Electronic Supplementary Material (ESI) for Polymer Chemistry.

Ring Opening Polymerization of β-acetoxy-δ-methylvalerolactone, a Triacetic Acid Lactone Derivative

Hussnain Sajjad,[a] *Emily A. Prebihalo,*[a] *William B. Tolman,**[b] *and Theresa M. Reineke**[a]

[a]Department of Chemistry and Center for Sustainable Polymers, University of Minnesota, 207 Pleasant St. SE, Minneapolis, Minnesota 55455-0431. Email: treineke@umn.edu

[b]Department of Chemistry, Washington University in St. Louis, One Brookings Drive, Campus Box 1134, St. Louis, MO 63130-4899. Email: wbtolman@wustl.edu

Supporting Information

Experimental

Materials. 4-Hydroxy-6-methyl-2-pyrone ("Triacetic Acid Lactone" (TAL)) was purchased from Oakwood Chemical and used without further purification. Pd/C (10 wt% loading) was purchased from Sigma-Aldrich and dried under vacuum prior to use. 4-(dimethylamino)pyridine (DMAP), acetic anhydride, and vinylmagnesium bromide (1M, THF solution) were obtained from Millipore-Sigma and used without further purification.

Characterization. All reported ^{1}H NMR and ^{13}C NMR spectra were collected on Bruker Avance III HD 500 MHz and Bruker Avance III HD 400 MHz spectrometers in deuterated chloroform ($CDCl_3$). ^{1}H NMR chemical shifts are referenced to tetramethylsilane (TMS) at 0.00 ppm and ^{13}C NMR spectra are referenced to the $CDCl_3$ carbon resonance at 77.16 ppm Spectra of small molecules were collected at 22 °C with a D1 = 1s (16 scans) and spectra of polymers were collected at 22 °C with a D1= 10s (64 scans).

THF size-exclusion chromatography (SEC) was performed in uninhibited THF utilizing a Waters Styragel guard column and three consecutive Waters Styragel columns at a flow rate of 1 mL min^{-1} at 22 °C. The instrument was equipped with an Agilent 1260 Infinity liquid chromatography coupled with a Wyatt Dawn Heleos II multiangle light scattering detector (18 angles from 10° to 160° and a 662.6 nm laser) and a Wyatt Optilab T-rEX refractive index detector. Reported dn/dc values were calculated from the RI signal using a known sample concentration and assuming 100% mass recovery from the column and used for molar mass determination.

Thermal gravimetric analysis (TGA) was performed on a TA Instruments Q500 series at a heating rate of 10 °C min^{-1} under 60/40 nitrogen/oxygen flow.

Differential scanning calorimetry (DSC) experiments were conducted with a TA Instruments Discovery DSC, using samples hermetically sealed in aluminum pans, at a heating/cooling rate of 10 °C min^{-1}. Reported T_g values are from the second heating/cooling ramps.

Hydrogenation of 4-hydroxy-6-methyl-2-pyrone (Triacetic Acid Lactone (TAL, 1)). Uninhibited THF was stirred over activated 3Å molecular sieves for 24 hours and filtered through a bed of Celite prior to use. A 300 mL high-pressure reactor vessel was charged with TAL (**1**) (20.0 g, 159 mmol), Pd/C (2.0 g, 10% by mass), and 200 mL of THF. The reactor was sealed, and first pressurized and de-pressurized with Argon (3X) to remove O_2, then pressurized with gaseous H_2 to 100 PSI, heated to 50 °C, then pressurized to 500 PSI. Over the next 48 h, the reactor vessel was periodically re-pressurized to 500 PSI, after which time the vessel was cooled to room temperature and purged with Argon to remove H_2. The reaction mixture was then filtered through a bed of Celite to remove the Pd/C. The THF was removed under vacuum and the resultant liquid was crystallized using ethyl acetate and hexanes to afford 4-hydroxy-6-methyl-2-lactone (**2**) (14 g, 68% isolated yield). ^{1}H NMR (500 MHz, Chloroform-d) δ 4.44 – 4.29 (m, 1H), 4.25 (ddt, J = 9.3, 7.8, 5.7 Hz, 1H), 2.97 (s, 1H), 2.91 – 2.83 (m, 1H), 2.45 (ddd, J = 17.1, 5.9, 1.3 Hz, 1H), 2.28 (dddd, J = 13.8, 5.6, 3.0, 1.3 Hz, 1H), 1.63 – 1.52 (m, 1H), 1.41 (d, J = 6.3, 1.8 Hz, 3H).

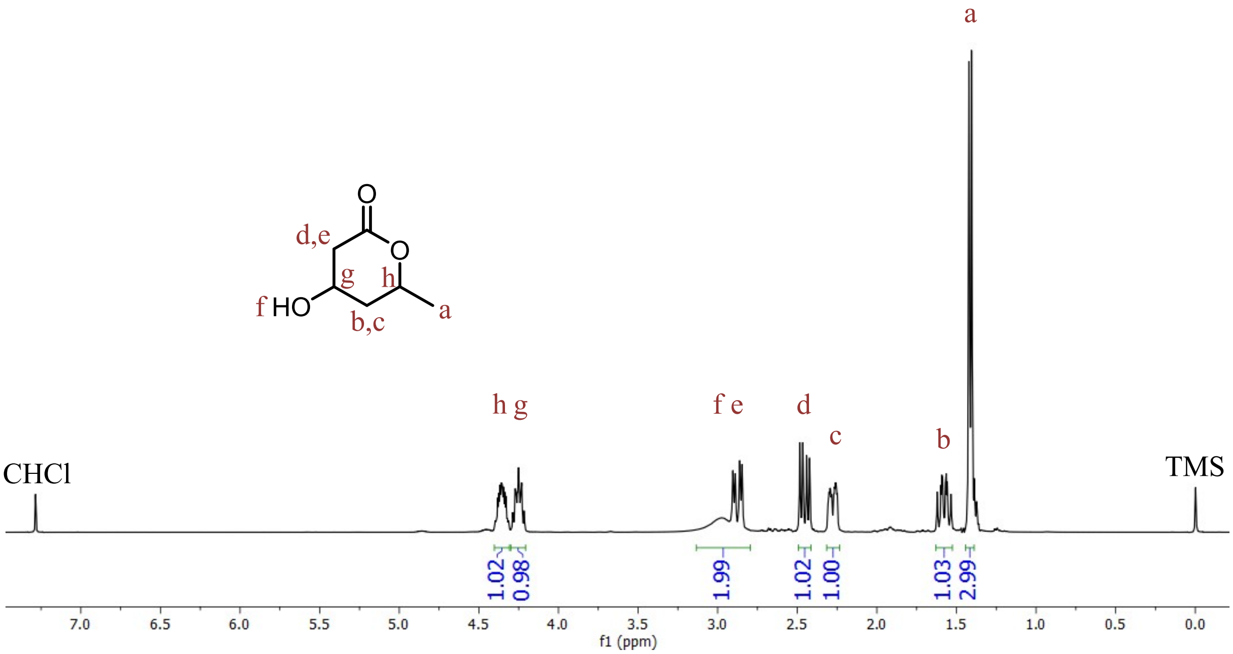


Figure S1. ^{1}H NMR spectrum of the **2** ($CDCl_3$, 500 MHz).

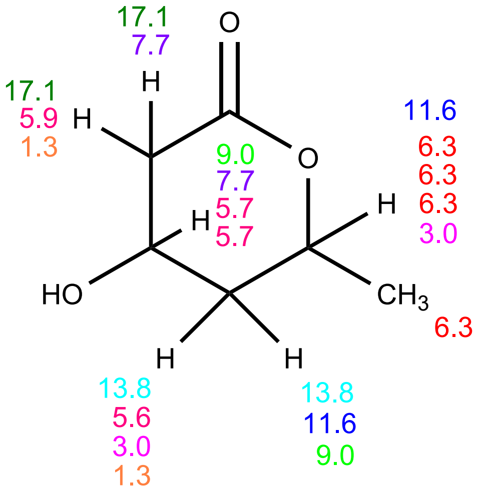


Figure S2. J-coupling constants for each proton pair (color-coded) as determined from the ^{1}H NMR spectrum of (3).

Synthesis of β-acetoxy-δ-methylvalerolactone (4). (**3**) (10.0 g, 76.8 mmol) and 4-(dimethylamino)pyridine (DMAP) (0.94 g, 7.7 mmol) were dissolved in 40 mL of anhydrous ethyl acetate in an oven-dried 100 mL round bottom flask. The flask was sealed with a rubber septum and submerged in an ice-bath, then acetic anhydride (11.0 mL, 11.9 g, 116.4 mmol) was added drop-wise via needle/syringe to the stirring solution over a period of 10 minutes. After 12 h, the reaction mixture was concentrated under vacuum to yield a yellow liquid. The yellow liquid was loaded on to a column of basic alumina (2” diameter x 10” length) and a mixture of ethyl acetate/hexanes (3:1) was used as the eluent. The desired compound eluted from the column first and DMAP, the acetic acid byproduct, and excess acetic anhydride were left behind on the column. The solvents were then removed under vacuum to afford (**4**) and a small impurity of parasorbic acid (ca. 5% by ^{1}H NMR analysis). The parasorbic acid impurity was removed from the sample by applying high vacuum for 2 – 3 days, or until it was undetectable by ^{1}H NMR analysis, to yield (**4**) (6.5 g, 49% isolated yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.22 (dq, *J* = 8.6, 6.4 Hz, 1H), 4.40 (dqd, *J* = 11.6, 6.3, 2.9 Hz, 1H), 2.93 (ddd, *J* = 17.3, 6.4, 0.9 Hz, 1H), 2.59 (dd, *J* = 17.3, 6.7 Hz, 1H), 2.40 (dddd, *J* = 14.0, 6.2, 2.9, 0.9 Hz, 1H), 2.08 (s, 3H), 1.64 (dddd, *J* = 14.0, 6.2, 2.9, 0.9 Hz, 1H), 1.44 (d, *J* = 6.3 Hz, 3H).

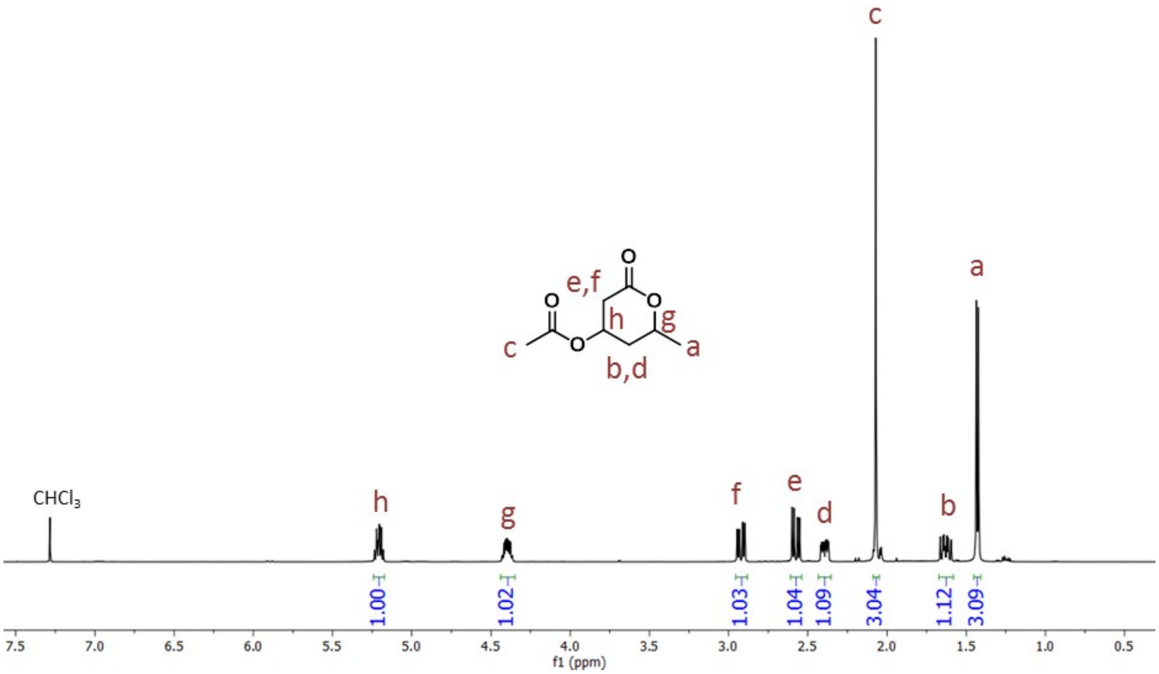


Figure S3. ^{1}H NMR spectrum of β-acetoxy-δ-methylvalerolactone (**4**) (CDCl$_3$, 500 MHz).

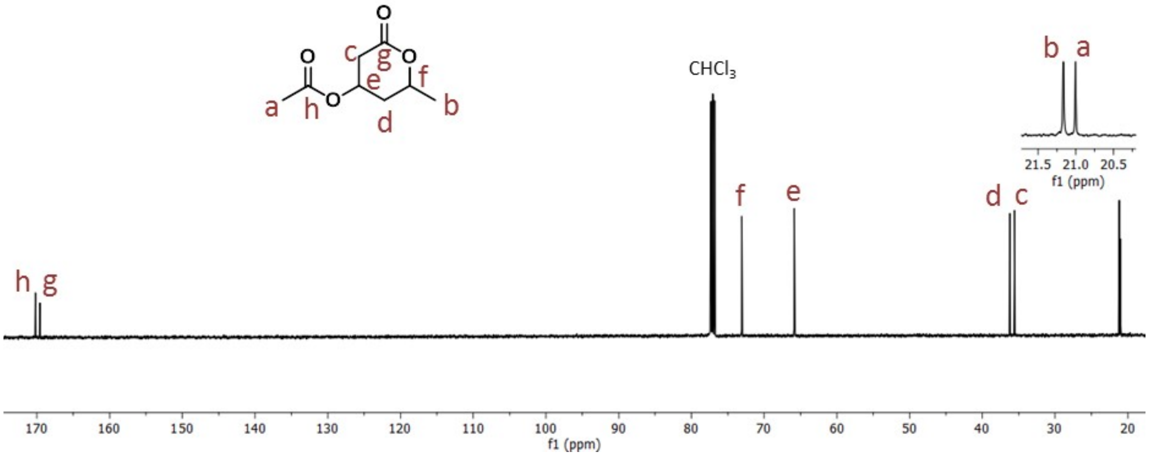


Figure S4. ^{13}C{^{1}H} NMR spectrum of β-acetoxy-δ-methylvalerolactone (**4**) (CDCl$_3$, 126 MHz).

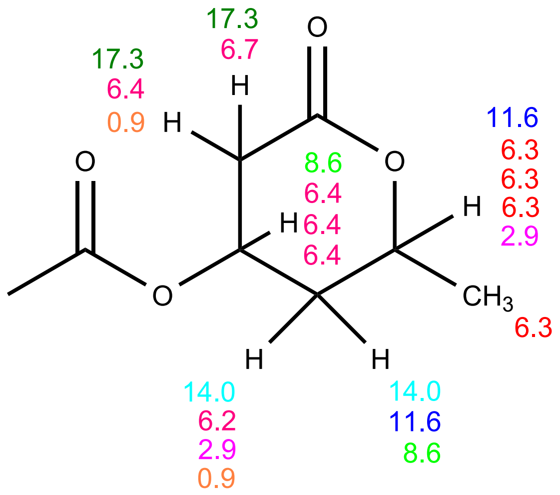


Figure S5. J-coupling constants for each proton pair (color-coded) as determined from the ^{1}H NMR spectrum of β-acetoxy-δ-methylvalerolactone (**4**).

General procedure for the synthesis of Poly(4). The following is a representative example: β-acetoxy-δ-methylvalerolactone (**4**) (200 mg, 1.16 mmol, 200 equiv), benzyl alcohol (0.63 mg, 5.82 μmol, 1 equiv), and diphenyl phosphate (DPP) (14.5 mg, 0.058 mmol, 5 equiv) were combined together in a 5 mL vial and the contents were thoroughly mixed using a vortex mixer until the DPP was fully dissolved. The solution was stirred for 14 days (during which time the conversion was periodically monitored via ^{1}H NMR spectroscopy) and then quenched by the addition of a solution of NEt_3 in THF (ca. 2 μL/mL). The polymer was precipitated from the THF solution into a 50/50 mixture of H_2O/methanol. The majority of the supernatant liquid was decanted from the suspension and the remaining solvents were removed on a rotary evaporator. The polymer was re-dissolved in THF and the precipitation procedure was repeated twice more (i.e. precipitated a total of 3 times). Drying in a vacuum oven at 40 °C for 12 h yielded **poly(4)** as a slightly tacky solid.

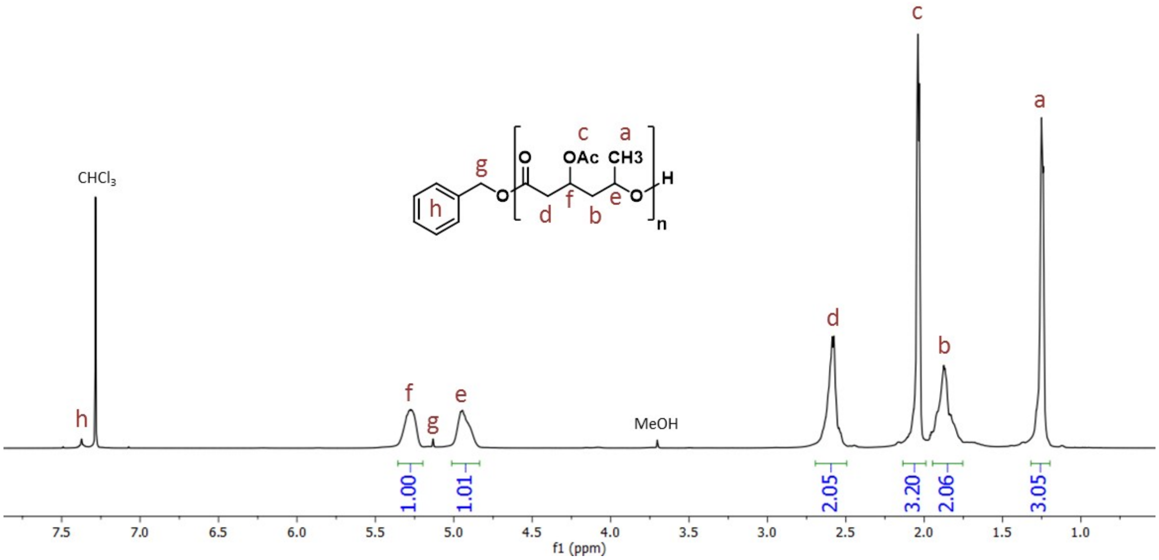


Figure S6. ^{1}H NMR spectrum of poly(4) ($CDCl_3$, 500 MHz).

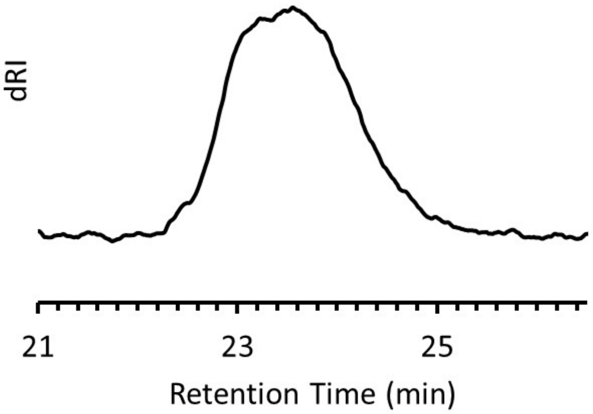


Figure S7. THF SEC trace of **poly(4)** with differential refractive index (M_n = 10 kDa, (Đ) = 1.2).

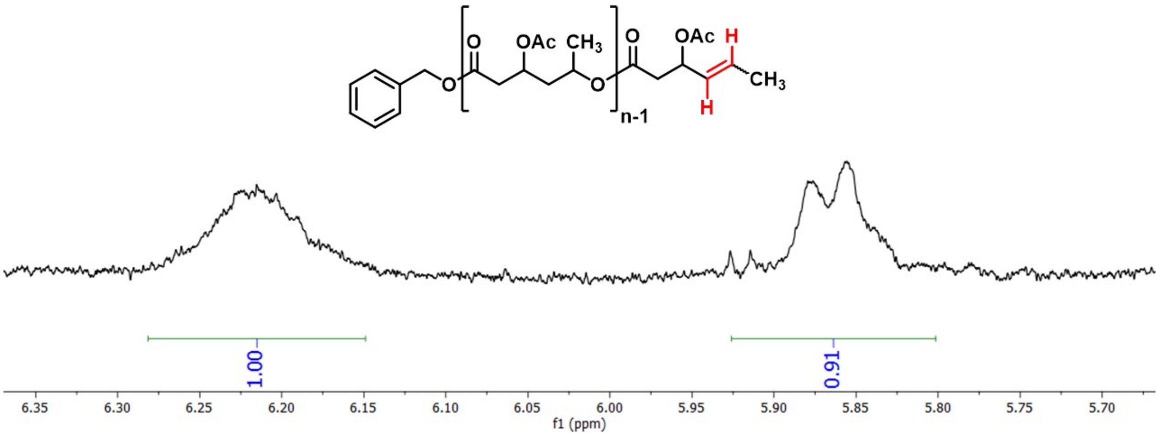
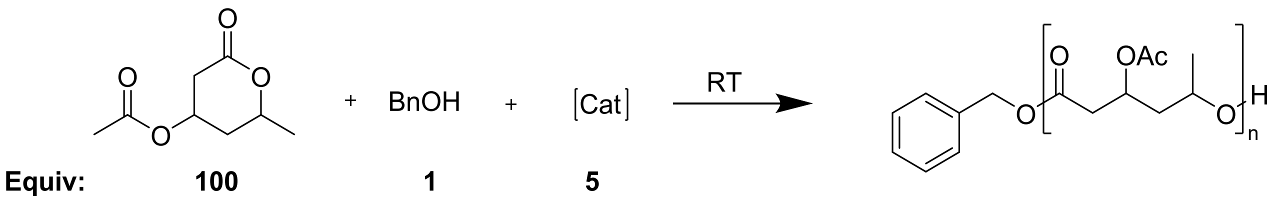
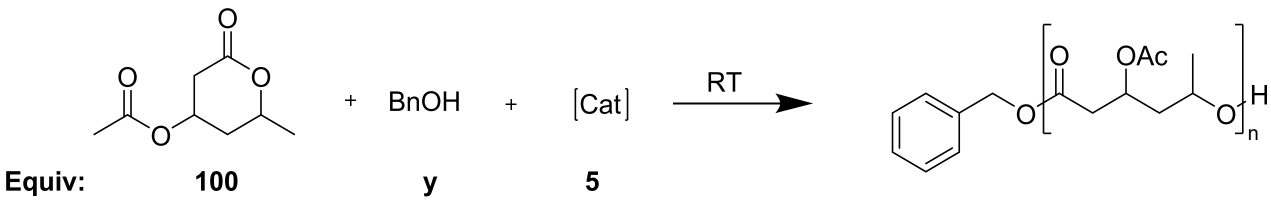


Figure S8. ^{1}H NMR spectrum of **poly(4)**, expanding the baseline in the alkene region, indicating the presence of terminal olefins formed through an elimination reaction of the secondary propagating alcohol during polymerization.



Catalyst	**Time** (Days)	**Conversion** (%)
DPP	3	38
TBD	X	X
Ti(OiPr)$_4$	3	25
Sn(Oct)$_2$	X	X
Al(OiPr)$_3$	X	X
Sc(OTf)$_3$	4	7
BF3·OEt$_2$	3	39
BBr$_3$	X	X
Bi subsalicylate	X	X
NNO-Zn-Et	X	X
Nomura's catalyst	X	X
C3 Ad- iOPr	X	X
C3 Ind-BnOH	X	X

Table S1: Catalysts tested for polymerization, with monomer conversions listed for successful polymerizations. Catalyst loading was kept consistent at a 100:1:5 ratio of monomer:initiator:catalyst.



Monomer : Initiator	Monomer consumption (%)	Yield (%)	$M_{n(theo)}$ (kDa)	$M_{n(NMR)}$ (kDa)
50	47	43	4.0	4.6
100	45	40	7.7	7.5
200	46	42	15.8	15.8
500	44	43	37.9	31.0
1000	46	40	79.2	65.4

Table S2: Monomer consumption, yield, and molecular weight data for various monomer:initator ratios tested. Catalyst loading was kept consistent at 100:y:5 ratio for monomer:initiator:catalyst.

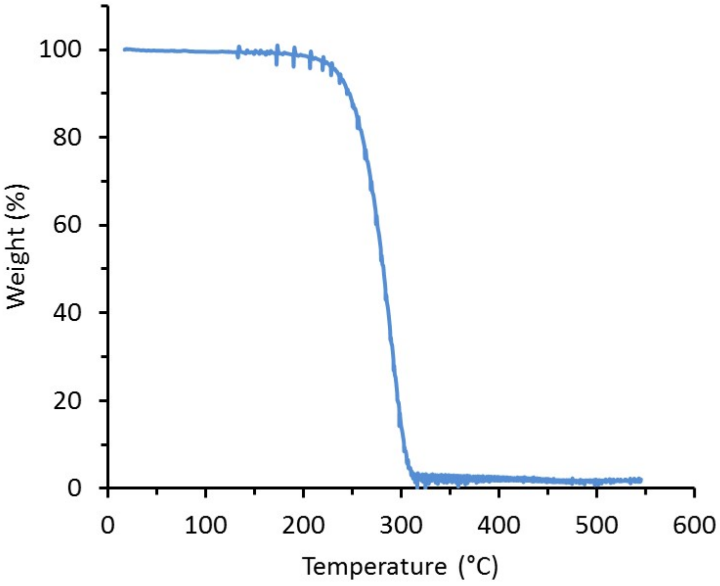


Figure S9. TGA thermogram of **poly(4)** at a heating rate of 10 °C min^{-1}.

Poly(4): Thermodynamics of Polymerization. β-acetoxy-δ-methylvalerolactone (**4**) (600 mg, 3.48 mmol, 50 equiv), benzyl alcohol (7.8 mg, 0.072 mmol, 1 equiv), and diphenyl phosphate (DPP, 44.6 mg, 0.167 mmol, 2.5 equiv) were combined together in a 5 mL vial. The contents were thoroughly mixed using a vortex mixer and then separated into 3, separate, 5 mL vials. After 10 days at 22 °C (RT), an aliquot was removed from one sample and immediately quenched by the addition of a solution of NEt_3 in $CDCl_3$ (ca. 2 μL/mL). The conversion was analyzed using ^1H NMR spectroscopy. Aliquots were periodically removed everyday over the next 7 days, and in each case, the conversion had not increased; therefore, the other two vials were quenched and analyzed by the same method. This entire process was repeated to measure the equilibrium conversion of polymerization of (**4**) at 10 °C in an oil bath which was chilled using a Thermo Neslab 100-C immersion cooler; aliquots were periodically analyzed over the course of 30 days using ^1H NMR until apparent equilibrium. The process was repeated again to measure the equilibrium conversion of polymerization at 0 °C; aliquots were periodically analyzed over the course of 60 days using ^1H NMR until apparent equilibrium. The data was plotted in Microsoft Excel and the LINEST function was used to calculate the uncertainty associated with the slope and Y-intercept of the best-fit line.

Poly(4): Kinetics of Polymerization. Benzyl alcohol (2.2 mg, 0.020 mmol) and β-acetoxy-δ-methylvalerolactone (**4**) (700 mg, 4.07 mmol) were mixed together in a 5 mL vial. Diphenyl phosphate (DPP, 1.5 mg, 6.0 μmol) was added to three separate 5 mL vials (i.e. each vial containing 1.5 mg DPP). 200 mg aliquot of the benzyl alcohol/(**4**) mixture was added to each vial and stirred until homogenous. Aliquots were removed from the stirred reaction mixture every 24 h and quenched by the addition of a solution of NEt_3 in $CDCl_3$ (ca. 2 μL/mL). Analysis by ^1H

NMR spectroscopy was used to determine monomer conversion at the given time point. K_{obs} was determined from the first 192 h of polymerization using the rate equation $[M] = [M]_0 - k_{obs}t$. β-acetoxy-δ-methylvalerolactone (**4**) has a ρ = 1.16 g/mL, MW = 172.18 g/mol; thus, a neat $[M]_0$ = 6.75 M.