

Supporting information:

Using Differential Scanning Calorimetry to Accelerate Polymerization Catalysis: a Toolkit for Miniaturized and Automated Kinetics Measurements

Thomas M. McGuire, David Ning and Charlotte K. Williams*

^a Department of Chemistry, Chemistry Research Laboratory, University of Oxford, 12 Mansfield Rd, Oxford, OX1 3TA, U.K

Corresponding Authors

Charlotte K. Williams: Email: charlotte.williams@chem.ox.ac.uk

| | |
|--|----------|
| Supporting information: | 1 |
| 1. Materials..... | 3 |
| 2. Methods | 4 |
| 2.1 Polymerization Method using a DSC pan | 4 |
| 2.2 Polymerization Method with Aliquot Analysis..... | 4 |
| 2.3 Polymerization Method using <i>in-situ</i> ATR-IR Spectroscopy | 4 |
| 2.4 Estimation of Activation Parameters using Dynamic Heating Rates | 4 |
| 3. Additional information | 11 |
| 3.1 Benchmarking DSC kinetics..... | 11 |
| 3.2 Isothermal kinetics for dVL, LLA and TMC ROP and PA/CHO ROCOP | 28 |
| 3.3 ROP of dVL, LLA and TMC under dynamic heating | 34 |
| 3.5 dVL ROP kinetics by single heating ramp | 37 |
| 3.5 LLA ROP kinetics by single heating ramp | 40 |
| 3.6 TMC ROP kinetics by single heating ramp | 44 |
| 3.7 LLA and TMC kinetics by multi-heating ramps..... | 48 |
| 3.8 Comparison of methods for determination of activation paramaters for the kinetics of dVL, TMC and LLA ROP..... | 49 |
| 3.9 Determination of equilibrium monomer conversions..... | 52 |
| 3.10 Examples for new users..... | 57 |
| 4. References | 59 |

1. Materials

All experiments were carried out, under N₂, using standard Schlenk/glovebox techniques, unless otherwise stated. All chemicals were stored, under N₂, unless otherwise stated. 1,2-Dichlorobenzene was purchased from Sigma-Aldrich. Prior to use, 1,2-dichlorobenzene was degassed, by N₂ purge, and stored over 3 Å molecular sieves under N₂. δ-Valerolactone (dVL) was purchased from Tokyo Chemical Industries. Prior to use, the lactone was stirred over calcium hydride, overnight, and then fractionally distilled under reduced pressure. L-Lactide (LLA) was purchased from Sigma-Aldrich. Prior to use, LLA was recrystallised from toluene, three times, then sublimed, under reduced pressure. Trimethylene carbonate (TMC) was purchased from Tokyo chemical industry. Prior to use, TMC was recrystallised from anhydrous diethylether, two times. Phthalic anhydride (PA) was purchased from Sigma-Aldrich. Prior to use, PA was purified by stirring in dry toluene, at room temperature, for 16 hours. The supernatant was filtered, and the toluene removed in vacuo. The resultant white powder was crystallised from hot (60 °C) chloroform then sublimed under vacuum at 80 °C. Cyclohexene oxide (CHO) was purchased from Acros Organics. Prior to use, the epoxide was stirred over calcium hydride overnight and fractionally distilled, under reduced pressure, twice. 4-methyl-1,3-dioxan-2-one (MDO) was synthesised according to literature.¹ Prior to use, MDO was dried over CaH₂ and fractionally distilled, under reduced pressure. 5,5-dimethyl-1,3-dioxan-2-one (DDO).¹ Prior to use, DDO was twice recrystallised from anhydrous diethyl ether. Tin(II) 2-ethylhexanoate (Sn(Oct)₂) was purchased from Sigma-Aldrich and used as received. Anhydrous benzyl alcohol was purchased from Sigma-Aldrich and used as received. (*R,R*)-(-)-*N,N'*-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminochromium(III) chloride ((salcy)CrCl) was purchased from strem chemicals and used as received. Tetrabutylammonium chloride was purchased from Sigma-Aldrich and used as received.

Size Exclusion Chromatography (SEC) was carried out on a Shimadzu LC-20AD instrument using two PSS SDV linear M columns in series, with a THF eluent. Measurements were conducted at 30 °C, with a flow rate of 1 mL/min. Samples were detected with a differential refractive index (RI) detector. Number-average molar mass ($M_{n,SEC}$) and dispersities (\mathcal{D}_M (M_w/M_n)) were determined using narrow molar mass polystyrene calibrants ($M_n = 500 - 1000000$ g mol⁻¹). The polymer samples were dissolved in HPLC-grade THF, at a concentration of ca 10 mg/mL, and filtered through a 0.2 µm microfilter prior to analysis.

Differential scanning calorimetry (DSC) was performed using a TA Discovery 25-Auto. See methodology section for detailed outline on DSC measurements. Dynamic kinetic analysis was performed using Trios software (v5.7.1.74) with the kinetics add-on package.

In-situ FTIR spectra were recorded using a Mettler-Toledo DiComp sentinel probe.

NMR spectra were obtained using a Bruker AVIII HD nanobay NMR spectrometer. Coupling constants are given in Hertz. Selectivities were determined by ¹H NMR spectroscopy.

Turnover Frequency (TOF) calculations were taken at 33% conversion for all reactions.

2. Methods

2.1 Polymerization Method using a DSC pan

N.B. For polymerizations with dVL, stock solutions were prepared in pure monomer. No reaction was observed between the monomer and Sn(Oct)₂ or monomer and benzyl alcohol.

In a glovebox, stock solutions of Sn(Oct)₂ (1.0 M, 40.5 mg diluted to 0.1 mL in dVL) and benzyl alcohol (0.1 M, 10.8 mg diluted to 0.1 mL in dVL) were prepared. 10 μ L of both stock solutions (0.01 mmol, 1 equiv.) were added to a vial containing dVL (88 mg) to bring the total mass of dVL to 100 mg (1.0 mmol, 100 equiv.) and the final loading of Sn(Oct)₂: BnOH: dVL to 1: 1: 100.

A DSC pan and hermetic lid were then tared and the dVL reaction solution was transferred to the DSC pan via micropipette (ca 3 μ L). The pan and lid were sealed, reweighed and the exact mass of the sample recorded. The pan was then transferred to a DSC instrument for polymerization. For isothermal measurements, the DSC cell was heated to the reaction temperature, before automated loading of the reference pan and sample pan. For dynamic measurements, the sample and reference pan were loaded at 40 °C. All measurements were carried out under N₂ flow (50 mL min⁻¹).

Once the reaction was complete, the pan was recovered and reweighed to confirm no mass loss had occurred during the reaction. Using a needle, the pan was carefully pierced and soaked in deuterated chloroform containing benzoic acid (catalyst quenching agent, ca 10 equiv.) and mesitylene (NMR spectroscopic standard, 10.0 μ L, 0.071 mmol). After recording the NMR spectrum, the sample was dried and diluted in THF (ca 1 mL) for SEC analysis.

For determination of activation parameters via isothermal methods, isotherms were held at temperatures between 80-150 °C until completion of the reaction.

2.2 Polymerization Method with Aliquot Analysis

In a glovebox, dVL (2.00 g, 20.0 mmol, 100 equiv.) was added to a vial containing Sn(Oct)₂ (80.9 mg, 0.200 mmol, 1.00 equiv.) and BnOH (21.6 mg, 0.200, 1.00 equiv.). The solution was divided equally between 8 vials. The vials were heated to the reaction temperature (100 °C) and individually quenched at pre-determined time intervals using benzoic acid. Conversion and molar mass of the polymer were determined using ¹H NMR spectroscopy and SEC.

2.3 Polymerization Method using *in-situ* ATR-IR Spectroscopy

In a glovebox, dVL was added (2.00 g, 20.0 mmol, 100 equiv.) to a Schlenk-tube containing Sn(Oct)₂ (80.9 mg, 0.200 mmol, 1.00 equiv.) and BnOH (21.6 mg, 0.200 mmol, 1.00 equiv.). Under a flow of N₂, the Schlenk-tube was fitted with a ATR-IR probe were then transferred to a preheated oil bath (100 °C). The carbonyl resonances of the monomer and polymer was monitored until the reaction reached completion. Once complete, the vessel was cooled to room temperature and the catalyst quenched through addition of benzoic acid. Final conversion was determined using ¹H NMR spectroscopy and molar mass was determined by SEC.

2.4 Estimation of Activation Parameters using Dynamic Heating Rates

Determination of activation parameters using dynamic heating methods was conducted according to either the Borchardt-Daniels (ASTM E2041, single ramp) or Flynn-Wall-Ozawa method (ASTM E698, multi ramp) with heating rates between 2 and 10 °C min⁻¹. Data for dynamic analysis was processed using the Trios Kinetics software package.

2.4.1 Borchardt-Daniles Method (ASTM E2041-23)

Following Borchardt-Daniels method (ASTM E2041-23):

Assuming that the reaction follows first order kinetics, the rate of reaction can be expressed as:

$$\frac{d\alpha}{dt} = k(1 - \alpha)$$

Equation S1

Where α is the fractional conversion, $\frac{d\alpha}{dt}$ is the reaction rate, k is the rate constant at a given temperature, t is time.

Taking the natural logarithm of both sides gives:

$$\ln \frac{d\alpha}{dt} = \ln k + \ln(1 - \alpha)$$

Equation S2

Equation S2 can be rearranged to:

$$\ln k = \ln \frac{d\alpha}{dt} - \ln(1 - \alpha)$$

Equation S3

The rate and fractional conversion is determined from the DSC exotherm (Fig. S1). Here, the determination was taken using 20 segments of the curve, evenly spaced by temperature, between 5% conversion and the conversion at maximum rate (Fig S2 and Table S1)..

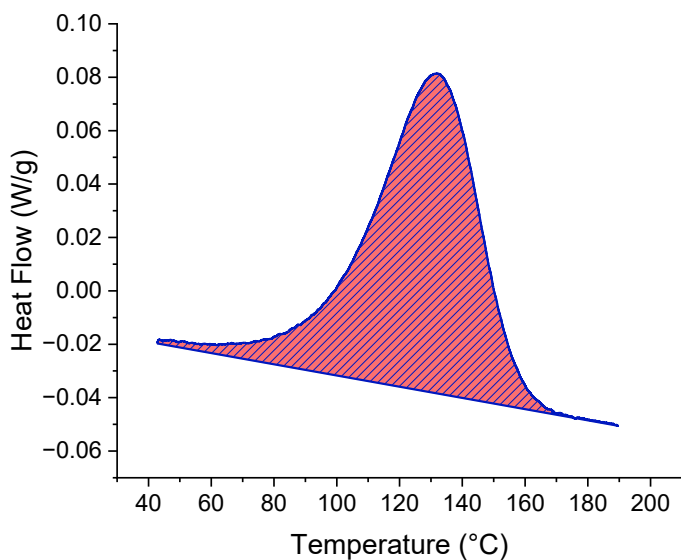


Figure S1. Heatflow vs temperature for the ROP of dVL conducted under a heating rate of 2 °C min⁻¹ between 40 – 200 °C ([Sn(Oct)₂]₀: [BnOH]₀: [dVL]₀ = 1:1:100, in neat dVL. [dVL]₀ = 9.98 M). Shade shows the area where the integral was taken to generate figure S2.

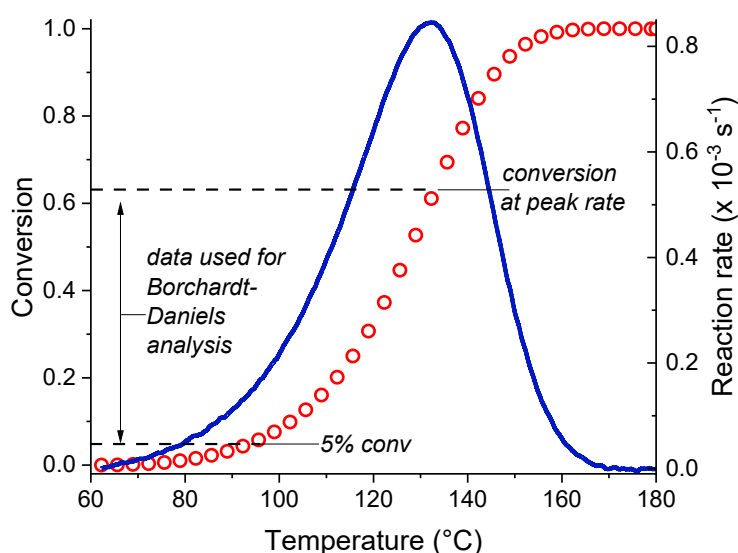


Figure S2. Conversion (red circles, left y axis) and reaction rate (blue line, right y axis) vs temperature for the ROP of dVL. Reaction conditions: heating rate of 2 °C min⁻¹, 40 – 200 °C, [Sn(Oct)₂]₀:[BnOH]₀:[dVL]₀ = 1:1:100, neat ([dVL]₀ = 9.98 M). Conversion was determined from the normalized integral of the heatflow vs time data in figure S1. The reaction rate is equivalent to the normalized heat flow in figure S1.

Table S1. Temperature, fraction conversion and rate determined at 20 evenly spaced sections between 5 and 65% conversion of dVL ROP conducted a heating rate of 2 °C min⁻¹ between 40 – 200 °C.

| Temp. (°C) ^[a] | 1/Temp (K ⁻¹) | Fractional conversion, α ^[a] | Rate (s ⁻¹) ^[a] | ln(1-α) | ln k ^[b] |
|---------------------------|---------------------------|---|--|----------|---------------------|
| 93.95 | 0.00272 | 0.05 | 1.46533E-4 | -0.05129 | -8.77696 |
| 96.05 | 0.00271 | 0.05999 | 1.6926E-4 | -0.06187 | -8.62221 |
| 98.15 | 0.00269 | 0.07121 | 1.93803E-4 | -0.07387 | -8.4748 |
| 100.25 | 0.00268 | 0.08426 | 2.21292E-4 | -0.08802 | -8.32801 |
| 102.35 | 0.00266 | 0.09925 | 2.52517E-4 | -0.10453 | -8.17951 |
| 104.45 | 0.00265 | 0.11616 | 2.8659E-4 | -0.12348 | -8.03398 |
| 106.55 | 0.00263 | 0.13538 | 3.26368E-4 | -0.14547 | -7.88202 |
| 108.65 | 0.00262 | 0.15716 | 3.66525E-4 | -0.17097 | -7.74047 |
| 110.75 | 0.0026 | 0.18164 | 4.12015E-4 | -0.20045 | -7.594 |
| 112.85 | 0.00259 | 0.20898 | 4.56898E-4 | -0.23444 | -7.45661 |
| 114.95 | 0.00258 | 0.23984 | 5.10818E-4 | -0.27423 | -7.30527 |
| 117.05 | 0.00256 | 0.27326 | 5.64097E-4 | -0.31918 | -7.1611 |
| 119.15 | 0.00255 | 0.31056 | 6.17955E-4 | -0.37188 | -7.01721 |
| 121.25 | 0.00254 | 0.35111 | 6.71662E-4 | -0.43249 | -6.87327 |
| 123.35 | 0.00252 | 0.39526 | 7.2416E-4 | -0.50295 | -6.72755 |
| 125.45 | 0.00251 | 0.44229 | 7.71317E-4 | -0.58391 | -6.5835 |
| 127.55 | 0.0025 | 0.49202 | 8.07068E-4 | -0.67731 | -6.44479 |
| 129.65 | 0.00248 | 0.54375 | 8.34108E-4 | -0.78471 | -6.30444 |
| 131.76 | 0.00247 | 0.59702 | 8.4425E-4 | -0.90888 | -6.16818 |
| 133.86 | 0.00246 | 0.65 | 8.38415E-4 | -1.04982 | -6.03418 |

Reaction conditions: [Sn(Oct)₂]₀: [BnOH]₀: [dVL]₀ = 1: 1: 100 in neat dVL. [dVL]₀ = 9.98 M. ^[a] Determined from 20 evenly spaced segments in area indicated in figure S2 ^[b] $\ln k = \ln \frac{d\alpha}{dt} - \ln(1 - \alpha)$

Assuming the reaction follows arrhenius behaviour:

$$k = A e^{-\frac{\Delta H^\ddagger}{RT}}$$

Equation S4

Where T is temperature, A is the pre-exponential factor, ΔH^\ddagger is the activation energy and R is the gas constant.

Taking the natural logarithm gives:

$$\ln k = \ln(A) - \frac{\Delta H^\ddagger}{RT}$$

Equation S5

Using the estimated values of k (Table S1), a plot of $\ln k$ vs $1/T$ yields a straight line. The ΔH^\ddagger and A are estimated from the slope and intercept, respectively.

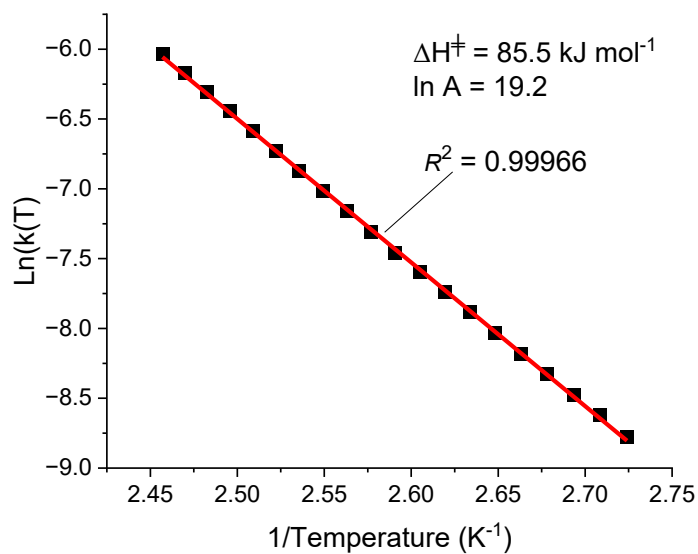


Figure S3. Plot of $\ln k$ vs $1/\text{temperature}$ for for the ROP of dVL. Reaction conditions: heating rate of $2 \text{ }^\circ\text{C min}^{-1}$, $40 - 200 \text{ }^\circ\text{C}$, $[\text{Sn}(\text{Oct})_2]_0: [\text{BnOH}]_0: [\text{dVL}]_0 = 1:1:100$, neat ($[\text{dVL}]_0 = 9.98 \text{ M}$). Data taken from Table S1.

2.4.2 Activation Parameters using Multi-heating-rate Method

Following the Flynn-Wall-Ozawa method (ASTM E698-05):

The fractional conversion and rate can be determined by integrating and normalising the DSC exotherms at different heating rates to give the data shown in Figures S4 and 5:

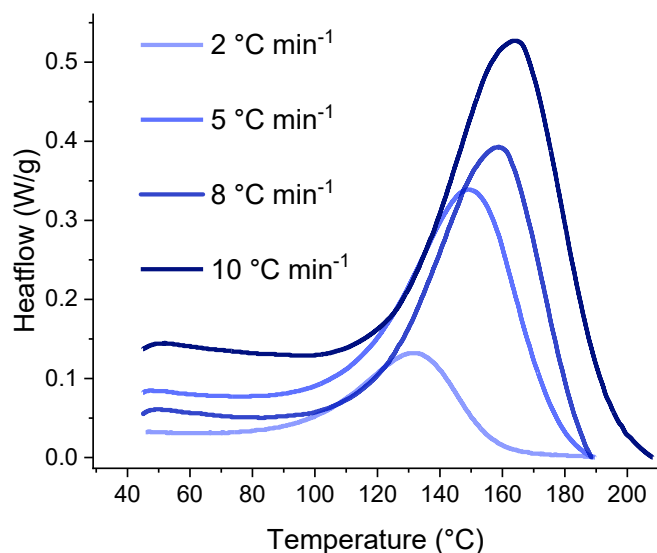


Figure S4. Plot of heatflow vs temperature for the ROP of dVL. Reaction conditions: heating rates of 2, 5, 8 and 10 °C min⁻¹, 40 – 220 °C, [Sn(Oct)₂]₀: [BnOH]₀: [dVL]₀ = 1:1:100, neat ([dVL]₀ = 9.98 M). Thermograms were integrated as shown in figure S1.

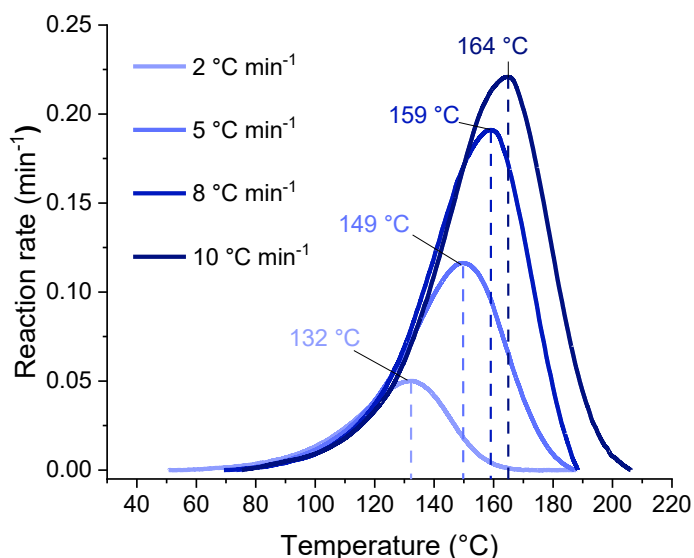


Figure S5. Plot of reaction rate vs temperature for ROP of dVL. Reaction conditions: heating rates of 2, 5, 8 and 10 °C min⁻¹, 40 – 220 °C, [Sn(Oct)₂]₀: [BnOH]₀: [dVL]₀ = 1:1:100, neat ([dVL]₀ = 9.98 M). The reaction rate is equivalent to the normalized heat flow in figure S4. The peak temperature for each heating rate is shown.

Table S2. Table showing heating rate, peak temperature taken from figure S5 for the ROP of dVL conducted under dynamic heating between 40 – 200 °C

| Heating rate, β ($^{\circ}\text{C min}^{-1}$) | Peak temperature ($^{\circ}\text{C}$) | 1/Temperature ($\times 10^{-3} \text{ K}^{-1}$) | Log β |
|---|---|---|-------------|
| 2 | 132 | 2.47 | 0.3 |
| 5 | 149 | 2.37 | 0.7 |
| 8 | 159 | 2.31 | 0.9 |
| 10 | 164 | 2.28 | 1 |

Reaction conditions: $[\text{Sn}(\text{Oct})_2]_0 : [\text{BnOH}]_0 : [\text{dVL}]_0 = 1 : 1 : 100$ in neat dVL. $[\text{dVL}]_0 = 9.98 \text{ M}$.

The log of the heating rate, β , was plotted against reciprocal temperature to give:.

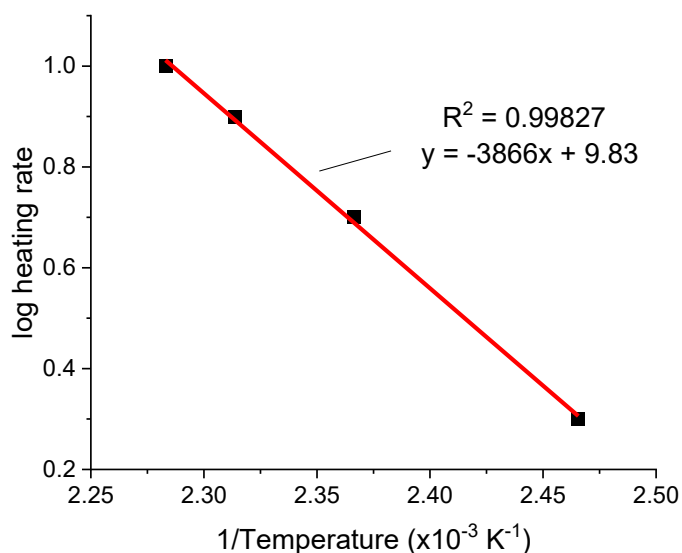


Figure S6. Plot of Log(heating rate) vs 1/temperature for the ROP dVL. Reaction conditions: heating rates of 2, 5, 8 and 10 $^{\circ}\text{C min}^{-1}$, 40 – 220 $^{\circ}\text{C}$, $[\text{Sn}(\text{Oct})_2]_0 : [\text{BnOH}]_0 : [\text{dVL}]_0 = 1 : 1 : 100$, neat, $[\text{dVL}]_0 = 9.98 \text{ M}$.

An initial ΔH^{\ddagger} is estimated from the gradient of figure S6 using:

$$\Delta H^{\ddagger}(\text{est1}) = -2.19 \times \text{gradient} \times R$$

Equation S6

$$= 70394.5 \text{ J mol}^{-1}$$

Where R is the gas constant.

The ΔH^{\ddagger} is refined as follows:

To calculate the correction factor, X, use:

$$X = \frac{\Delta H^{\ddagger}(\text{est1})}{RT}$$

Equation S7

Using $\Delta H^{\ddagger}(\text{est1})$, the peak temperature at the maximum heating rate and equation S7 gives:

$$X1 = \frac{\Delta H^\ddagger(est1)}{RT} \approx 20$$

Using Table X2.1 given in ASTM0698-05, X1 corresponds to a $D = 1.10$ (D1)

The ΔH^\ddagger is further refined using:

$$\Delta H^\ddagger(est2) = \frac{-2.303 \times R \times gradient}{D1}$$

Equation S8

$$= 67296 \text{ J mol}^{-1}$$

Using $\Delta H^\ddagger(est2)$ the peak temperature at the maximum heating rate and equation S7 gives:

$$X2 = \frac{\Delta H^\ddagger(est2)}{RT} \approx 19$$

Using Table X2.1 given in ASTM0698-05, this estimate of X2 corresponds to a $D = 1.1053$ (D2)

The ΔH^\ddagger (final) is given by:

$$\Delta H^\ddagger(final) = \frac{-2.303 \times R \times gradient}{D2}$$

$$= 66.9 \text{ J mol}^{-1}$$

The A value was calculated using:

$$A = \frac{\beta \times \Delta H^\ddagger \times e^{\Delta H^\ddagger/RT}}{RT^2}$$

Equation S9

$$= 699485 \text{ s}$$

$$\ln A = 13.5$$

3. Additional information

3.1 Benchmarking DSC kinetics

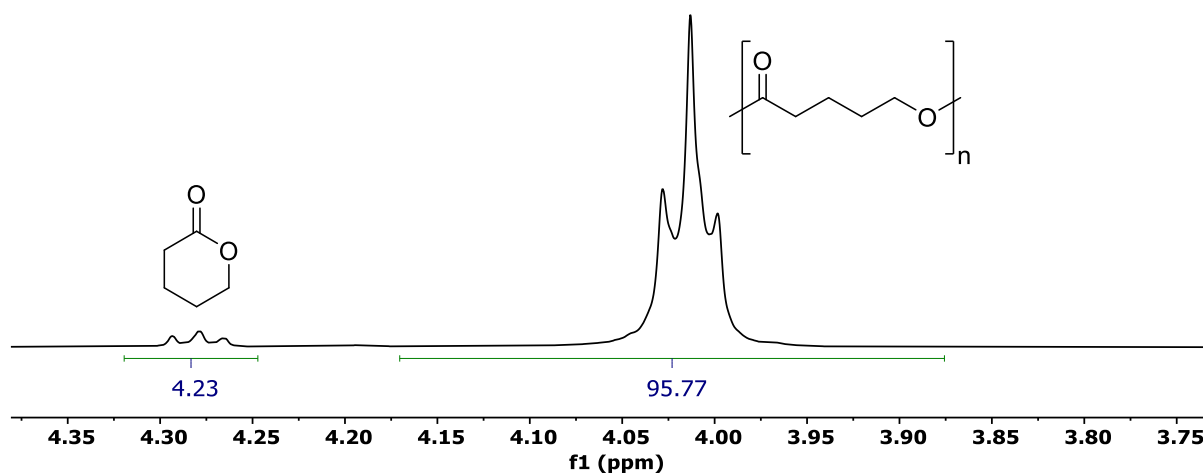


Figure S7. ¹H NMR spectrum of PVL (dVL ROP) conducted in a DSC. Reaction conditions: 100 °C, [Sn(Oct)₂]₀: [BnOH]₀: [dVL]₀ = 1:1:100, in neat dVL ([dVL]₀ = 9.98 M). The monomer conversion was used to determine [PVL] as [PVL] = [dVL]₀ - [dVL]_t.

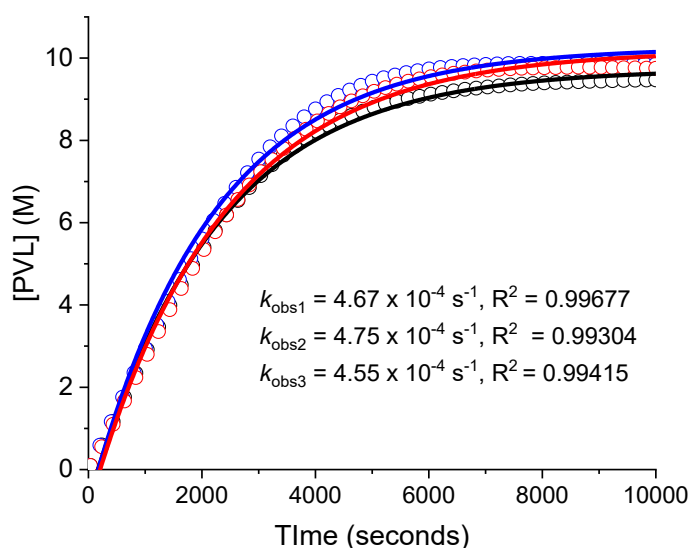


Figure S8. Plot of [PVL] vs time showing repeat, independent experiments (red, blue and black circles). The final conversion of dVL was determined by ¹H NMR spectroscopy (Fig. S7) and used to calculate the [PVL] vs time profile. The red, blue and black lines each show the first-order exponential fit to the data which was used to extract k_{obs} values.

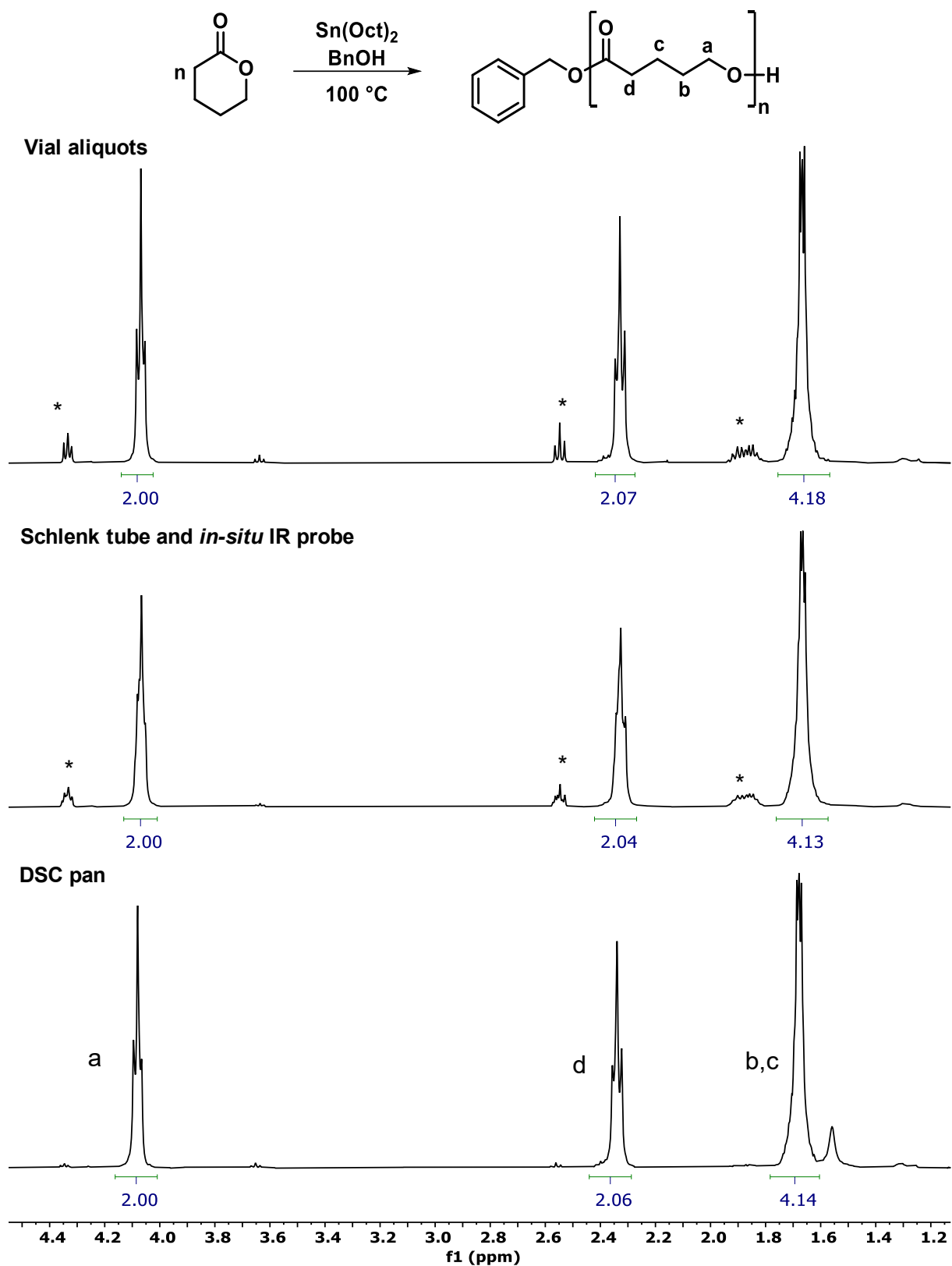


Figure S9. Stacked crude ^1H NMR spectra from dVL ROP conducted in vial (top), Schlenk (middle) and DSC pan (bottom). Reaction conditions: $120\text{ }^\circ\text{C}$, $[\text{Sn}(\text{Oct})_2]_0:[\text{BnOH}]_0:[\text{dVL}]_0 = 1:1:100$, in neat dVL ($[\text{dVL}]_0 = 9.98\text{ M}$). * indicates residual monomer

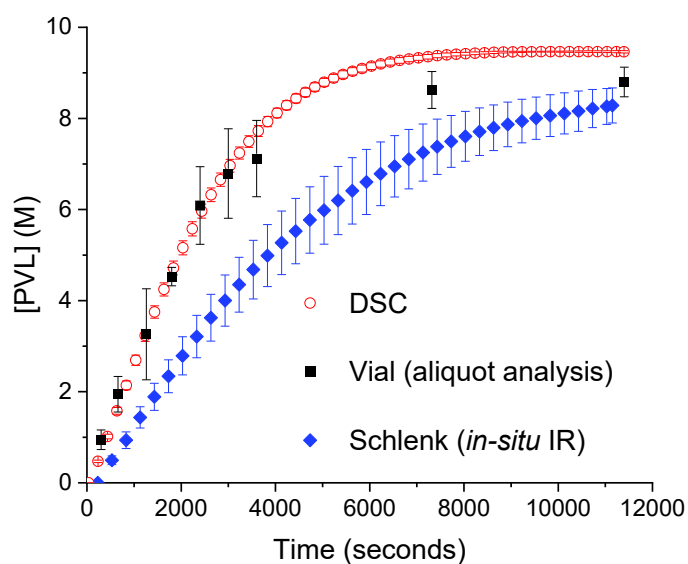


Figure S10. Plot of [PVL] vs time for the ROP of dVL. Reaction conditions: 100 °C, $[\text{Sn}(\text{Oct})_2]_0:[\text{BnOH}]_0:[\text{dVL}]_0 = 1:1:100$, in neat monomer ($[\text{dVL}]_0 = 9.98 \text{ M}$). (Table 1, entries 1 – 2 and Table S3). Reactions were monitored by DSC (red, conducted in DSC), ^1H NMR spectroscopy (black, conducted in vial) and in-situ IR spectroscopy (red, conducted in Schlenk). The error bars are the standard deviation of the mean taken from three repeat runs (note: error on DSC runs is significantly smaller).

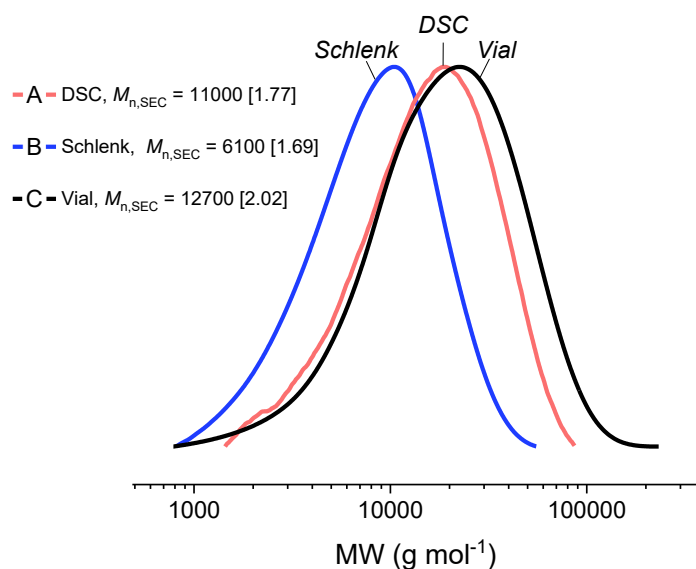


Figure S11. SEC chromatograms of PVL formed in DSC pan (red), vial (black) or Schlenk tube (blue). Reaction conditions: $[\text{Sn}(\text{Oct})_2]_0:[\text{BnOH}]_0:[\text{dVL}]_0 = 1:1:100$, in neat monomer ($[\text{dVL}]_0 = 9.98 \text{ M}$).

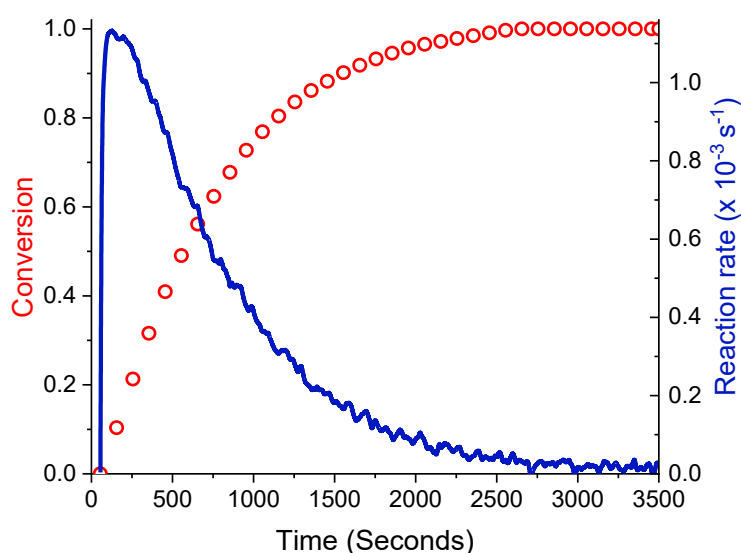


Figure S13. Plot of PLLA conversion (red circles, left y axis) and reaction rate (blue line, right y axis) vs time for the ROP of LLA. Reaction conditions: 120 °C, $[\text{Sn}(\text{Oct})_2]_0:[\text{BnOH}]_0:[\text{LLA}]_0 = 1:1:100$, in 1,2-dimethoxybenzene, $[\text{LLA}]_0 = 1.0 \text{ M}$. Conversion was determined from the normalized integral of the heatflow vs time data in figure S12. The reaction rate is equivalent to the normalized heat flow in figure S12.

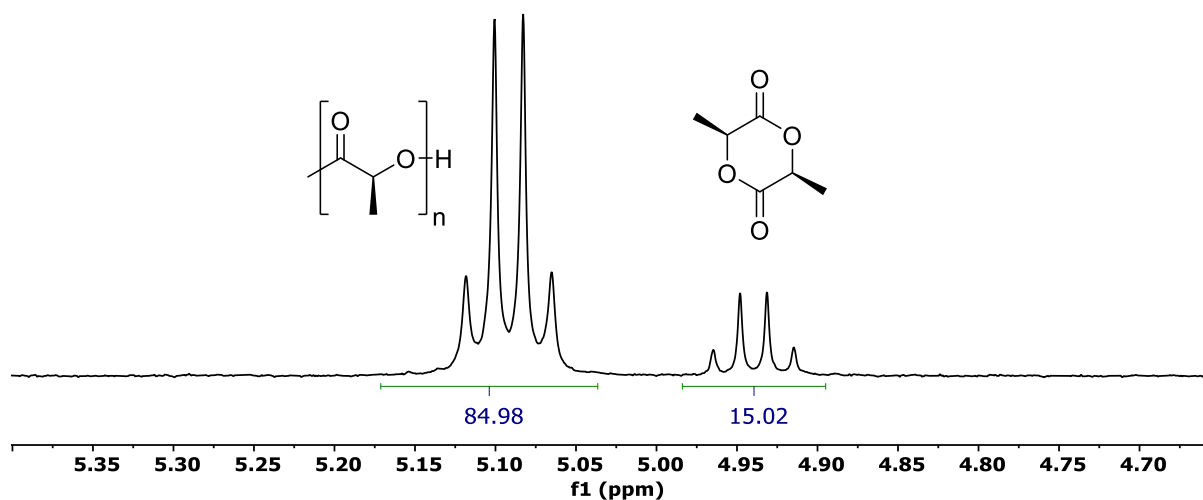


Figure S14. ^1H NMR spectrum of PLLA (LLA ROP) conducted in a DSC. Reaction conditions: 120 °C, $[\text{Sn}(\text{Oct})_2]_0:[\text{BnOH}]_0:[\text{LLA}]_0 = 1:1:100$, $[\text{LLA}]_0 = 1.0 \text{ M}$ in 1,2-dimethoxybenzene. The monomer conversion (83%) was used to determine $[\text{PLLA}]$ as $[\text{PLLA}] = [\text{LLA}]_0 - [\text{LLA}]_t$

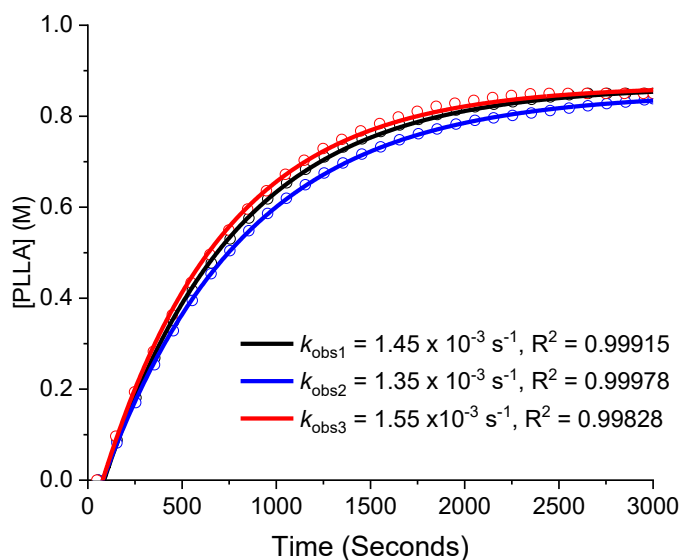


Figure S15. Plots of [PLLA] vs time showing repeat, independent experiments (red, blue and black circles). The final conversion of LLA was determined by ^1H NMR spectroscopy (Fig. S14) which was used to calculate the [PLLA] vs time profile. The red, blue and black lines each show the first-order exponential fit to the data which was used to extract k_{obs} values

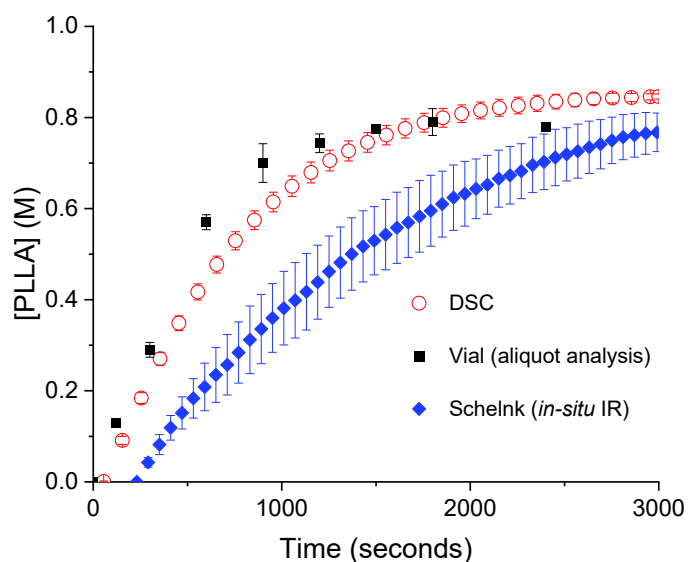


Figure S16. Plots of [PLLA] vs time for the ROP of LLA. Reaction conditions: $120\text{ }^\circ\text{C}$, $[\text{Sn}(\text{Oct})_2]_0:[\text{BnOH}]_0:[\text{LLA}]_0 = 1:1:100$, $[\text{LLA}]_0 = 1.0\text{ M}$ in 1,2-dimethoxybenzene. (Table 1, entries 3 – 4 and Table S3). Reactions were monitored by DSC (red, conducted in DSC), ^1H NMR spectroscopy (black, conducted in vial) and in-situ IR spectroscopy (blue, conducted in Schlenk). The error bars are the standard deviation of the mean taken from three repeat runs (note: error on DSC runs is significantly smaller).

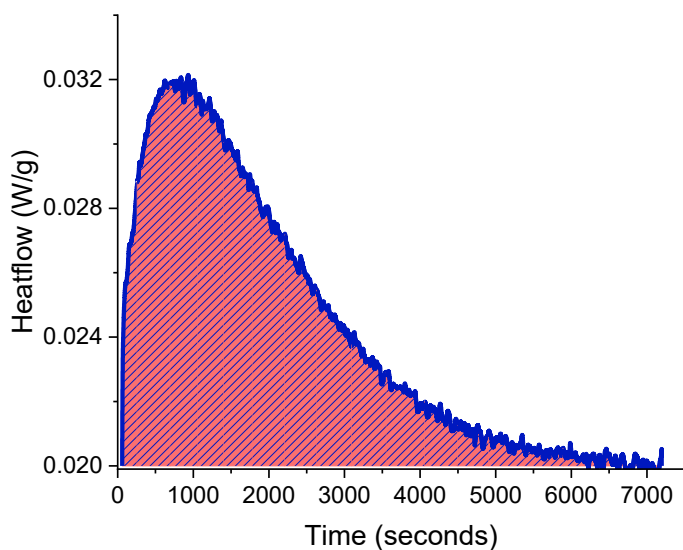
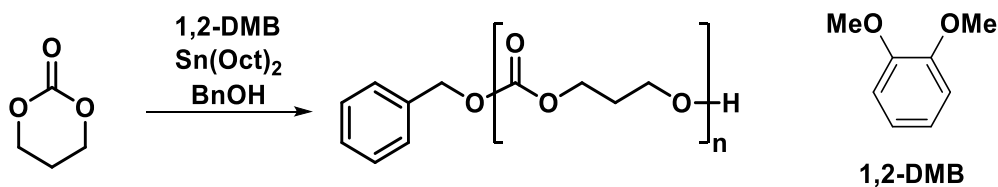


Figure S17 Plots of heatflow vs time for ROP of TMC. Reaction conditions: 120 °C, $[\text{Sn}(\text{Oct})_2]_0 : [\text{BnOH}]_0 : [\text{TMC}]_0 = 1 : 1 : 100$, $[\text{TMC}]_0 = 2.0 \text{ M}$ in 1,2-dimethoxybenzene. (Table 1, entries 5). The shaded area shows the region where the integral was taken to generate figure S18.

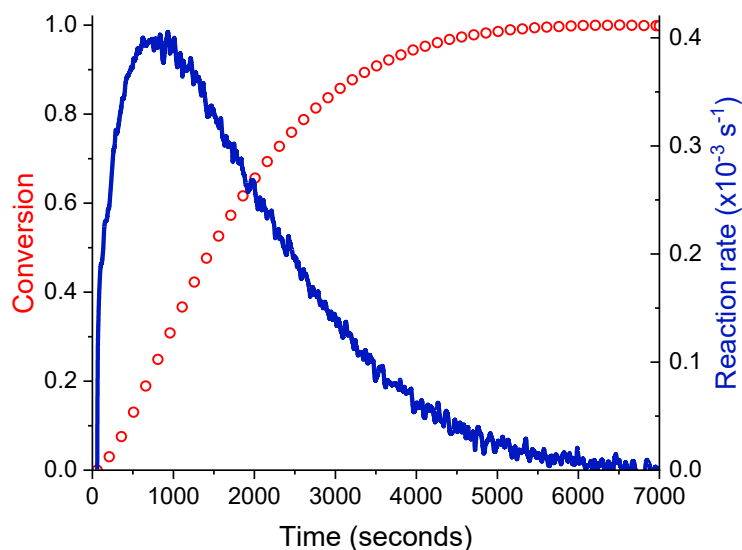


Figure S18. Plot of PTMC conversion (red circles, left y axis) and reaction rate (blue line, right y axis) vs time. Reaction conditions: 120 °C, $[\text{Sn}(\text{Oct})_2]_0 : [\text{BnOH}]_0 : [\text{TMC}]_0 = 1 : 1 : 100$, $[\text{TMC}]_0 = 2.0 \text{ M}$ in 1,2-dimethoxybenzene. Conversion was determined from the normalized integral of the heatflow vs time data in figure S17. The reaction rate is equivalent to the normalized heat flow in figure S17.

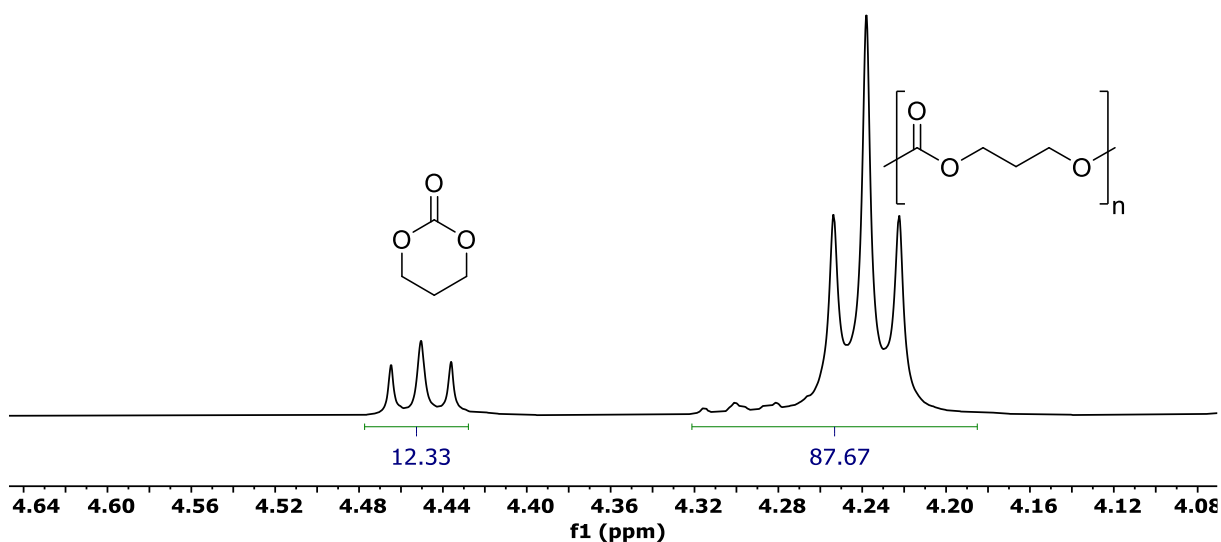


Figure S19. ^1H NMR spectrum of PTMC (TMC ROP) formed in a DSC. Reaction conditions: 120 °C, $[\text{Sn}(\text{Oct})_2]_0 : [\text{BnOH}]_0 : [\text{TMC}]_0 = 1 : 1 : 100$, $[\text{TMC}]_0 = 2.0$ M in 1,2-dimethoxybenzene. The monomer conversion (88%) was used to determine $[\text{PTMC}]$ as $[\text{PTMC}] = [\text{TMC}]_0 - [\text{TMC}]$; figure S20.

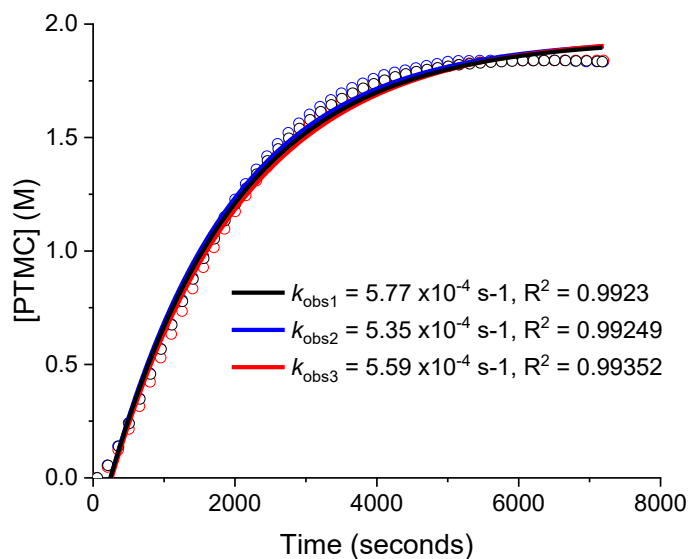


Figure S20. Plots of $[\text{PTMC}]$ vs time showing repeat, independent experiments (red, blue and black circles). The final conversion of TMC was determined by ^1H NMR spectroscopy (Fig. S19) which was used to calculate the $[\text{PTMC}]$ vs time profile. The red, blue and black lines each show the first-order exponential fit to the data which was used to extract k_{obs} values

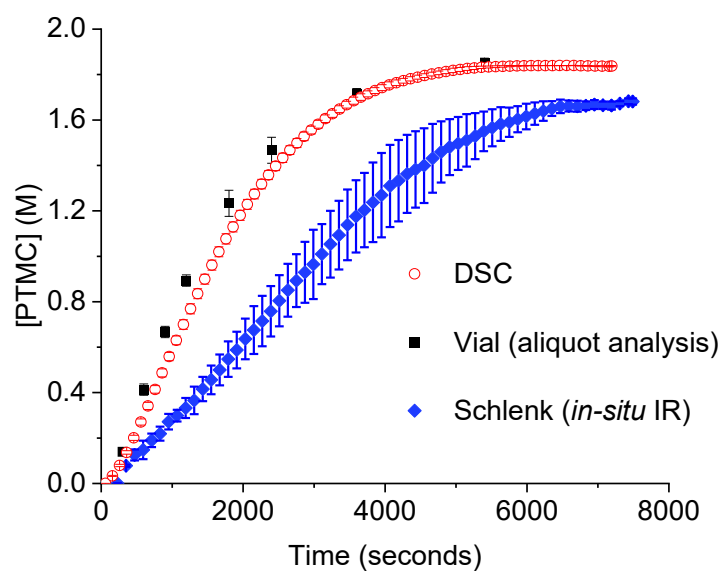


Figure S21. Plots of [PTMC] vs time. Reaction conditions: 120 °C, $[\text{Sn}(\text{Oct})_2]_0:[\text{BnOH}]_0:[\text{TMC}]_0 = 1:1:100$, $[\text{TMC}]_0 = 2.0 \text{ M}$ in 1,2-dimethoxybenzene (Table 1, entries, 5 – 6). Reactions were monitored by DSC (red, conducted in DSC), ^1H NMR spectroscopy (black, conducted in vial) and in-situ IR spectroscopy (blue, conducted in Schlenk). The error bars are the standard deviation of the mean taken from three repeat runs (note: error on DSC reactions is significantly smaller than vial or Schlenk reactions).

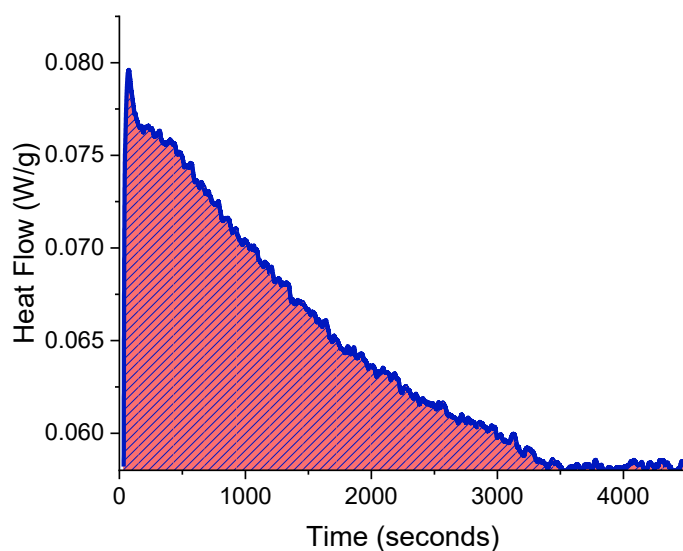
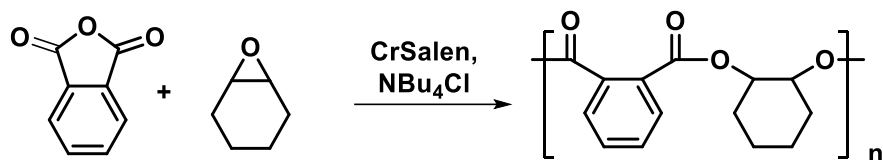


Figure S22. Plot of heatflow vs time for the ROCOP of CHO and PA at 85 °C $[(\text{salcy})\text{CrCl}]_0:[\text{PPNCl}]_0:[\text{PA}]_0:[\text{CHO}]_0 = 1: 50: 2000$ in neat CHO ($[\text{CHO}]_0 = 9.5 \text{ M}$, Table 1, entry 5). The shaded area shows the region where the integral was taken to generate figure S23. Note these loadings of PA/CHO were chosen to maximise the polymerization rate, as the reaction is first order in CHO and zero-order in anhydride, and ensure complete solubility of the PA monomer at room temperature.

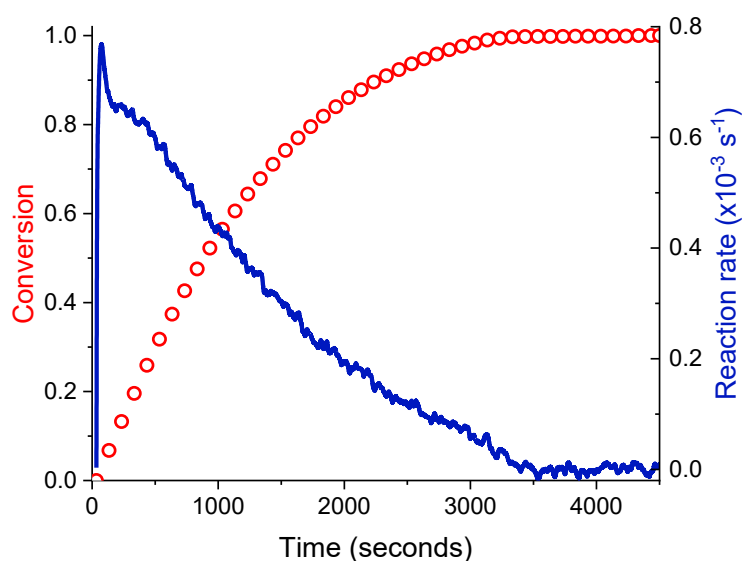


Figure S23. Plots of PA conversion (red circles, left y axis) and reaction rate (blue line, right y axis) vs time, for the ROCOP of PA and CHO. Reaction conditions: 85 °C, $[(\text{salcy})\text{CrCl}]_0:[\text{PPNCl}]_0:[\text{PA}]_0:[\text{CHO}]_0 = 1: 50: 2000$ in neat CHO ($[\text{CHO}]_0 = 9.5 \text{ M}$). Conversion was determined from the normalized integral of the heatflow vs time data in figure S22. The reaction rate is equivalent to the normalized heat flow in figure S22.

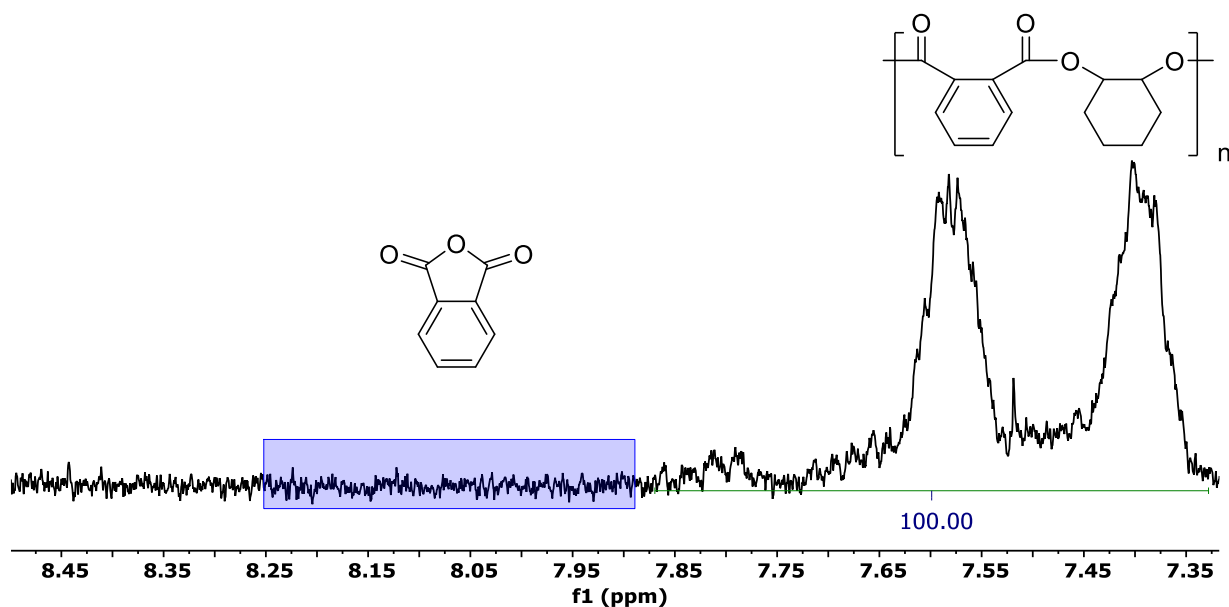


Figure S24. ^1H NMR spectrum of P(PA-*alt*-CHO) (PA/CHO ROCOP) conducted in a DSC. Reaction conditions: $85\text{ }^\circ\text{C}$, [(salcy)CrCl] $_0$: [PPNCl] $_0$: [PA] $_0$: [CHO] $_0$ = 1: 50: 2000, in neat CHO ([CHO] $_0$ = 9.5 M). The monomer conversion (100%) was used to determine [P(PA-*alt*-CHO)] as [P(PA-*alt*-CHO)] = [PA] $_0$ - [PA] $_t$ (note, shaded area shows region PA resonances appear).

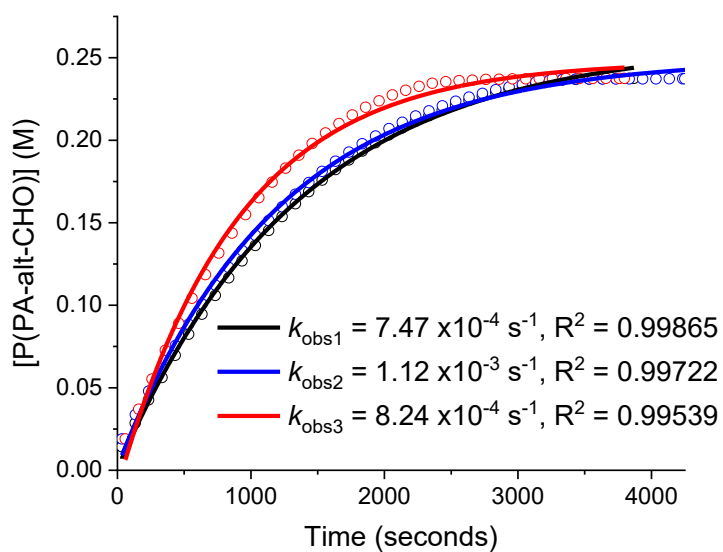


Figure S25. Plots of [P(PA-*alt*-CHO)] vs time showing repeat, independent experiments (red, blue and black circles). The final conversion of PA was determined by ^1H NMR spectroscopy (Fig. S24) which was used to calculate the [P(PA-*alt*-CHO)] vs time profile. The red, blue and black lines each show the first-order exponential fit to the data which was used to extract k_{obs} values.

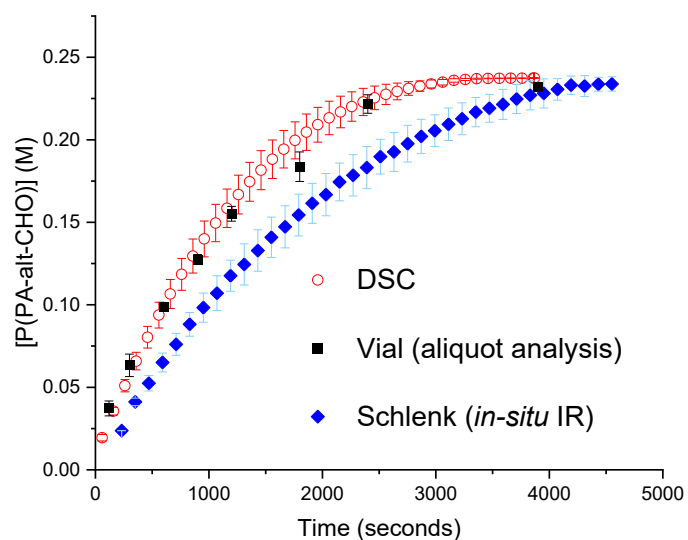


Figure S26. Plots of $[P(\text{PA-}i\text{alt-CHO})]$ vs time. Reaction conditions: 85 °C, $[(\text{salcy})\text{CrCl}]_0:[\text{PPNCl}]_0:[\text{PA}]_0:[\text{CHO}]_0 = 1:1:50:2000$, in neat CHO ($[\text{CHO}]_0 = 9.5$ M, Table 1, entries 5 – 6 and Table S3). Reactions were monitored by DSC (red, conducted in DSC), ^1H NMR spectroscopy (black, conducted in vial) and in-situ IR (blue, conducted in Schlenk). The error bars are the standard deviation of the mean taken from three repeat runs (note: error on DSC reactions is significantly smaller than vial or Schlenk reactions).

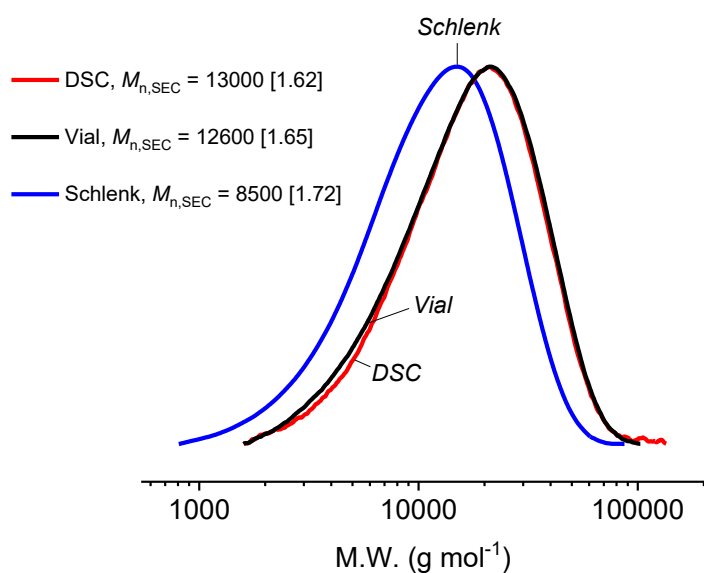


Figure S27. SEC chromatograms of PTMC formed in DSC (red), vial (black) or Schlenk tube (blue). Reaction conditions: 120 °C, $[\text{TMC}]_0 : [\text{BnOH}]_0 : [\text{Sn}(\text{Oct})_2]_0$ 1: 1: 100, $[\text{TMC}]_0 = 2$ M in 1,2-dimethoxybenzene.

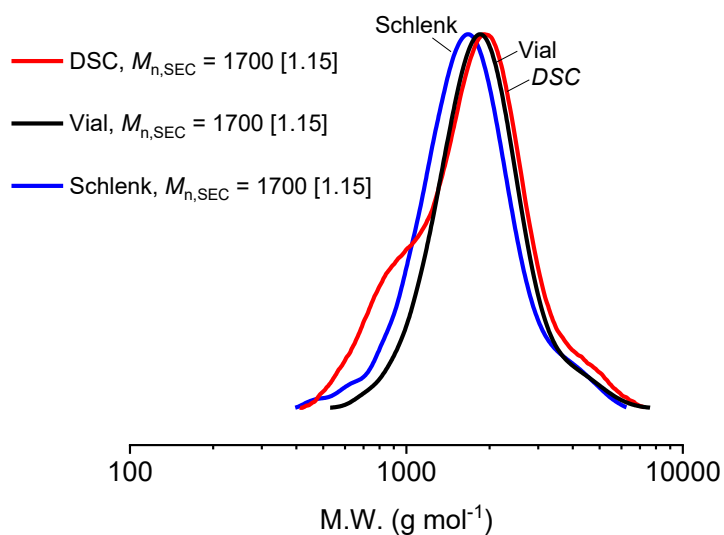


Figure S28. SEC chromatograms of P(PA-*alt*-CHO) formed in DSC (red), vial (black) or Schlenk tube (blue). Reaction conditions: 85 °C, $[(\text{salcy})\text{CrCl}]_0 : [\text{PPNCl}]_0 : [\text{PA}]_0 : [\text{CHO}]_0$ 1: 1: 50: 2000 in neat CHO ($[\text{CHO}]_0 = 9.5$ M).

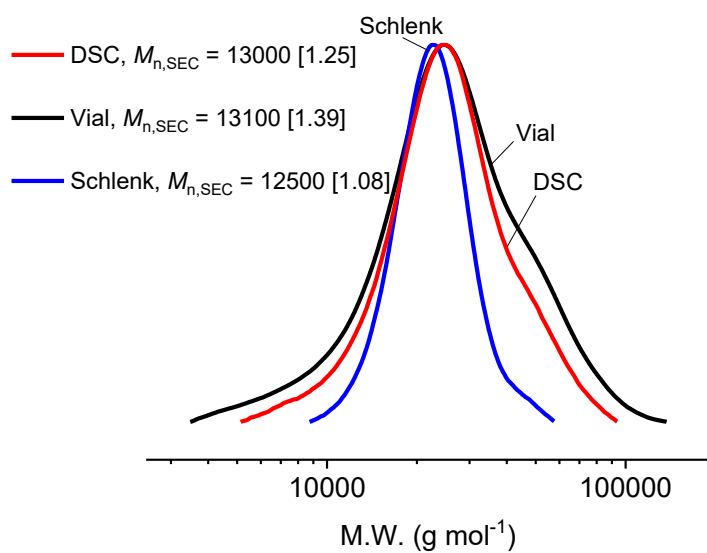


Figure S29. SEC chromatograms of PLLA formed in DSC pan (red), vial (black) or Schlenk tube (blue). Reaction conditions: 120 °C, $[\text{Sn}(\text{Oct})_2]_0 : [\text{BnOH}]_0 : [\text{LLA}]_0$ at 1: 1: 100 $[\text{LLA}]_0 = 1$ M in 1,2-dimethoxybenzene. Note: correction factor of 0.58 applied.²

Table S3. Summary of kinetic data using *in-situ* IR probe.

| # | Mon. | Temp. (°C) | k_{obs} ($\times 10^{-4} \text{ s}^{-1}$) ^[a] | TOF (h^{-1}) ^[b] | Poly. Conv. (%) ^[c] | $M_{n,\text{SEC}}$ (g mol^{-1}) [D_M] ^[d] | Overall Mass needed (g) ^[e] |
|------------------|------------|------------|---|--|--------------------------------|---|--|
| 1 ^[f] | dVL | 100 | 2.2 (± 0.5) | 37(± 7) | 91(± 2) | 6100 [1.69] | 6.00 |
| 2 ^[g] | LLA | 120 | 8.6 (± 2.1) | 133 (± 30) | 82(± 3) | 12500 [1.08] ^[h] | 6.00 |
| 3 ^[i] | TMC | 120 | 2.4 (± 0.5) | 54 (± 5) | 90(± 3) | 8500 [1.72] | 6.00 |
| 4 ^[j] | PA/ CHO | 100 | 5.1 (± 0.9) | 125(± 9) | >99% | 1700 [1.15] | 6.00 |

[a] The rate constants are all obtained by exponential fits to the polymer/monomer conversion vs time data. [b] Catalytic Activity obtained as turn-over-frequency, TOF= # moles monomer consumed/# moles catalyst/time. For all experiments the TOF was determined at 33% monomer conversion from the rate constant monitoring. [c] The polymer conversion was determined at the end of the reaction using ¹H NMR spectroscopy, with mass balance confirmed by weighing. [d] Polymer molecular weight (M_n) determined by SEC, with a THF eluent and polystyrene standards (PVL, P(PA-*alt*-CHO), PTMC) or with CHCl_3 eluent and polystyrene standards (PLLA). [e] The total mass used for the combined triplicate measurements. [f] Polymerization conditions: $[\text{Sn}(\text{Oct})_2]_0 : [\text{BnOH}]_0 : [\text{dVL}]_0 = 1:1:100$ at 100 °C, $[\text{dVL}]_0 = \text{bulk}$ (9.98 M) [g] Polymerization conditions $[\text{Sn}(\text{Oct})_2]_0 : [\text{BnOH}]_0 : [\text{LLA}]_0 = 1:1:100$ at 120 °C, $[\text{LLA}]_0 = 1.0 \text{ M}$ in 1,2-dimethoxybenzene.[h] correction factor of 0.58 applied². [i] Polymerization conditions $[\text{Sn}(\text{Oct})_2]_0 : [\text{BnOH}]_0 : [\text{TMC}]_0 = 1:1:100$ at 120 °C, $[\text{TMC}]_0 = 2.0 \text{ M}$ in 1,2-dimethoxybenzene. [j] $[(\text{salcy})\text{CrCl}]_0 : [\text{NBu}_4\text{Cl}]_0 : [\text{PA}]_0 : [\text{CHO}]_0 = 1: 1: 50: 2000$ at 85 °C, $[\text{CHO}]_0 = 9.5 \text{ M}$ in neat CHO.

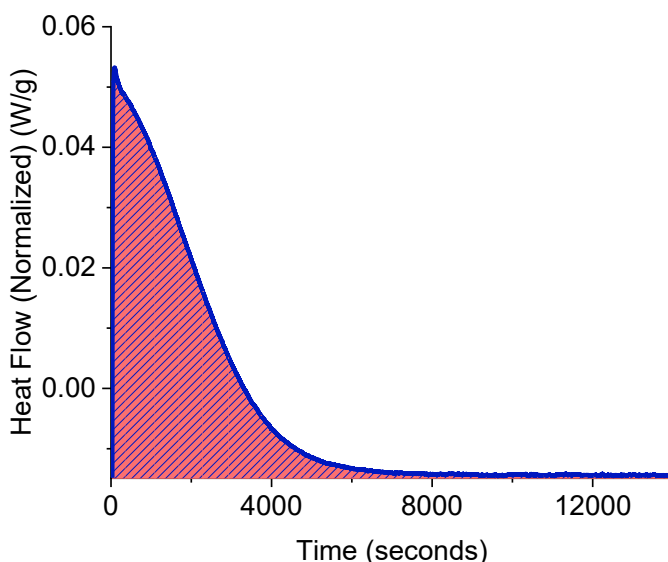


Figure S30. Plot of heatflow vs time for the ROP of dVL. Reaction conditions: 160 °C, $[\text{Sn}(\text{Oct})_2]_0 : [\text{BnOH}]_0 : [\text{dVL}]_0 = 1:1:1000$, in neat dVL. $[\text{dVL}]_0 = 9.98 \text{ M}$). The shaded area shows the integral that was used to generate figure S31.

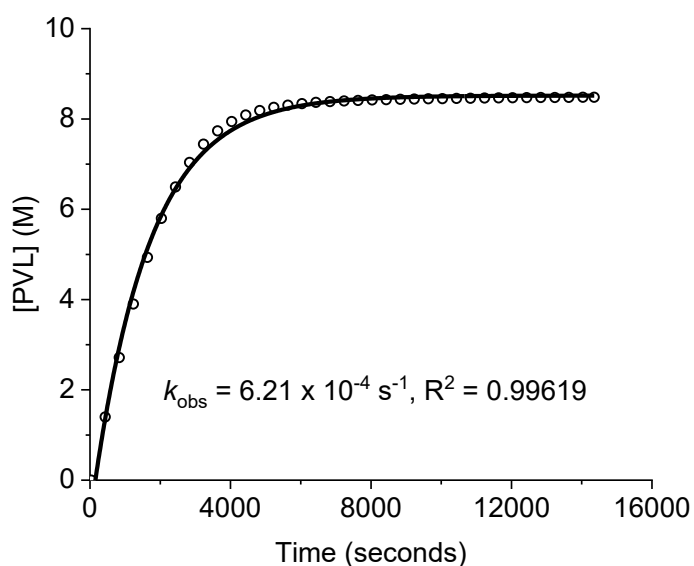


Figure S31. Plot of [PVL] vs time (black circles, 160 °C, [Sn(Oct)₂]₀:[BnOH]₀:[dVL]₀ = 1:1:1000, in neat monomer, [dVL]₀ = 9.98 M). The final conversion of dVL was determined by ¹H NMR spectroscopy and used to calculate the [PVL] vs time profile. The black line show the first-order exponential fit to the data which was used to extract *k*_{obs} values.

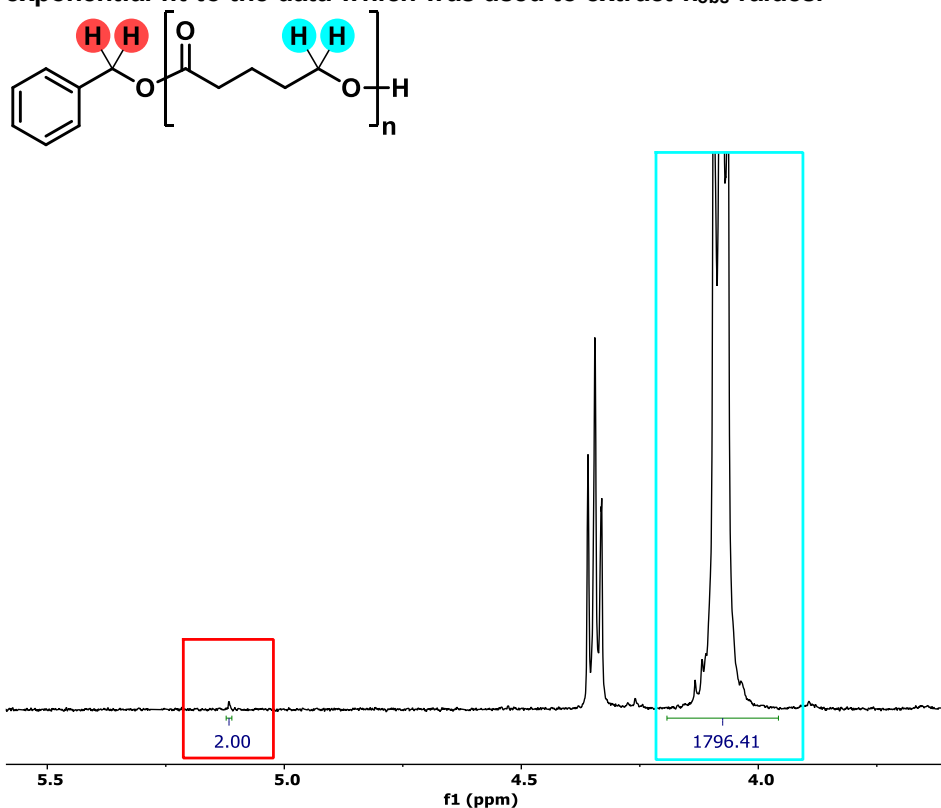


Figure S32. ¹H NMR spectrum of PVL (dVL ROP) conducted in a DSC. Reaction conditions: 160 °C, [Sn(Oct)₂]₀:[BnOH]₀:[dVL]₀ = 1:1:1000, in neat dVL ([dVL]₀ = 9.98 M). The highted integrals show the benzyl alcohol end group and PVL repeat unit which gives a degree of polymerization of 898 and *M*_{n,NMR} of 89,900 g mol⁻¹. Note residual monomer is detected at 4.25 ppm.

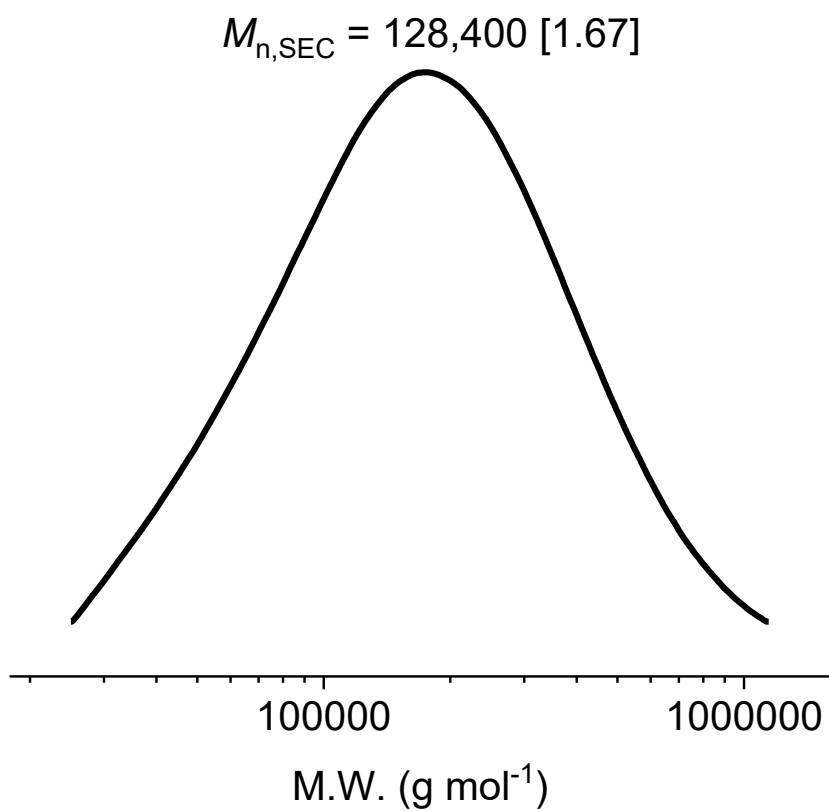


Figure S33. SEC chromatograms of PVL formed in DSC pan determined in chloroform eluent. Reaction conditions: 160 °C, $[\text{Sn}(\text{Oct})_2]_0:[\text{BnOH}]_0:[\text{dVL}]_0 = 1:1:1000$, in neat monomer ($[\text{dVL}]_0 = 9.98 \text{ M}$).

3.2 Isothermal kinetics for dVL, LLA and TMC ROP and PA/CHO ROCOP

Table S4. ROP of dVL using Sn(Oct)₂/BnOH catalyst at 100, 105, 110, 115 and 120 °C

| Entry | Temp. (°C) | k_{obs} [a] ($\times 10^{-4} \text{ s}^{-1}$) | k_{obs} [b] ($\times 10^{-4} \text{ s}^{-1}$) | TOF[c] (h^{-1}) |
|-------|------------|---|---|----------------------------|
| 1 | 100 | 4.66636 | 4.7 | 100±10 |
| | | 4.75489 | ± | |
| | | 4.55581 | 0.1 | |
| 2 | 105 | 4.66636 | 5.3 | 150±20 |
| | | 4.66636 | ± | |
| | | 6.57562 | 0.9 | |
| 3 | 110 | 7.62195 | 6.5 | 160±10 |
| | | 6.08643 | ± | |
| | | 5.91017 | 0.8 | |
| 4 | 115 | 9.53289 | 8.7 | 190±10 |
| | | 8.01282 | ± | |
| | | 8.66551 | 0.6 | |
| 5 | 120 | 13.33333 | 11.9 | 250±10 |
| | | 11.17318 | ± | |
| | | 11.23848 | 1.0 | |

Reactions conducted in DSC pans with Sn(Oct)₂: BnOH: dVL loadings of 1: 1: 100 in neat dVL, [dVL]₀ = 9.98 M.^[a] Determined from exponential fit of conversion vs time profiles from 0 – 90% conversion.^[b] k_{obs} , error = standard deviation from 3 repeats ^[d] TOF = moles of dVL consumed/time * moles of catalyst. Determined from 0 – 30% conversion.

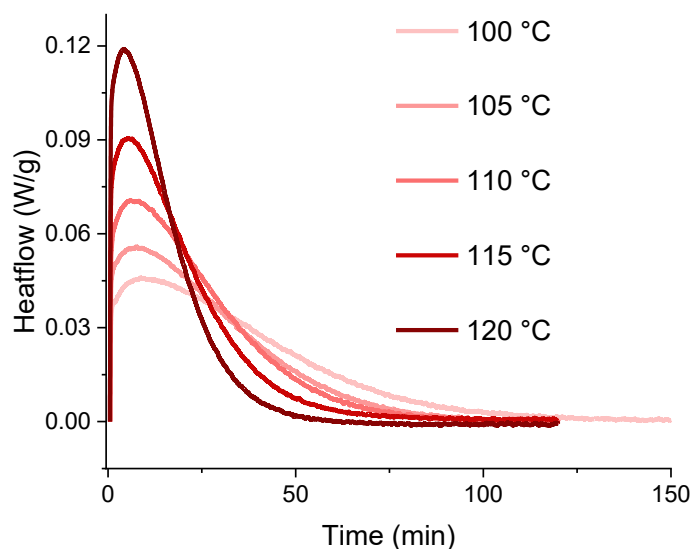


Figure S34. Plots of heatflow vs time for the ROP of dVL. Reactions were performed at 100, 105, 110, 115 and 120 °C with loadings of [Sn(Oct)₂]₀: [BnOH]₀: [dVL]₀ = 1: 1: 100 in neat dVL. [dVL]₀ = 9.98 M.

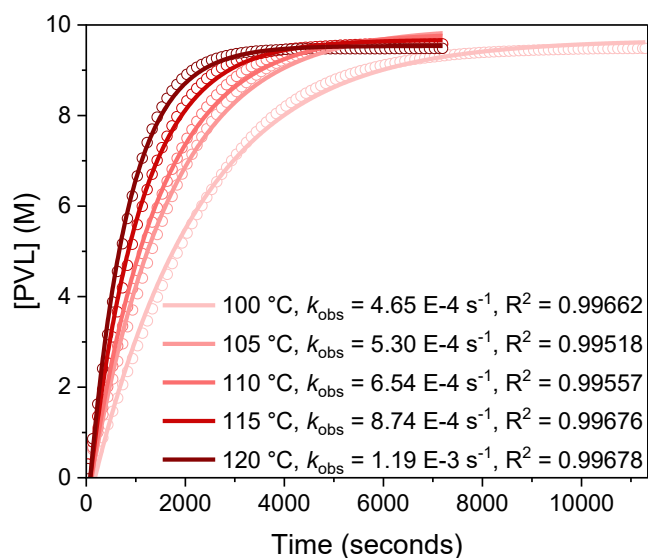


Figure S35. Plots of [PVL] vs time. Reactions were performed at 100, 105, 110, 115 and 120 °C with loadings of $[\text{Sn}(\text{Oct})_2]_0 : [\text{BnOH}]_0 : [\text{dVL}]_0 = 1 : 1 : 100$ in neat dVL. $[\text{dVL}]_0 = 9.98 \text{ M}$

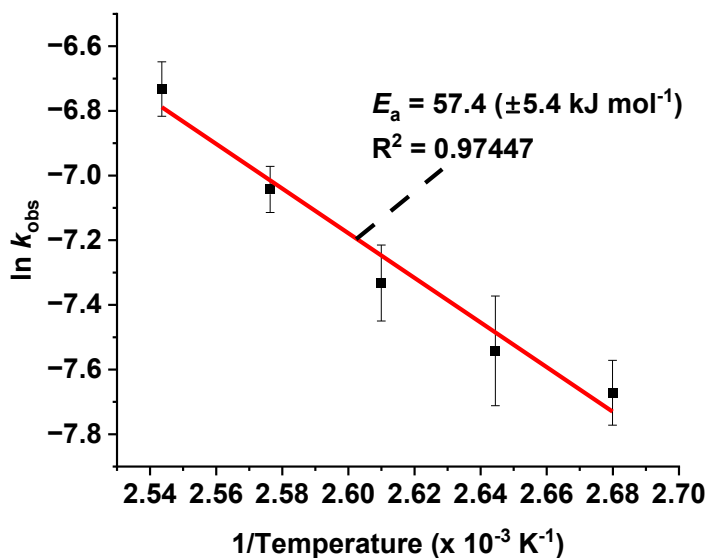


Figure S36. Plot of $\ln k_{\text{obs}}$ vs $1/\text{Temperature}$ for the ROP of dVL. Reactions were performed at 100, 105, 110, 115 and 120 °C with loadings of $[\text{Sn}(\text{Oct})_2]_0 : [\text{BnOH}]_0 : [\text{dVL}]_0 = 1 : 1 : 100$ in neat dVL. $[\text{dVL}]_0 = 9.98 \text{ M}$. Data taken from table S4.

Table S5. ROP of LLA using Sn(Oct)₂/BnOH catalyst at 120, 125, 130, 135 and 140 °C

| Entry | Temp. (°C) | $k^{[a]}$ ($\times 10^{-3} \text{ s}^{-1}$) | $k_{\text{obs}}^{[b]}$ ($\times 10^{-3} \text{ s}^{-1}$) | TOF ^[c] (h^{-1}) |
|-------|------------|--|---|--|
| 1 | 120 | 1.45 | 1.5 ± 0.1 | 260 ± 10 |
| | | 1.35 | | |
| | | 1.55 | | |
| 2 | 125 | 1.89 | 1.9 ± 0.1 | 330 ± 10 |
| | | 1.74 | | |
| | | 1.94 | | |
| 3 | 130 | 2.42 | 2.1 ± 0.2 | 370 ± 20 |
| | | 1.94 | | |
| | | 1.94 | | |
| 4 | 135 | 3.07 | 3.1 ± 0.5 | 470 ± 20 |
| | | 3.68 | | |
| | | 2.43 | | |
| 5 | 140 | 3.76 | 3.6 ± 0.2 | 570 ± 30 |
| | | 3.70 | | |
| | | 3.27 | | |

Reactions conducted in DSC pans with Sn(Oct)₂: BnOH: LLA loadings of 1: 1: 100, [LLA]₀ = 1 M in 1,2-dimethoxybenzene.^[a] Determined from exponential fit of conversion vs time profiles from 0 – 90% conversion.^[b] k_{obs} = average of 3 repeats, error = standard deviation from 3 repeats ^[d] TOF = moles of LLA consumed/time * moles of catalyst. Determined from 0 – 30% conversion.

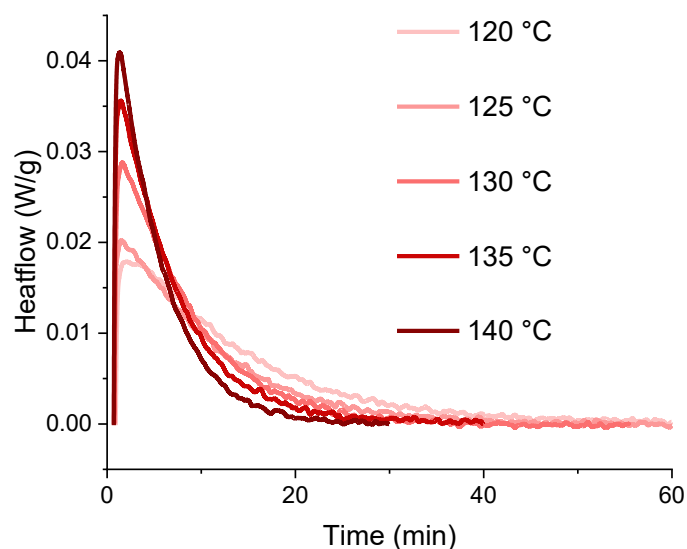


Figure S37. Plots of heatflow vs time for the ROP of LLA. Reactions were performed at 120, 125, 130, 135 and 140 °C with loadings of [Sn(Oct)₂]₀: [BnOH]₀: [LLA]₀ = 1: 1: 100. [LLA]₀ = 1 M in 1,2-dimethoxybenzene.

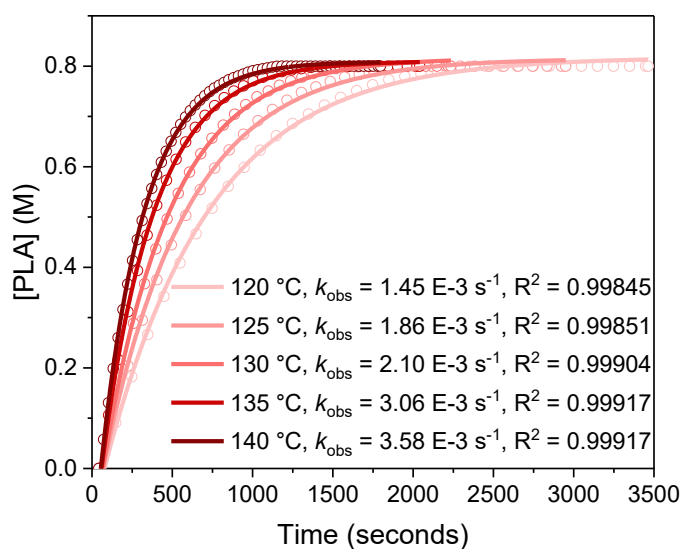


Figure S38. Plots of [PLLA] vs time. Reactions were performed at 120, 125, 130, 135 and 140 °C with loadings of $[\text{Sn}(\text{Oct})_2]_0$: $[\text{BnOH}]_0$: $[\text{LLA}]_0 = 1$: 1: 100. $[\text{LLA}]_0 = 1$ M in 1,2-dimethoxybenzene.

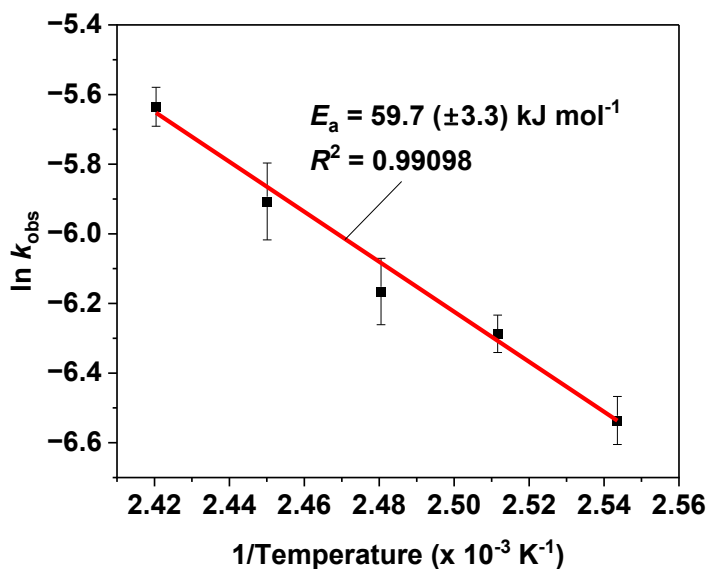


Figure S39. Plot of $\ln k_{\text{obs}}$ vs $1/\text{temperature}$ for the ROP of LLA. Reactions were performed at 120, 125, 130, 135 and 140 °C with loadings of $[\text{Sn}(\text{Oct})_2]_0$: $[\text{BnOH}]_0$: $[\text{LLA}]_0 = 1$: 1: 100. $[\text{LLA}]_0 = 1$ M in 1,2-dimethoxybenzene. Data taken from table S5

Table S6. Solution ROP of TMC using Sn(Oct)₂/BnOH catalyst at 120, 130, 135, 140 and 150 °C

| Entry | Temp. (°C) | $k^{[a]}$ ($\times 10^{-3} \text{ s}^{-1}$) | $k_{\text{obs}}^{[b]}$ ($\times 10^{-3} \text{ s}^{-1}$) | TOF ^[c] (h^{-1}) |
|-------|------------|--|---|--|
| 1 | 120 | 0.577 | 0.56 ± 0.01 | 110 ± 10 |
| | | 0.536 | | |
| | | 0.559 | | |
| 2 | 130 | 1.00 | 1.0 ± 0.1 | 180 ± 10 |
| | | 1.10 | | |
| | | 0.980 | | |
| 3 | 135 | 1.56 | 1.56 ± 0.1 | 250 ± 10 |
| | | 1.56 | | |
| | | 1.57 | | |
| 4 | 140 | 1.80 | 1.8 ± 0.1 | 300 ± 10 |
| | | 1.79 | | |
| | | 1.81 | | |
| 5 | 150 | 3.14 | 3.2 ± 0.08 | 540 ± 40 |
| | | 3.32 | | |
| | | 3.13 | | |

Reactions conducted in DSC pans with Sn(Oct)₂: BnOH: TMC loadings of 1: 1: 100, [TMC]₀ = 2 M, in 1,2-dimethoxybenzene.^[a] Determined from exponential fit of conversion vs time profiles from 0 – 90% conversion.^[b] k_{obs} = average of 3 repeats, error = standard deviation from 3 repeats ^[c] TOF = moles of TMC consumed/time * moles of catalyst. Determined from 0 – 30% conversion.

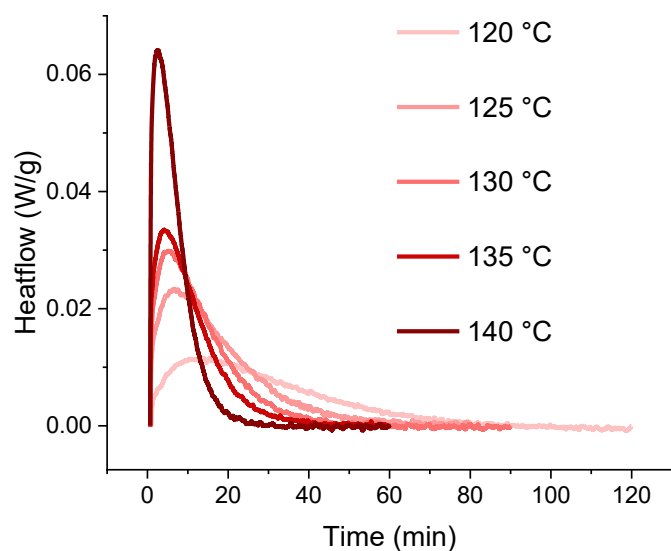


Figure S40. Plot of heatflow vs time for the ROP of TMC. Reactions were performed at 120, 130, 135, 140 and 150 °C with loadings of [Sn(Oct)₂]₀: [BnOH]₀: [TMC]₀ = 1: 1: 100 [TMC]₀ = 2 M, in 1,2-dimethoxybenzene.

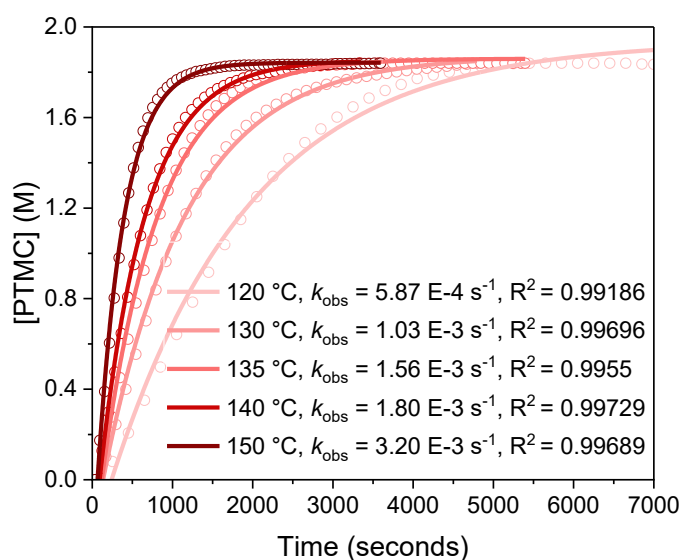


Figure S41. Plots of [PTMC] vs time. Reactions were performed at 120, 130, 135, 140 and 150 °C with loadings of $[\text{Sn}(\text{Oct})_2]_0$: $[\text{BnOH}]_0$: $[\text{TMC}]_0 = 1: 1: 100$. $[\text{TMC}]_0 = 2 \text{ M}$, 1,2-dimethoxybenzene.

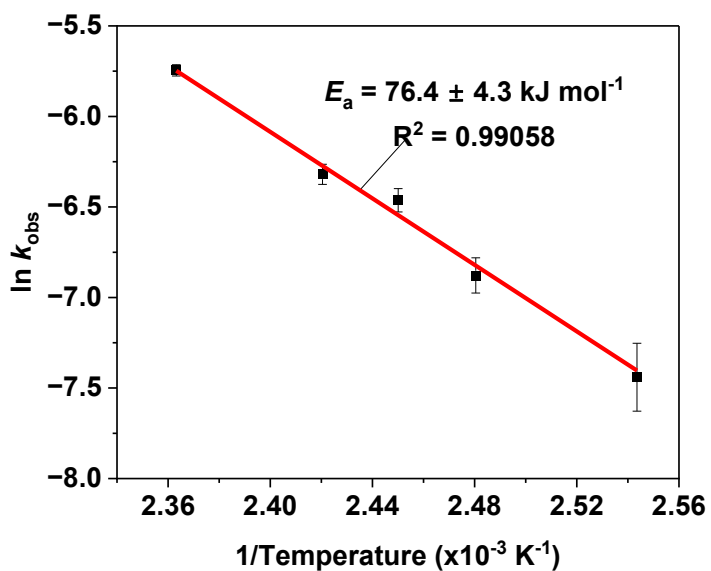


Figure S42. Plot of $\ln k_{\text{obs}}$ vs $1/\text{temperature}$ for the ROP of TMC. Reactions were performed at 120, 130, 135, 140 and 150 °C with loadings of $[\text{Sn}(\text{Oct})_2]_0$: $[\text{BnOH}]_0$: $[\text{TMC}]_0 = 1: 1: 100$. $[\text{TMC}]_0 = 2 \text{ M}$ in 1,2-dimethoxybenzene. Data taken from table S6

3.3 ROP of dVL, LLA and TMC under dynamic heating

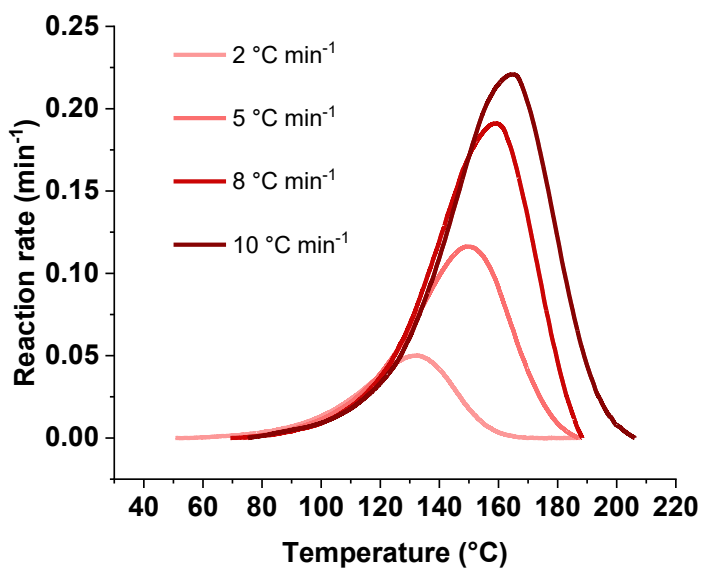


Figure S43. Plots of reaction rate vs temperature for the ROP of dVL with heating rates of 2, 5, 8 and 10 °C min⁻¹. [Sn(Oct)₂]₀: [BnOH]₀: [dVL]₀ = 1: 1: 100 in neat dVL. [dVL]₀ = 9.98 M.

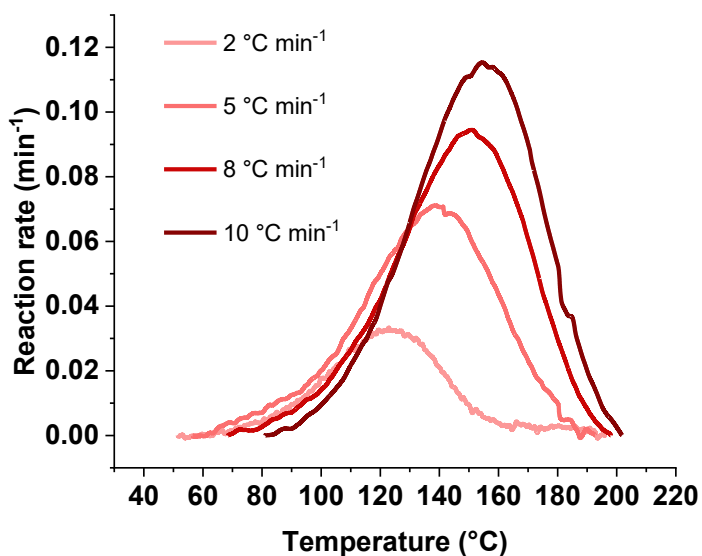


Figure S44. Plots of reaction rate vs temperature for the ROP of LLA with heating rates of 2, 5, 8 and 10 °C min⁻¹. [Sn(Oct)₂]₀: [BnOH]₀: [LLA]₀ = 1: 1: 100. [LLA]₀ = 1 M in 1,2-dimethoxybenzene

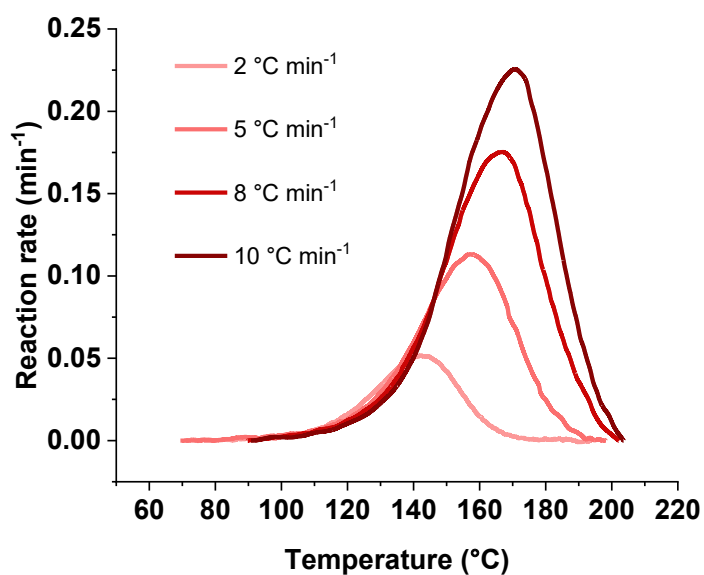


Figure S45. Plots of reaction rate vs temperature for the ROP of TMC with heating rates of 2, 5, 8 and 10 °C min⁻¹. [Sn(Oct)₂]₀ : [BnOH]₀ : [TMC]₀ = 1 : 1 : 100. [TMC]₀ = 2 M in 1,2-dimethoxybenzene.

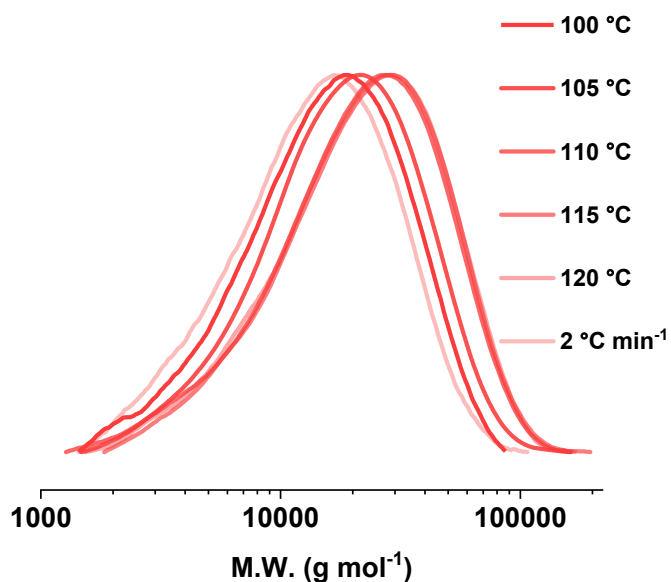


Figure S46. Representative SEC chromatograms of polymer formed in DSC pan at different isotherms or under dynamic heating rates. Polymerizations were conducted at 105, 110, 115 120 °C and at 2 °C min⁻¹ 40 -200 °C using [Sn(Oct)₂]₀ : [BnOH]₀ : [dVL]₀ 1 : 1 : 100. [dVL]₀ = 9.98 M

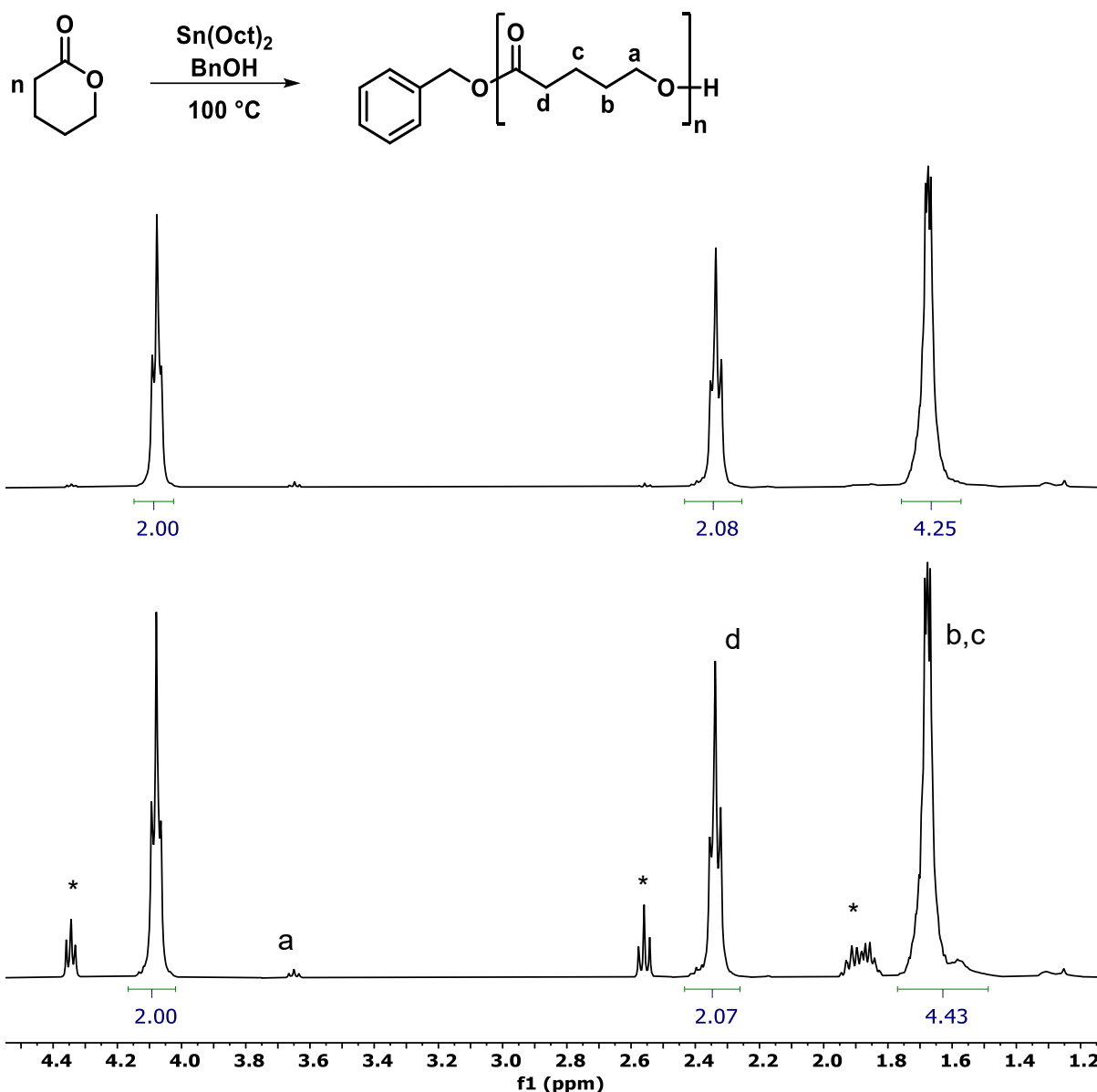


Figure S47. Stacked crude ^1H NMR spectra from dVL ROP conducted in DSC pan at $120\text{ }^\circ\text{C}$ or at heating rate of $2\text{ }^\circ\text{C min}^{-1}$ between $40 - 200\text{ }^\circ\text{C}$. Reactions were conducted at $[\text{Sn}(\text{Oct})_2]_0 : [\text{BnOH}]_0 : [\text{dVL}]_0 = 1 : 1 : 100$, in neat dVL. $[\text{dVL}]_0 = 9.98\text{ M}$. * indicates residual monomer

3.5 dVL ROP kinetics by single heating ramp

Table S7. Temperature, fraction conversion and rate determined at 20 evenly spaced sections between 5 and 65% conversion of dVL ROP conducted a heating rate of 5 °C min⁻¹ between 40 – 200 °C.

| Temp. (°C) ^[a] | 1/Temp (K ⁻¹) | Fractional conversion, α ^[a] | Rate (s ⁻¹) ^[a] | ln(1- α) | ln k ^[b] |
|---------------------------|---------------------------|--|--|------------------|-----------------------|
| 108.56 | 0.00262 | 0.04999 | 3.31E-4 | -0.05128 | -7.96172 |
| 110.85 | 0.0026 | 0.05975 | 3.8E-4 | -0.06161 | -7.81365 |
| 113.14 | 0.00259 | 0.07095 | 4.37667E-4 | -0.07359 | -7.66036 |
| 115.43 | 0.00257 | 0.08385 | 5.02E-4 | -0.08758 | -7.50922 |
| 117.72 | 0.00256 | 0.09861 | 5.71667E-4 | -0.10382 | -7.3633 |
| 120.01 | 0.00254 | 0.1153 | 6.49667E-4 | -0.12251 | -7.21648 |
| 122.29 | 0.00253 | 0.13421 | 7.38667E-4 | -0.14411 | -7.06589 |
| 124.58 | 0.00251 | 0.15582 | 8.34167E-4 | -0.16939 | -6.91936 |
| 126.87 | 0.0025 | 0.1801 | 9.39667E-4 | -0.19857 | -6.77085 |
| 129.16 | 0.00249 | 0.20745 | 0.00105 | -0.2325 | -6.62504 |
| 131.45 | 0.00247 | 0.23795 | 0.00118 | -0.27174 | -6.47443 |
| 133.74 | 0.00246 | 0.27194 | 0.0013 | -0.31737 | -6.32858 |
| 136.03 | 0.00244 | 0.30931 | 0.00143 | -0.37006 | -6.18064 |
| 138.32 | 0.00243 | 0.35019 | 0.00156 | -0.43108 | -6.03479 |
| 140.61 | 0.00242 | 0.3946 | 0.00167 | -0.50187 | -5.89118 |
| 142.9 | 0.0024 | 0.44189 | 0.00178 | -0.5832 | -5.74982 |
| 145.19 | 0.00239 | 0.49197 | 0.00186 | -0.67721 | -5.6095 |
| 147.47 | 0.00238 | 0.54365 | 0.00192 | -0.7845 | -5.47093 |
| 149.76 | 0.00236 | 0.59679 | 0.00194 | -0.9083 | -5.33755 |
| 152.05 | 0.00235 | 0.64989 | 0.00192 | -1.04951 | -5.20624 |

Reaction conditions: [Sn(Oct)₂]₀: [BnOH]₀: [dVL]₀ = 1: 1: 100 in neat dVL. [dVL]₀ = 9.98 M. ^[a] Determined from 5 °C min⁻¹ ramp in figure S43 ^[b] $\ln k = \ln \frac{d\alpha}{dt} - \ln (1 - \alpha)$

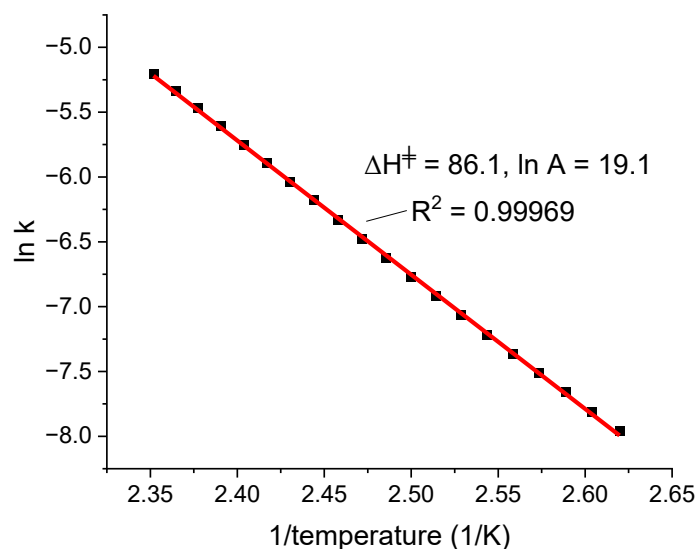


Figure S48. Plot of ln k vs 1/temperature for for the ROP of dVL. Reaction conditions: heating rate of 5 °C min⁻¹, 40 – 200 °C, [Sn(Oct)₂]₀: [BnOH]₀: [dVL]₀ = 1: 1: 100 in neat dVL ([dVL]₀ = 9.98 M). Data taken from table S7.

Table S8. Temperature, fraction conversion and rate determined at 20 evenly spaced sections between 5 and 65% conversion of dVL ROP conducted a heating rate of 8 °C min⁻¹ between 40 – 200 °C.

| Temp. (°C) ^[a] | 1/Temp (K ⁻¹) | Fractional conversion, α ^[a] | Rate (s ⁻¹) ^[a] | ln(1- α) | ln k ^[b] |
|---------------------------|---------------------------|--|--|------------------|-----------------------|
| 117.04 | 0.00256 | 0.05003 | 5.07833E-4 | -0.05132 | -7.53449 |
| 119.28 | 0.00255 | 0.05921 | 5.86833E-4 | -0.06104 | -7.38013 |
| 121.53 | 0.00253 | 0.0698 | 6.76E-4 | -0.07236 | -7.22689 |
| 123.78 | 0.00252 | 0.08204 | 7.75833E-4 | -0.0856 | -7.07672 |
| 126.02 | 0.00251 | 0.09606 | 9.03833E-4 | -0.10099 | -6.90756 |
| 128.27 | 0.00249 | 0.11246 | 0.00103 | -0.1193 | -6.75572 |
| 130.52 | 0.00248 | 0.13115 | 0.00119 | -0.14058 | -6.59024 |
| 132.76 | 0.00246 | 0.15258 | 0.00137 | -0.16556 | -6.43 |
| 135.01 | 0.00245 | 0.17711 | 0.00155 | -0.19493 | -6.27252 |
| 137.25 | 0.00244 | 0.20485 | 0.00175 | -0.22922 | -6.1211 |
| 139.5 | 0.00242 | 0.23592 | 0.00194 | -0.26908 | -5.97351 |
| 141.75 | 0.00241 | 0.27038 | 0.00215 | -0.31523 | -5.82602 |
| 143.99 | 0.0024 | 0.30838 | 0.00236 | -0.36872 | -5.6783 |
| 146.24 | 0.00238 | 0.3497 | 0.00256 | -0.43032 | -5.53848 |
| 148.49 | 0.00237 | 0.39467 | 0.00275 | -0.50198 | -5.39619 |
| 150.73 | 0.00236 | 0.44184 | 0.0029 | -0.58311 | -5.25878 |
| 152.98 | 0.00235 | 0.49188 | 0.00302 | -0.67704 | -5.12597 |
| 155.23 | 0.00233 | 0.54341 | 0.00311 | -0.78397 | -4.98887 |
| 157.47 | 0.00232 | 0.59623 | 0.00317 | -0.90691 | -4.84625 |
| 159.72 | 0.00231 | 0.64999 | 0.00318 | -1.04979 | -4.70074 |

Reaction conditions: [Sn(Oct)₂]₀ : [BnOH]₀ : [dVL]₀ = 1 : 1 : 100 in neat dVL. [dVL]₀ = 9.98 M. ^[a] Determined from from 8 °C min⁻¹ ramp in figure S43 ^[b] ln $k = \ln \frac{d\alpha}{dt} - \ln (1 - \alpha)$

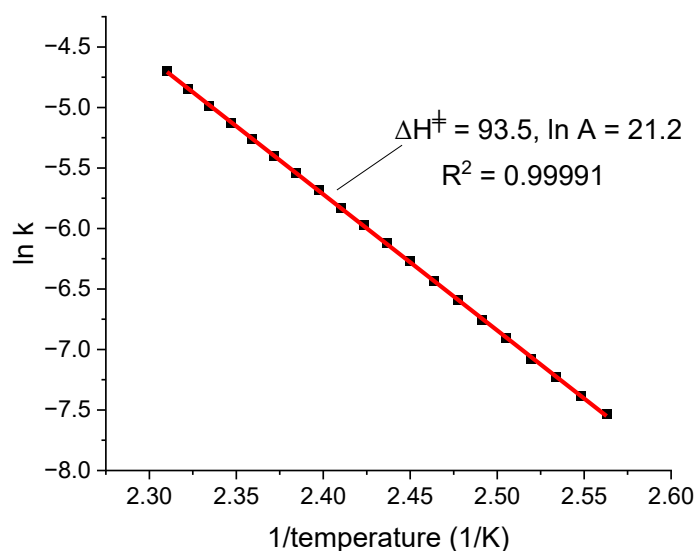


Figure S49. Plot of ln k vs 1/temperature for for the ROP of dVL. Reaction conditions: heating rate of 5 °C min⁻¹, 40 – 200 °C, [Sn(Oct)₂]₀ : [BnOH]₀ : [dVL]₀ = 1 : 1 : 100 in neat dVL ([dVL]₀ = 9.98 M). Data taken from table S8.

Table S9. Temperature, fraction conversion and rate determined at 20 evenly spaced sections between 5 and 65% conversion of dVL ROP conducted a heating rate of 10 °C min⁻¹ between 40 – 200 °C.

| Temp. (°C) ^[a] | 1/Temp (K ⁻¹) | Fractional conversion, α ^[a] | Rate (s ⁻¹) ^[a] | ln(1- α) | ln k ^[b] |
|---------------------------|---------------------------|--|--|------------------|---------------------|
| 120.57 | 0.00254 | 0.04997 | 5.72667E-4 | -0.05126 | -7.4135 |
| 122.98 | 0.00252 | 0.05888 | 6.58833E-4 | -0.06068 | -7.26485 |
| 125.38 | 0.00251 | 0.06904 | 7.56833E-4 | -0.07154 | -7.11534 |
| 127.79 | 0.00249 | 0.08082 | 8.86E-4 | -0.08427 | -6.94503 |
| 130.19 | 0.00248 | 0.09454 | 0.00103 | -0.09931 | -6.77689 |
| 132.6 | 0.00246 | 0.11074 | 0.0012 | -0.11737 | -6.60488 |
| 135 | 0.00245 | 0.12928 | 0.00139 | -0.13843 | -6.43813 |
| 137.41 | 0.00244 | 0.15091 | 0.00159 | -0.16359 | -6.28331 |
| 139.81 | 0.00242 | 0.17516 | 0.00181 | -0.19257 | -6.12375 |
| 142.22 | 0.00241 | 0.20306 | 0.00204 | -0.22698 | -5.9669 |
| 144.62 | 0.00239 | 0.23405 | 0.0023 | -0.26664 | -5.8104 |
| 147.02 | 0.00238 | 0.26883 | 0.00254 | -0.31311 | -5.66361 |
| 149.43 | 0.00237 | 0.30725 | 0.00279 | -0.36709 | -5.5135 |
| 151.83 | 0.00235 | 0.34888 | 0.00303 | -0.42906 | -5.37049 |
| 154.24 | 0.00234 | 0.39411 | 0.00325 | -0.50106 | -5.22816 |
| 156.64 | 0.00233 | 0.44219 | 0.00342 | -0.58374 | -5.0944 |
| 159.05 | 0.00231 | 0.49272 | 0.00355 | -0.67869 | -4.96388 |
| 161.45 | 0.0023 | 0.54405 | 0.00363 | -0.78537 | -4.83337 |
| 163.86 | 0.00229 | 0.59707 | 0.00368 | -0.90899 | -4.69709 |
| 166.26 | 0.00228 | 0.65002 | 0.00366 | -1.04988 | -4.55973 |

Reactions conditions: [Sn(Oct)₂]₀ : [BnOH]₀ : [dVL]₀ = 1 : 1 : 100 in neat dVL. [dVL]₀ = 9.98 M. ^[a] Determined from from 10 °C min⁻¹ ramp in figure S43 ^[b] $\ln k = \ln \frac{d\alpha}{dt} - \ln(1 - \alpha)$

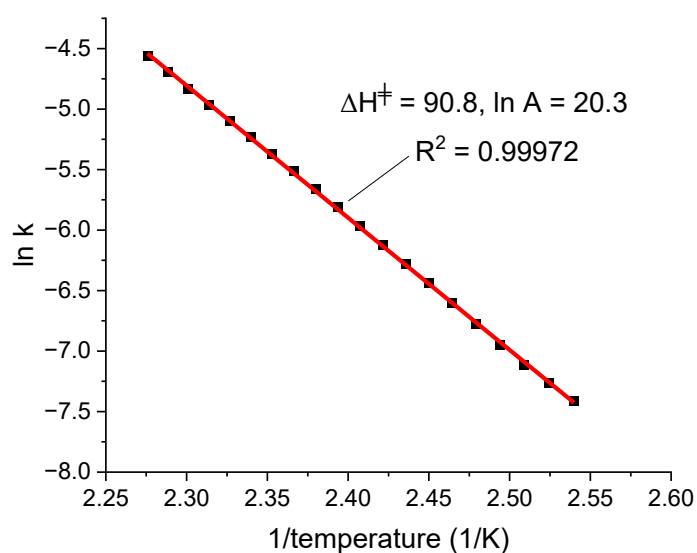


Figure S50. Plot of ln k vs 1/temperature for for the ROP of dVL. Reaction conditions: heating rate of 10 °C min⁻¹, 40 – 200 °C, [Sn(Oct)₂]₀ : [BnOH]₀ : [dVL]₀ = 1 : 1 : 100 in neat dVL ([dVL]₀ = 9.98 M). Data taken from table S9.

3.5 LLA ROP kinetics by single heating ramp

Table S10. Temperature, fraction conversion and rate determined at 20 evenly spaced sections between 5 and 40% conversion of LLA ROP conducted a heating rate of 2 °C min⁻¹ between 40 – 200 °C.

| Temp. (°C) ^[a] | 1/Temp (K ⁻¹) | Fractional conversion, α ^[a] | Rate (s ⁻¹) ^[a] | ln(1- α) | ln k ^[b] |
|---------------------------|---------------------------|--|--|------------------|-----------------------|
| 89.54 | 0.00276 | 0.04997 | 1.5E-4 | -0.05126 | -8.7527 |
| 91.24 | 0.00274 | 0.05816 | 1.66167E-4 | -0.05992 | -8.64224 |
| 92.95 | 0.00273 | 0.06724 | 1.82E-4 | -0.06961 | -8.54211 |
| 94.65 | 0.00272 | 0.07709 | 2.05333E-4 | -0.08022 | -8.41011 |
| 96.35 | 0.00271 | 0.08813 | 2.28833E-4 | -0.09226 | -8.29041 |
| 98.05 | 0.00269 | 0.10019 | 2.53333E-4 | -0.10557 | -8.17493 |
| 99.76 | 0.00268 | 0.11375 | 2.92333E-4 | -0.12076 | -8.01697 |
| 101.46 | 0.00267 | 0.12878 | 2.93833E-4 | -0.13786 | -7.99411 |
| 103.16 | 0.00266 | 0.14478 | 3.29833E-4 | -0.1564 | -7.86043 |
| 104.87 | 0.00265 | 0.16212 | 3.525E-4 | -0.17688 | -7.77345 |
| 106.57 | 0.00263 | 0.18074 | 3.72667E-4 | -0.19935 | -7.69539 |
| 108.27 | 0.00262 | 0.20053 | 4.04E-4 | -0.22381 | -7.59003 |
| 109.97 | 0.00261 | 0.2224 | 4.44167E-4 | -0.25154 | -7.46777 |
| 111.68 | 0.0026 | 0.24509 | 4.435E-4 | -0.28116 | -7.43959 |
| 113.38 | 0.00259 | 0.26827 | 4.585E-4 | -0.31234 | -7.37498 |
| 115.08 | 0.00258 | 0.29274 | 4.88667E-4 | -0.34636 | -7.27715 |
| 116.78 | 0.00256 | 0.31844 | 5.09167E-4 | -0.38337 | -7.19917 |
| 118.49 | 0.00255 | 0.34507 | 5.23E-4 | -0.42323 | -7.13263 |
| 120.19 | 0.00254 | 0.37241 | 5.38167E-4 | -0.46587 | -7.06154 |
| 121.89 | 0.00253 | 0.39987 | 5.40667E-4 | -0.51061 | -7.01206 |

Reaction conditions: [Sn(Oct)₂]₀: [BnOH]₀: [LLA]₀ = 1: 1: 100. [LLA]₀ = 1 M in 1,2-dimethoxybenzene. ^[a] Determined from 2 °C min⁻¹ ramp in figure S44 ^[b] $\ln k = \ln \frac{d\alpha}{dt} - \ln(1 - \alpha)$

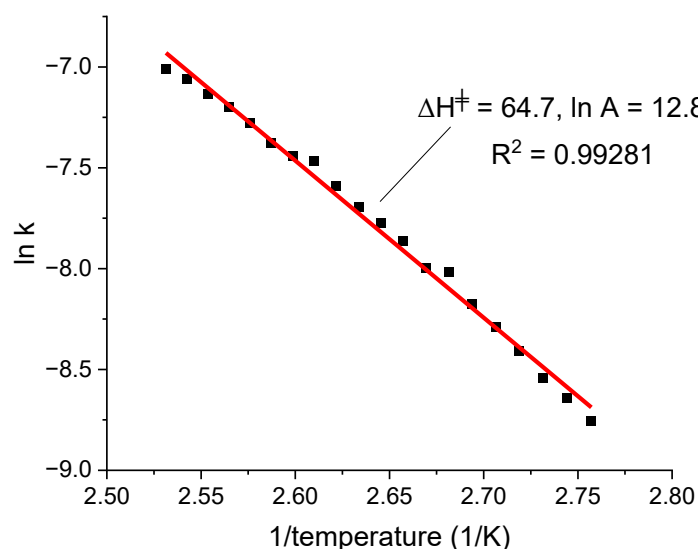


Figure S51. Plot of ln k vs 1/temperature for for the ROP of LLA. Reaction conditions: heating rate of 2 °C min⁻¹, 40 – 200 °C, [Sn(Oct)₂]₀: [BnOH]₀: [LLA]₀ = 1:1:100, [LLA]₀ = 1 M in 1,2-dimethoxybenzene. Data taken from table S10.

Table S11. Temperature, fraction conversion and rate determined at 20 evenly spaced sections between 5 and 40% conversion of LLA ROP conducted a heating rate of 5 °C min⁻¹ between 40 – 200 °C.

| Temp. (°C) ^[a] | 1/Temp (K ⁻¹) | Fractional conversion, α ^[a] | Rate (s ⁻¹) ^[a] | ln(1- α) | ln k ^[b] |
|---------------------------|---------------------------|--|--|------------------|-----------------------|
| 95.22 | 0.00271 | 0.05 | 2.62167E-4 | -0.05129 | -8.19551 |
| 97.38 | 0.0027 | 0.05725 | 2.95833E-4 | -0.05895 | -8.06711 |
| 99.53 | 0.00268 | 0.06521 | 3.28333E-4 | -0.06743 | -7.95382 |
| 101.68 | 0.00267 | 0.07413 | 3.665E-4 | -0.07702 | -7.83431 |
| 103.84 | 0.00265 | 0.08419 | 4.05667E-4 | -0.08795 | -7.72184 |
| 105.99 | 0.00264 | 0.09503 | 4.455E-4 | -0.09985 | -7.61636 |
| 108.15 | 0.00262 | 0.10752 | 5.10667E-4 | -0.11375 | -7.46595 |
| 110.3 | 0.00261 | 0.12127 | 5.58333E-4 | -0.12928 | -7.36114 |
| 112.46 | 0.00259 | 0.1365 | 6.19E-4 | -0.14676 | -7.24057 |
| 114.61 | 0.00258 | 0.15315 | 6.68833E-4 | -0.16623 | -7.1435 |
| 116.76 | 0.00256 | 0.17152 | 7.50667E-4 | -0.18816 | -7.00615 |
| 118.92 | 0.00255 | 0.19178 | 8.05167E-4 | -0.21292 | -6.91148 |
| 121.07 | 0.00254 | 0.21334 | 8.59667E-4 | -0.23996 | -6.81914 |
| 123.23 | 0.00252 | 0.23642 | 9.23333E-4 | -0.26974 | -6.718 |
| 125.38 | 0.00251 | 0.26071 | 9.6E-4 | -0.30207 | -6.64655 |
| 127.53 | 0.0025 | 0.28619 | 0.00102 | -0.33714 | -6.54857 |
| 129.69 | 0.00248 | 0.31323 | 0.00106 | -0.37576 | -6.4702 |
| 131.84 | 0.00247 | 0.34117 | 0.0011 | -0.41729 | -6.39593 |
| 134 | 0.00246 | 0.37021 | 0.00114 | -0.46237 | -6.31195 |
| 136.15 | 0.00244 | 0.39998 | 0.00117 | -0.51079 | -6.24393 |

Reaction conditions: [Sn(Oct)₂]₀:[BnOH]₀:[LLA]₀ = 1:1:100. [LLA]₀ = 1 M in 1,2-dimethoxybenzene. ^[a] Determined from 5 °C min⁻¹ ramp in figure S44 ^[b] $\ln k = \ln \frac{d\alpha}{dt} - \ln(1 - \alpha)$

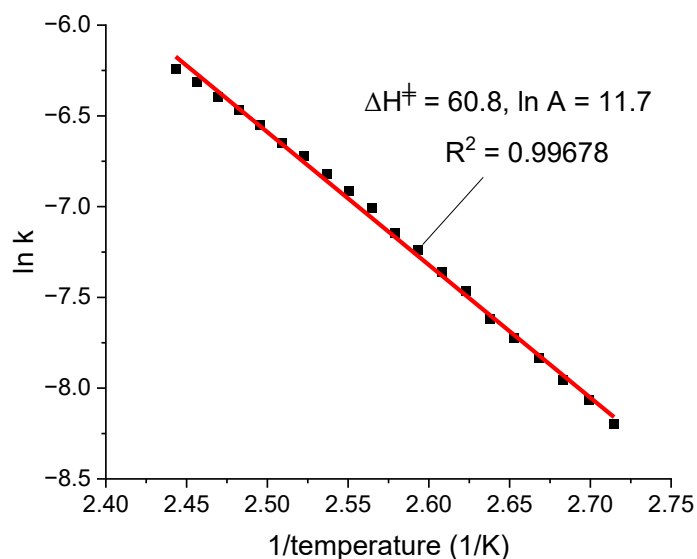


Figure S52. Plot of ln k vs 1/temperature for for the ROP of LLA. Reaction conditions: heating rate of 5 °C min⁻¹, 40 – 200 °C, [Sn(Oct)₂]₀:[BnOH]₀:[LLA]₀ = 1:1:100, [LLA]₀ = 1 M in 1,2-dimethoxybenzene. Data taken from table S11.

Table S12. Temperature, fraction conversion and rate determined at 20 evenly spaced sections between 5 and 40% conversion of LLA ROP conducted a heating rate of 8 °C min⁻¹ between 40 – 200 °C.

| Temp. (°C) ^[a] | 1/Temp (K ⁻¹) | Fractional conversion, α ^[a] | Rate (s ⁻¹) ^[a] | ln(1- α) | ln k ^[b] |
|---------------------------|---------------------------|--|--|------------------|-----------------------|
| 110.86 | 0.0026 | 0.05001 | 4.63333E-4 | -0.0513 | -7.62613 |
| 113.09 | 0.00259 | 0.0582 | 5.13167E-4 | -0.05996 | -7.51471 |
| 115.33 | 0.00257 | 0.06724 | 5.63333E-4 | -0.06961 | -7.41232 |
| 117.56 | 0.00256 | 0.07718 | 6.30333E-4 | -0.08032 | -7.2891 |
| 119.79 | 0.00254 | 0.08827 | 6.92167E-4 | -0.09241 | -7.18332 |
| 122.02 | 0.00253 | 0.10049 | 7.73E-4 | -0.10591 | -7.05906 |
| 124.26 | 0.00252 | 0.11424 | 8.61833E-4 | -0.12131 | -6.93518 |
| 126.49 | 0.0025 | 0.1293 | 9.415E-4 | -0.13846 | -6.82954 |
| 128.72 | 0.00249 | 0.14572 | 0.00102 | -0.1575 | -6.7342 |
| 130.95 | 0.00247 | 0.16338 | 0.00112 | -0.17839 | -6.6198 |
| 133.19 | 0.00246 | 0.18278 | 0.00119 | -0.20185 | -6.53292 |
| 135.42 | 0.00245 | 0.20333 | 0.00126 | -0.22731 | -6.453 |
| 137.65 | 0.00243 | 0.22491 | 0.00133 | -0.25478 | -6.36829 |
| 139.88 | 0.00242 | 0.24764 | 0.00139 | -0.28454 | -6.29336 |
| 142.12 | 0.00241 | 0.27148 | 0.00145 | -0.31674 | -6.21983 |
| 144.35 | 0.0024 | 0.29608 | 0.0015 | -0.35109 | -6.15043 |
| 146.58 | 0.00238 | 0.32171 | 0.00155 | -0.38818 | -6.08446 |
| 148.81 | 0.00237 | 0.34765 | 0.00156 | -0.42717 | -6.03591 |
| 151.05 | 0.00236 | 0.37401 | 0.00157 | -0.46842 | -5.98548 |
| 153.28 | 0.00235 | 0.40007 | 0.00154 | -0.51094 | -5.96532 |

Reaction conditions: [Sn(Oct)₂]₀:[BnOH]₀:[LLA]₀ = 1:1:100. [LLA]₀ = 1 M in 1,2-dimethoxybenzene. ^[a] Determined from 8 °C min⁻¹ ramp in figure S44 ^[b] $\ln k = \ln \frac{d\alpha}{dt} - \ln(1 - \alpha)$

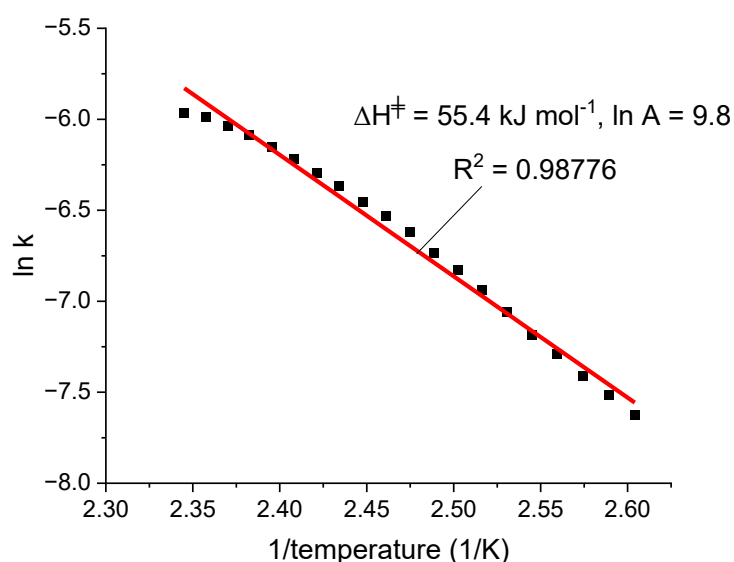


Figure S53. Plot of ln k vs 1/temperature for for the ROP of LLA. Reaction conditions: heating rate of 8 °C min⁻¹, 40 – 200 °C, [Sn(Oct)₂]₀:[BnOH]₀:[LLA]₀ = 1:1:100, [LLA]₀ = 1 M in 1,2-dimethoxybenzene. Data taken from table S12.

Table S13. Temperature, fraction conversion and rate determined at 20 evenly spaced sections between 5 and 35% conversion of LLA ROP conducted a heating rate of 10 °C min⁻¹ between 40 – 200 °C.

| Temp. (°C) ^[a] | 1/Temp (K ⁻¹) | Fractional conversion, α ^[a] | Rate (s ⁻¹) ^[a] | ln(1- α) | ln k ^[b] |
|---------------------------|---------------------------|--|--|------------------|-----------------------|
| 119.65 | 0.00255 | 0.04999 | 6.49333E-4 | -0.05128 | 0.04102 |
| 121.54 | 0.00253 | 0.05793 | 7.41333E-4 | -0.05968 | 0.0472 |
| 123.42 | 0.00252 | 0.06676 | 8.12667E-4 | -0.06909 | 0.05224 |
| 125.31 | 0.00251 | 0.07629 | 8.80167E-4 | -0.07936 | 0.05715 |
| 127.2 | 0.0025 | 0.0867 | 9.62167E-4 | -0.09069 | 0.0632 |
| 129.08 | 0.00249 | 0.09807 | 0.00105 | -0.10322 | 0.06998 |
| 130.97 | 0.00247 | 0.11052 | 0.00115 | -0.11712 | 0.07774 |
| 132.86 | 0.00246 | 0.12416 | 0.00124 | -0.13257 | 0.0848 |
| 134.74 | 0.00245 | 0.13852 | 0.00133 | -0.1491 | 0.09243 |
| 136.63 | 0.00244 | 0.15411 | 0.0014 | -0.16737 | 0.09956 |
| 138.52 | 0.00243 | 0.17043 | 0.00148 | -0.18685 | 0.10729 |
| 140.4 | 0.00242 | 0.18422 | 0.00155 | -0.20361 | 0.11566 |
| 142.29 | 0.00241 | 0.20583 | 0.00165 | -0.23046 | 0.12444 |
| 144.18 | 0.0024 | 0.2248 | 0.00171 | -0.25463 | 0.13257 |
| 146.06 | 0.00239 | 0.24452 | 0.00177 | -0.2804 | 0.14084 |
| 147.95 | 0.00237 | 0.26506 | 0.00183 | -0.30797 | 0.14913 |
| 149.84 | 0.00236 | 0.28587 | 0.00185 | -0.33669 | 0.15535 |
| 151.72 | 0.00235 | 0.30687 | 0.00188 | -0.36654 | 0.16251 |
| 153.61 | 0.00234 | 0.32833 | 0.00192 | -0.39799 | 0.1711 |
| 155.5 | 0.00233 | 0.35002 | 0.00191 | -0.43081 | 0.17659 |

Reaction conditions: [Sn(Oct)₂]₀: [BnOH]₀: [LLA]₀ = 1:1:100. [LLA]₀ = 1 M in 1,2-dimethoxybenzene. ^[a]
Determined from 10 °C min⁻¹ ramp in figure S44 ^[b] $\ln k = \ln \frac{d\alpha}{dt} - \ln(1 - \alpha)$

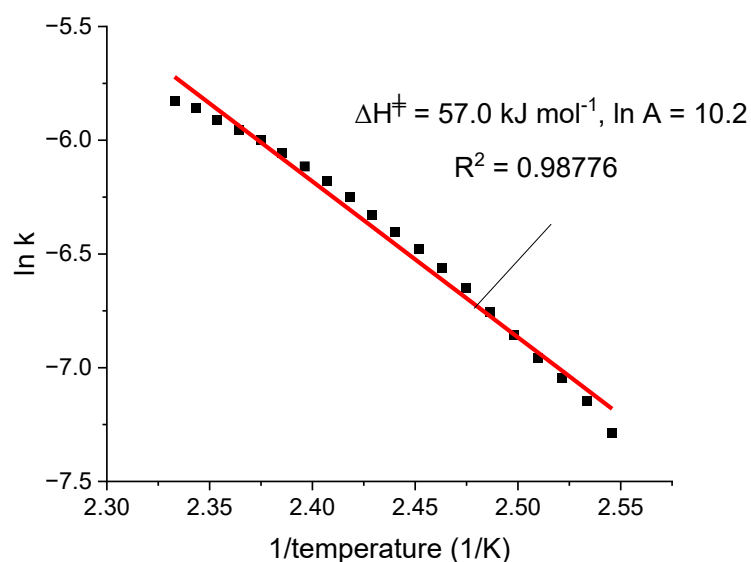


Figure S54. Plot of ln k vs 1/temperature for for the ROP of LLA. Reaction conditions: heating rate of 10 °C min⁻¹, 40 – 200 °C, [Sn(Oct)₂]₀: [BnOH]₀: [LLA]₀ = 1:1:100, [LLA]₀ = 1 M in 1,2-dimethoxybenzene. Data taken from table S13.

3.6 TMC ROP kinetics by single heating ramp

Table S14. Temperature, fraction conversion and rate determined at 20 evenly spaced sections between 5 and 55% conversion of TMC ROP conducted a heating rate of 2 °C min⁻¹ between 40 – 200 °C.

| Temp. (°C) ^[a] | 1/Temp (K ⁻¹) | Fractional conversion, α ^[a] | Rate (s ⁻¹) ^[a] | ln(1- α) | ln k ^[b] |
|---------------------------|---------------------------|--|--|------------------|-----------------------|
| 114.69 | 0.00258 | 0.05 | 1.705E-4 | -0.05129 | -8.62556 |
| 116.29 | 0.00257 | 0.05876 | 1.88833E-4 | -0.06056 | -8.51375 |
| 117.89 | 0.00256 | 0.0686 | 2.21167E-4 | -0.07107 | -8.34562 |
| 119.49 | 0.00255 | 0.0802 | 2.57333E-4 | -0.0836 | -8.1811 |
| 121.09 | 0.00254 | 0.09326 | 2.9E-4 | -0.0979 | -8.04742 |
| 122.69 | 0.00253 | 0.10811 | 3.26833E-4 | -0.11441 | -7.91059 |
| 124.3 | 0.00252 | 0.12502 | 3.78E-4 | -0.13355 | -7.74693 |
| 125.9 | 0.00251 | 0.14435 | 4.24833E-4 | -0.15589 | -7.60763 |
| 127.5 | 0.0025 | 0.16593 | 4.73167E-4 | -0.18144 | -7.47434 |
| 129.1 | 0.00249 | 0.19 | 5.275E-4 | -0.21072 | -7.33629 |
| 130.7 | 0.00248 | 0.21658 | 5.76E-4 | -0.24409 | -7.21477 |
| 132.31 | 0.00247 | 0.2459 | 6.375E-4 | -0.28223 | -7.07589 |
| 133.91 | 0.00246 | 0.27771 | 6.87333E-4 | -0.32533 | -6.95716 |
| 135.51 | 0.00245 | 0.31201 | 7.395E-4 | -0.37398 | -6.83521 |
| 137.11 | 0.00244 | 0.3486 | 7.84167E-4 | -0.42863 | -6.72198 |
| 138.71 | 0.00243 | 0.38693 | 8.12E-4 | -0.48928 | -6.62622 |
| 140.32 | 0.00242 | 0.42704 | 8.42667E-4 | -0.55694 | -6.52187 |
| 141.92 | 0.00241 | 0.46797 | 8.61E-4 | -0.63106 | -6.42635 |
| 143.52 | 0.0024 | 0.50905 | 8.515E-4 | -0.71141 | -6.35696 |
| 145.12 | 0.00239 | 0.54987 | 8.41333E-4 | -0.79822 | -6.28222 |

Reaction conditions: [Sn(Oct)₂]₀: [BnOH]₀: [TMC]₀ = 1:1:100. [TMC]₀ = 2 M in 1,2-dimethoxybenzene. ^[a] Determined from 2 °C min⁻¹ ramp in figure S45 ^[b] $\ln k = \ln \frac{d\alpha}{dt} - \ln(1 - \alpha)$

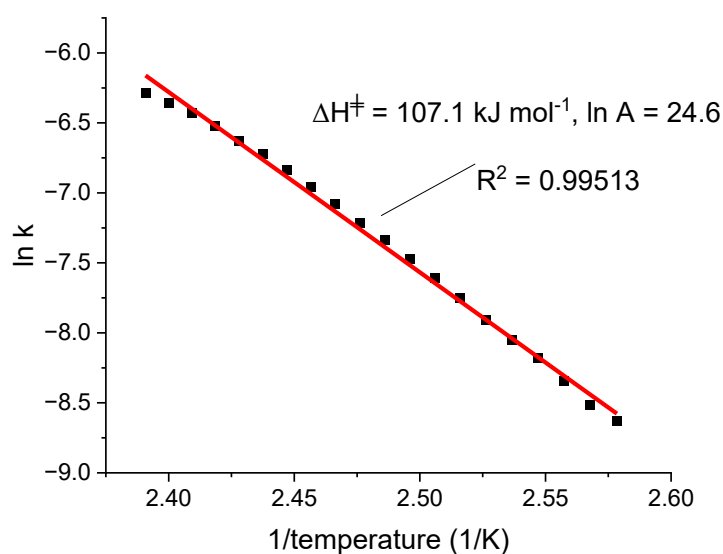


Figure S55. Plot of ln k vs 1/temperature for for the ROP of TMC. Reaction conditions: heating rate of 2 °C min⁻¹, 40 – 200 °C, [Sn(Oct)₂]₀: [BnOH]₀: [TMC]₀ = 1:1:100, [TMC]₀ = 2 M in 1,2-dimethoxybenzene. Data taken from table S14.

Table S15. Temperature, fraction conversion and rate determined at 20 evenly spaced sections between 5 and 55% conversion of TMC ROP conducted a heating rate of 5 °C min⁻¹ between 40 – 200 °C.

| Temp. (°C) ^[a] | 1/Temp (K ⁻¹) | Fraction conversion ^[a] | Rate (sec ⁻¹) ^[a] | ln(1-fraction conversion) | ln k ^[b] |
|---------------------------|---------------------------|------------------------------------|--|---------------------------|---------------------|
| 124.78 | 0.00251 | 0.04998 | 3.21833E-4 | -0.05127 | -7.98994 |
| 126.66 | 0.0025 | 0.05771 | 3.65667E-4 | -0.05944 | -7.85358 |
| 128.55 | 0.00249 | 0.06671 | 4.275E-4 | -0.06904 | -7.68878 |
| 130.43 | 0.00248 | 0.07729 | 5.025E-4 | -0.08044 | -7.51582 |
| 132.31 | 0.00247 | 0.08938 | 5.77E-4 | -0.09363 | -7.36445 |
| 134.19 | 0.00245 | 0.10345 | 6.64167E-4 | -0.1092 | -7.20798 |
| 136.07 | 0.00244 | 0.11942 | 7.635E-4 | -0.12717 | -7.05063 |
| 137.95 | 0.00243 | 0.13788 | 8.75167E-4 | -0.14836 | -6.89267 |
| 139.83 | 0.00242 | 0.15891 | 9.84E-4 | -0.17306 | -6.75104 |
| 141.71 | 0.00241 | 0.18242 | 0.00111 | -0.20141 | -6.60491 |
| 143.59 | 0.0024 | 0.20888 | 0.00123 | -0.23431 | -6.46438 |
| 145.47 | 0.00239 | 0.23814 | 0.00137 | -0.27199 | -6.32028 |
| 147.35 | 0.00238 | 0.27053 | 0.0015 | -0.31544 | -6.18491 |
| 149.23 | 0.00237 | 0.30568 | 0.0016 | -0.36482 | -6.07011 |
| 151.11 | 0.00236 | 0.34291 | 0.00171 | -0.41993 | -5.95276 |
| 152.99 | 0.00235 | 0.38256 | 0.00179 | -0.48217 | -5.8429 |
| 154.87 | 0.00234 | 0.42338 | 0.00184 | -0.55057 | -5.74925 |
| 156.75 | 0.00233 | 0.46555 | 0.00188 | -0.62652 | -5.64757 |
| 158.64 | 0.00232 | 0.5083 | 0.00188 | -0.70989 | -5.56927 |
| 160.52 | 0.00231 | 0.55007 | 0.00183 | -0.79866 | -5.50523 |

Reaction conditions: [Sn(Oct)₂]₀: [BnOH]₀: [TMC]₀ = 1:1:100. [TMC]₀ = 2 M in 1,2-dimethoxybenzene. ^[a] Determined from 5 °C min⁻¹ ramp in figure S45 ^[b] $\ln k = \ln \frac{d\alpha}{dt} - \ln(1 - \alpha)$

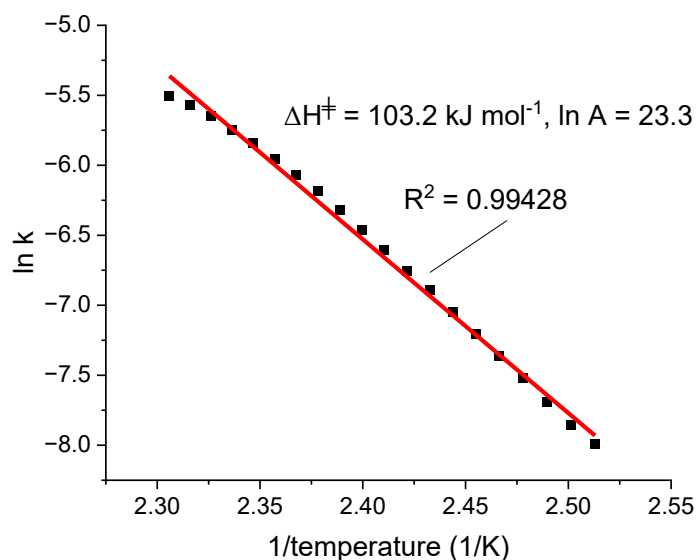


Figure S56. Plot of ln k vs 1/temperature for for the ROP of TMC. Reaction conditions: heating rate of 5 °C min⁻¹, 40 – 200 °C, [Sn(Oct)₂]₀: [BnOH]₀: [TMC]₀ = 1:1:100, [TMC]₀ = 2 M in 1,2-dimethoxybenzene. Data taken from table S15.

Table S16. Temperature, fraction conversion and rate determined at 20 evenly spaced sections between 5 and 55% conversion of TMC ROP conducted a heating rate of 8 °C min⁻¹ between 40 – 200 °C.

| Temp. (°C) ^[a] | 1/Temp (K ⁻¹) | Fractional conversion, α ^[a] | Rate (s ⁻¹) ^[a] | ln(1- α) | ln k ^[b] |
|---------------------------|---------------------------|--|--|------------------|-----------------------|
| 133.06 | 0.00246 | 0.05001 | 5.445E-4 | -0.0513 | -7.46466 |
| 134.94 | 0.00245 | 0.05829 | 6.31667E-4 | -0.06006 | -7.30759 |
| 136.82 | 0.00244 | 0.0678 | 7.45833E-4 | -0.07021 | -7.1304 |
| 138.7 | 0.00243 | 0.07905 | 8.56667E-4 | -0.08235 | -6.97972 |
| 140.59 | 0.00242 | 0.09208 | 9.765E-4 | -0.0966 | -6.83534 |
| 142.47 | 0.00241 | 0.10672 | 0.00111 | -0.11286 | -6.69331 |
| 144.35 | 0.0024 | 0.12341 | 0.00126 | -0.13172 | -6.54554 |
| 146.23 | 0.00238 | 0.14222 | 0.00143 | -0.15341 | -6.39572 |
| 148.11 | 0.00237 | 0.16393 | 0.00165 | -0.17904 | -6.22946 |
| 149.99 | 0.00236 | 0.18844 | 0.00182 | -0.2088 | -6.10132 |
| 151.87 | 0.00235 | 0.21533 | 0.00202 | -0.24249 | -5.96112 |
| 153.75 | 0.00234 | 0.24512 | 0.0022 | -0.2812 | -5.84031 |
| 155.63 | 0.00233 | 0.2776 | 0.00239 | -0.32518 | -5.7119 |
| 157.51 | 0.00232 | 0.31227 | 0.00253 | -0.37436 | -5.60491 |
| 159.39 | 0.00231 | 0.34892 | 0.00266 | -0.42912 | -5.49894 |
| 161.27 | 0.0023 | 0.38738 | 0.00279 | -0.49001 | -5.3933 |
| 163.15 | 0.00229 | 0.42724 | 0.00286 | -0.55729 | -5.29875 |
| 165.03 | 0.00228 | 0.46792 | 0.0029 | -0.63096 | -5.21077 |
| 166.91 | 0.00227 | 0.50904 | 0.00292 | -0.71139 | -5.12464 |
| 168.8 | 0.00226 | 0.55005 | 0.00288 | -0.79862 | -5.05045 |

Reaction conditions: [Sn(Oct)₂]₀: [BnOH]₀: [TMC]₀ = 1:1:100. [TMC]₀ = 2 M in 1,2-dimethoxybenzene. ^[a] Determined from 8 °C min⁻¹ ramp in figure S45 ^[b] $\ln k = \ln \frac{d\alpha}{dt} - \ln(1 - \alpha)$

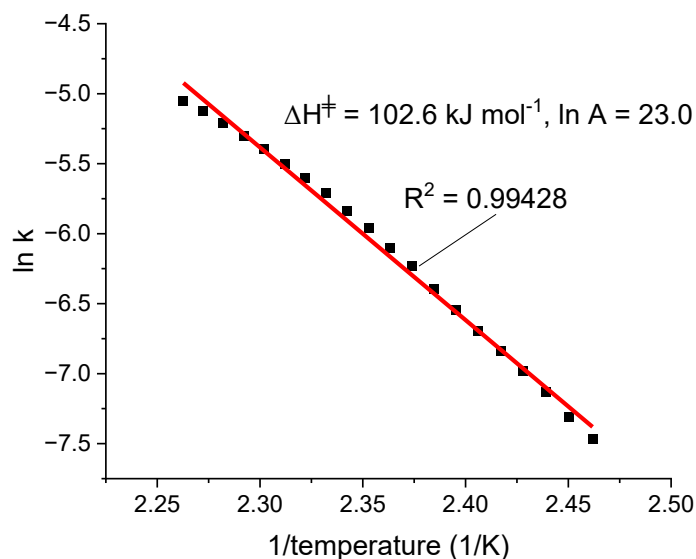


Figure S57. Plot of ln k vs 1/temperature for for the ROP of TMC. Reaction conditions: heating rate of 8 °C min⁻¹, 40 – 200 °C, [Sn(Oct)₂]₀: [BnOH]₀: [TMC]₀ = 1:1:100, [TMC]₀ = 2 M in 1,2-dimethoxybenzene. Data taken from table S16.

Table S17. Temperature, fraction conversion and rate determined at 20 evenly spaced sections between 5 and 55% conversion of TMC ROP conducted a heating rate of 10°C min⁻¹ between 40 – 200 °C.

| Temp. (°C) ^[a] | 1/Temp (K ⁻¹) | Fractional conversion, α ^[a] | Rate (s ⁻¹) ^[a] | ln(1- α) | ln k ^[b] |
|---------------------------|---------------------------|--|--|------------------|-----------------------|
| 137.68 | 0.00243 | 0.05003 | 6.96833E-4 | -0.05132 | -7.21828 |
| 139.49 | 0.00242 | 0.05815 | 8.08667E-4 | -0.05991 | -7.05993 |
| 141.31 | 0.00241 | 0.06764 | 9.375E-4 | -0.07004 | -6.90255 |
| 143.12 | 0.0024 | 0.07872 | 0.00109 | -0.08199 | -6.73747 |
| 144.93 | 0.00239 | 0.09141 | 0.00126 | -0.09586 | -6.5778 |
| 146.75 | 0.00238 | 0.10647 | 0.0015 | -0.11258 | -6.38716 |
| 148.56 | 0.00237 | 0.12388 | 0.00172 | -0.13225 | -6.23421 |
| 150.38 | 0.00236 | 0.14378 | 0.00196 | -0.15523 | -6.0786 |
| 152.19 | 0.00235 | 0.16633 | 0.0022 | -0.18192 | -5.93761 |
| 154 | 0.00234 | 0.19148 | 0.00242 | -0.21255 | -5.81224 |
| 155.82 | 0.00233 | 0.21904 | 0.00266 | -0.24723 | -5.6824 |
| 157.63 | 0.00232 | 0.24918 | 0.00291 | -0.28659 | -5.55458 |
| 159.44 | 0.00231 | 0.28173 | 0.00307 | -0.33091 | -5.45676 |
| 161.26 | 0.0023 | 0.31617 | 0.00324 | -0.38005 | -5.35203 |
| 163.07 | 0.00229 | 0.35195 | 0.00339 | -0.43379 | -5.25353 |
| 164.88 | 0.00228 | 0.38972 | 0.00353 | -0.49384 | -5.15305 |
| 166.7 | 0.00227 | 0.42878 | 0.00363 | -0.55998 | -5.05776 |
| 168.51 | 0.00226 | 0.46847 | 0.00371 | -0.632 | -4.96455 |
| 170.32 | 0.00225 | 0.50922 | 0.00376 | -0.71176 | -4.87243 |
| 172.14 | 0.00225 | 0.5501 | 0.00373 | -0.79873 | -4.79288 |

Reaction conditions: [Sn(Oct)₂]₀: [BnOH]₀: [TMC]₀ = 1:1:100. [TMC]₀ = 2 M in 1,2-dimethoxybenzene. ^[a] Determined from 10 °C min⁻¹ ramp in figure S45 ^[b] $\ln k = \ln \frac{d\alpha}{dt} - \ln(1 - \alpha)$

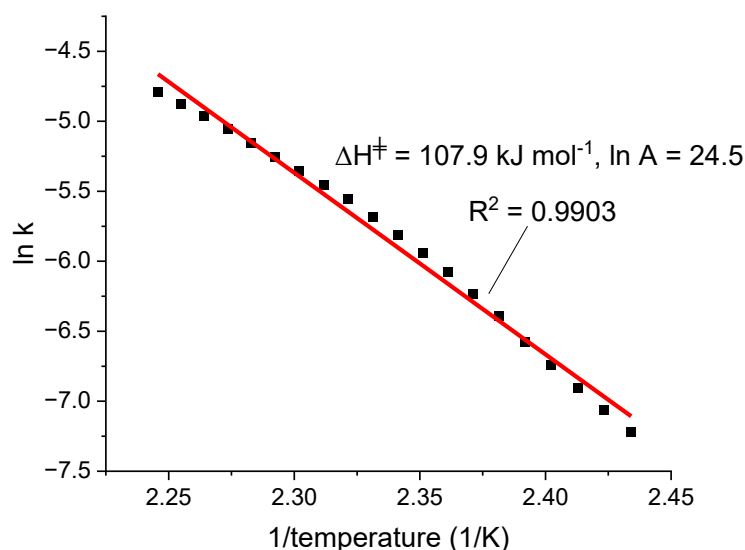


Figure S58. Plot ln k vs 1/temperature for for the ROP of TMC. Reaction conditions: heating rate of 10°C min⁻¹, 40 – 200 °C, [Sn(Oct)₂]₀: [BnOH]₀: [TMC]₀ = 1:1:100, [TMC]₀ = 2 M in 1,2-dimethoxybenzene. Data taken from table S17.

3.7 LLA and TMC kinetics by multi-heating ramps

Table S18. Heating rate, peak temperature taken from figure S44 for the ROP of LLA conducted under dynamic heating between 40 – 200 °C.

| Heating rate, β ($^{\circ}\text{C min}^{-1}$) | Peak temperature ($^{\circ}\text{C}$) | 1/Temperature ($\times 10^{-3} \text{ K}^{-1}$) | Log β |
|---|---|---|-------------|
| 2 | 123 | 2.53 | 0.3 |
| 5 | 139 | 2.43 | 0.7 |
| 8 | 151 | 2.36 | 0.9 |
| 10 | 155 | 2.34 | 1 |

Reaction conditions: $[\text{Sn}(\text{Oct})_2]_0 : [\text{BnOH}]_0 : [\text{LLA}]_0 = 1:1:100$. $[\text{LLA}]_0 = 1 \text{ M}$ in 1,2-dimethoxybenzene

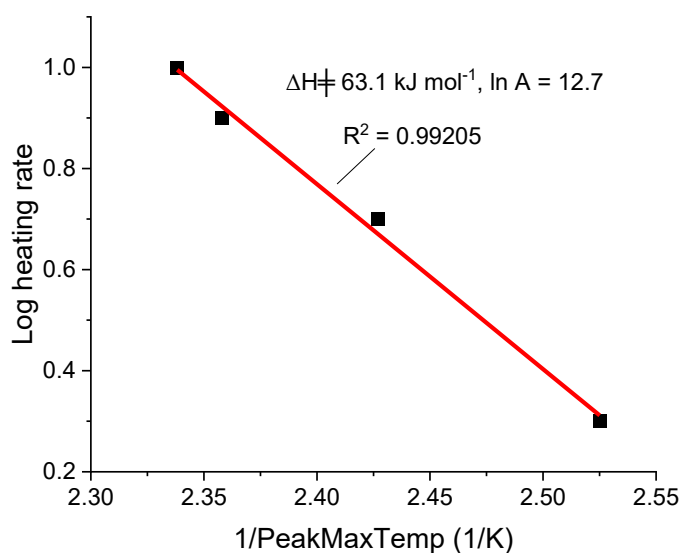


Figure S59. Log heating rate vs 1/temperature for the ROP LLA. Reaction conditions: heating rates of 2, 5, 8 and 10 $^{\circ}\text{C min}^{-1}$, 40 – 200 $^{\circ}\text{C}$, $[\text{Sn}(\text{Oct})_2]_0 : [\text{BnOH}]_0 : [\text{LLA}]_0 = 1:1:100$, $[\text{LLA}]_0 = 1 \text{ M}$ in 1,2-dimethoxybenzene. Data taken from table S18.

Table S19. Heating rate, peak temperature taken from figure S45 for the ROP of TMC conducted under dynamic heating between 40 – 200 $^{\circ}\text{C}$. X

| Heating rate, β ($^{\circ}\text{C min}^{-1}$) | Peak temperature ($^{\circ}\text{C}$) | 1/Temperature ($\times 10^{-3} \text{ K}^{-1}$) | Log β |
|---|---|---|-------------|
| 2 | 142 | 2.41 | 0.3 |
| 5 | 158 | 2.32 | 0.7 |
| 8 | 167 | 2.27 | 0.9 |
| 10 | 171 | 2.25 | 1 |

$[\text{Sn}(\text{Oct})_2]_0 : [\text{BnOH}]_0 : [\text{TMC}]_0 = 1:1:100$. $[\text{TMC}]_0 = 2 \text{ M}$ in 1,2-dimethoxybenzene.

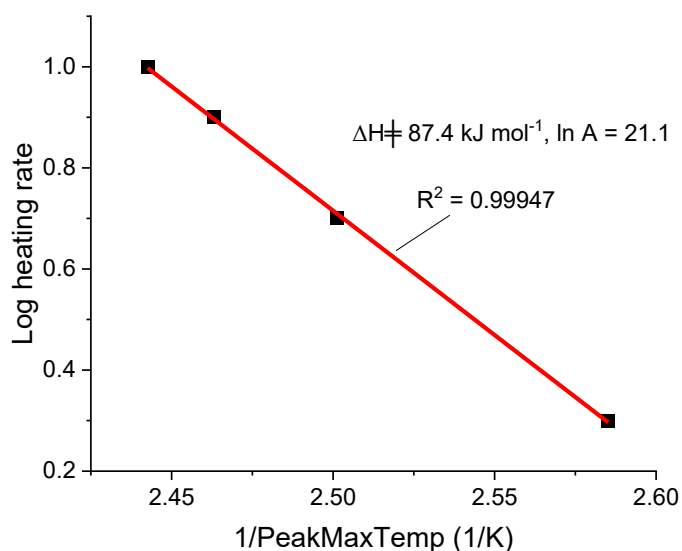


Figure S60. Plot showing log heating rate vs 1/temperature for the ROP TMC. Reaction conditions: heating rates of 2, 5, 8 and 10 °C min⁻¹, 40 – 200 °C, [Sn(Oct)₂]₀: [BnOH]₀: [TMC]₀ = 1:1:100, [TMC]₀ = 2 M in 1,2-dimethoxybenzene. Data taken from table S19.

3.8 Comparison of methods for determination of activation parameters for the kinetics of dVL, TMC and LLA ROP

Table S20. Comparison of methods for determination of ΔH^\ddagger and Ln A for the ROP of dVL using a Sn(Oct)₂/BnOH catalyst

| DSC method | Model | Figure | ΔH^\ddagger | Ln A |
|---------------------------------------|----------------------|--------|---------------------|------------|
| Isothermal | Arrhenius isothermal | S36 | 57.4 (±5.4) | 10.8 ± 1.7 |
| 2 °C min ⁻¹ ramp | Borchardt-Daniels | S2 | 85.5 | 19.2 |
| 5 °C min ⁻¹ ramp | Borchardt-Daniels | S48 | 86.1 | 19.1 |
| 8 °C min ⁻¹ ramp | Borchardt-Daniels | S49 | 93.5 | 21.2 |
| 10 °C min ⁻¹ ramp | Borchardt-Daniels | S50 | 90.8 | 20.3 |
| 2, 5, 8, 10 °C min ⁻¹ ramp | Flynn-Wall-Ozawa | S6 | 66.8 | 13.5 |

Reaction conditions: [Sn(Oct)₂]₀: [BnOH]₀: [dVL]₀ = 1: 1: 100 in neat dVL. [dVL]₀ = 9.98 M. Borchardt-Daniels, taken between 5 – 65% conversion, with 20 intervals. Reaction order set to 1. Flynn-Wall-Ozawa: calculated from peak temperature

Table S21. Comparison of methods for determination of ΔH^\ddagger and Ln A for the ROP of LLA using a Sn(Oct)₂/BnOH catalyst/initiator

| DSC method | Model | Figure | ΔH^\ddagger | Ln A |
|---|----------------------|--------|---------------------|------------|
| Isothermal | Arrhenius isothermal | S39 | 59.7 ± 3.3 | 11.7 ± 1.0 |
| 2 °C min ⁻¹ ramp | Borchardt-Daniels | S51 | 64.7 | 12.8 |
| 5 °C min ⁻¹ ramp | Borchardt-Daniels | S52 | 60.8 | 11.6 |
| 8 °C min ⁻¹ ramp | Borchardt-Daniels | S53 | 55.5 | 9.8 |
| 10 °C min ⁻¹ ramp ^[a] | Borchardt-Daniels | S54 | 53.7 | 9.3 |
| 2, 5, 8, 10 °C min ⁻¹ ramp | Flynn-Wall-Ozawa | S59 | 63.1 | 15.9 |

Reaction conditions: [Sn(Oct)₂]₀: [BnOH]₀: [LLA]₀ = 1: 1: 100. [LLA]₀ = 1 M in 1,2-dimethoxybenzene. Borchardt-Daniels, taken between onset of reaction and peak rate (5-40% conversion), with 20 interval. Reaction order set to 1. Flynn-Wall-Ozawa: calculated from peak temperature

^[a] calculated from 5 – 35% conversion

Table S22. Comparison of methods for determination of ΔH^\ddagger and Ln A for the ROP of TMC using a Sn(Oct)₂/BnOH catalyst/initiator

| DSC method | Model | Figure | ΔH^\ddagger | Ln A |
|---------------------------------------|----------------------|--------|---------------------|------------|
| Isothermal | Arrhenius isothermal | S42 | 76.4 ± 4.3 | 16.0 ± 1.2 |
| 2 °C min ⁻¹ ramp | Borchardt-Daniels | S55 | 107.1 | 24.6 |
| 5 °C min ⁻¹ ramp | Borchardt-Daniels | S56 | 103.2 | 23.3 |
| 8 °C min ⁻¹ ramp | Borchardt-Daniels | S57 | 102.6 | 23.0 |
| 10 °C min ⁻¹ ramp | Borchardt-Daniels | S58 | 107.9 | 24.5 |
| 2, 5, 8, 10 °C min ⁻¹ ramp | Flynn-Wall-Ozawa | S60 | 87.5 | 16.3 |

Reaction conditions: [Sn(Oct)₂]₀: [BnOH]₀: [TMC]₀ = 1:1:100. [TMC]₀ = 2 M in 1,2-dimethoxybenzene. Borchardt-Daniels, taken between onset of reaction and peak rate (5-55% conversion), with 20 intervals. Reaction order set to 1. Flynn-Wall-Ozawa: calculated from peak temperature

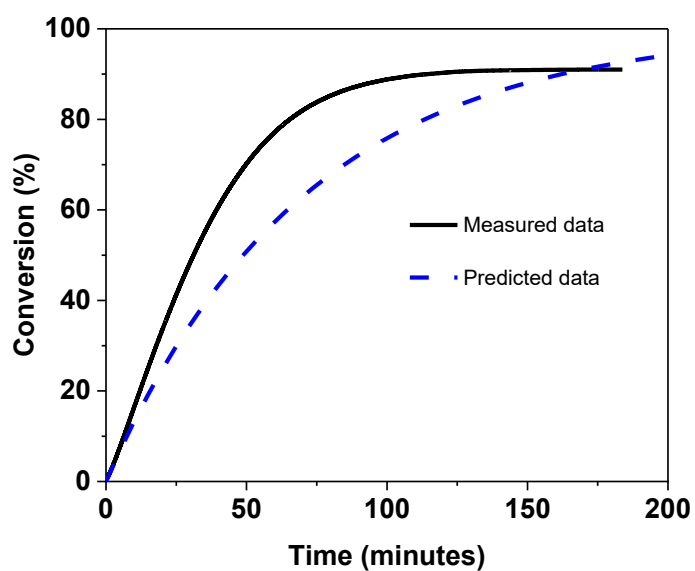


Figure S61. Conversion vs time for the ROP of dVL ($[\text{Sn}(\text{Oct})_2]_0$: $[\text{BnOH}]_0$: $[\text{dVL}]_0$ 1: 1: 100, 120 °C, in neat dVL, $[\text{dVL}]_0 = 9.98 \text{ M}$). Dashed black line shows measured data, blue dashed line shows predicted data from activation parameters determined for a $2 \text{ }^\circ\text{C min}^{-1}$ ramp ($\Delta H^\ddagger = 85.5$, $\ln A = 19.2$)

3.9 Determination of equilibrium monomer conversions

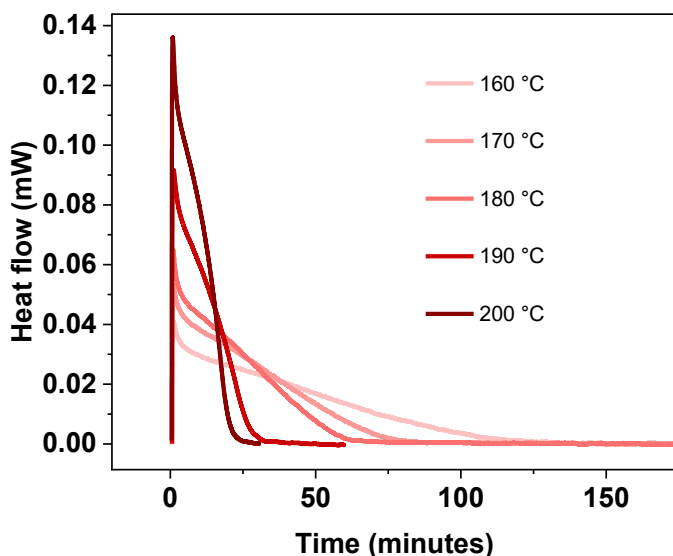


Figure S62. Plots showing heat flow vs time for the polymerization of MDO. Reaction conditions: 160 – 200 °C, [Sn(Oct)₂]: [benzyl alcohol]₀: [MDO]₀ loadings of 1:1:100, in neat MDO, [MDO]₀ = 8.61 M.

Table S23. Equilibrium monomer concentrations for the ROP of MDO at 160, 170, 180, 190 and 200 °C

| Entry | Temp. (°C) | [Monomer] _{eq} ^[a] (M) | [Monomer] _{eq} ^[b] (M) |
|-------|------------|--|--|
| 1 | 160 | 1.145991 | 1.17 ±0.03 |
| | | 1.210566 | |
| | | 1.164072 | |
| 2 | 170 | 1.337133 | 1.35 ±0.02 |
| | | 1.332828 | |
| | | 1.387071 | |
| 3 | 180 | 1.43787 | 1.5 ±0.04 |
| | | 1.464561 | |
| | | 1.529997 | |
| 4 | 190 | 1.539468 | 1.56 ±0.03 |
| | | 1.599738 | |
| 5 | 200 | 1.887312 | 1.87 ±0.08 |
| | | 1.775382 | |
| | | 1.961358 | |

Reactions conducted in DSC pans with [Sn(Oct)₂]: [BnOH]₀: [MDO]₀ = 1: 1: 100. [MDO]₀ = 8.61 M. ^[a]Determined by ¹H NMR spectroscopy. ^[b]average of at least three repeats. Error taken as standard deviation of the mean.

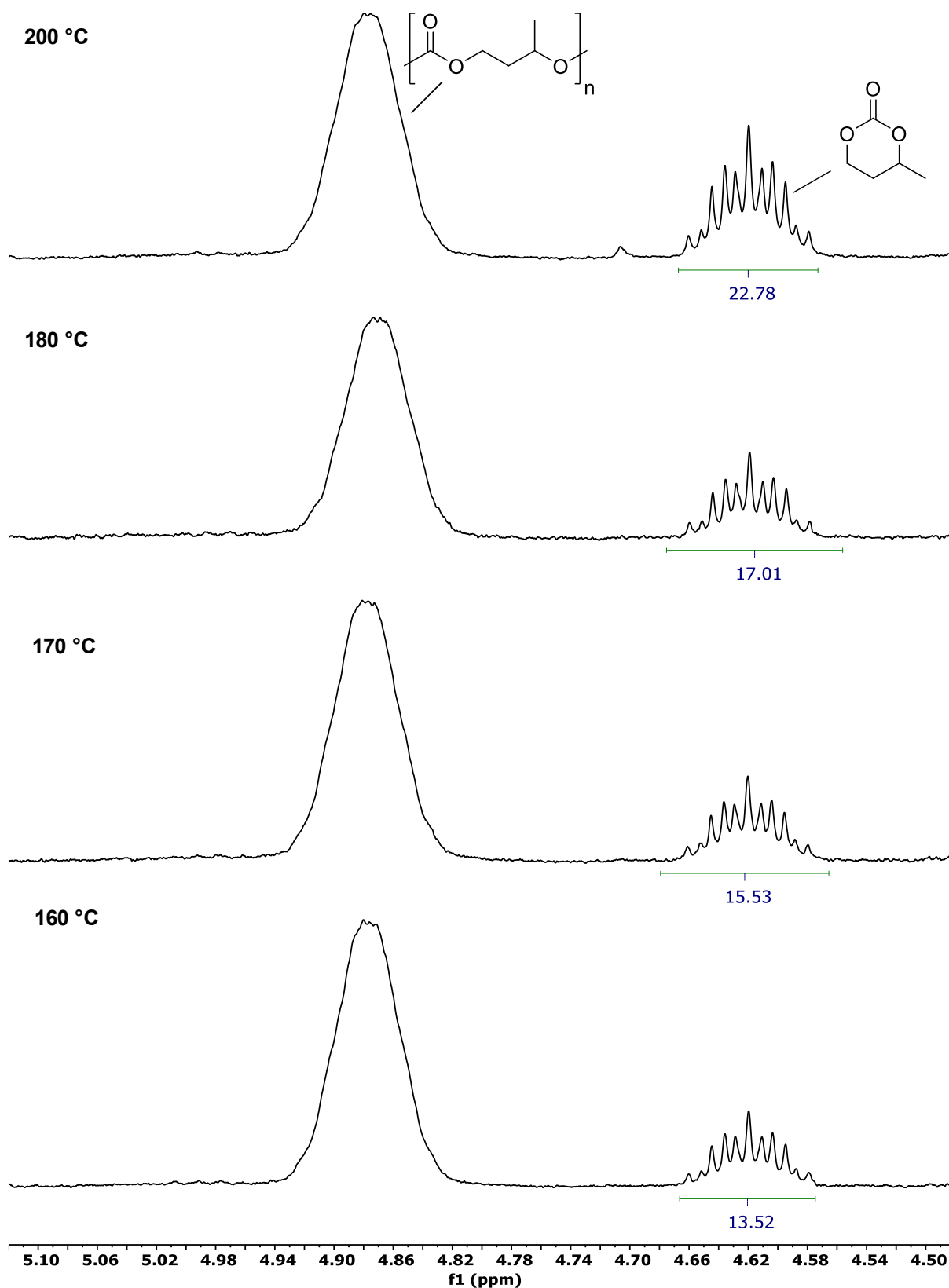


Figure S63. Selected ^1H NMR spectra (CDCl_3) showing MDO integrals used to determine equilibrium monomer concentration. Reaction conditions: 160 – 200 °C, $[\text{Sn}(\text{Oct})_2]$: $[\text{benzyl alcohol}]_0$: $[\text{MDO}]_0 = 1:1:100$ in neat MDO, $[\text{MDO}]_0 = 8.61 \text{ M}$

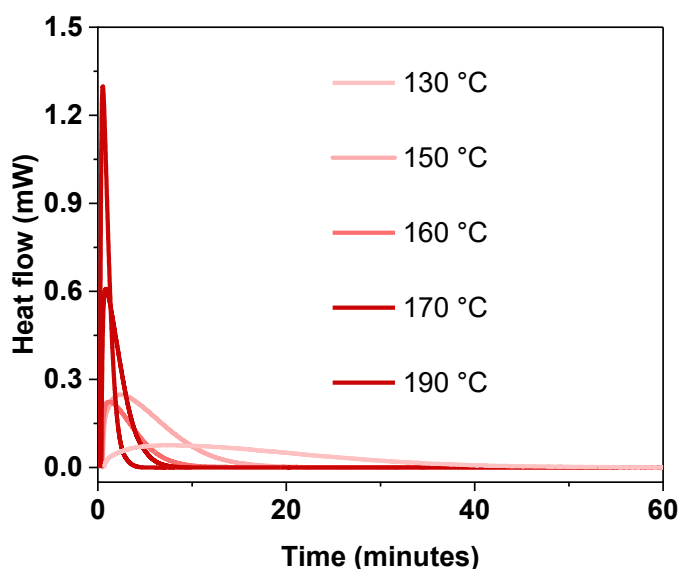


Figure S64. Plots of heat flow vs time for the polymerization of DDO. Reaction conditions: 130 – 190 °C, $[\text{Sn}(\text{Oct})_2]: [\text{benzyl alcohol}]_0: [\text{DDO}]_0$ loadings of 1:1:500, $[\text{DDO}]_0 = 7.68 \text{ M}$.

Table S24. Equilibrium monomer concentrations for the ROP of DDO at 130, 150, 160, 170 and 190 °C

| Entry | Temp. (°C) | $[\text{Monomer}]_{\text{eq}}^{[\text{a}]} (\text{M})$ | $[\text{Monomer}]_{\text{eq}}^{[\text{b}]} (\text{M})$ |
|-------|------------|--|--|
| 1 | 130 | 0.301824 | 0.31 ±0.01 |
| | | 0.324096 | |
| 2 | 150 | 0.457728 | 0.43 ±0.02 |
| | | 0.415488 | |
| | | 0.410112 | |
| 3 | 160 | 0.507648 | 0.52 ±0.01 |
| | | 0.52224 | |
| | | 0.523008 | |
| 4 | 170 | 0.615936 | 0.59 ±0.02 |
| | | 0.596736 | |
| | | 0.570624 | |
| 5 | 190 | 0.807168 | 0.80 ±0.01 |
| | | 0.797952 | |
| | | 0.805632 | |

Reactions conducted in DSC pans with $[\text{Sn}(\text{Oct})_2]: [\text{BnOH}]_0: [\text{DDO}]_0 = 1: 1: 100$. $[\text{DDO}]_0 = 7.68 \text{ M}$. ^[a]Determined by ^1H NMR spectroscopy. ^[b]average of at least three repeats. Error taken as standard deviation of the mean.

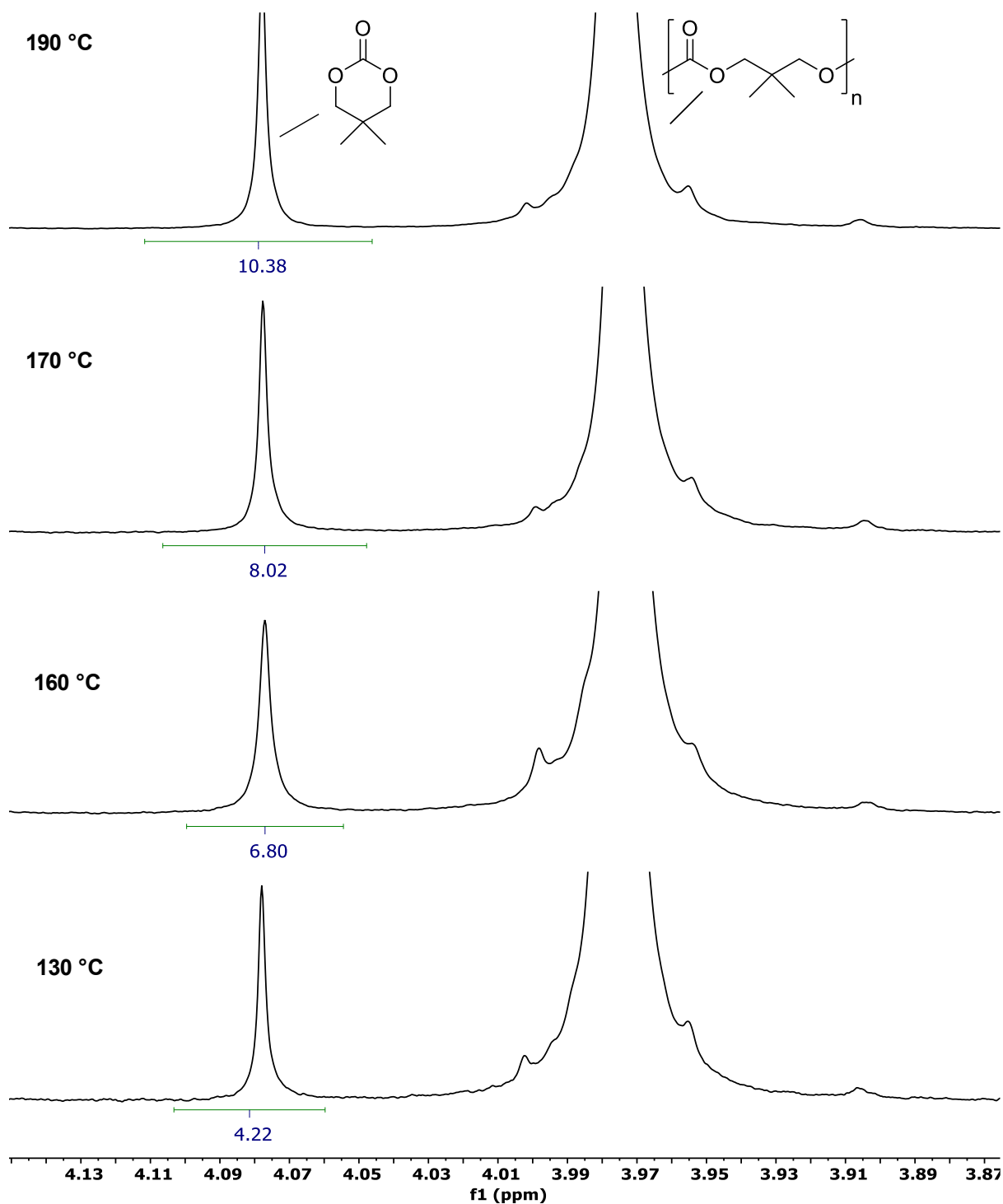


Figure S65. Selected ^1H NMR spectra (CDCl_3) showing DDO integrals used to determine equilibrium monomer concentration. Reaction conditions: 130 – 190 °C, $[\text{Sn}(\text{Oct})_2]: [\text{benzyl alcohol}]_0: [\text{DDO}]_0 = 1:1:100$ in neat MDO, $[\text{DDO}]_0 = 7.68 \text{ M}$.

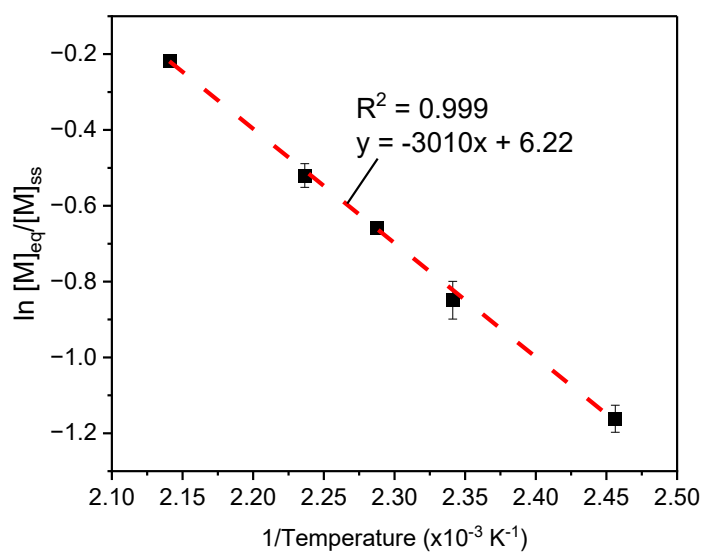


Figure S66. Plot of $\ln [M]_{\text{eq}}/[M]_{\text{ss}}$ vs $1/\text{temperature}$ for the ROP of DDO. Reactions conditions: 130 – 190 °C, $[\text{Sn}(\text{Oct})_2]_0 : [\text{BnOH}]_0 : [\text{DDO}]_0 = 1 : 1 : 100$, $[\text{DDO}]_0 = 7.68 \text{ M}$. $[M]_{\text{ss}} = 1.0 \text{ M}$.

3.10 Examples for new users

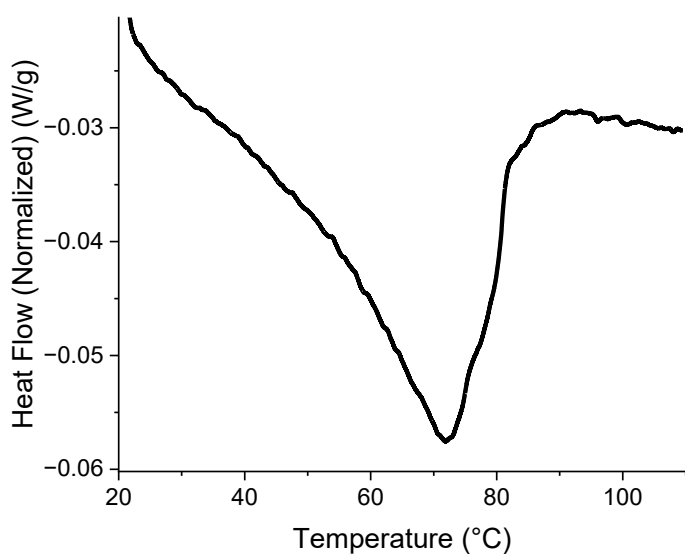


Figure S67. Heatflow vs temperature showing the exotherm of dissolving PA in CHO and toluene. The mixture was initially heterogeneous with PA suspended in a solution of $[\text{CHO}]_0 = 5 \text{ M}$ in toluene. The initial molar ratio of PA: CHO = 1: 5

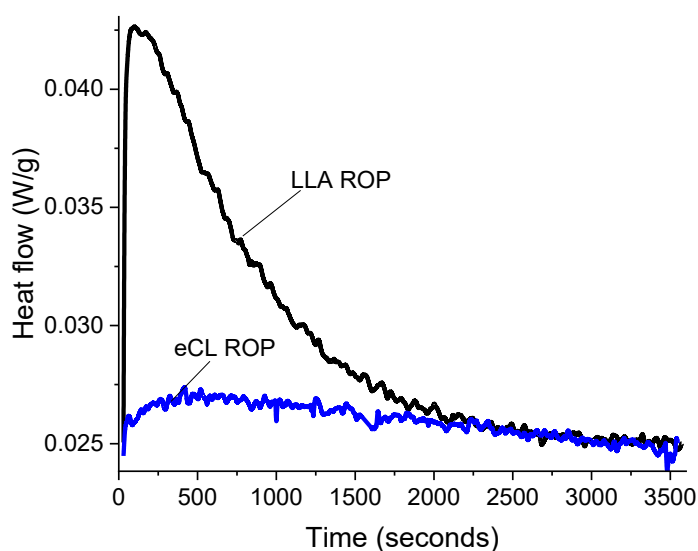
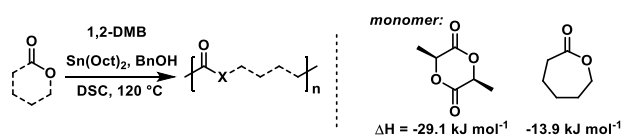


Figure S68. Heatflow vs time for the ROP of LLA (black), and *epsilon*-caprolactone (blue). Reactions conditions: $120 \text{ }^\circ\text{C}$, $[\text{Sn}(\text{Oct})_2]_0: [\text{BnOH}]_0: [\text{monomer}]_0 = 1: 1: 100$, $[\text{monomer}]_0 = 1 \text{ M}$ in 1,2-dimethoxybenzene. *e*CL ROP reached 100% conversion in the shown timeframe but the exotherm is not detected owing to the lower enthalpy of the *e*CL polymerization.

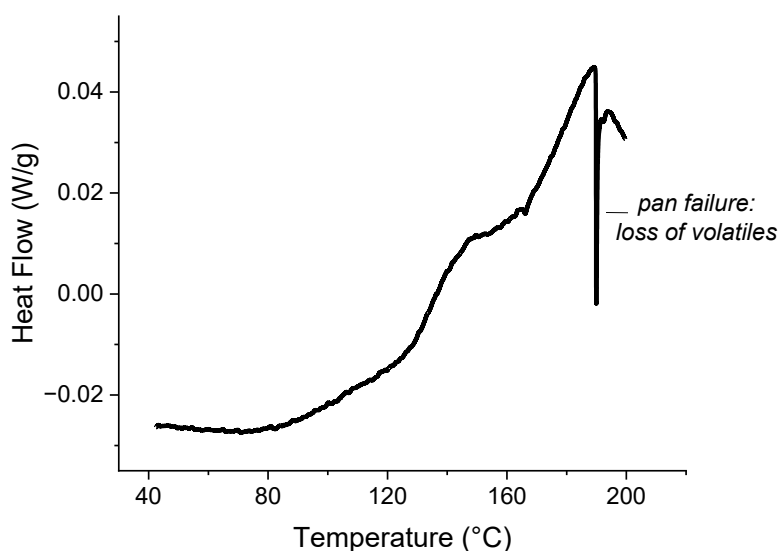


Figure S69. Heatflow vs temperature for the ROP of CHO in neat CHO. Reaction conditions: heating rate of $2\text{ }^{\circ}\text{C min}^{-1}$, $[\text{KO}^t\text{Bu}]_0 : [\text{CHO}]_0 = 1 : 50$, $[\text{CHO}]_0 = 10.2\text{ M}$. Escape of volatiles causes spike in thermogram around $200\text{ }^{\circ}\text{C}$.

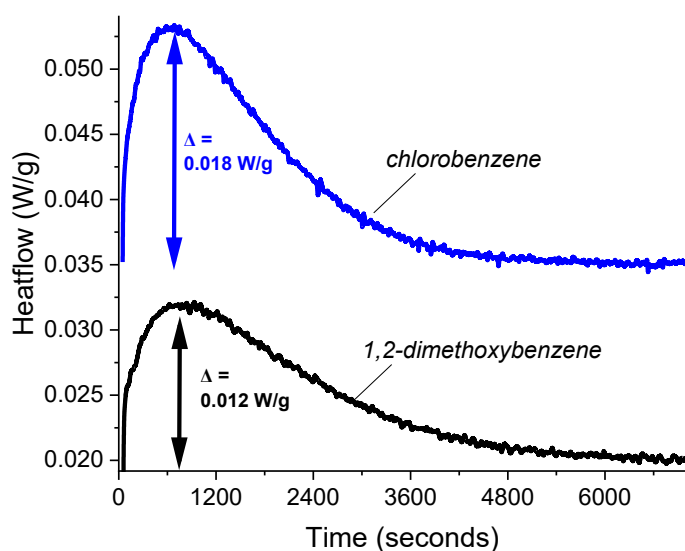
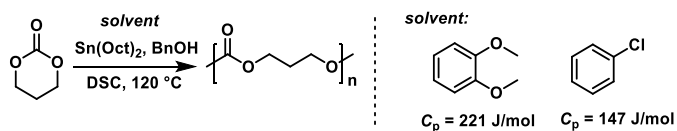


Figure S70. Heatflow vs time for the ROP of TMC in 1,2-dimethoxybenzene (black) and chlorobenzene (blue). Reaction conditions: $120\text{ }^{\circ}\text{C}$, $[\text{Sn}(\text{Oct})_2]_0 : [\text{BnOH}]_0 : [\text{eCl}]_0 = 1 : 1 : 100$, $[\text{monomer}]_0 = 2\text{ M}$ in 1,2-dimethoxybenzene.

4. References

- (1) Olsson, J. V.; Hult, D.; Cai, Y.; García-Gallego, S.; Malkoch, M. Reactive imidazole intermediates: simplified synthetic approach to functional aliphatic cyclic carbonates. *Polym. Chem.* **2014**, *5* (23), 6651-6655. DOI: <https://doi.org/10.1039/C4PY00911H>.
- (2) Kowalski, A.; Duda, A.; Penczek, S. Polymerization of 1,1-Lactide Initiated by Aluminum Isopropoxide Trimer or Tetramer. *Macromolecules* **1998**, *31* (7), 2114-2122. DOI: 10.1021/ma971737k.