Supporting Information

Redox-Triggered Crosslinking of a Degradable Polymer

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I. General Considerations.

Unless stated otherwise, all reactions were carried out in oven-dried glassware in nitrogen-filled glove box or using standard Schlenk line techniques.[1] Solvents were used after passage through a solvent purification system under a blanket of argon and then degassed briefly by exposure to vacuum. Acros Organics supplied the glyoxylic acid. zinc, allyl bromide, 2-bromopropionyl bromide, triethylamine, sodium carbonate, and rhodium on activated carbon were purchased from Sigma-Aldrich. TCI America provided bismuth(III) chloride. Fisher Scientific supplied hydrochloric acid, magnesium sulfate, and solvents. 1,2-epoxy-5-hexene was purchased from Gelest, Inc. Hoveyda-Grubbs 2nd Generation and Zhan's catalysts were purchased through Strem. (*rac*)-Lactide was supplied by Frinton Laboratories and was recrystallized from ethyl acetate followed by recrystallization from toluene and dried *in vacuo* prior to use. Zinc was activated with hydrochloric acid, dried over P_2O_5, and stored under an inert atmosphere.

Nuclear magnetic resonance (NMR) spectra were recorded at ambient temperature on a Varian spectrometer (^{1}H and ^{1}H{^{1}H} 500 MHz, and ^{13}C{^{1}H} 125 MHz) in $CDCl_3$ and are referenced versus shifts of solvents containing residual protic impurities. The line listing for the ^{1}H NMR spectra are reported as: chemical shift in ppm (multiplicity, number of protons, coupling constant in Hz, assignment).

High-resolution mass spectra were obtained at the Boston College Mass Spectrometry Facility using JEOL AccuTOF DART.

Automated flash column chromatography was carried out using a Teledyne ISCO CombiFlash® R_f using RediSep Rf Gold columns. Thin layer chromatography (TLC) was done using Merck TLC Silica gel 60 F_{254} glass plates and stained with potassium permanganate or phosphoromolybdoic acid (PMA) stains.

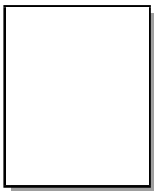
Gel permeation chromatography (GPC) was performed on an Agilent GPC220 in THF at 40 °C with three PL gel columns (10μm) in series and recorded with a refractive index detector. Molecular weights and molecular weight distributions were determined from the signal response of the RI detector relative to polystyrene standards.

Gas chromatography (GC) was performed with a Shimadzu GC-2014 GC-FID (SHRXI-5MS column 15 m x 0.25 mm x 0.25 μm). The GC method used was a ramp of

10 ºC per minute from 80 ºC to 250 ºC where it was held for 3 minutes with tetradecane as an internal standard.

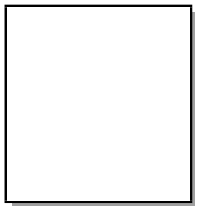
All differential scanning calorimetry (DSC) measurements were performed on a TA instruments Q10-0311 for three heating cycles from -80°C to 300°C at a ramp of 10°C/min. Thermogravimetric analysis (TGA) measurements were performed on a TA Instruments Q50 from room temperature to 800°C at a ramp of 20°C/min. TGA and DSC were performed at MIT using instruments in the Swager group.

II. Synthetic and Experimental Procedures

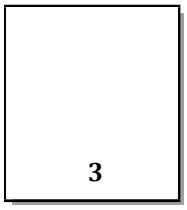


Synthesis of 2-Hydroxypent-4-enoic Acid In a dry atmosphere glove box, glyoxylic acid monohydrate (20 g, 0.22 mol) was added to a 3-neck round bottom flask (1L) with a 180º joint, rubber septum, and a thermometer. The round bottom flask was brought out of the glove box and connected to a Schlenk line, and dry THF (590 mL) was added. Zinc (30 g, 0.46 mol) and bismuth trichloride (96 g, 0.30 mol) were cooled to 0 °C. The zinc was added in two portions to the round bottom flask via the side arm under a positive pressure of nitrogen. Bismuth trichloride was added in four portions to the round bottom flask under a positive pressure of nitrogen, making sure the temperature did not rise above 10 °C. The reaction slurry turned gray upon the addition of zinc and turned dark blue/black upon addition of the bismuth trichloride. The reaction slurry stirred for 3 hours at 0 °C. Allyl bromide (26 mL, 0.30 mol) was added drop wise to the flask. The reaction was sealed under nitrogen and stirred overnight at 4 °C. The reaction was quenched with 1 M HCl (1000 mL) and stirred for 3 hours at 25 °C. The reaction slurry was filtered through celite. The organic phase was extracted three times with diethyl ether (100 mL). The combined organic phases were washed three times with brine (100 mL), dried over magnesium sulfate, filtered, and concentrated to give white crystals (16.9 g, 67%). The product was used without further purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.83 (ddt, J = 17.2, 10.0, 7.2 Hz, 1H, CH), 5.21 (dd, J = 13.5, 9.1 Hz, 2H, CH_2), 4.36 (dd, J = 6.1, 4.9 Hz, 1H, CH), 2.72 – 2.43 (m, 2H, CH_2).; ^{13}C NMR (150 MHz, $CDCl_3$): δ 38.51, 69.86, 119.67, 132.03, 178.90; IR (neat) 3451.74, 3401.12, 2909.37, 1707.29, 1209.51, 1070.59, 917.76, 874.37

cm^{-1}; HRMS (ESI+) Calcd. for $C_5H_9O_3$ $[M+H]^+$: 117.05517; Found 117.05574. Spectroscopic data matches what is reported in the literature.[2]



Synthesis of 2-(2-Bromopropanoyloxy)pent-4-enoic Acid On the Schlenk line under nitrogen, 2-bromopropionyl bromide (12.25 mL, 117 mmol) and dichloromethane (329 mL) were added to a 2-neck round bottom flask (1L) and cooled to 0 °C. A solution of triethylamine (16.3 mL, 11.82 g, 117 mmol) and 2-hydroxypent-4-enoic acid (13.59 g, 117 mmol) in dichloromethane (120 mL) was added drop wise to the round bottom flask. The reaction solution was stirred at 25 °C for 24 hours. The organic phase was washed three times with water (100 mL) and washed once with brine (300 mL). The organic phase was extracted three times from the aqueous phase using dichloromethane (100 mL). The combined organic phases were dried over magnesium sulfate, filtered, and concentrated to give a dark yellow oil as a mixture of diastereomers (29 g, quant.). The product was used without further purification. ^{1}H NMR (500 MHz, $CDCl_3$), a mixture of two diastereomers that could not be resolved. δ 10.92 (s, 1H), 5.88 – 5.68 (m, 1H, CH), 5.19 (dd, J = 2.5, 1.3 Hz, 1H, CH), 5.13 (t, J = 9.4, 8.1, 3.0 Hz, 2H, CH_2), 4.54 – 4.28 (q, 1H, CH), 2.77 – 2.42 (m, 2H, CH_2), 1.82 (d, J = 9.9, 7.6, 5.5 Hz, 3H, CH_3).; ^{13}C (150 MHz, $CDCl_3$): δ 175.58, 174.44, 169.87, 169.59, 131.48, 131.41, 119.46, 72.64, 72.55, 39.96, 39.71, 39.30, 35.28, 21.86, 21.65; HRMS (ESI+) Calcd. for $C_8H_{12}BrO_4$ $[M+H]^+$: 250.99190; Found 250.99164. Spectroscopic data matches what is reported in the literature.[2]



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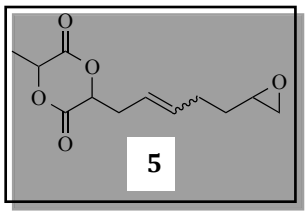
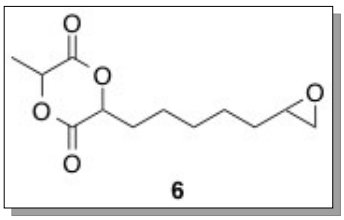
*Synthesis of 3-Allyl-6-methyl-1,4-dioxane-2,5-dione (**3**)* A solution of 2-(2-Bromopropanoyloxy)pent-4-enoic acid (25.0 g, 99.6 mmol) in DMF (800 mL) was added drop wise using an addition funnel over 5 hours to a slurry of sodium carbonate (4.80 g, 43.3 mmol) in DMF (3200 mL) in a 3-neck round bottom flask (5L) at 0 ºC. The reaction slurry was stirred at 25 °C for 24 hours. The reaction solution was concentrated, and acetone was added to precipitate the sodium salts. The mixture was filtered and concentrated to give a yellow oil. The product was purified by flash column chromatography using elution gradient as a mixture of diastereomers (100% hexanes to 70% hexanes and 30% ethyl acetate, $KMnO_4$ stain) to

give a colorless oil (R_f = 0.37 in 70/30 hexanes/EtOAc, 9.3 g, 55%). ^{1}H NMR (600 MHz, $CDCl_3$) diastereomers could not be resolved. δ 5.82 (m, J = 17.1, 10.2, 7.0 Hz, 1H, CH), 5.33 – 5.18 (m, 2H, CH_2), 5.08 – 4.99 (m, 1H, CH), 4.95 (d, J = 7.3, 4.5 Hz, 1H, CH), 2.85 – 2.66 (m, 2H, CH_2), 1.65 (d, J = 21.1, 6.9 Hz, 3H, CH_3).; ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.52, 166.65, 166.06, 165.30, 130.76, 130.00, 121.01, 119.83, 76.01, 75.12, 72.74, 72.25, 36.09, 33.99, 17.59, 15.65; IR (neat) 1752.40, 1227.14, 1072.27 cm^{-1}; HRMS (ESI+) Calcd. for $C_8H_{11}O_4$ $[M+H]^+$: 171.06573; Found 171.06503. Spectroscopic data matches what is reported in the literature.[2]



*Synthesis of 3-methyl-6-(5-(oxiran-2-yl)pent-2-en-1-yl)-1,4-dioxane-2,5-dione (**5**)* Compound **3** (2.000 g, 11.75 mmol) and 1,2-epoxy-5-hexene (**2**) (4.00 mL, 3.480 g 35.5 mmol) were dissolved in dichloromethane (30 mL) in a 2-neck round bottom flask (50 mL). The solution was degassed by freeze-pump-thaw three times. The Hoveyda-Grubbs second-generation catalyst (**4**) (220 mg, 0.35 mmol) was added as a solid in one portion via the side arm. The reaction solution was stirred for 24 hours at 25 °C with brief exposure to vacuum periodically until the TLC of the reaction mixture indicated no further conversion. The crude reaction mixture was purified by column chromatography using a gradient of solvents (15% ethyl acetate and 85% hexanes to 30% ethyl acetate and 70% hexanes) to afford a light brown oil as a mixture of diastereomers (R_f = 0.30 and 0.31, 1.8 g, 65%) Reaction followed using 30% hexanes/70% ethyl acetate and staining with $KMnO_4$. The unreacted starting material was also collected from the column (R_f =0.73, 0.50 g, 30%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.71 (dt, *J* = 19.0, 10.0 Hz, 1H, CH), 5.53 (dt, *J* = 24.1, 8.1 Hz, 1H, CH), 5.08 – 4.94 (m, 1H, CH), 4.90 (dd, *J* = 7.0, 4.6 Hz, 1H, CH), 2.91 (dd, *J* = 6.3, 3.8 Hz, 1H, CH), 2.74 (m, 3H, CH and CH_2), 2.48 (dd, *J* = 8.7, 5.9 Hz, 1H, CH), 2.38 – 2.08 (m, 2H, CH_2), 1.78 – 1.42 (m, 5H, CH_3 and CH_2).; ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.43, 166.54, 135.02, 122.87, 75.59, 72.31, 51.77, 47.08, 33.09, 31.99, 29.03, 15.84; IR (neat) 2923.55, 1758.82, 1274.80, 1231.34; HRMS (ESI+) Calcd. for $C_{12}H_{16}O_5$ $[M+H]^+$: 241.10760; Found 241.10853.



Synthesis of 3-methyl-6-(5-(oxiran-2-yl)pentyl)-1,4-dioxane-2,5-dione (**6**) Rhodium on activated carbon (170 mg) and ethyl acetate (10 mL) were added to a 2-neck, 50 mL, round bottom flask, equipped with a septum and a 3-way joint, under nitrogen. The solution was degassed by brief exposure to vacuum and backfilling with nitrogen three times. Compound **5** (1.7 g, 7.1 mmol) was then added to the flask via the side arm under a positive pressure nitrogen. The flask was evacuated and backfilled with hydrogen (1 atm) from a balloon through the 3-way joint three times. The reaction was allowed to stir under hydrogen for 4 hours at 25 °C and monitored by staining with $KMnO_4$ until the compound no longer stained, indicating absence of alkenes. Reaction mixture then filtered through celite and concentrated to afford a colorless oil that was >95% pure with a small amount of an aldehyde impurity (1.6 g, 96%). ^{1}H NMR (600 MHz, $CDCl_3$) diastereomers could not be resolved. δ 5.01 (m, J = 11.9, 6.9 Hz, 1H, CH), 4.93 – 4.82 (m, 1H, CH), 2.87 (s, 1H, CH), 2.72 (dd, J = 4.9, 4.0 Hz, 1H, CH), 2.43 (dd, J = 5.0, 2.7 Hz, 1H, CH), 2.18 – 1.87 (m, 2H, CH_2), 1.65 (d, J = 14.8, 7.6 Hz, 3H, CH_3), 1.61 – 1.27 (m, 8H, 4 CH_2).; ^{13}C NMR (150 MHz, $CDCl_3$):; IR (neat) 2931.95, 2860.66, 1758.31, 1450.59, 1233.69; HRMS (ESI+) Calcd. for $C_{12}H_{18}O_5$ $[M+H]^+$:243.12329; Found 243.12325.

Representative procedure for redox-triggered polymerization of ***6****.* In the glovebox, a 7 mL vial with a stir bar was charged with **6** (100 mg, 0.413 mmol) as a solution in dichloromethane (1.36 mL). In a separate 4 mL vial, a solution of **1** (5.5 mg, 8.2 μmol) in dichloromethane (1 mL) was prepared and immediately added to the solution of **6**. The reaction was allowed to stir at room temperature for 24 hours. Ferrocenium hexafluorophosphate (2.7 mg, 8.2 μmol) was then added the vial, and the reaction was stirred for four hours at room temperature. The reaction was brought out of the glove box and concentrated (quantitative). To obtain pre-crosslinked polymer, reaction mixture was removed from glovebox prior to oxidation and dried *in vacuo*.

Procedure for redox-triggered polymerization of ***6*** *starting with* ***1-ox****.* In the glovebox, a 7 mL vial with a stir bar was charged with **6** (100 mg, 0.413 mmol) as a solution in dichloromethane (1.00 mL). In a separate 4 mL vial, a solution of **1-ox** (6.7 mg, 8.2 μmol) in dichloromethane (1.0 mL) was prepared and immediately added to the solution of **6**. The reaction was allowed to stir at room temperature for 48 hours.

Cobaltocene (1.6 mg, 8.2 μmol) was then added the vial, and the reaction was stirred for four hours at room temperature. The reaction was concentrated (quantitative) in the glovebox. To obtained pre-crosslinked polymer, reaction mixture was removed from glovebox prior to reduction and dried *in vacuo*.

*Representative procedure for redox-triggered copolymerization of **6** and lactide.* In a 7 mL vial with stir bar was added **6** (60.6 mg, 250 μmol) and lactide (36 mg, 0.25 mmol), which was dissolved in dichloromethane (0.5 mL). In a separate 4 mL vial, **1** (6.7 mg, 10 μmol) was dissolved in dichloromethane (1 mL), and the catalyst solution was added to the solution containing the monomers. The reaction was allowed to stir at room temperature for 24 hours, a sample was taken at 2 hours for use in determining the reactivity ratios. Ferrocenium hexafluorophosphate (13.3 mg, 10.0 μmol) was then added to the vial, and the reaction was stirred for 4 hours at room temperature. The solvent was removed concentrated to give an insoluble polymer mass. To obtained pre-crosslinked polymer, reaction mixture was removed from glovebox prior to oxidation and dried *in vacuo*.

*Procedure for redox-triggered polymerization of **6** using ferrocenium hexafluorophosphate.* In the glovebox, a 7 mL vial with a stir bar was charged with **6** (121 mg, 0.50 mmol) as a solution in dichloromethane (1.0 mL). In a separate 4 mL vial, a solution of **1** (6.7 mg, 10 μmol) in dichloromethane (1.0 mL) was prepared and immediately added to the solution of **6**. The reaction was allowed to stir at room temperature for 24 hours. The reaction was then removed from the glovebox and the polymer was precipitated into methanol. The resulting polyester 7 was brought back into the box and dissolved in dichloromethane (1.0 mL). Ferrocenium hexafluorophosphate (3.3 mg, 10 μmol) was then dissolved in dichloromethane (0.5 mL) and added the vial, and the reaction was stirred for twentyfour hours at room temperature. The reaction was brought out of the glove box and concentrated (quantitative).

*Procedure for copolymerization of lactide and saturated **3**.* In a 7 mL vial with stir bar was added lactide (36 mg, 250 μmol) and saturated **3** (43 mg, 250 μmol), which was dissolved in dichloromethane (0.5 mL). In a separate 4 mL vial, **1** (6.7 mg, 10 μmol) was dissolved in dichloromethane (1 mL), and the catalyst solution was added to the

solution containing the monomers. The reaction was allowed to stir at room temperature for 24 hours. The solvent was removed and dried *in vacuo*.

Representative procedure for swelling experiments. A known mass of polymer (5-10mg) was added to a vial and submerged in tetrahydrofuran (THF). After soaking for 24 hours, THF was carefully removed and swollen polymer was briefly dried to remove surface solvent. Polymer vial was reweighed and mass of absorbed THF was calculated. This was repeated three times.

Procedure for degradation experiments. In a 20 mL vial, 30mg of cross-linked polymer was added and stirred in 10% hydrochloric acid in tetrahydrofuran for 36h. This time and acid concentration were determined to fully degrade polyester linkages. This yielded an oligomeric polyether with a M_n= 500 and a polydispersity of 2.0 and a yield of 93%.

III. Supplemental Figures

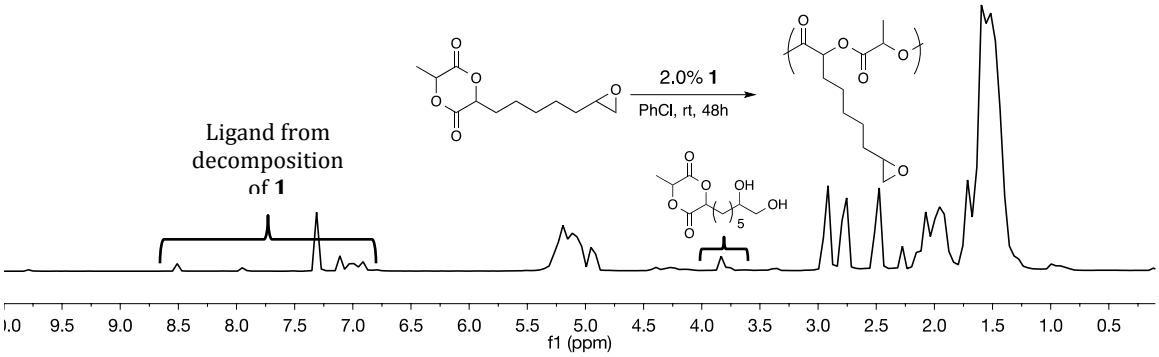


Figure S1. Representative ^{1}H NMR (500 MHz, $CDCl_3$ of the polymerization of **6** before oxidation.

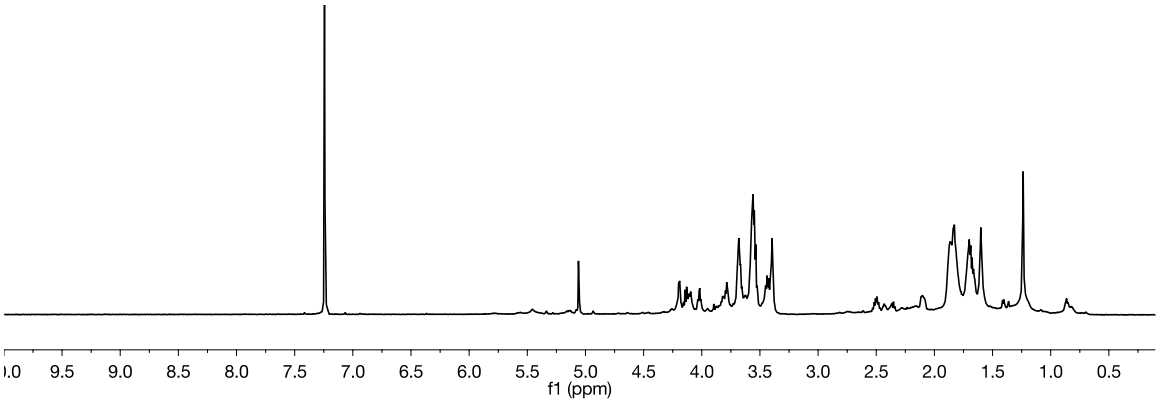


Figure S2. Representative ^{1}H NMR (500 MHz, $CDCl_3$) of cross-linked polymer after degradation in 10% HCl/THF for 36 hours.

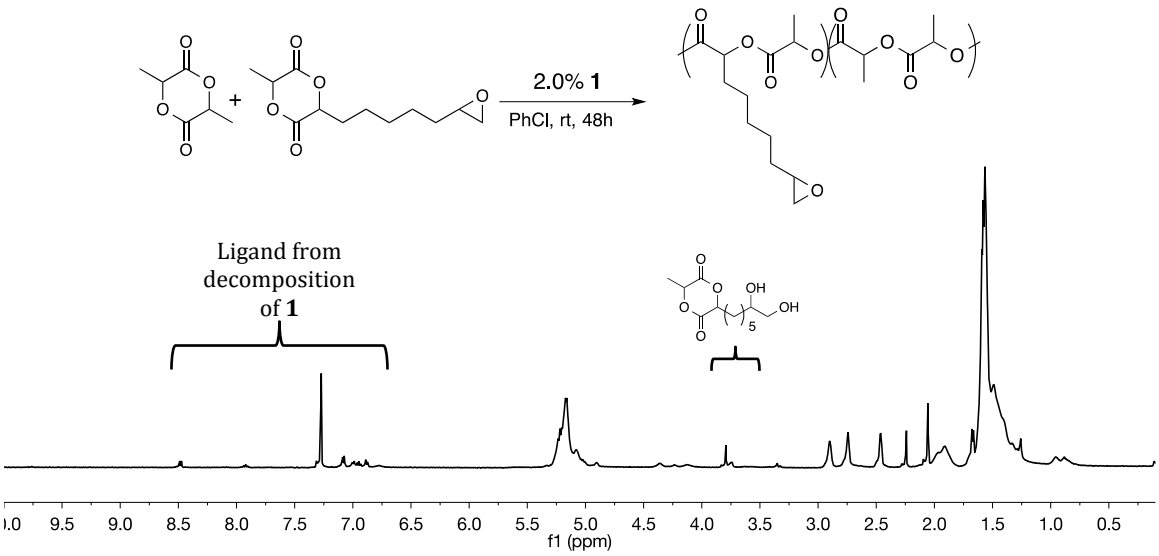


Figure S3. Representative ^{1}H NMR of the copolymerization of **6** with lactide before oxidation.

IV. Determination of Reactivity Ratios

The reactivity ratios were determined assuming the terminal model of copolymerization following the method described previously.[3] In order to determine reactivity ratios, polymerization reactions were carried out and conversion was analyzed by GC at low conversions (ideally below 70%). At high conversion the co-monomer feed will affect the copolymer composition, but at low conversion the copolymer composition will be based on the inherent reactivity of each monomer to undergo polymerization. The primary assumption of this method is that copolymerization rate is only dependent on the last unit of the propagating chain. Based on this there are four possible propagation reactions:

1: $M_1^* + M_1 \xrightarrow{k_{11}} M_1^*$ 2: $M_1^* + M_2 \xrightarrow{k_{12}} M_2^*$ 3: $M_2^* + M_1 \xrightarrow{k_{21}} M_1^*$

4: $M_2^* + M_2 \xrightarrow{k_{22}} M_2^*$

Here 1 and 4 are considered self-propagation and 2 and 3 are cross propagation. Above each reaction is the rate constant for each reaction.

$$r_1 = \frac{k_{11}}{k_{12}} \quad r_2 = \frac{k_{22}}{k_{21}}$$

Reactivity ratios are abbreviated as r_1 and r_2.

If r>1 then the monomer preferentially adds itself, but if r<1 it will more likely add the comonomer. The reactivity ratios are incorporated into the copolymerization equation:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2](r_2[M_2] + [M_1])}$$

Here $\frac{d[M_1]}{d[M_2]}$ is equal to the copolymer composition. Further manipulation of this equation using linear least-squares regression analysis can give equations G and F.

$$G = \frac{\frac{[M_1]}{[M_2]}\left(\frac{d[M_1]}{d[M_2]} - 1\right)}{\left(\frac{d[M_1]}{d[M_2]}\right)} \qquad F = \frac{\left(\frac{[M_1]}{[M_2]}\right)^2}{\left(\frac{d[M_1]}{d[M_2]}\right)}$$

Here $\frac{[M_1]}{[M_2]}$ is the initial comonomer feed. A plot of G is plotted against F to yield a straight line with slope r_1 and the intercept r_2.

Representative experimental procedure. In a 7 mL vial with stir bar was added **6** and the appropriate amount of lactide so as to maintain a 500 μmol total monomer along with tetradecane (100 mg, 505 μmol). The reaction mixture was dissolved in dichloromethane (0.5 mL) and an aliquot was removed and analyzed by GC for a t = 0 data point (See Figure S4). In a separate 4 mL vial, **1** (6.7 mg, 10 μmol) was dissolved in dichloromethane (1 mL), and the catalyst solution was added to the solution containing the monomers. The reaction was allowed to stir at room temperature for 2 hours, at which point a sample was taken and analyzed by GC. Conversion was determined by comparing the relative ratios of lactide and **6** to tetradecane standard obtained at the t = 2 hour data point to the analogous ratios obtained for the t = 0 data point.

Compound	**Retention Time (min)**
tetradecane	9.04
(*rac*)-lactide	7.35
6 (two diastereomers)	11.92, 12.27

Feed Ratio [**6**:lactide]	**6** % Conversion	Lactide Conversion
9:1	0.73	0.2
3:1	0.63	0.32
1:1	0.34	0.76
1:9	0.4	0.75

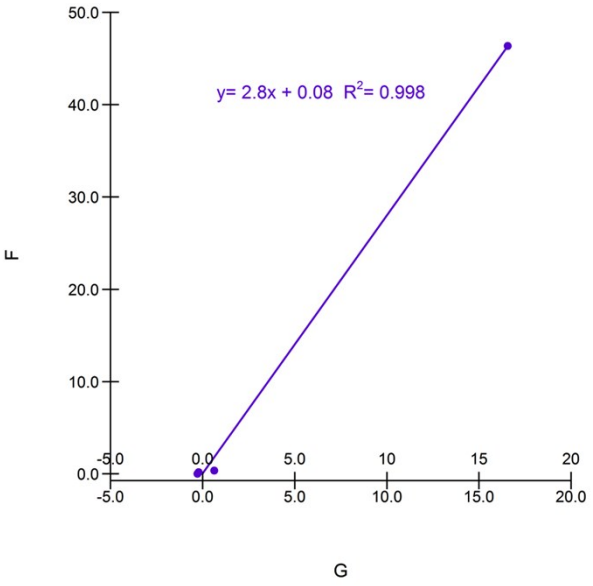


Figure S4. Determination of reactivity ratios for copolymerization **6** and lactide catalyzed by **1**. **6** had two retention times at 11.92 min and 12.30 min

V. GPC, DSC and TGA traces.

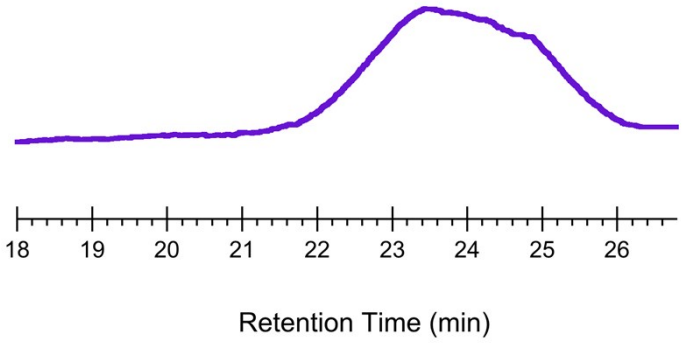


Figure S5. GPC trace of a **6** homopolymerization before oxidation.

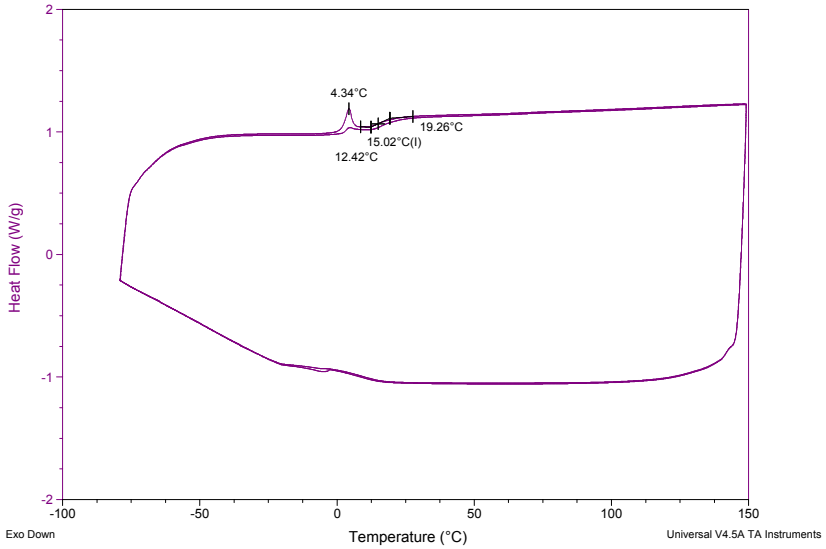


Figure S6. DSC trace of a **6** homopolymerization catalyzed by **1**.

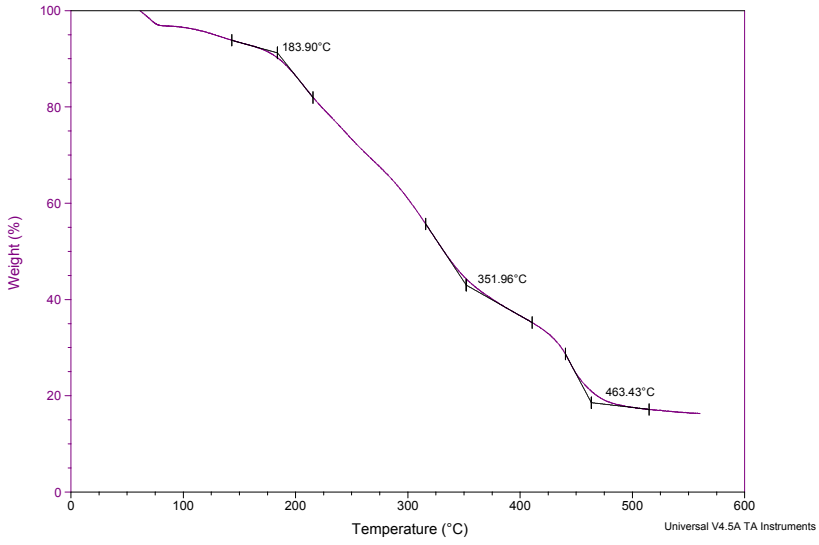


Figure S7. TGA trace of a **6** homopolymerization catalyzed by **1**.

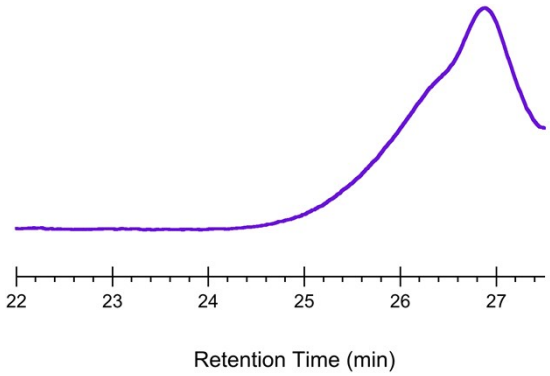


Figure S8. GPC trace of a **6** homopolymerization catalyzed by **1-ox**.

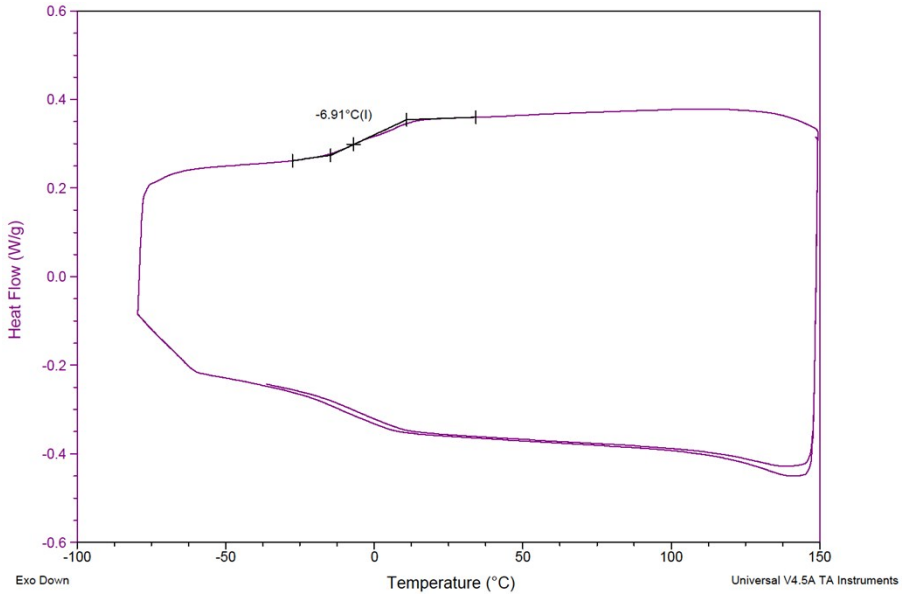


Figure S9. DSC trace of a **6** homopolymerization catalyzed by **1-ox**.

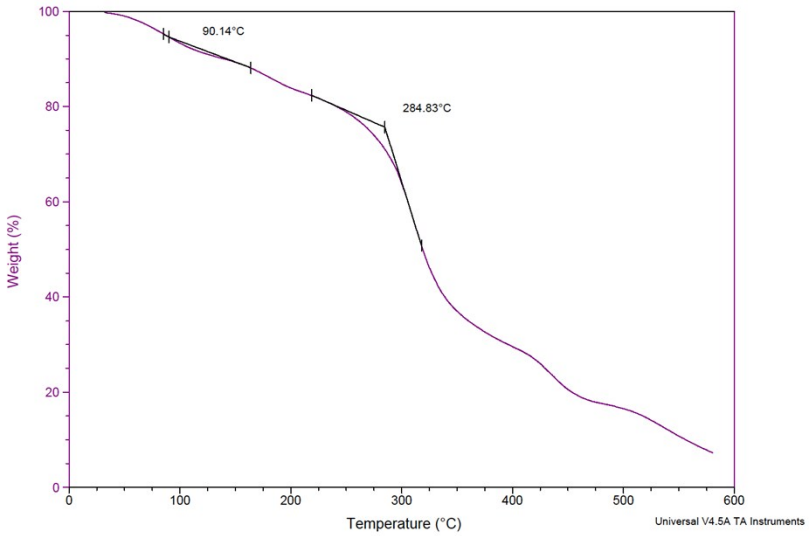


Figure S10. TGA trace of **6** homopolymerization catalyzed by **1-ox**.

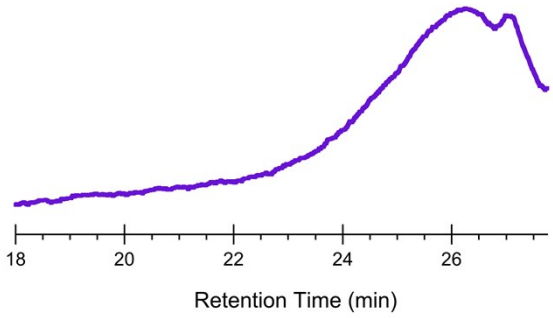


Figure 11. GPC trace of a **6**:lactide (9:1) copolymerization before oxidation.

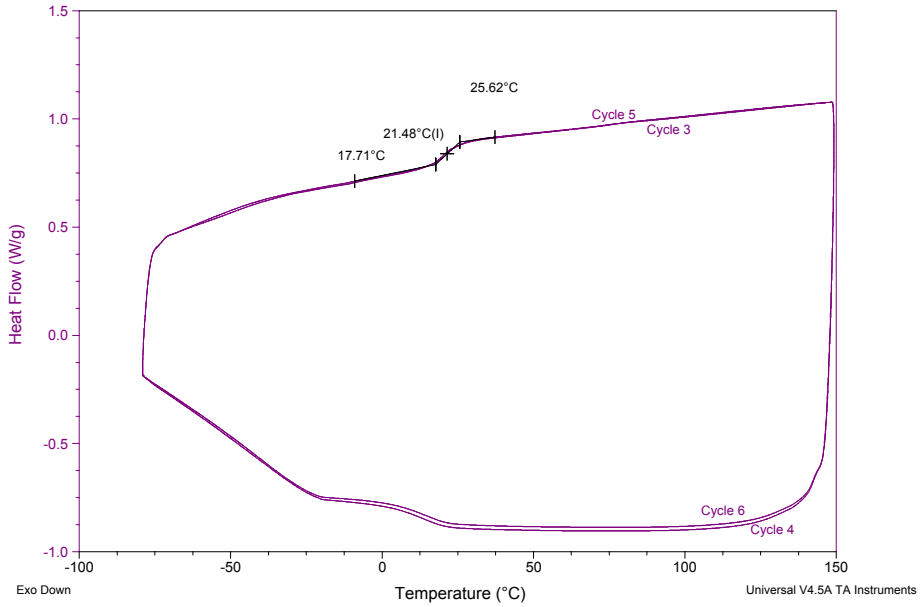


Figure S12. DSC trace of a **6**:lactide (9:1) copolymerization before oxidation.

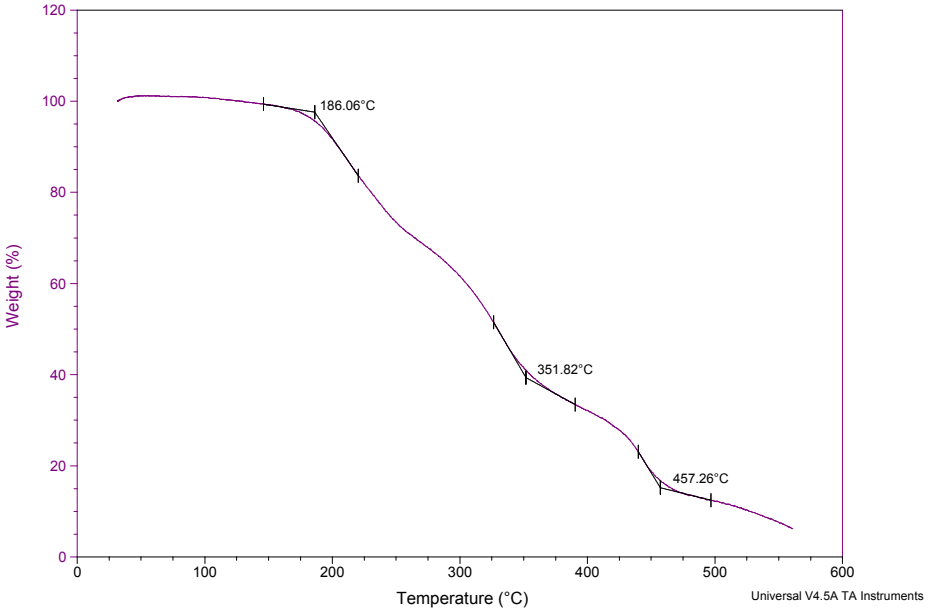


Figure S13. TGA trace of a **6**:lactide (9:1) copolymerization before oxidation.

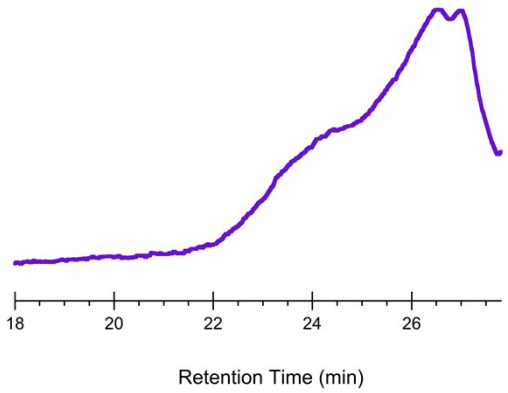


Figure S14. GPC trace of a **6**:lactide (3:1) copolymerization before oxidation.

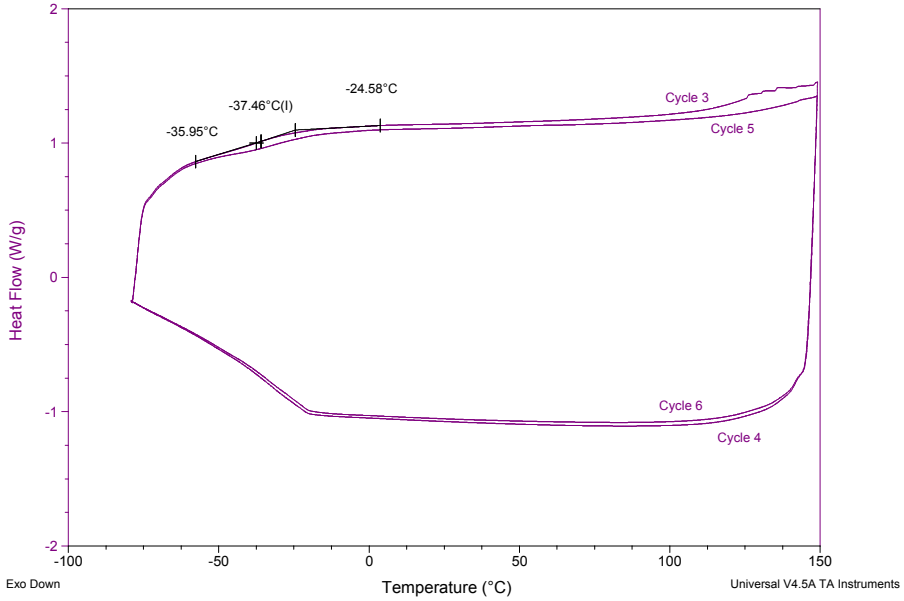


Figure S15. DSC trace of a **6**:lactide (3:1) copolymerization before oxidation.

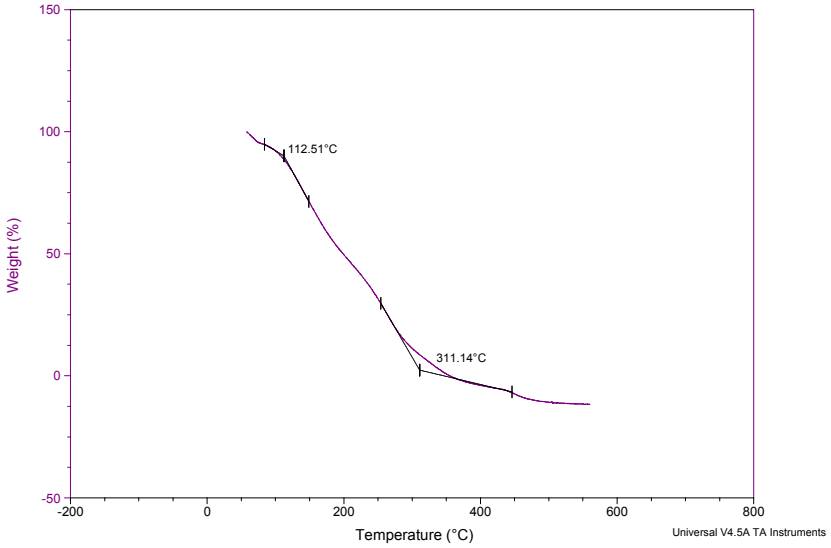


Figure S16. TGA trace of a **6**:lactide (3:1) copolymerization before oxidation.

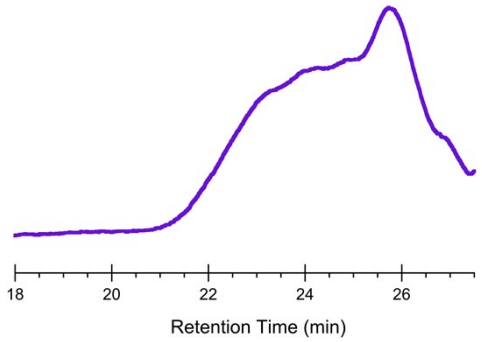


Figure S17. GPC trace of a **6**:lactide (1:1) copolymerization before oxidation.

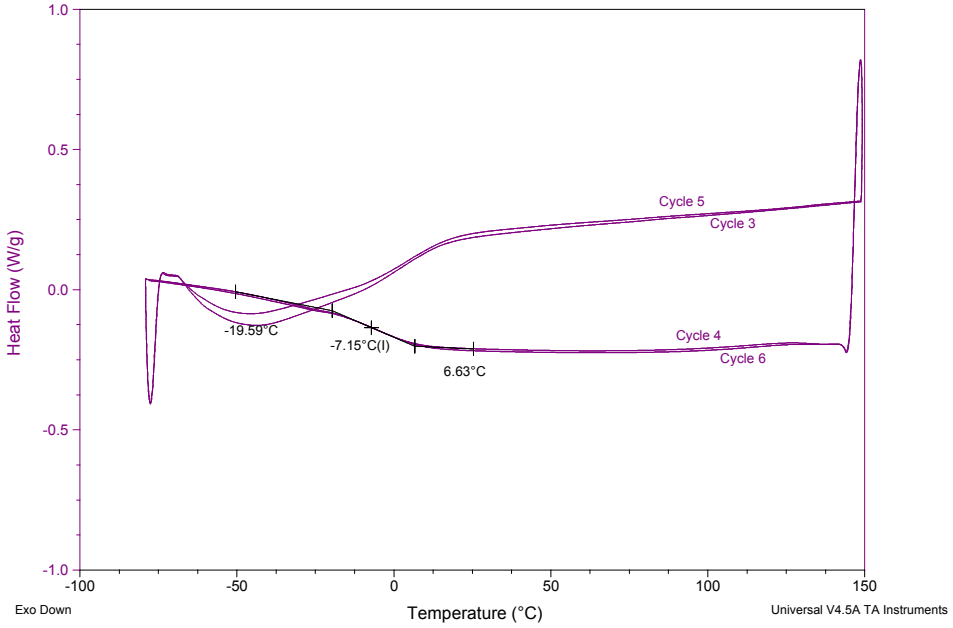


Figure S18. DSC trace of a **6**:lactide (1:1) copolymerization before oxidation.

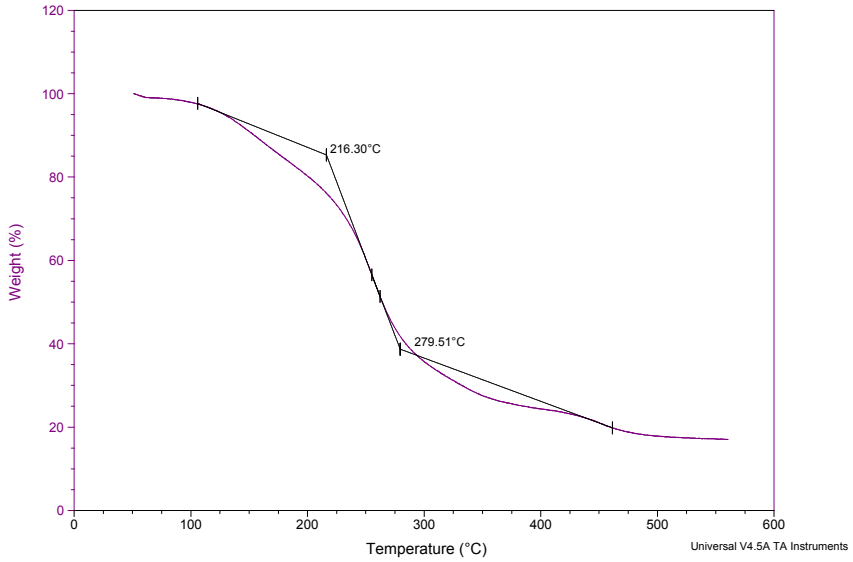


Figure S19. TGA trace of a **6**:lactide (1:1) copolymerization before oxidation.

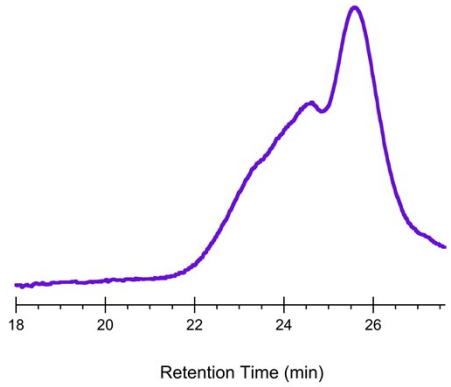


Figure S20. GPC trace of a **6**:lactide (1:3) copolymerization before oxidation.

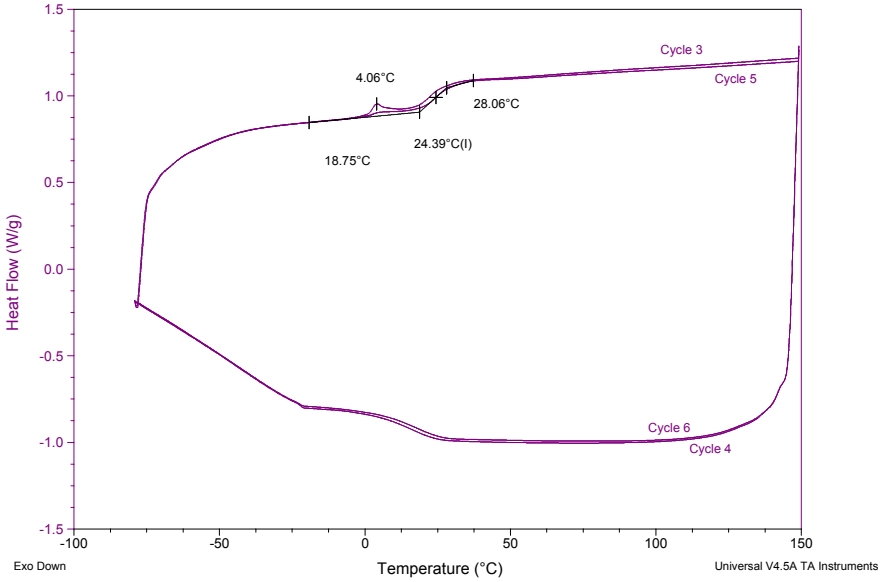


Figure S21. DSC trace of a **6**:lactide (1:3) copolymerization before oxidation.

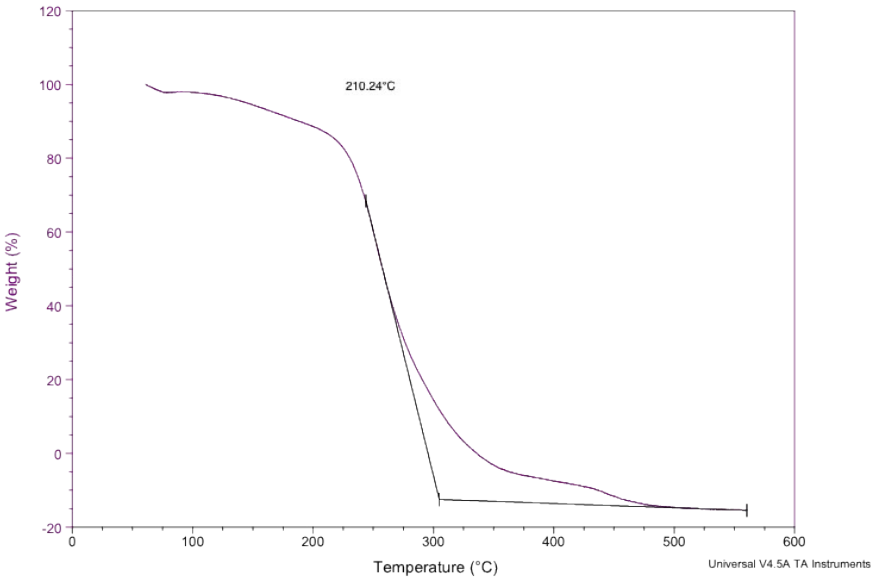


Figure S22. TGA trace of a **6**:lactide (1:3) copolymerization before oxidation.

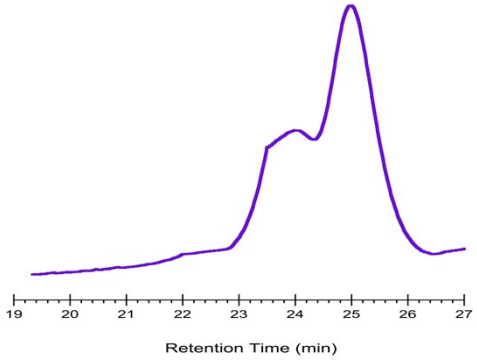


Figure S23. GPC trace of a **6**:lactide (1:9) copolymerization before oxidation.

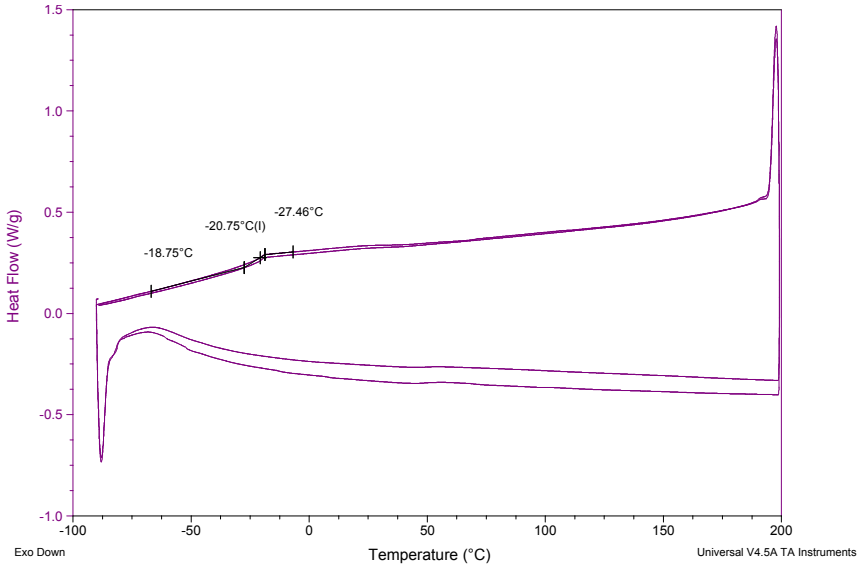


Figure S24. DSC trace of a **6**:lactide (1:9) copolymerization before oxidation.

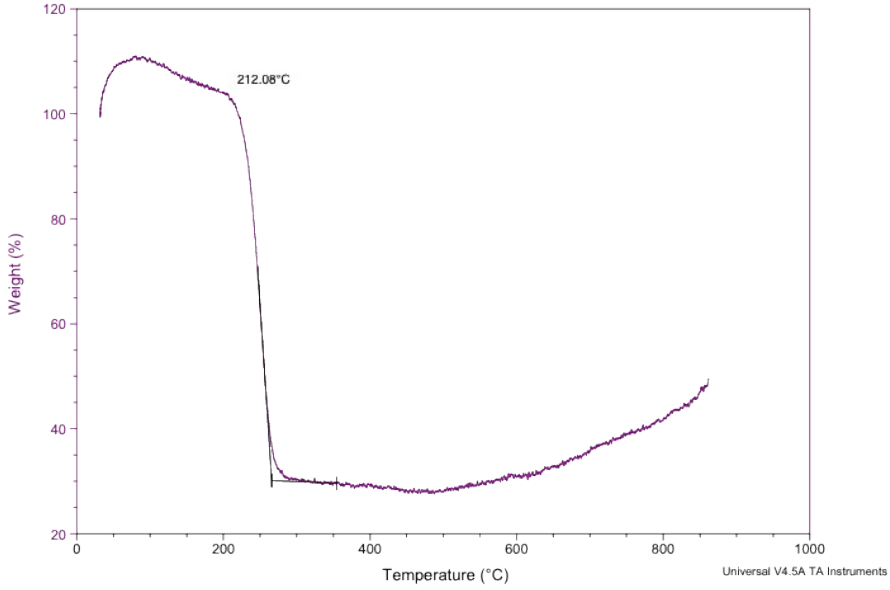


Figure S25. TGA trace of a **6**:lactide (1:9) copolymerization before oxidation.

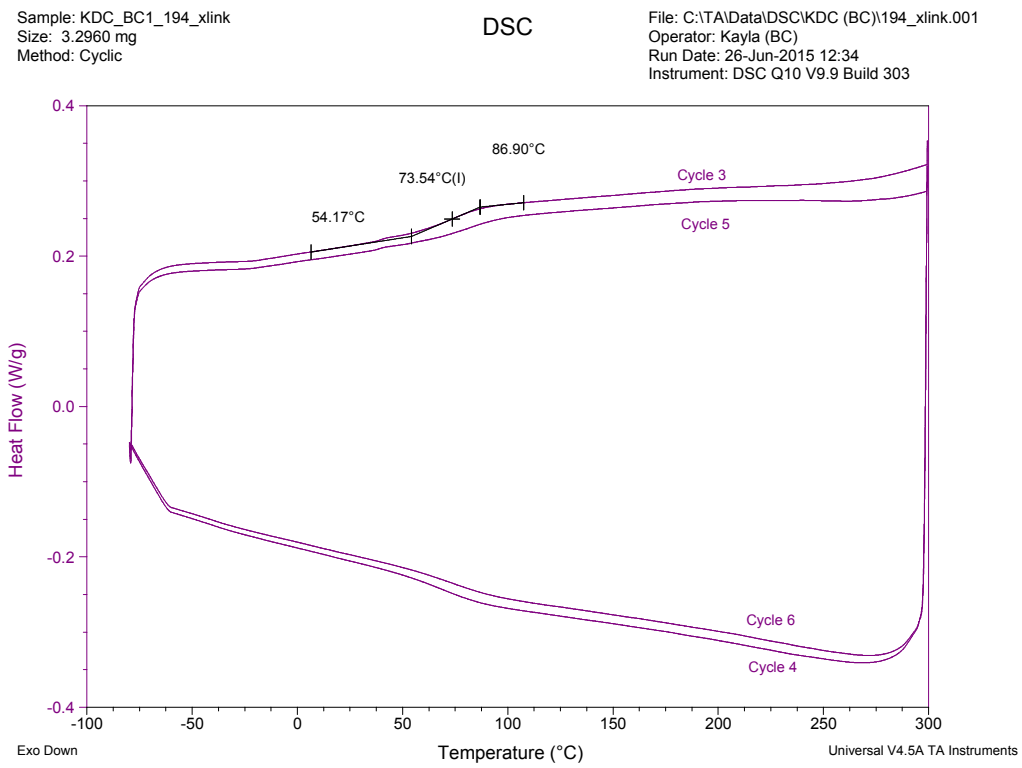


Figure S26. DSC trace of a **6** homopolymerization after the iron(II) to iron(III) switch.

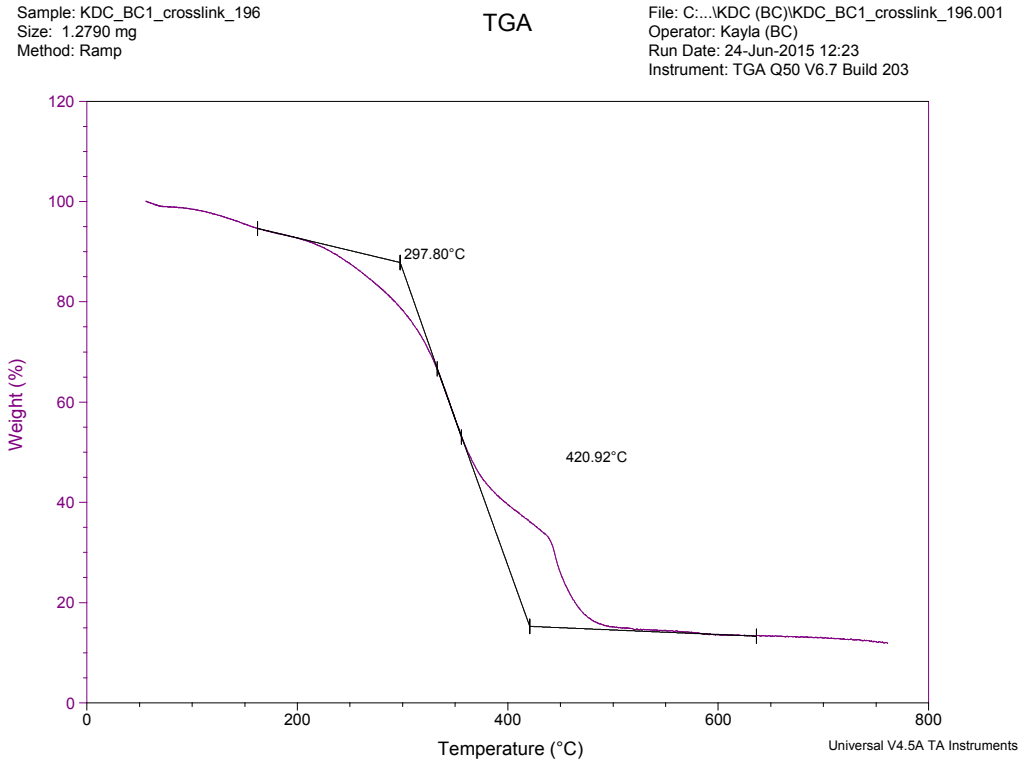


Figure S27. TGA trace of a **6** homopolymerization after the iron(II) to iron(III) switch.

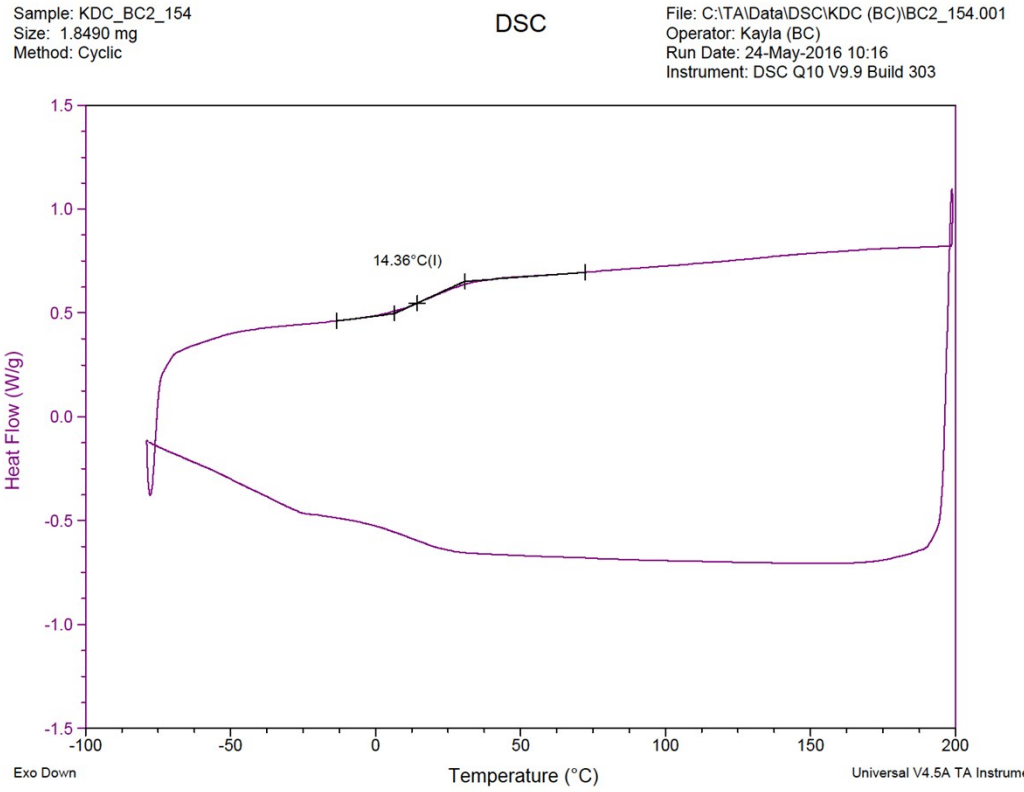


Figure S28. DSC trace of a **6** homopolymerization obtained after the iron(III) to iron(II) switch.

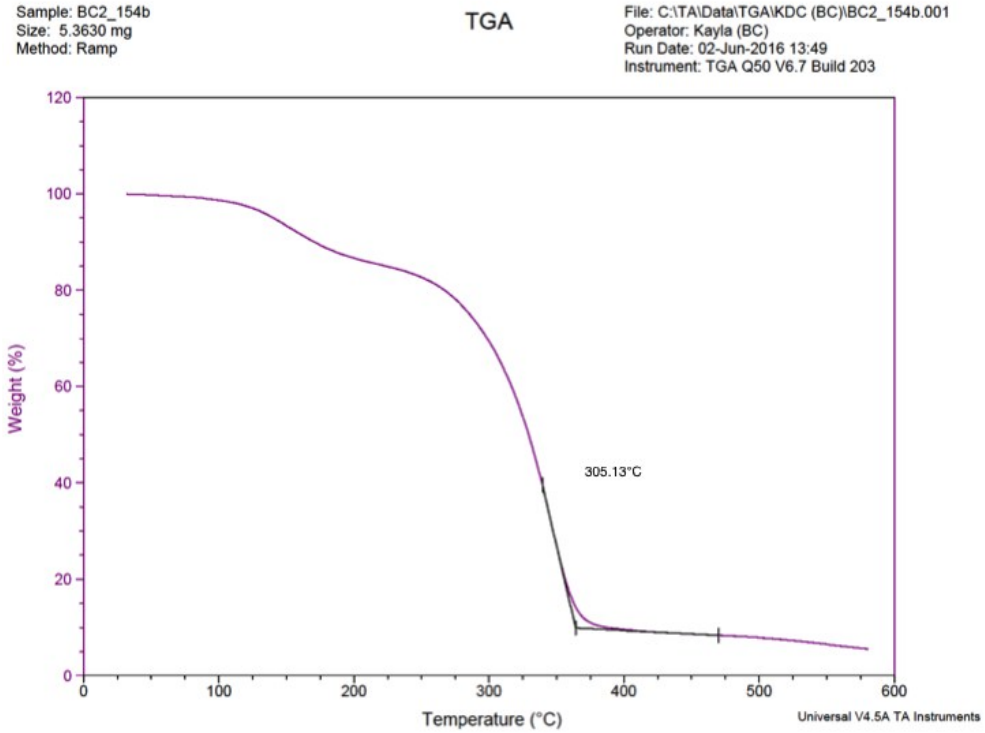


Figure S29. TGA trace of a **6** homopolymerization obtained after the iron(III) to iron(II) switch.

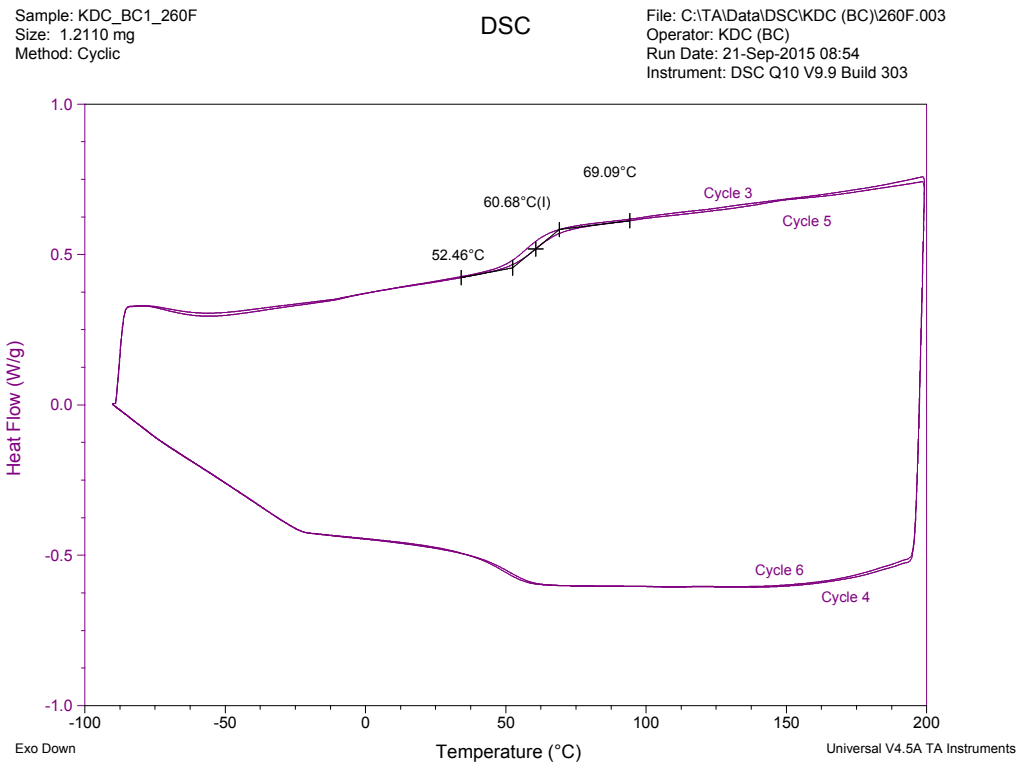


Figure S30. DSC trace of a **6**:lactide (9:1) copolymerization after oxidation.

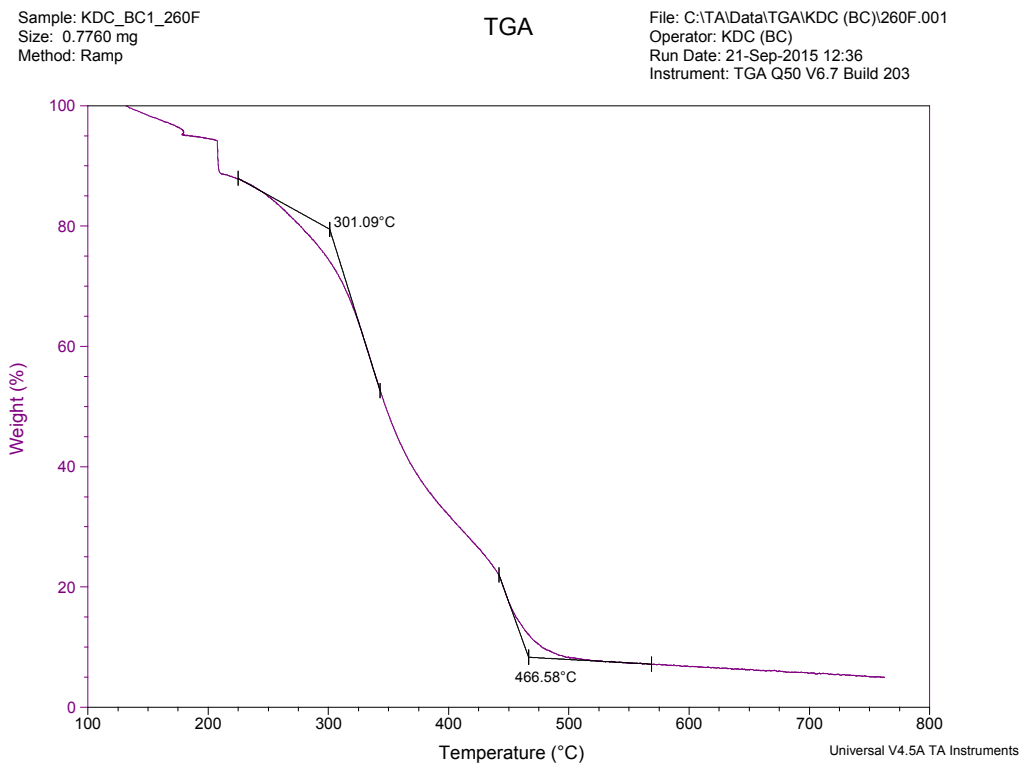


Figure S31. TGA trace of a **6**:lactide (9:1) copolymerization after oxidation.

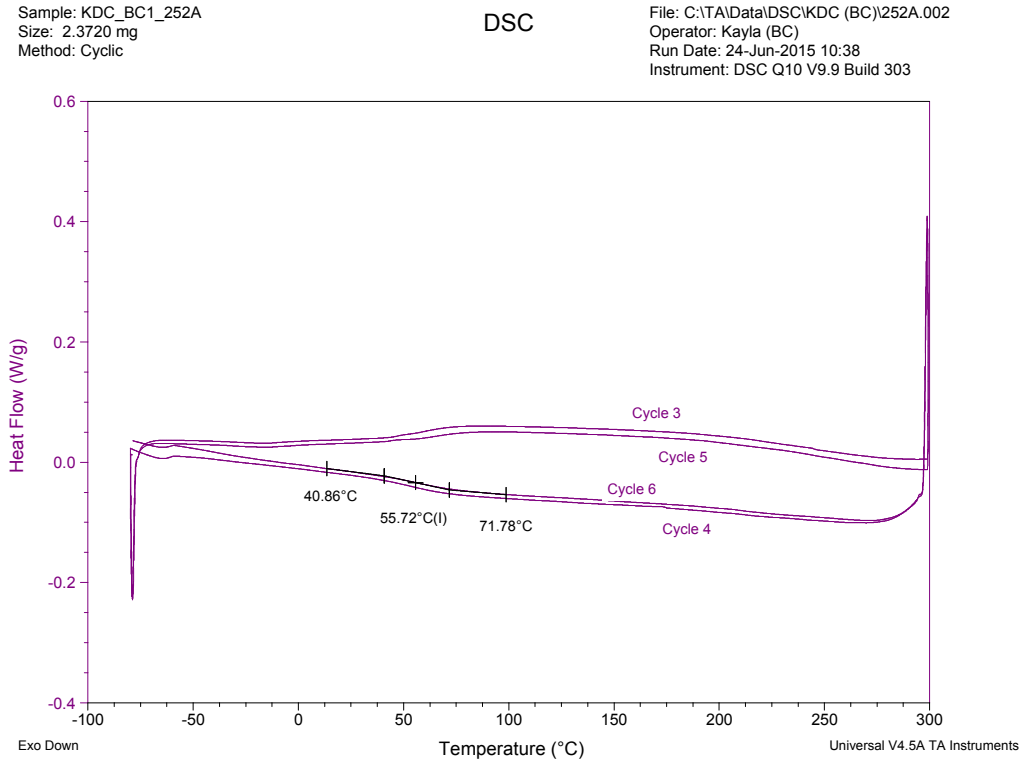


Figure S32. DSC trace of a **6**:lactide (3:1) copolymerization after oxidation.

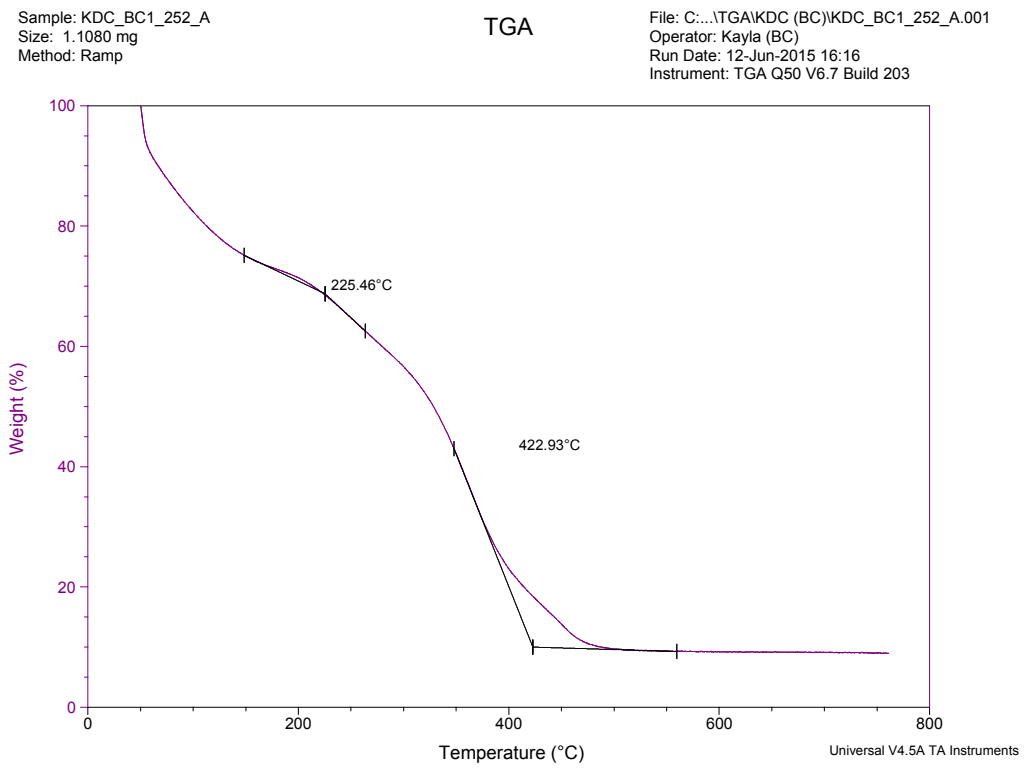


Figure S33. TGA trace of a **6**:lactide (3:1) copolymerization after oxidation.

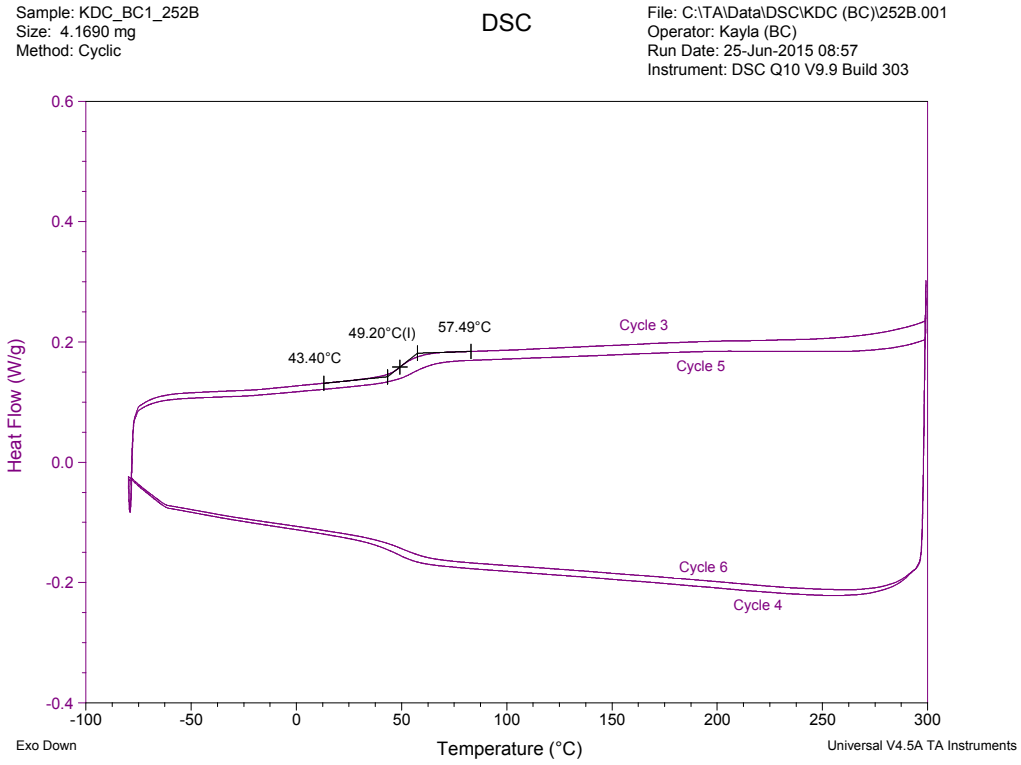


Figure S34. DSC trace of a **6**:lactide (1:1) copolymerization after oxidation.

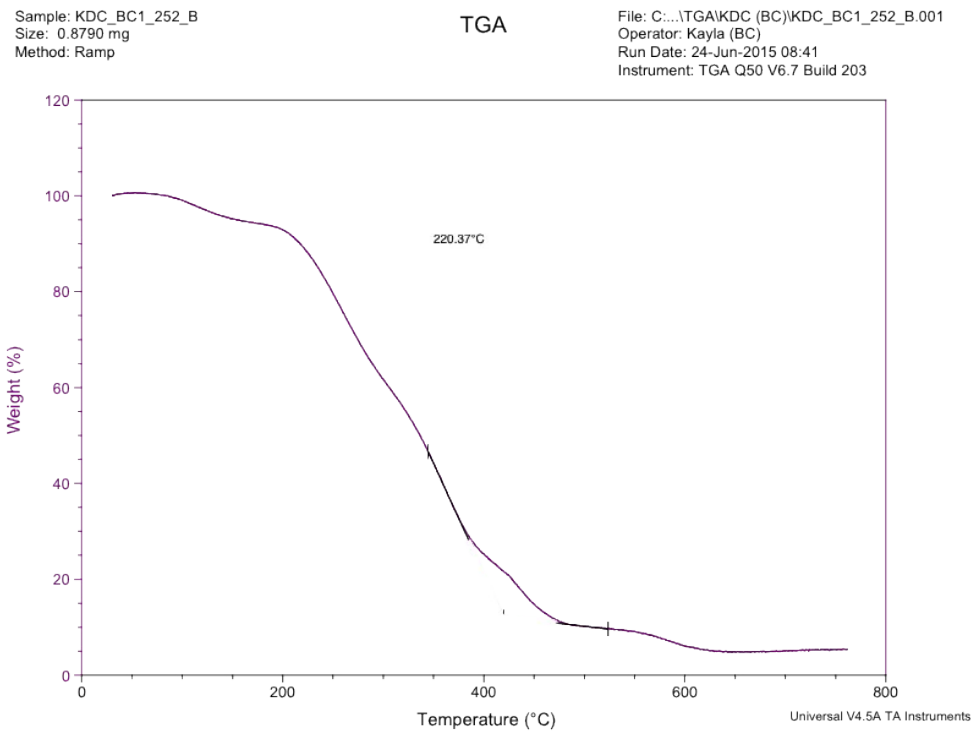


Figure S35. TGA trace of a **6**:lactide (1:1) copolymerization after oxidation.

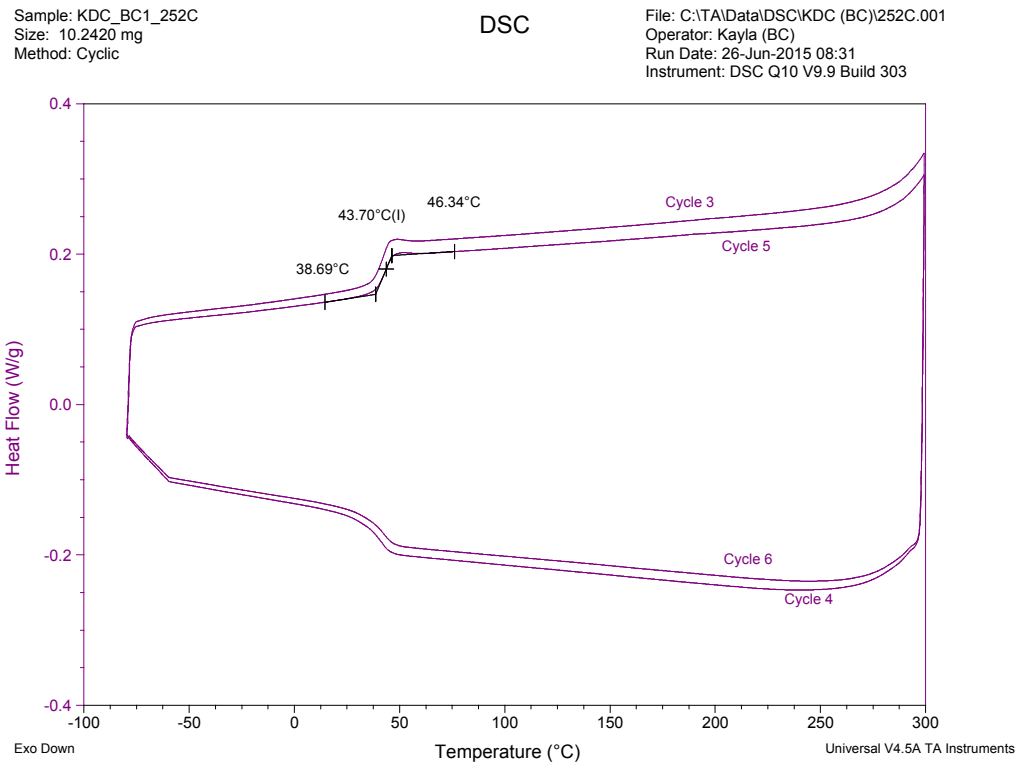


Figure S36. DSC trace of a **6**:lactide (1:3) copolymerization after oxidation.

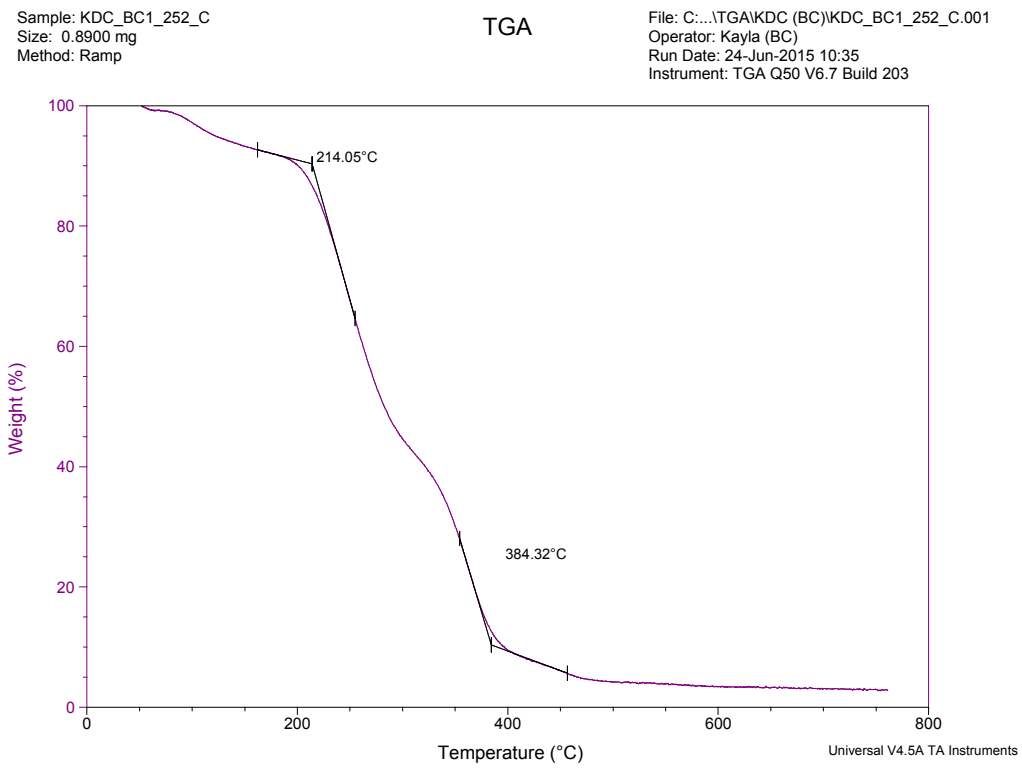


Figure S37. TGA trace of a **6**:lactide (1:3) copolymerization after oxidation.

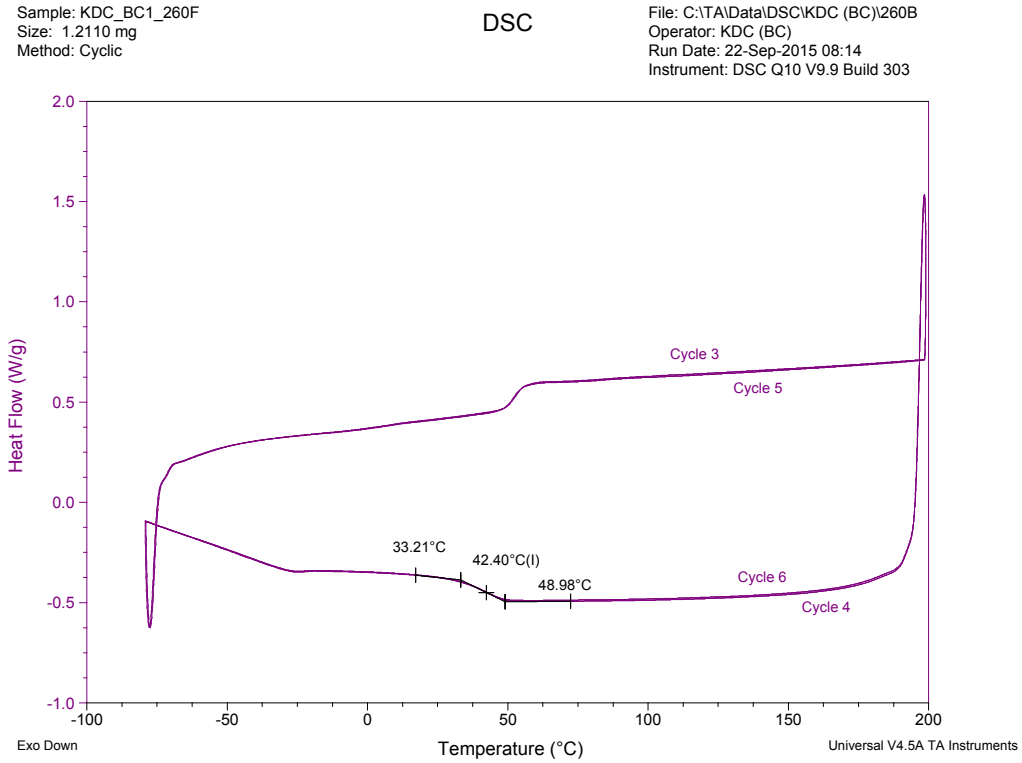


Figure S38. DSC trace of a **6**:lactide (1:9) copolymerization after oxidation.

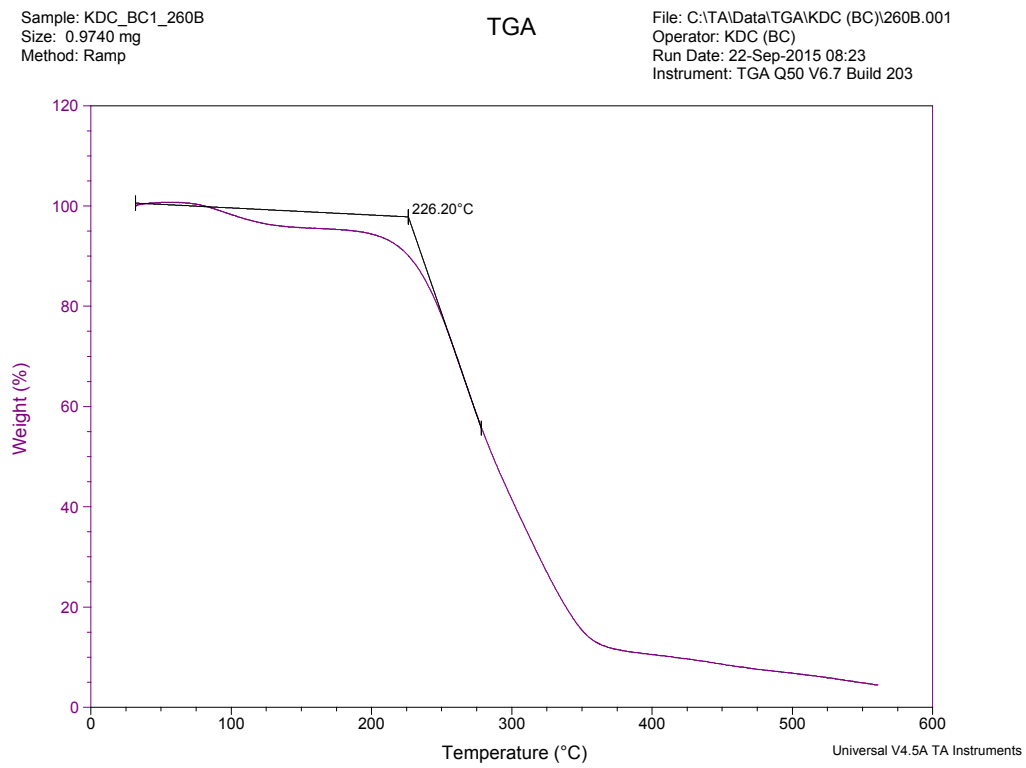
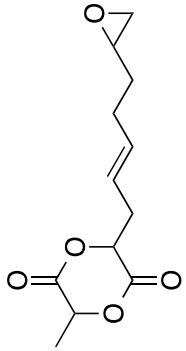
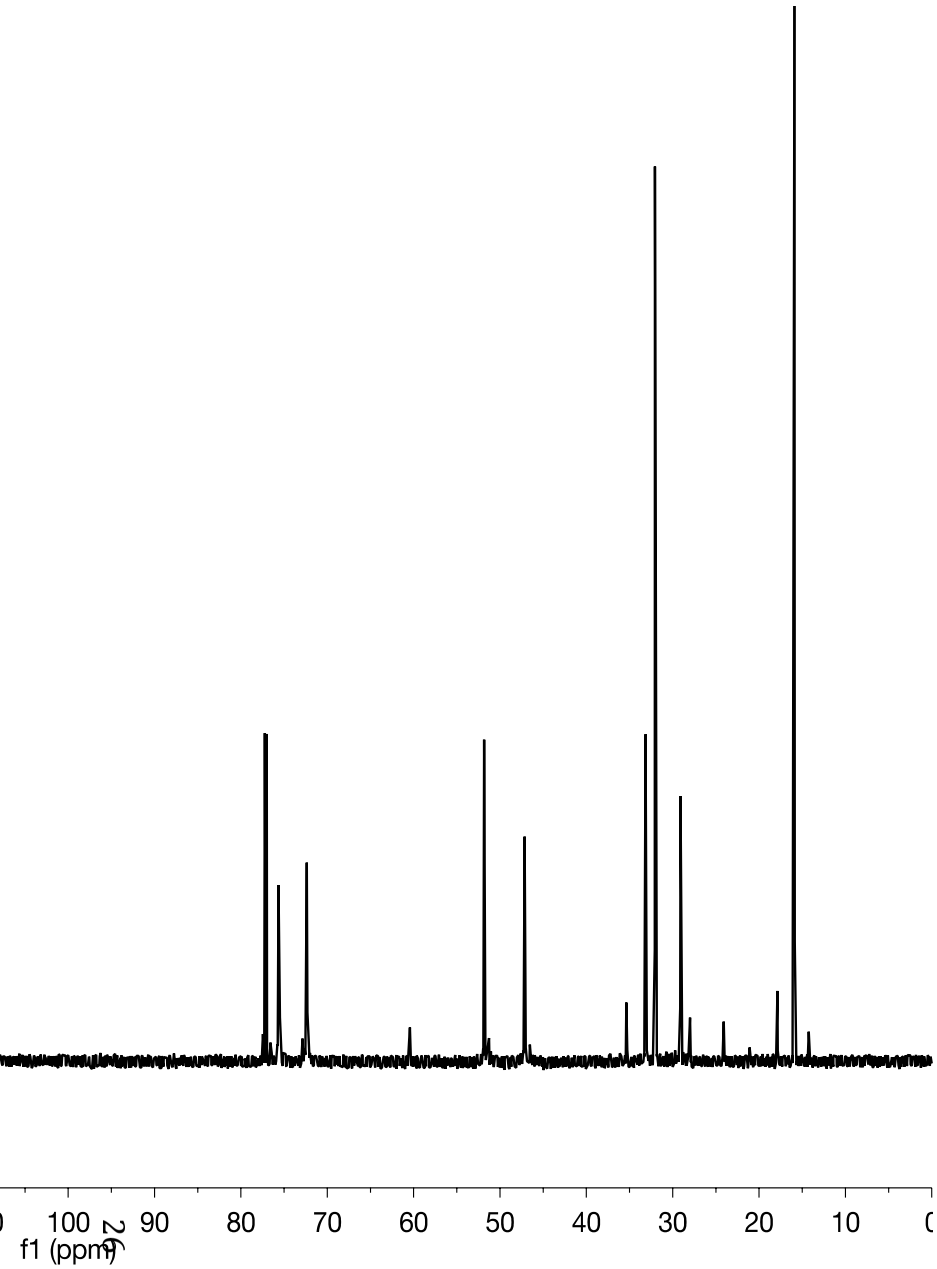


Figure S39. TGA trace of a **6**:lactide (1:9) copolymerization after oxidation.

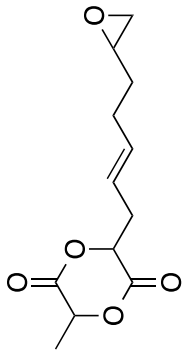
VI. ^{1}H NMR and ^{13}C NMR of 5 and 6.

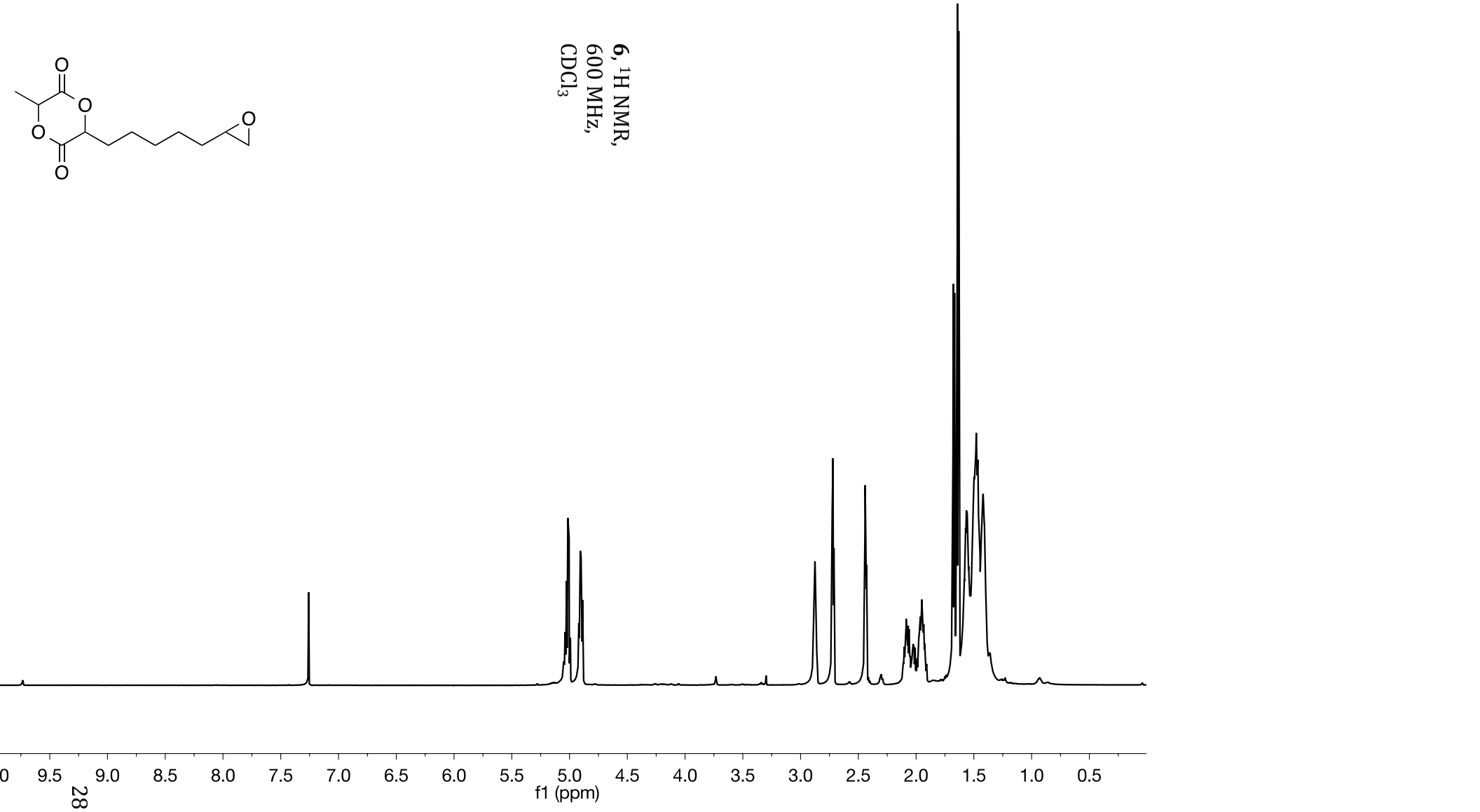
5, ^{1}H NMR,
600 MHz,
$CDCl_3$

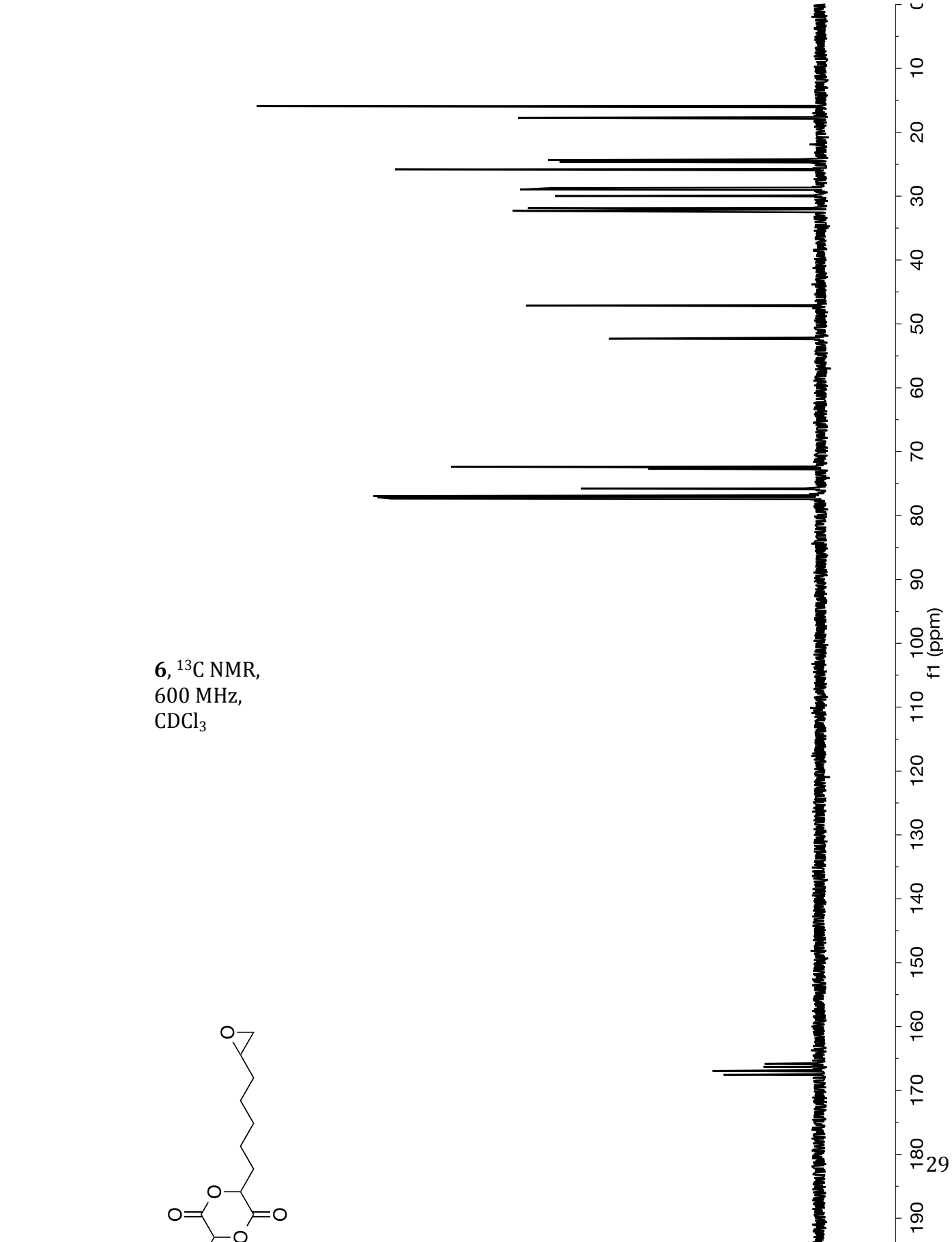



100
90
80
70
60
50
40
30
20
10
f1 (ppm)

5, ^{13}C NMR,
600 MHz,
$CDCl_3$




O
O
O
O
O
6, 1H NMR,
600 MHz,
CDCl3
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



6, ^{13}C NMR,
600 MHz,
$CDCl_3$

VII. References

[1]Burger, B. J. & Bercaw, J. E. *Vacuum Line Techniques for Handling Air-Sensitive Organometallic Compounds*; American Chemical Sociey, **1987**.

[2] Zou, J.; Hew, C. C.; Themistou, E.; Li, Y.; Chen, C.; Alexandridis, P.; Cheng, C. *Adv. Mater.* **2011**, *23*, 4274-4277

[3] Odian, G. Principles of Polymerization, 4th ed.; John Wiley & Sons: Hoboken, 2004