 (s, 9H, CH_3 TMB), 2.53 (m, 2H, COCH_2 PHB), 1.28 (t, 3H, OCHCH_3 PHB).

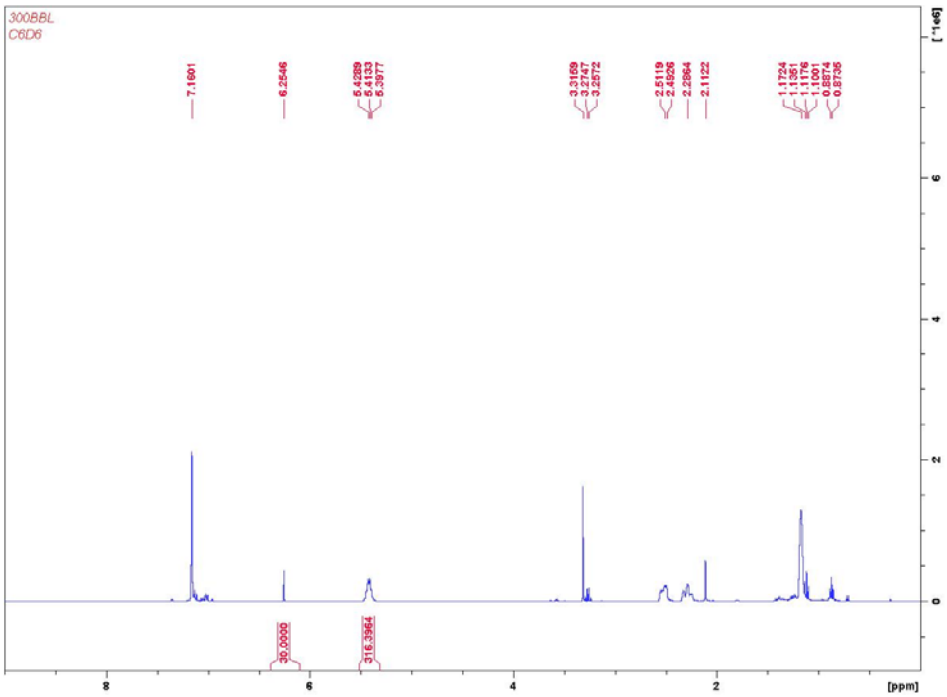


Figure S27. ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$) spectrum of β-butyrolactone (BBL) polymerization. Standard is 1,3,5-trimethoxybenzene (TMB). Initiator: TMB: BBL ratio is 1:10:300. δ (ppm): 6.09 (s, 3H, Ph*H* TMB), 5.26 (m, 1H, OC*H*CH_3 PHB), 3.77 (s, 9H, CH_3 TMB), 2.53 (m, 2H, COCH_2 PHB), 1.28 (t, 3H, OCHCH_3 PHB).

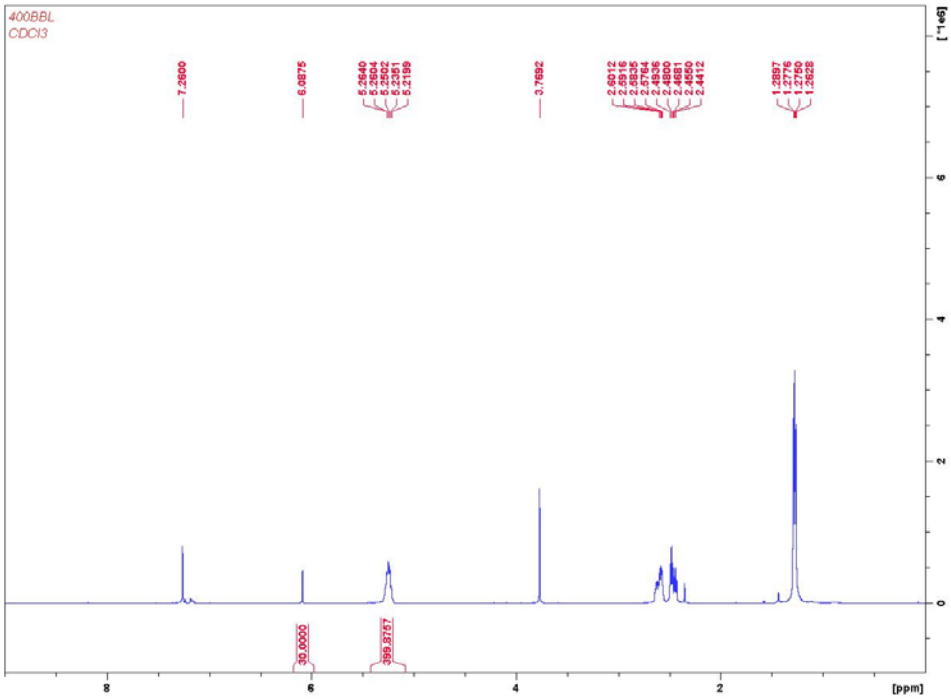


Figure S28. ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$) spectrum of β-butyrolactone (BBL) polymerization. Standard is 1,3,5-trimethoxybenzene (TMB). Initiator: TMB: BBL ratio is 1:10:400. δ (ppm): 6.09 (s, 3H, Ph*H* TMB), 5.26 (m, 1H, OC*H*CH_3 PHB), 3.77 (s, 9H, CH_3 TMB), 2.53 (m, 2H, COCH_2 PHB), 1.28 (t, 3H, OCHCH_3 PHB).

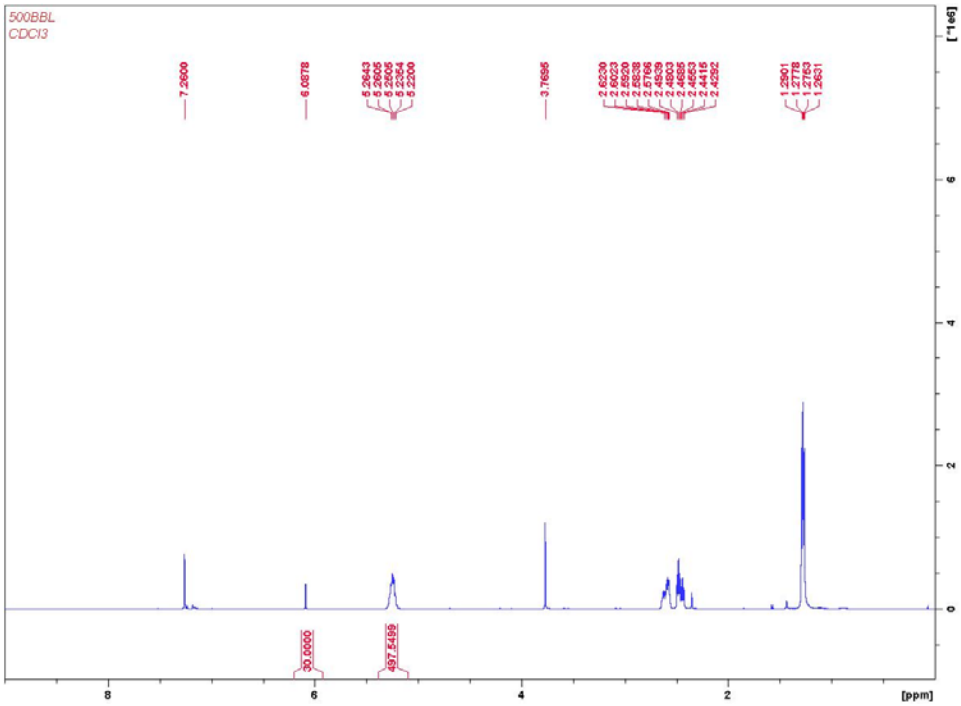


Figure S29. ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$) spectrum of β-butyrolactone (BBL) polymerization. Standard is 1,3,5-trimethoxybenzene (TMB). Initiator: TMB: BBL ratio is 1:10:500. δ (ppm): 6.09 (s, 3H, Ph*H* TMB), 5.26 (m, 1H, OC*H*CH_3 PHB), 3.77 (s, 9H, CH_3 TMB), 2.53 (m, 2H, COCH_2, PHB), 1.28 (t, 3H, OCHCH_3, PHB).

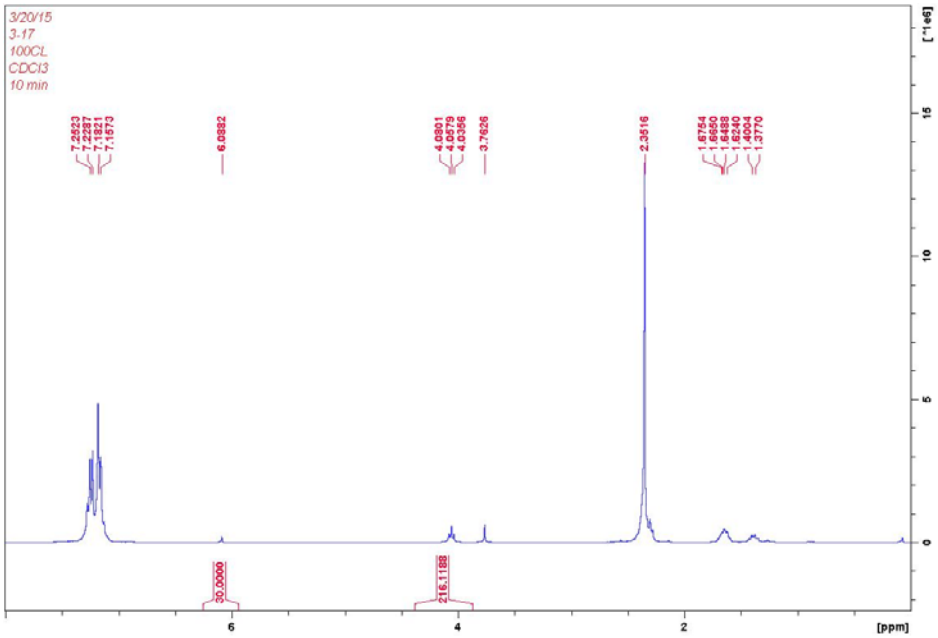


Figure S30. ^{1}H NMR (300 MHz, 0 °C, $CDCl_3$) spectrum of ε -caprolactone (CL) polymerization. Standard is 1,3,5-trimethoxybenzene (TMB). Initiator: TMB: CL ratio is 1:10:100. δ (ppm): 6.25 (s, 3H, Ph*H* TMB), 3.99 (t, 2H, OCH_2 PCL), 3.32 (s, 9H, CH_3 TMB), 2.12 (t, 2H, COCH_2, PCL), 1.53 (q, 2H, CH_2 PCL), 1.43 (q, 2H, CH_2 PCL), 1.19 (q, 2H, CH_2 PCL).

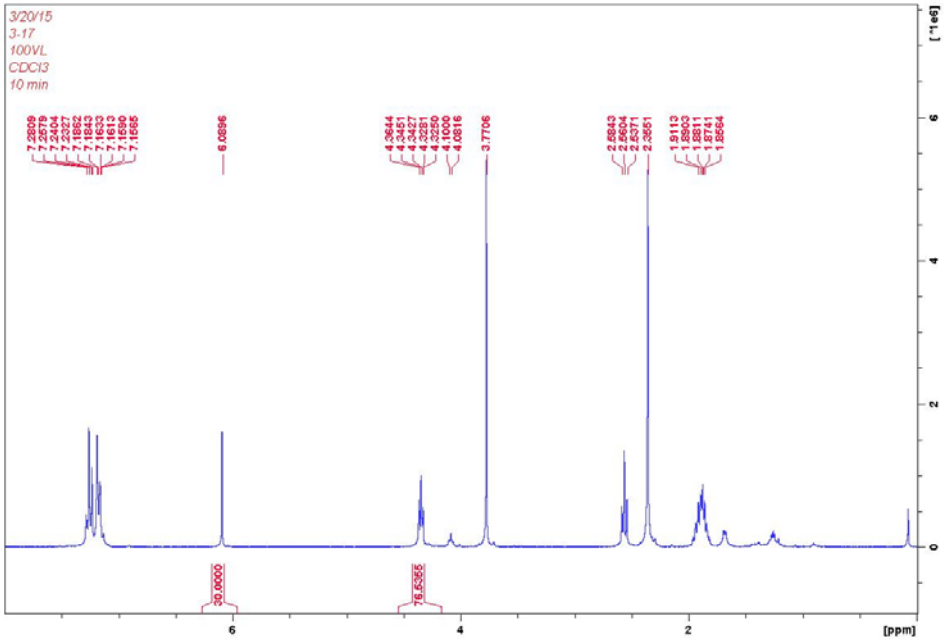


Figure S31. ^{1}H NMR (300 MHz, 0 °C, $CDCl_3$) spectrum of δ-valerolactone (VL) polymerization. Standard is 1,3,5-trimethoxybenzene (TMB). Initiator: TMB: VL ratio is 1:10:100. δ (ppm): 6.26 (s, 3H, Ph*H* TMB), 3.96 (m, 2H, OCH_2 PVL), 3.50 (t, 2H, OCH_2 VL), 3.32 (s, 9H, CH_3 TMB), 2.08 (m, 2H, COCH_2, PVL), 1.55 (m, 2H, CH_2 PVL), 1.43 (m, 2H, CH_2 PVL), 1.23 (m, 2H, CH_2 PVL). Aliquots were difficult to extract from the heterogeneous mixture of solid polymer and polymerization solution.

Cyclic Voltammetry Data

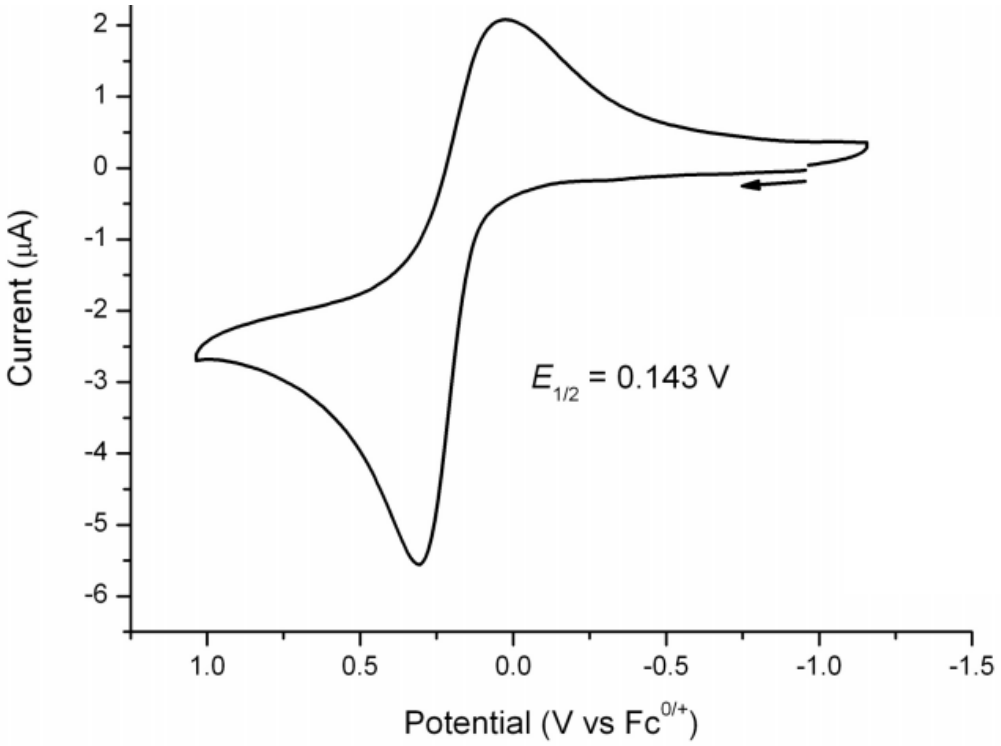


Figure S32. Cyclic voltammogram of 1.0 mM (salfen)InCl recorded with a glassy carbon electrode at 100 mV/s in THF, 0.010 M $[(C_3H_7)_4N][BAr^F{}_4]$.

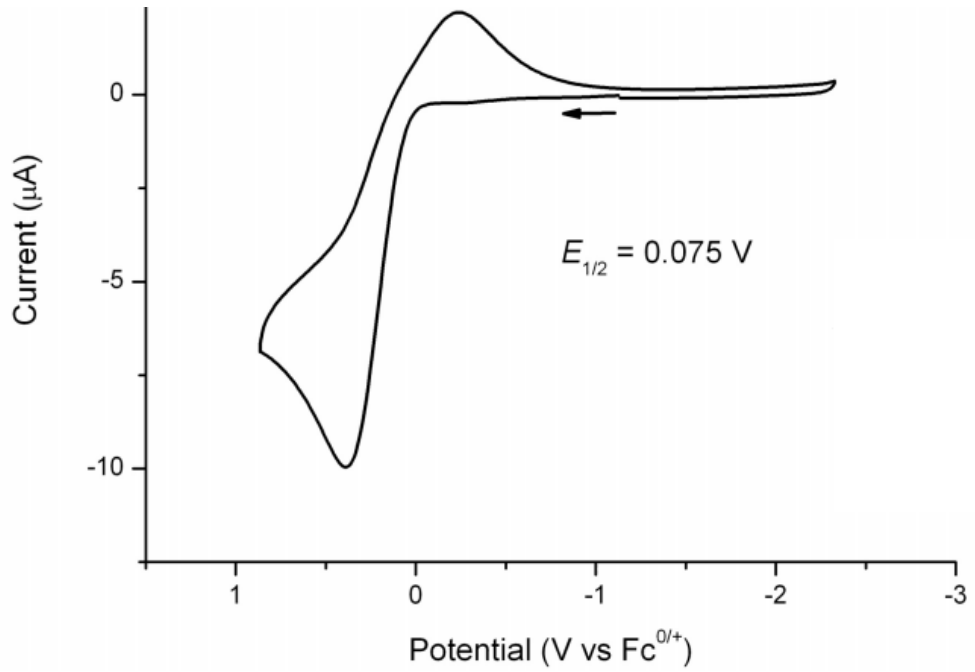


Figure S33. Cyclic voltammogram of 1.0 mM (salfen)In(O^{t}Bu) recorded with a glassy carbon electrode at 100 mV/s in THF, 0.010 M $[(C_3H_7)_4N][B[3,5\text{-}(CF_3)_2C_6H_3]_4]$.

Calculation of P_m values

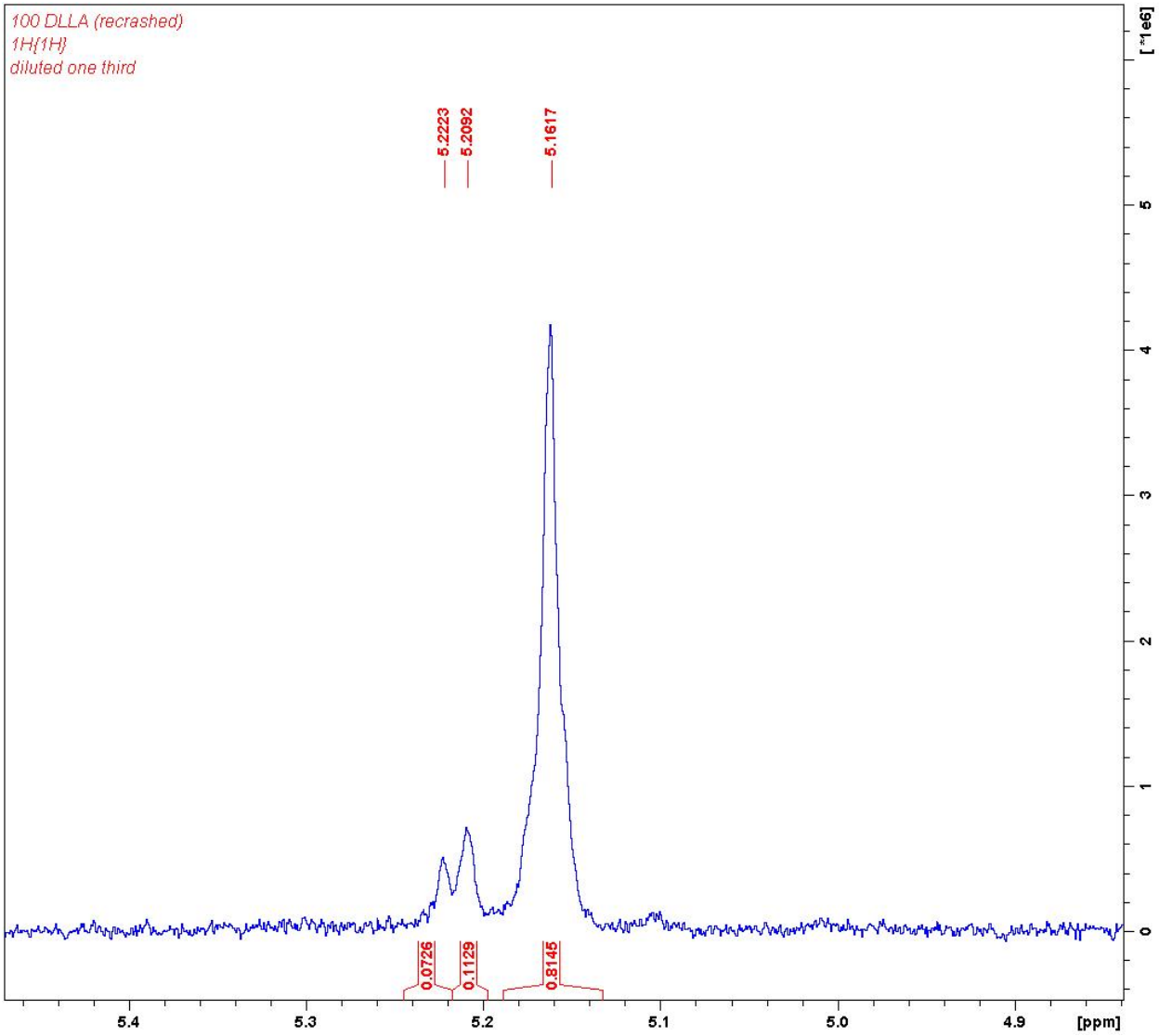


Figure S34. $^1H\{^1H\}$ NMR (500 MHz, 25 °C, C_6D_6) spectrum of PLA.

mmr/rmr = 5.22 ppm, 0.0726
rmm = 5.21 ppm, 0.1129

[rmr] = $P_r^2/2$
[mmr] = $(P_rP_m)/2$

$P_m = 0.59$
$P_r = 0.38$

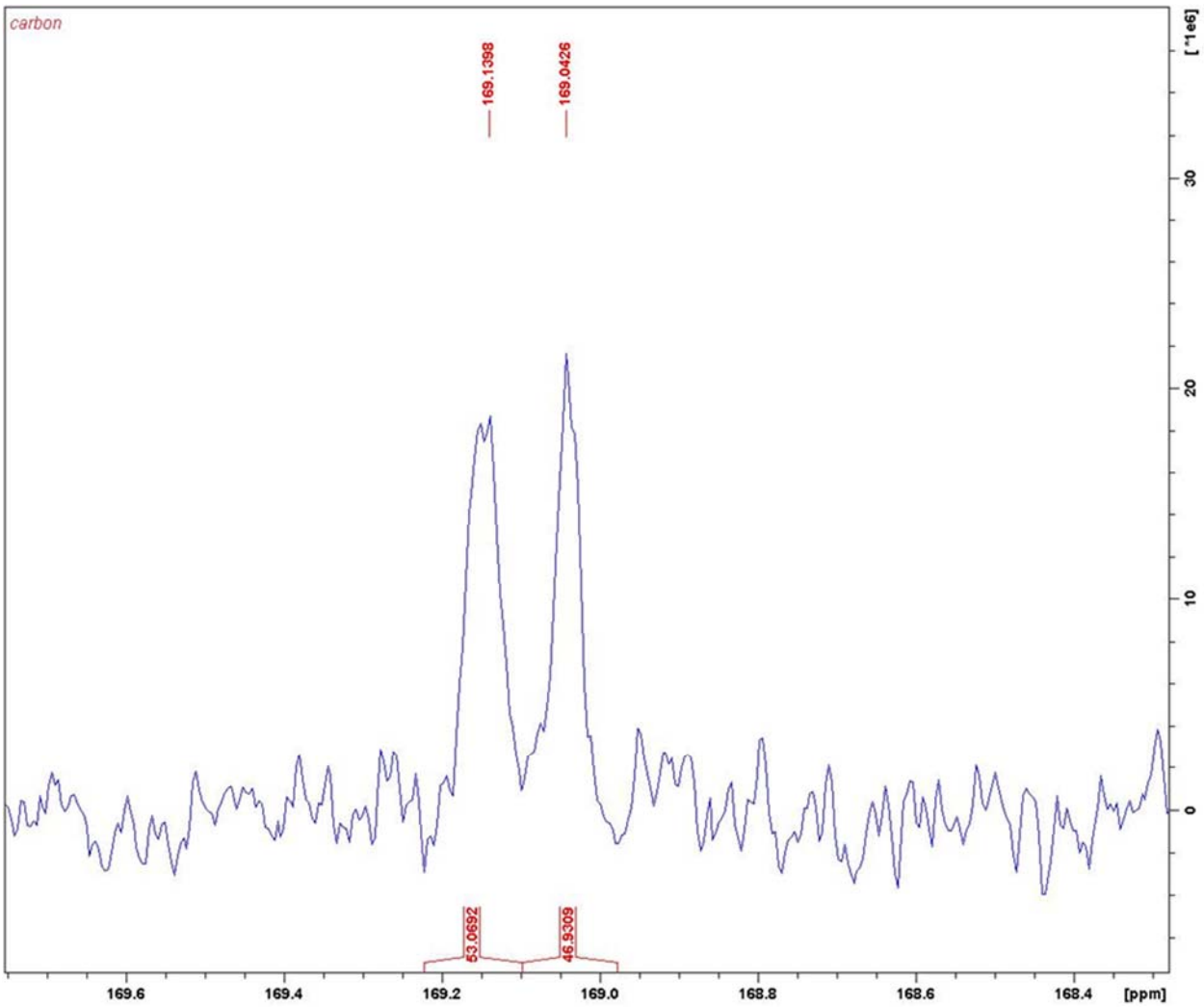


Figure S35. ^{13}C NMR (500 MHz, 25 °C, C_6D_6) spectrum of PHB.

r = 169.1 ppm, 53.1
m = 169.0 ppm, 46.9

$P_m = m/(r+m)$
$P_m = 0.47$

For more detail on methods used see reference.[4]

Kinetic Study

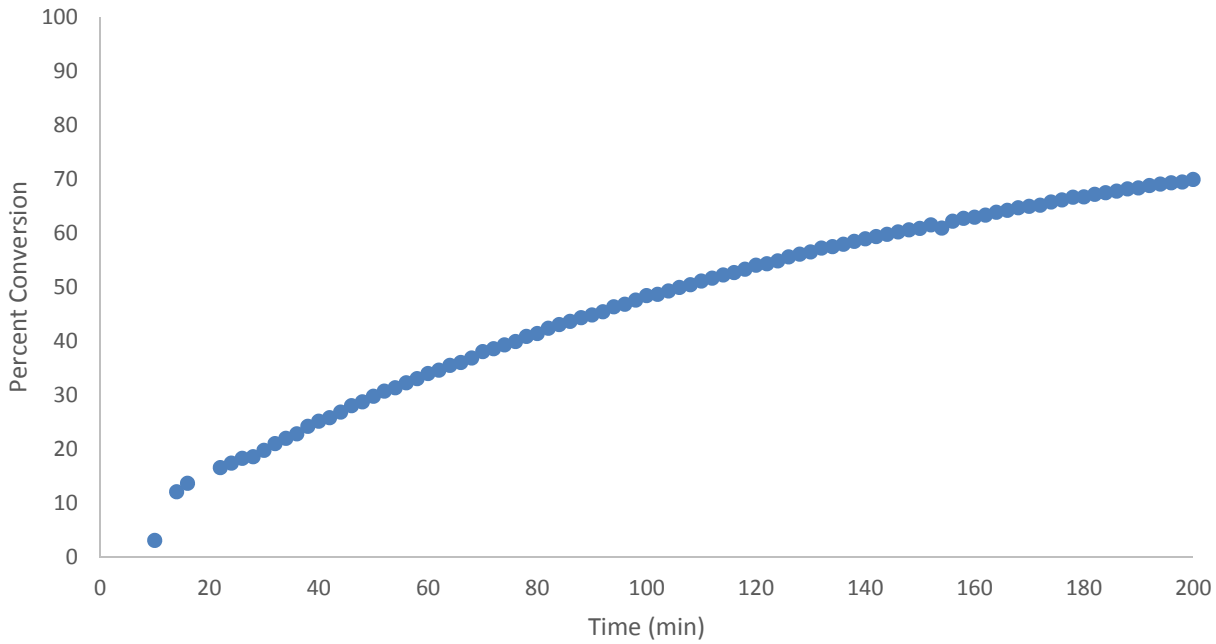


Figure S36. Polymerization of 50 equivalents of rac-lactide over 200 minutes.

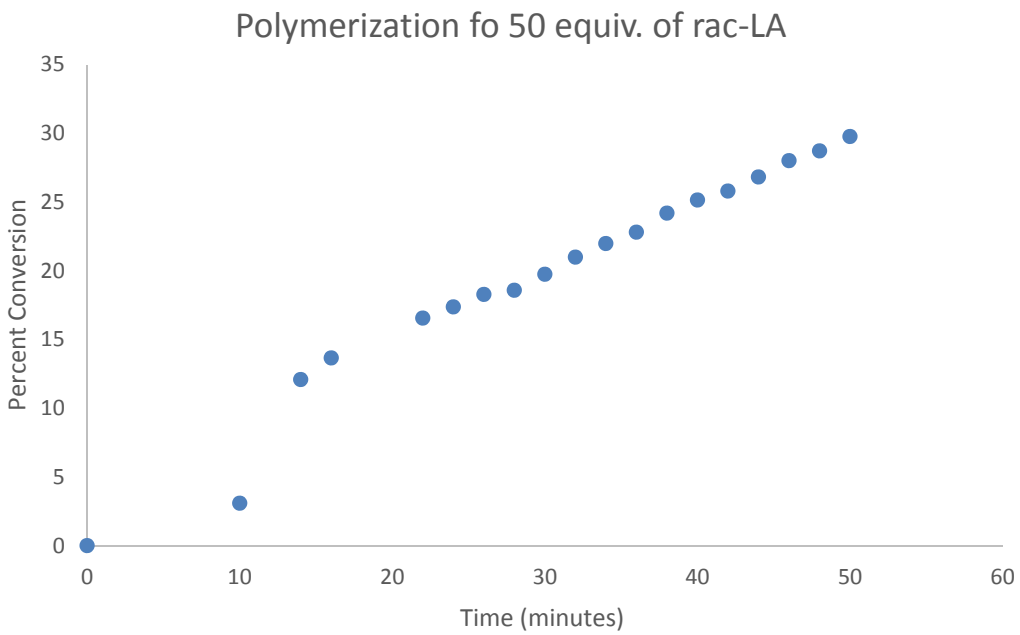


Figure S37. Polymerization of 50 equivalents of rac-lactide, first 50 minutes.

Gel Permeation Chromatography

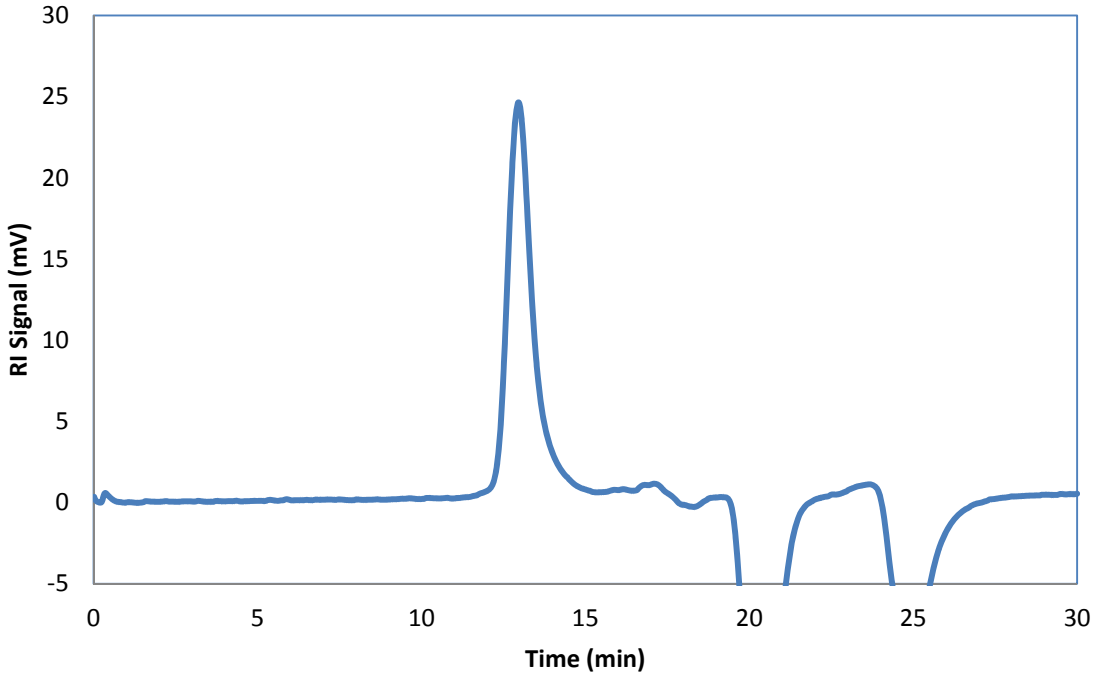


Figure S38. Polymerization of 50 equivalents of L-lactide; M_n = 15878, M_w = 18875, PDI = 1.189.

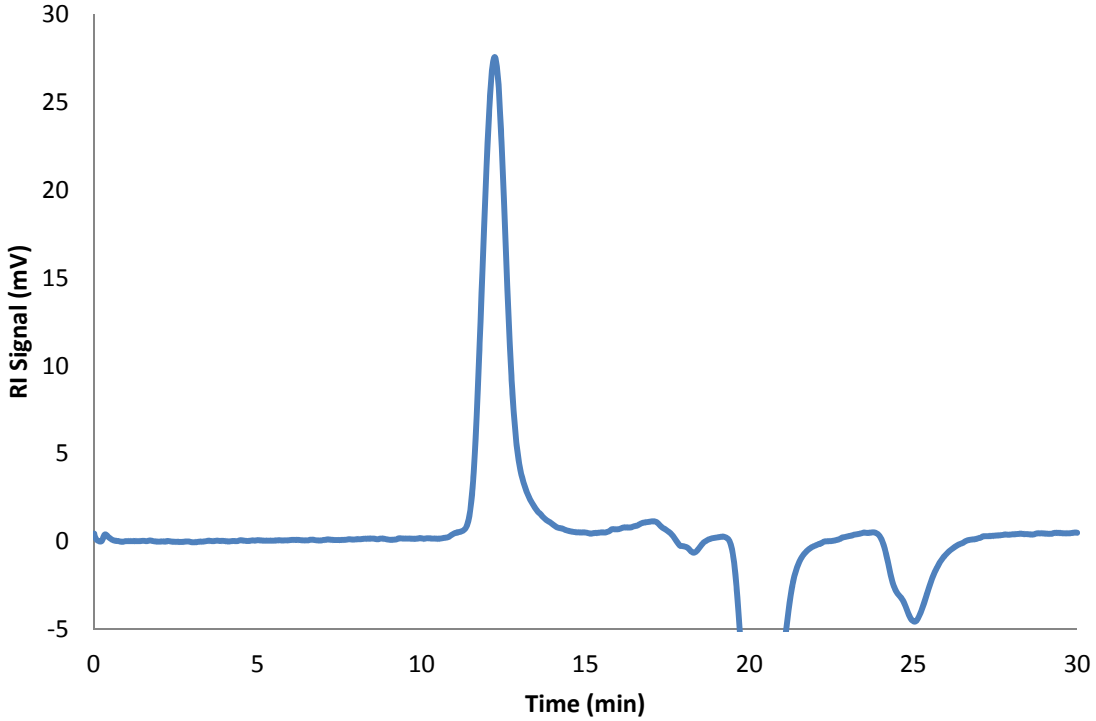


Figure S39. Polymerization of 100 equivalents of L-lactide; M_n = 32818, M_w = 38153, PDI = 1.163.

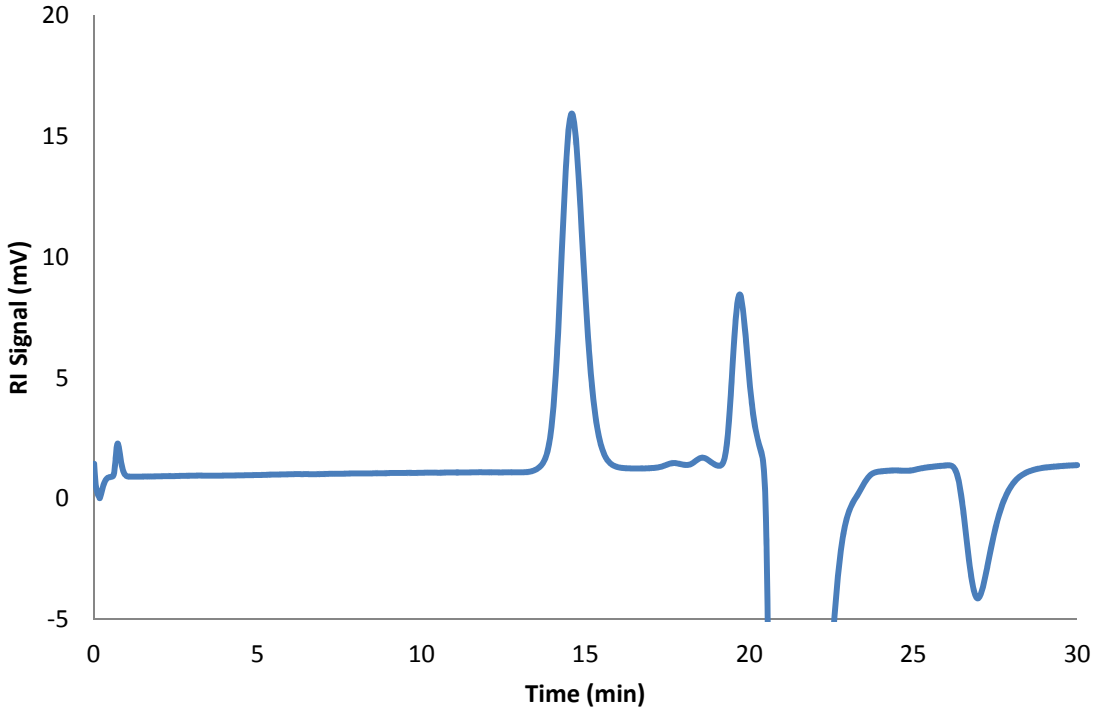


Figure S40. Polymerization of 50 equivalents of D,L-lactide; M_n = 15443, M_w = 16571, PDI = 1.073.

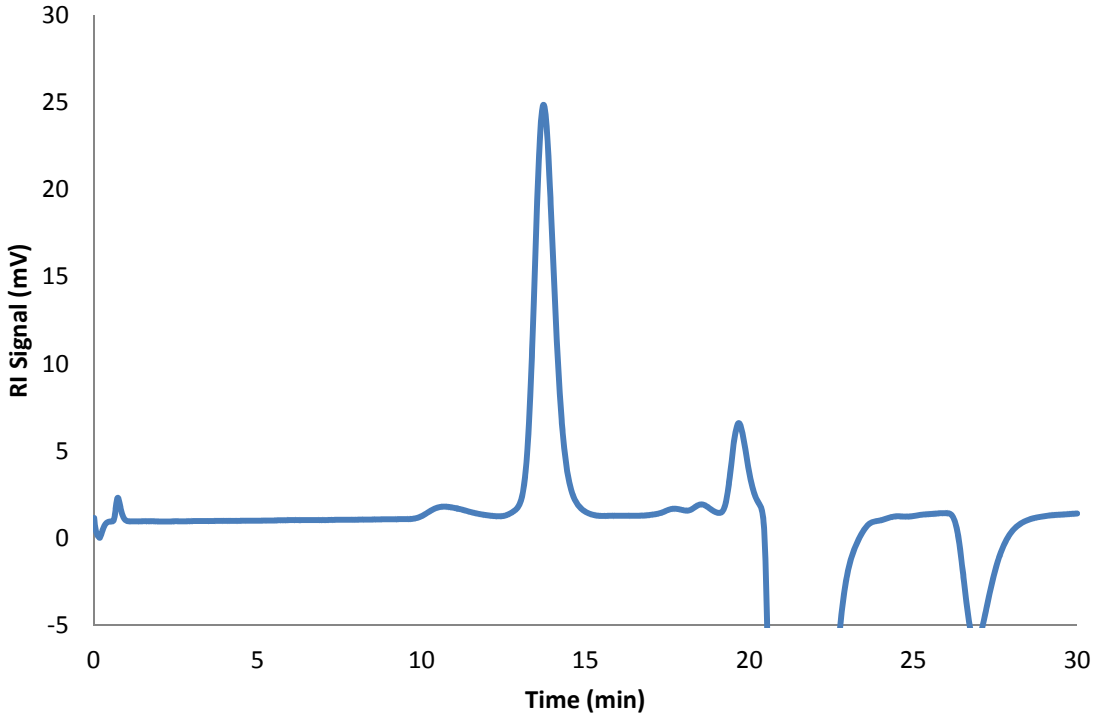


Figure S41. Polymerization of 100 equivalents of D,L-lactide; M_n = 32221, M_w = 34136, PDI = 1.059.

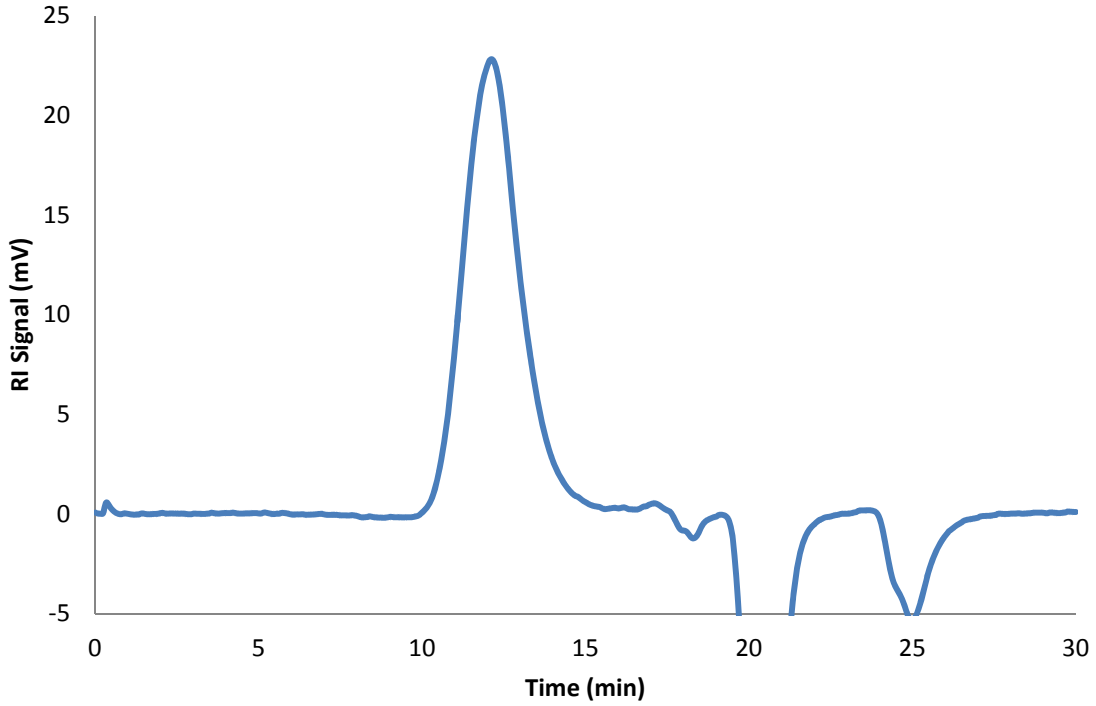


Figure S42. Polymerization of 50 equivalents of TMC; $M_n = 28096$, $M_w = 49176$, PDI = 1.75.

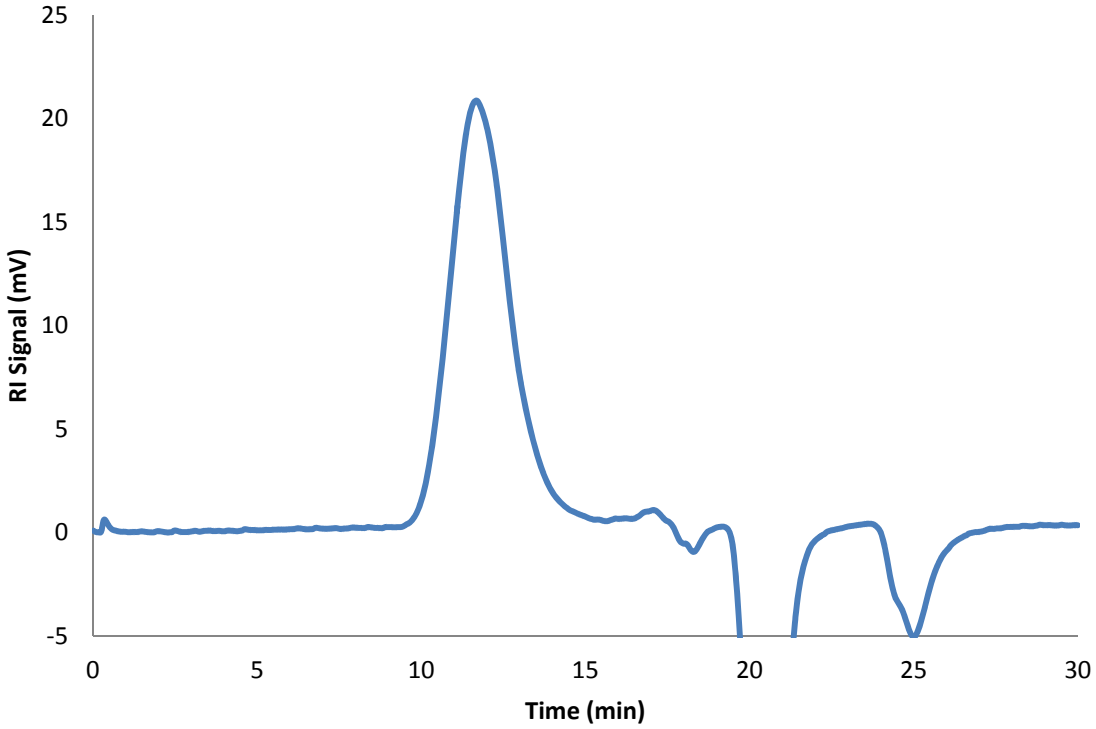


Figure S43. Polymerization of 100 equivalents of TMC; $M_n = 39745$, $M_w = 67642$, PDI = 1.70.

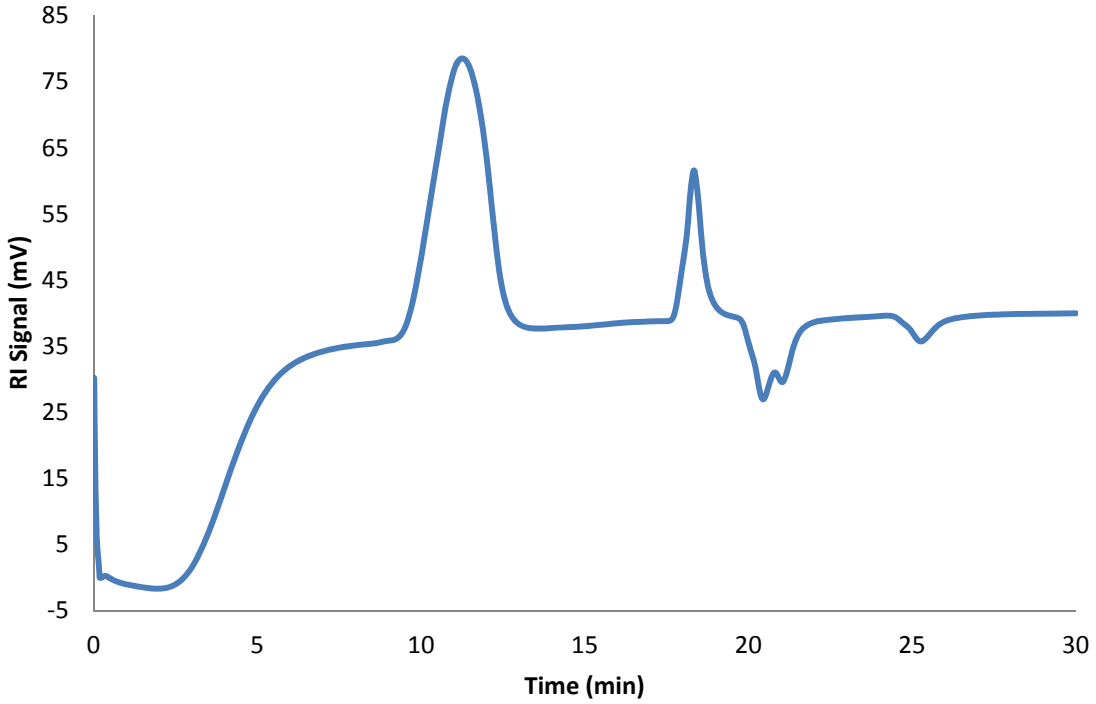


Figure S44. Polymerization of 100 equivalents of CL; M_n = 79793, M_w = 108641, PDI = 1.36.

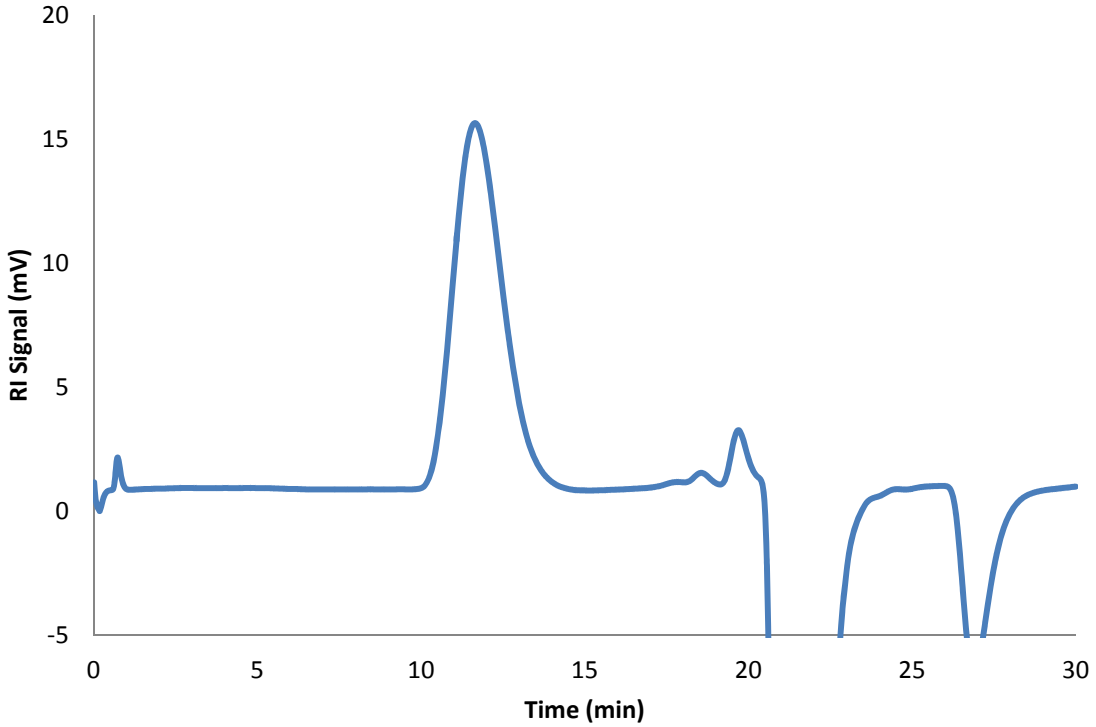


Figure S45. Polymerization of 250 equivalents of CL; M_n = 148077, M_w = 184490, PDI = 1.25.

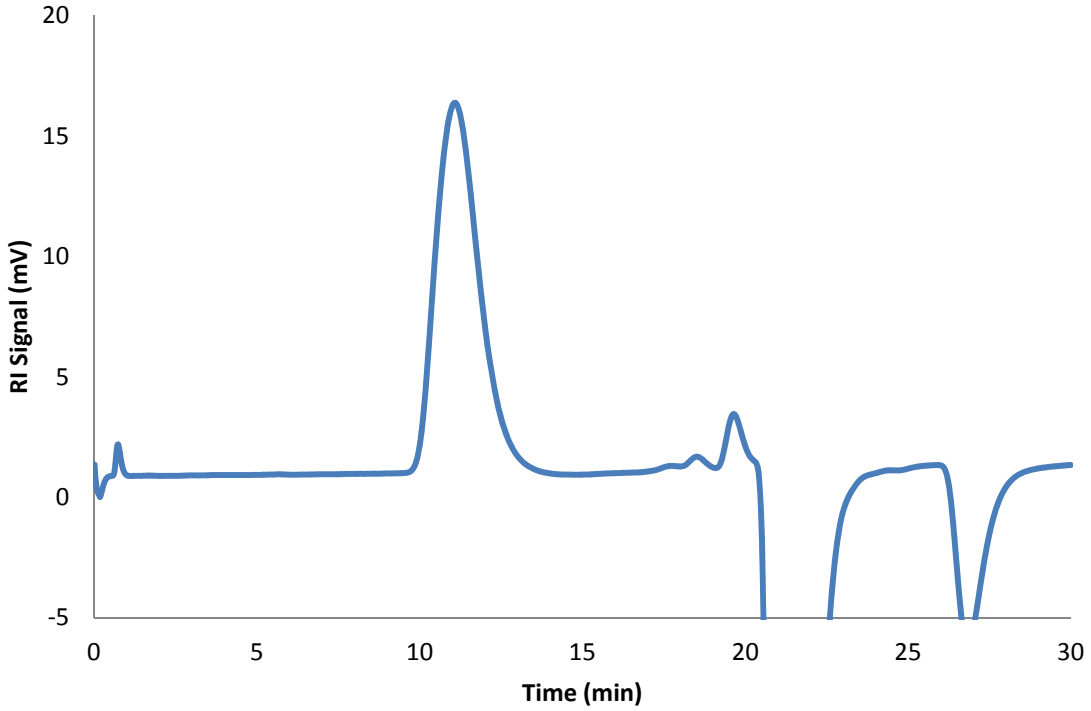


Figure S46. Polymerization of 500 equivalents of CL; M_n = 232714, M_w = 276139, PDI = 1.19.

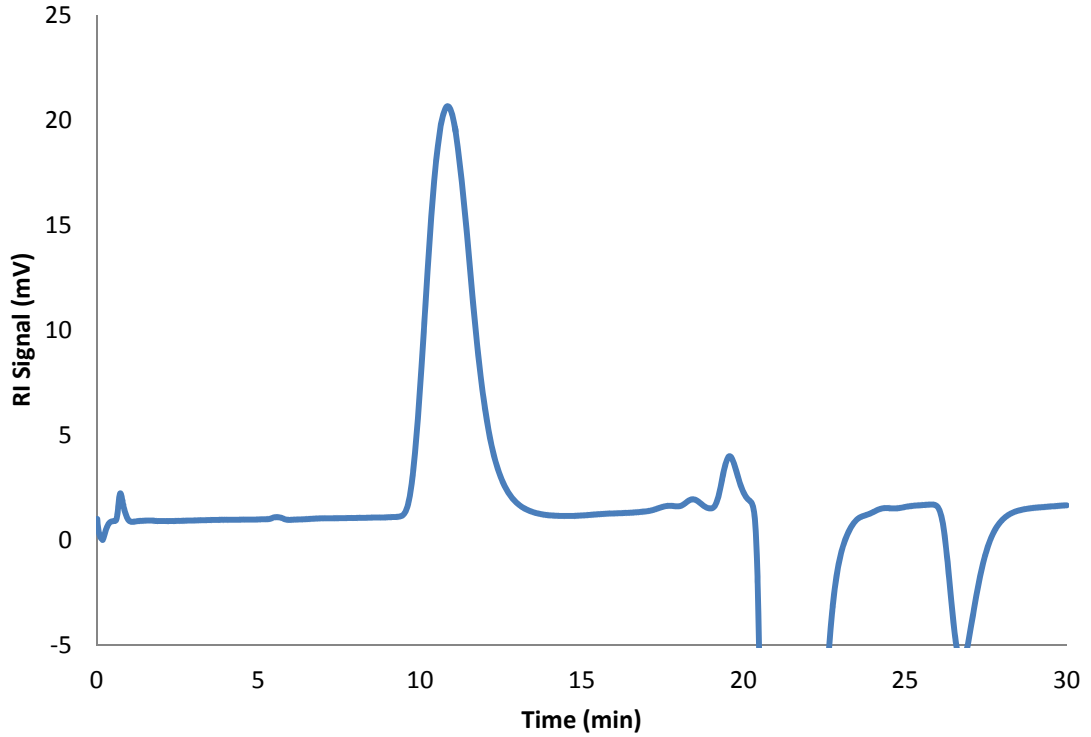


Figure S47. Polymerization of 750 equivalents of CL; M_n = 266257, M_w = 323628, PDI = 1.21.

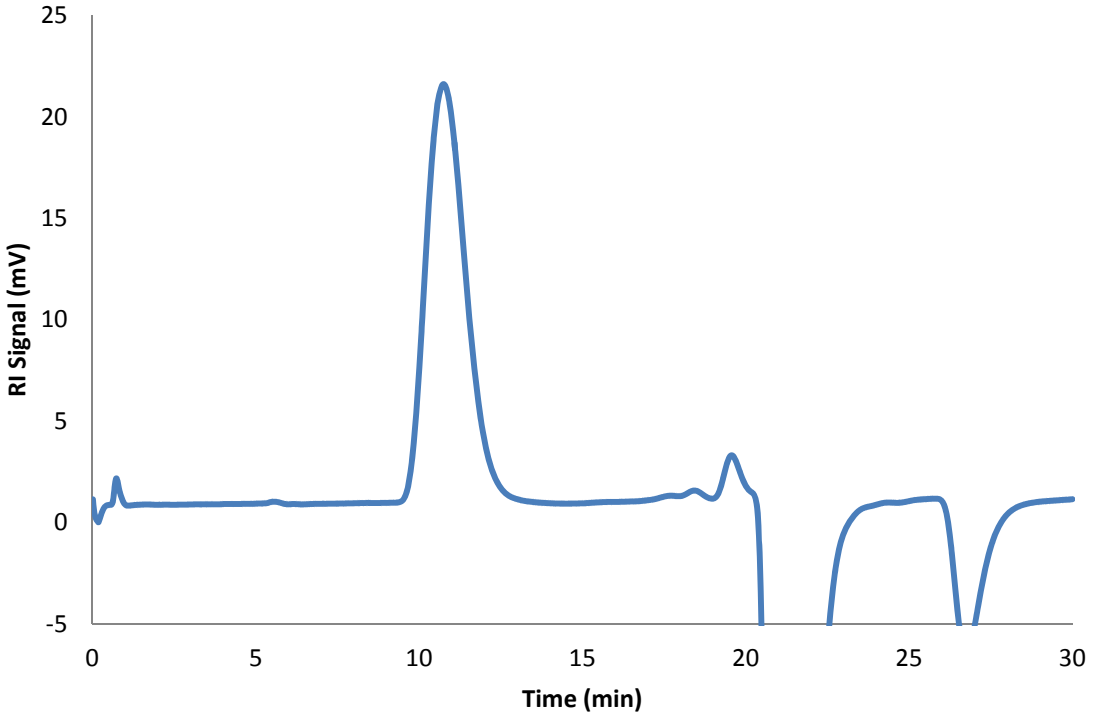


Figure S48. Polymerization of 1000 equivalents of CL; M_n = 298113, M_w = 346426, PDI = 1.16.

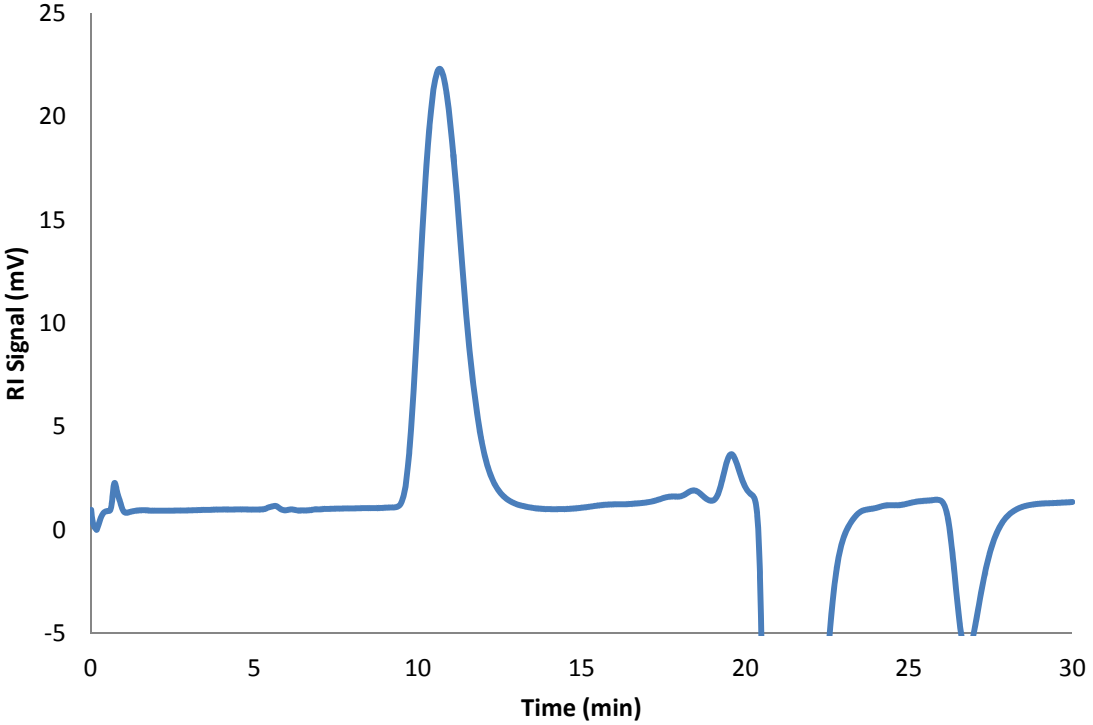


Figure S49. Polymerization of 1500 equivalents of CL; M_n = 310026, M_w = 364419, PDI = 1.17.

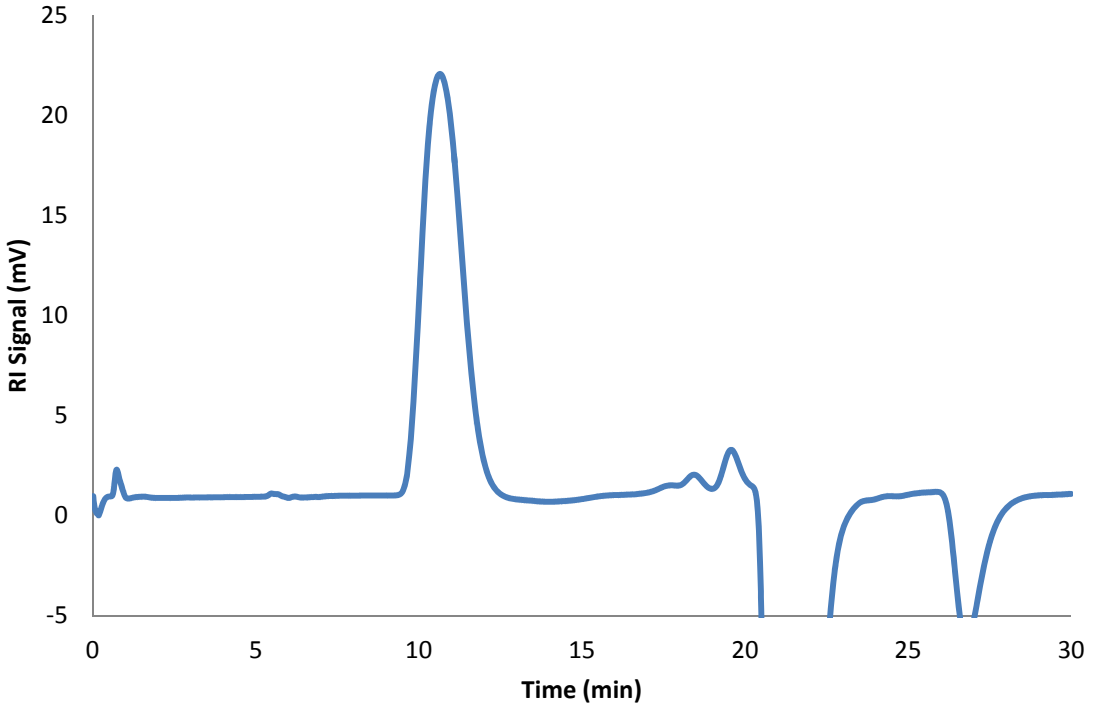


Figure S50. Polymerization of 2000 equivalents of CL; M_n = 322508, M_w = 371653, PDI = 1.15.

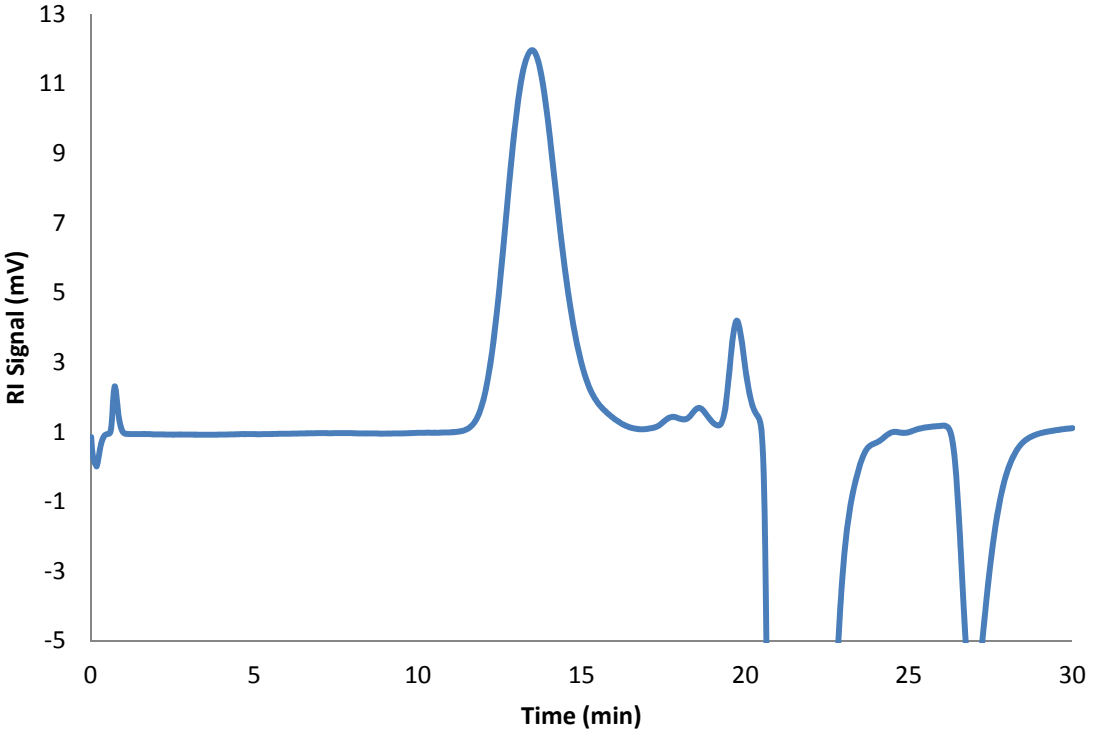


Figure S51. Polymerization of 100 equivalents of VL; M_n = 31785, M_w = 46478, PDI = 1.46.

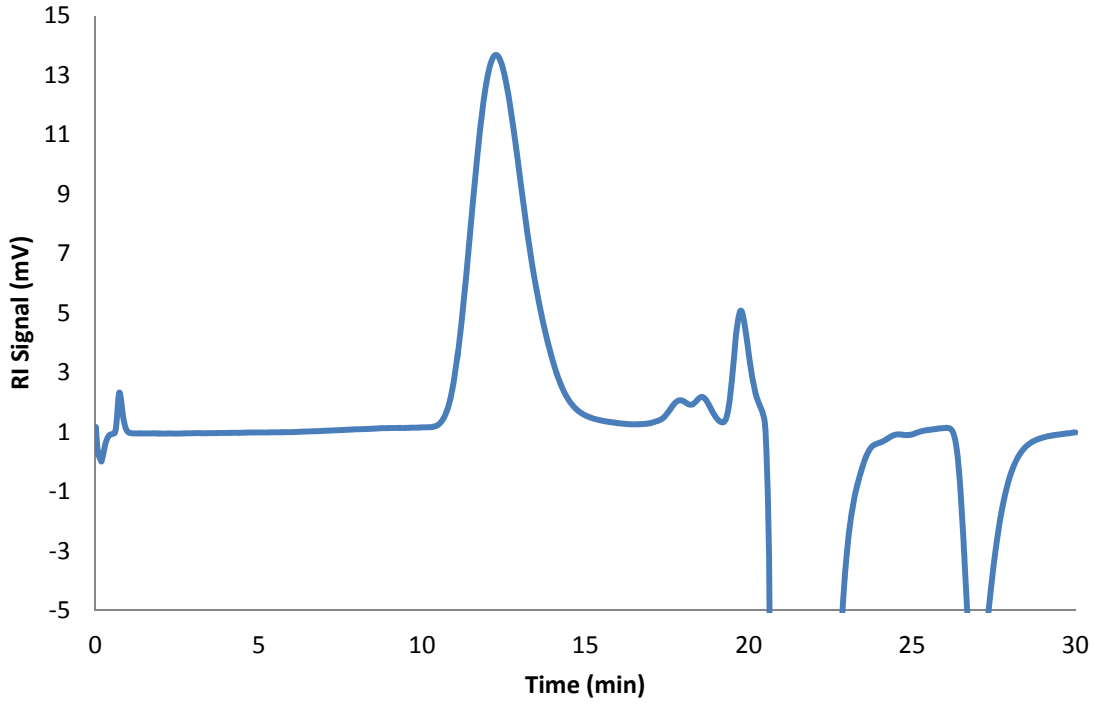


Figure S52. Polymerization of 250 equivalents of VL; M_n = 77505, M_w = 113255, PDI = 1.46.

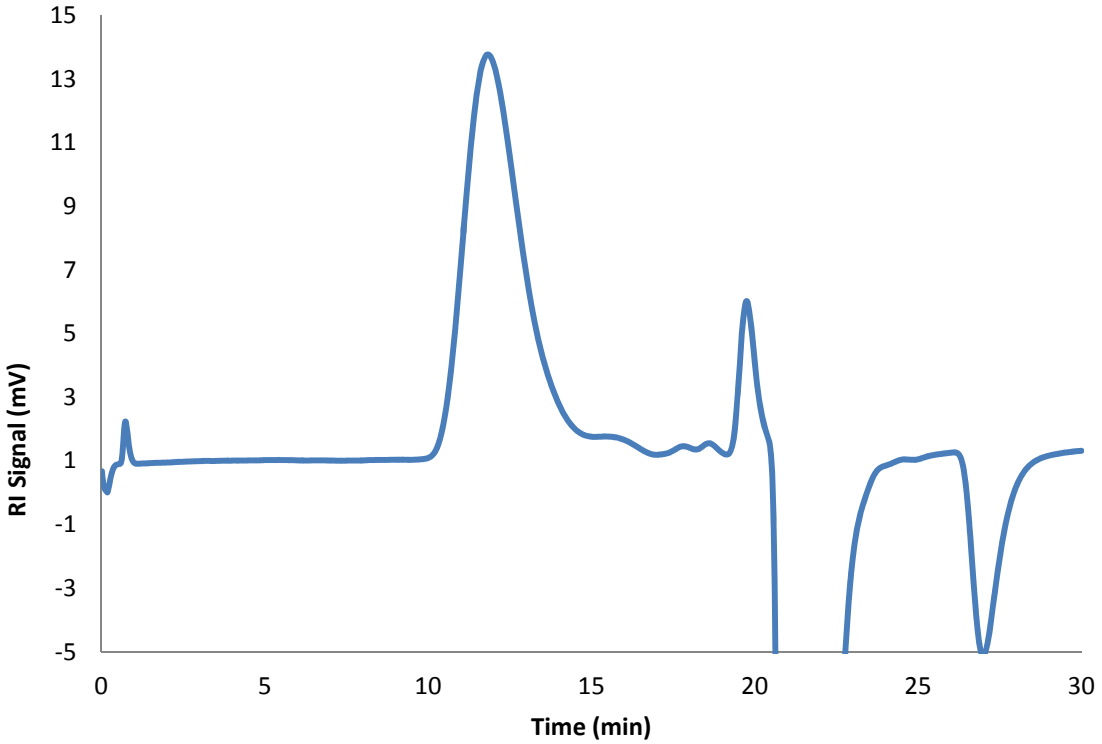


Figure S53. Polymerization of 500 equivalents of VL; M_n = 112642, M_w = 156177, PDI = 1.39.

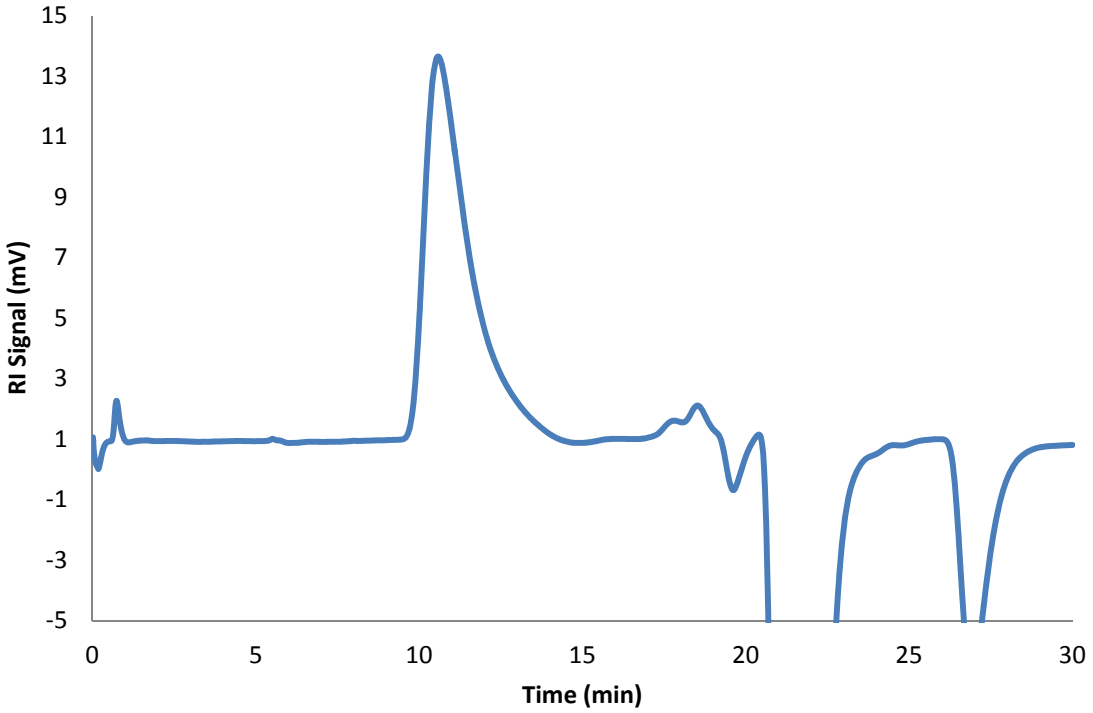


Figure S54. Polymerization of 750 equivalents of VL; M_n = 218497, M_w = 312867, PDI = 1.43.

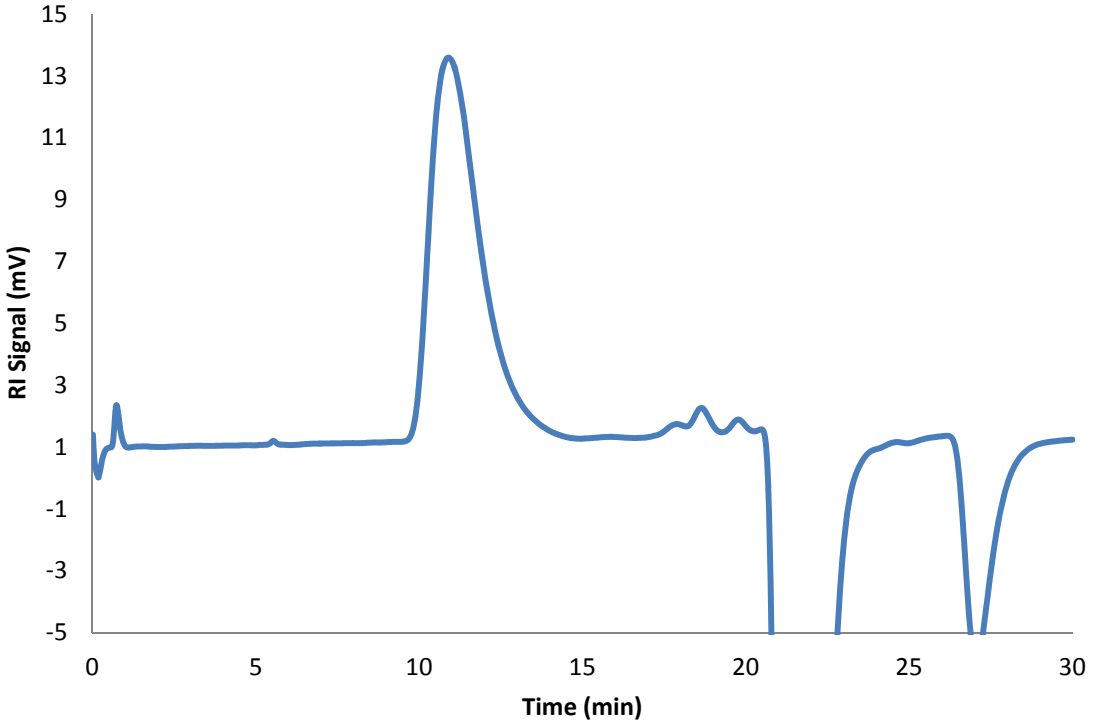


Figure S55. Polymerization of 1000 equivalents of VL; M_n = 190257, M_w = 272250, PDI = 1.43.

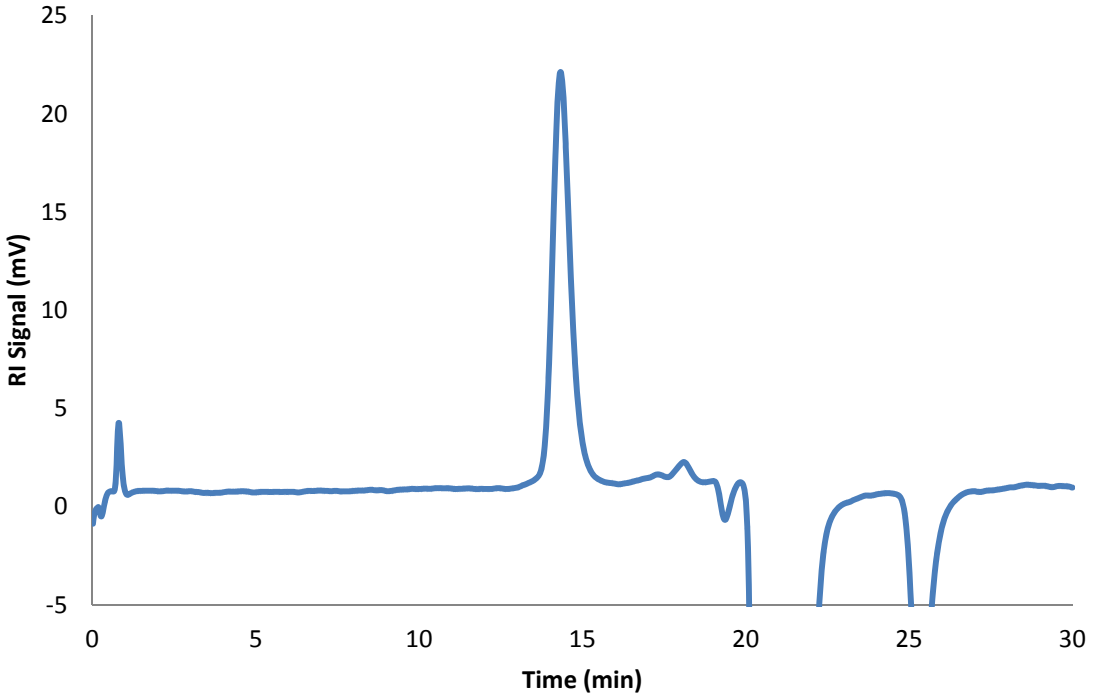


Figure S56. Polymerization of 100 equivalents of BBL; M_n = 15054, M_w = 16402, PDI = 1.09.

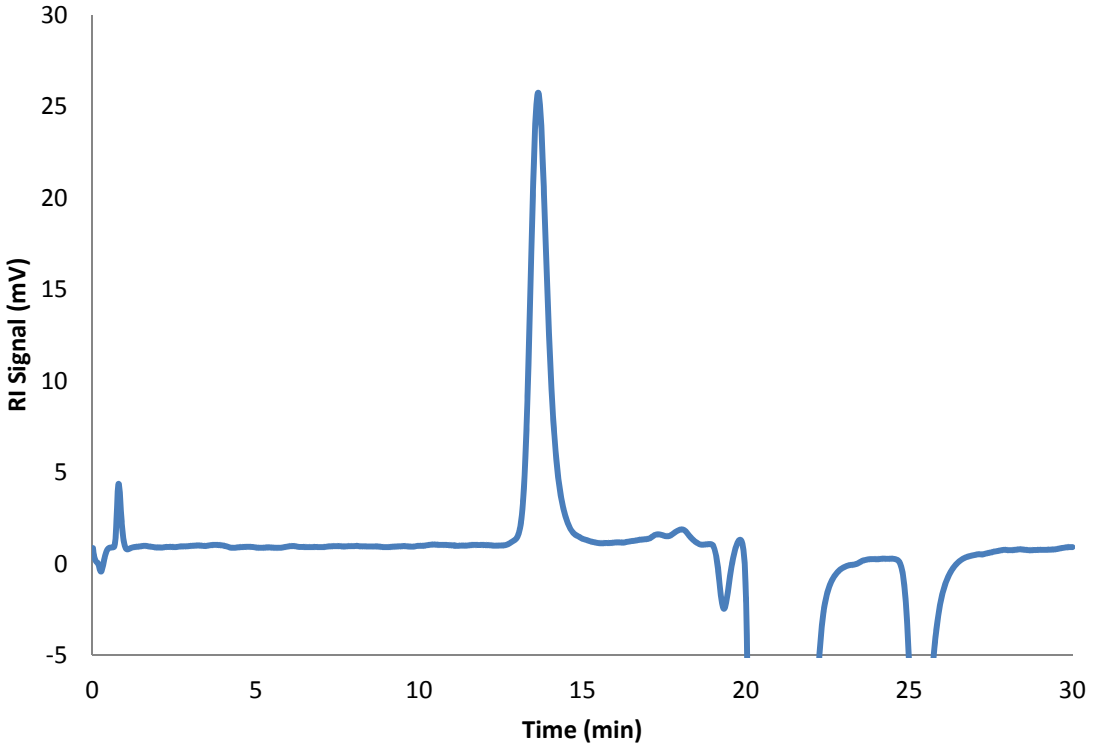


Figure S57. Polymerization of 200 equivalents of BBL; M_n = 27760, M_w = 29659, PDI = 1.07.

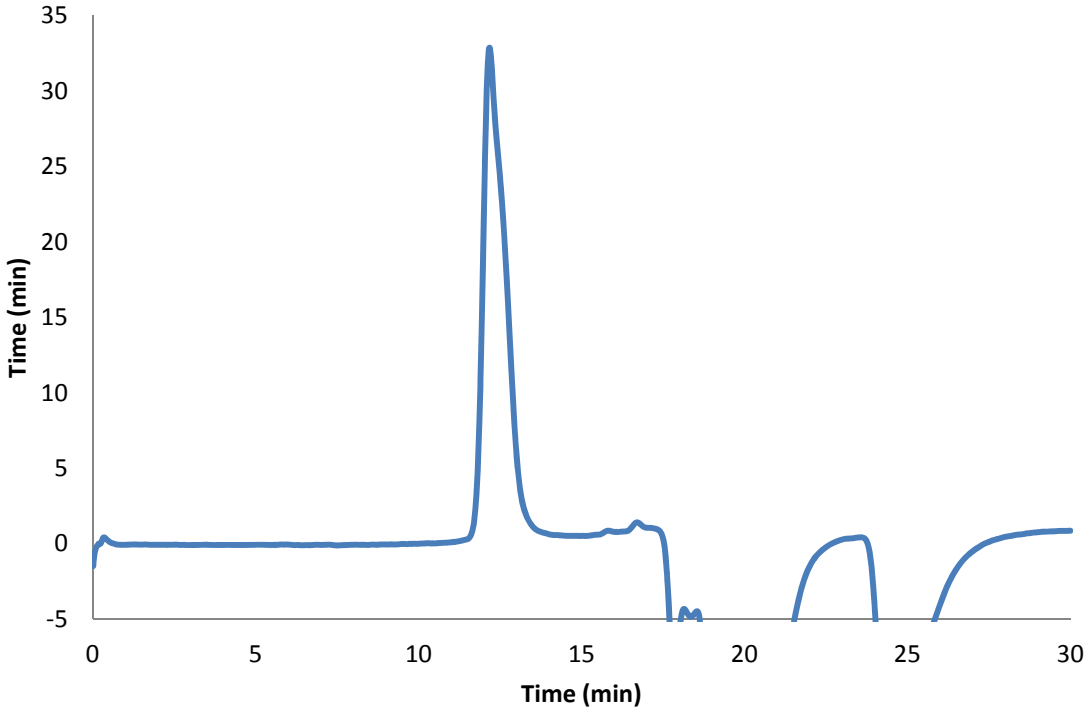


Figure S58. Polymerization of 300 equivalents of BBL; M_n = 31232, M_w = 34355, PDI = 1.10.

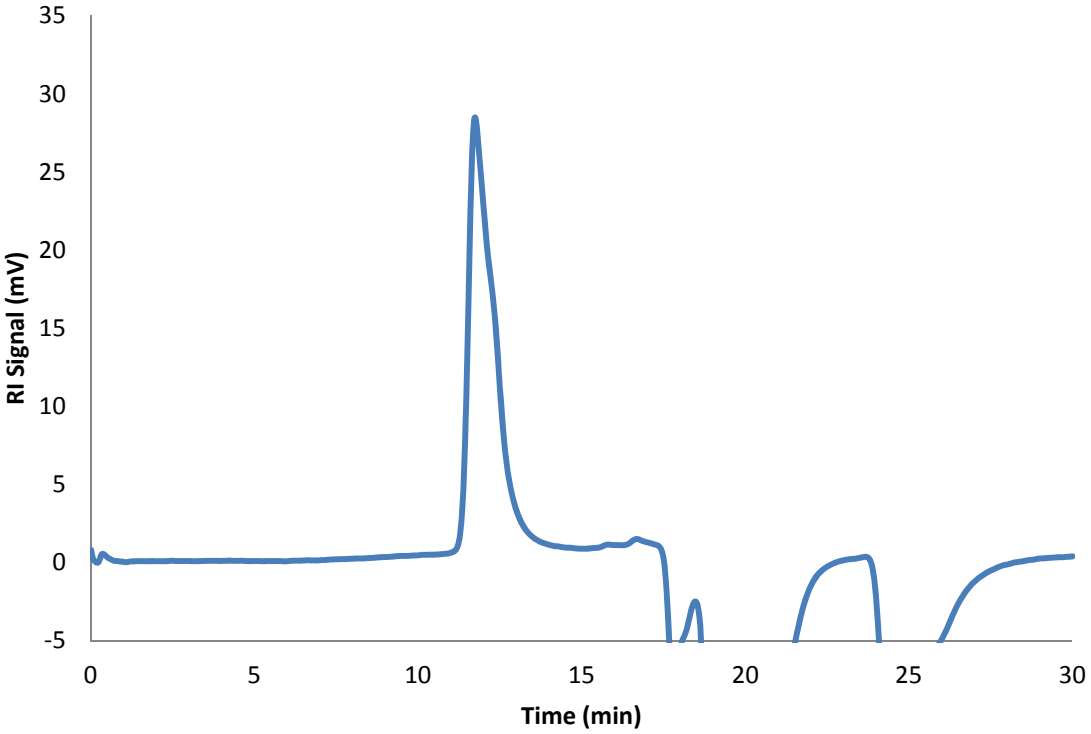


Figure S59. Polymerization of 400 equivalents of BBL; M_n = 42418, M_w = 48060, PDI = 1.13.

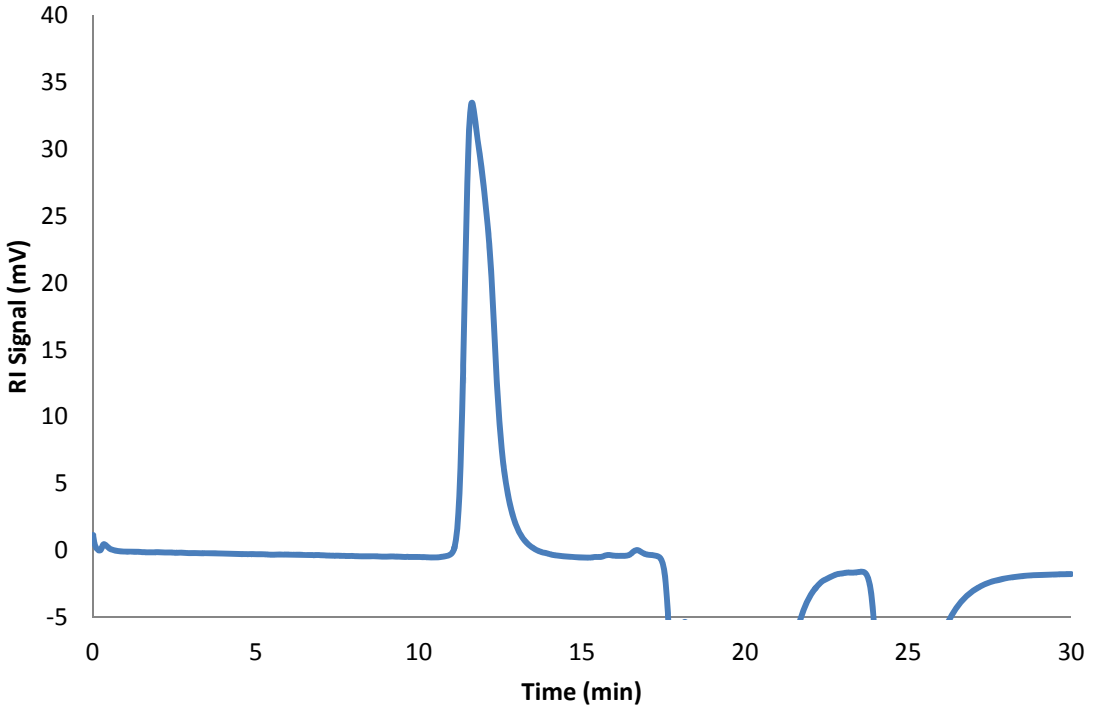


Figure S60. Polymerization of 500 equivalents of BBL; M_n = 47235, M_w = 53345, PDI = 1.13.

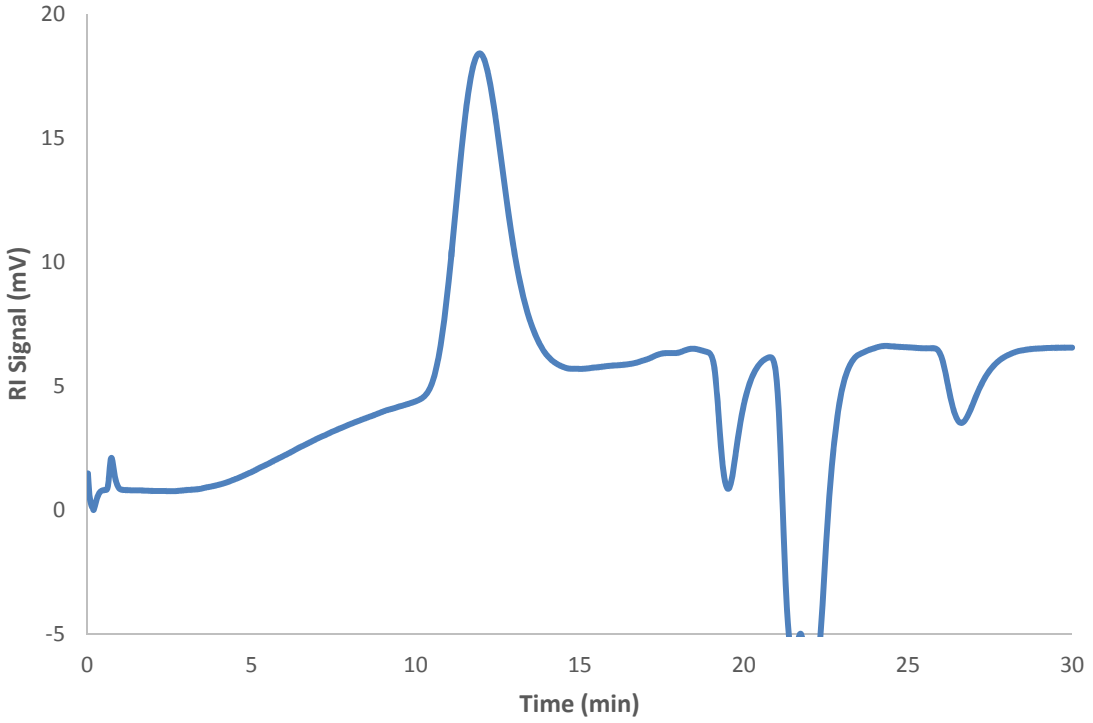


Figure S61. Polymerization of 100 equivalents of CL at 0 °C; M_n =116276, M_w = 160234, PDI = 1.38.

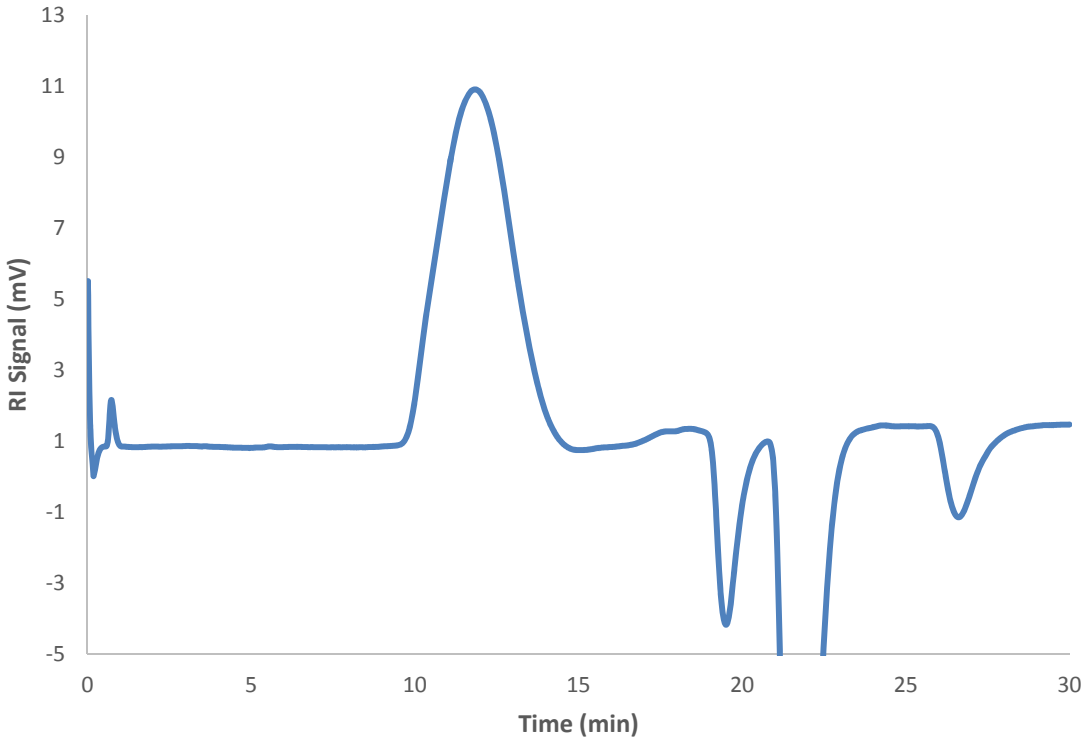


Figure S62. Polymerization of 100 equivalents of VL at 0 °C; M_n = 124487, M_w = 205393, PDI = 1.65.

X-ray Structure Data

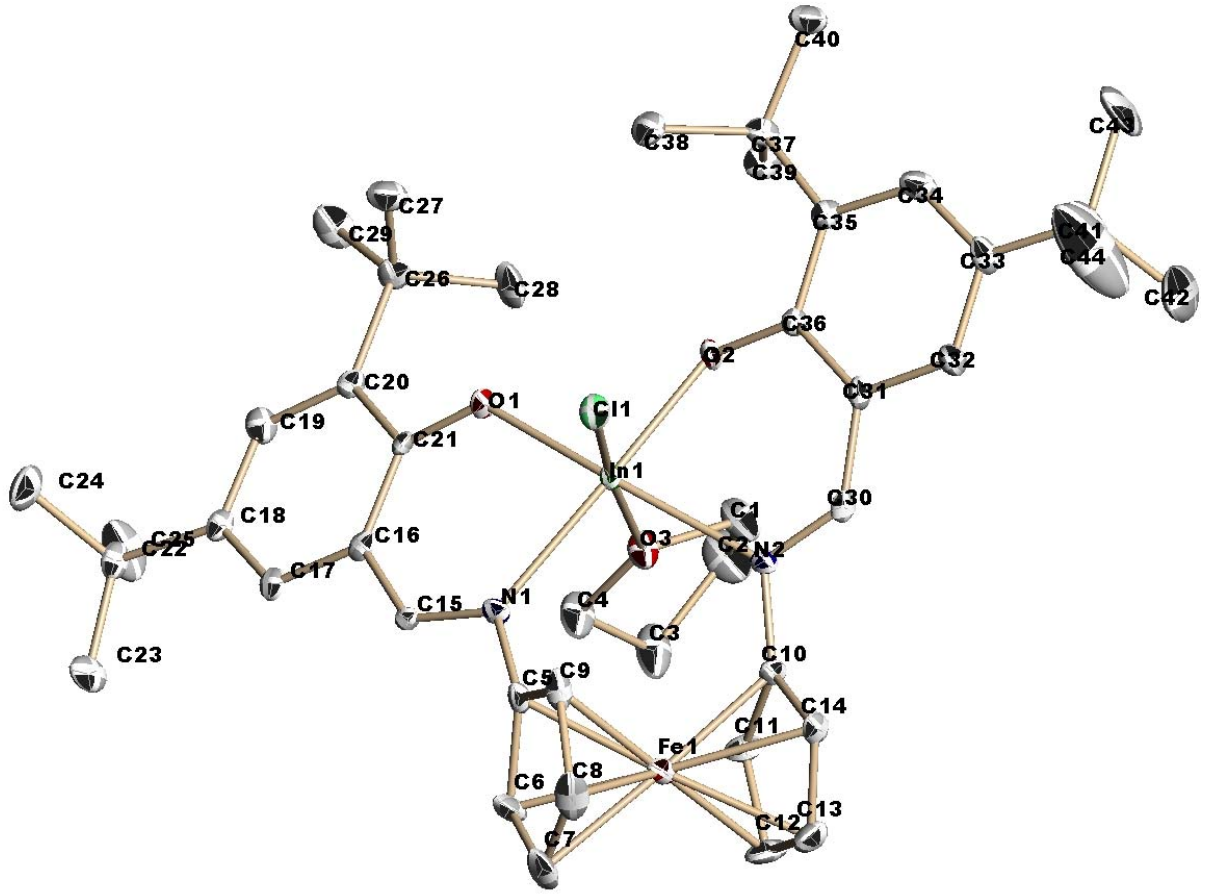


Figure S63. Thermal-ellipsoid (50% probability) representation of (salfen)InCl. Hydrogen atoms were omitted for clarity.

Single crystals suitable for X-ray diffraction were grown from a concentrated diethyl ether solution at -35 °C. Crystal data for $C_{48}H_{68}ClFeInN_2O_4$; M_r = 943.16; orthorhombic; space group P2(1)2(1)2(1); *a* = 10.3658(10) Å; *b* = 18.6942(18) Å; *c* = 23.794(2) Å; α = 90°; β = 90°; γ = 90°; V = 4610.8(8) Å^3; Z = 4; T = 120(2) K; λ = 0.71073 Å; μ = 0.916 mm^{-1}; d_{calc} = 1.359 g.cm^{-3}; 50963 reflections collected; 9383 unique (R_{int} = 0.0289) giving R_1 = 0.0225, wR_2 = 0.0506 for 9156 data with [I>2σ(I)] and R_1 = 0.0234, wR_2 = 0.0510 for all 9383 data. Residual electron density (e$^-$.Å^{-3}) max/min: 0.623/-0.727.

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