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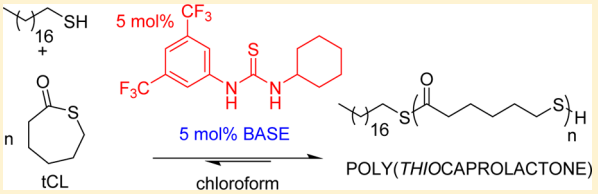
Poly(thioester) by Organocatalytic Ring-Opening Polymerization

Timothy J. Bannin and Matthew K. Kiesewetter*

Department of Chemistry, University of Rhode Island, Kingston, Rhode Island 02881, United States

Supporting Information

ABSTRACT: Organocatalysts typically used for the ring-opening polymerization (ROP) of cyclic ester monomers are applied to a thiolactone, ε-thiocaprolactone (tCL). In the absence of an H-bond donor, a nucleophilic polymerization mechanism is proposed. Despite the decreased ability of thioesters and thiols (versus esters and alcohols) to H-bond, H-bonding organocatalysts—a thiourea in combination with an H-bond accepting base—are also effective for the ROP of tCL. The increased nucleophilicity of thiols (versus alcohols) is implicated in the increased M_w/M_n of the poly(thiocaprolactone) versus poly(caprolactone), but deleterious transesterification is suppressed in the presence of a thiourea. The thioester monomer, tCL, is shown to be thermodynamically similar to ε-caprolactam but kinetically similar to ε-caprolactone.



INTRODUCTION

Organic catalysts for polymerization have provided efficient methods for the synthesis of well-defined, functionalized polymers.[1,2] Cyclic esters and carbonates have been the most common monomers for organocatalytic ring-opening polymerization (ROP) methods; acrylates have also been employed.[3−6] Expanding the scope of monomers available for organocatalytic ROP increases the diversity of materials and their applications.[7,8] The increased nucleophilicity of thiols and altered electrophilicity of thioesters versus alcohols/esters make poly(thioester)s potentially attractive synthons for materials and a challenge for controlled ROP chemistry. The mild conditions of organocatalytic ROP provide a route to well-defined poly(thioester)s.

Sporadic entries to the literature concerning the ROP of tCL have appeared since the initial report in 1968.[9,10] Many reports feature late metal alkoxide (Sn, Cd, Mn, etc.) catalyzed ROP of tCL from alcohol or thiol initiators in solvent or bulk,[11,12] and a ring-expansion polymerization technique has also been demonstrated.[13] A recent report of the ROP of ε-thiocaprolactone, tCL, used a lipase typically employed in esterification[14,15] to yield poly(ε-thionocaprolactone) (PtCL) with higher M_w/M_n than poly(ε-caprolactone) (PCL) generated under identical conditions. This report demonstrates the extension of mild techniques for the ROP of esters to thioesters. Herein, we disclose the "living" ROP of tCL using organocatalysts; the application of thiourea H-bond donors is discussed and a polymerization mechanism is proposed.

RESULTS AND DISCUSSION

Polymerization Thermodynamics. The first reports by Overberger and Weise in 1968[9,10] suggested that strong base organocatalysts may be effective for the ROP of tCL; these reports demonstrated that strong alkoxide and alkyl−lithium bases effect the ROP of tCL in the bulk.[9] The reported polymerizations were uncontrolled, and access to molecular weight/dispersity information was limited. The effectiveness of strong alkoxide bases for ROP of tCL suggested that the strong base and potent transesterification agent, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD),[16] might also be effective for the ROP of tCL. Indeed, the introduction of TBD (5 mol %) into a $CDCl_3$ solution of tCL (1 M) and octadecylthiol (2 mol %)) results in full conversion to polymer in 30 s (M_n = 6000 g/mol; M_w/M_n = 1.7). If the reaction is not quenched, the M_w/M_n rapidly broadens post polymerization, and timing the quench of this rapid reaction is difficult.

As opposed to cyclic lactones, only the 7-membered thiolactone, ε-thiocaprolactone (tCL), is thought to be thermodynamically favored to undergo ROP.[9] However, the magnitude of the thermodynamic driving force has not been reported, but we were able to employ the rapid TBD-catalyzed ROP of tCL to measure the thermodynamics of polymerization. The equilibrium monomer concentration of a solution of tCL (1 M), octadecylthiol (2 mol %) and TBD (20 mol %)) in $CDCl_3$ was measured versus temperature,[17] and the resulting Van't Hoff analysis yielded the thermodynamics of ROP for tCL: $\Delta H^\circ_P = -2.43 \pm 0.69$ kcal/mol; $\Delta S^\circ_P = -0.35 \pm 0.22$ cal/mol·K; $[M]_{eq}$ = 0.018 at 293 K and T_c = 7,000 K. This data describes a polymerization reaction that highly favors polymer and suggests that tCL is energetically more similar to caprolactam (no ceiling temperature) than it is ε-caprolactone (CL) or δ-valerolactone (VL) ($T_c \sim 534$ K and $T_c \sim 422$ K, respectively).[17]

Organic Base Catalyzed ROP. A screen of base catalysts revealed that only strong, nucleophilic bases are active for the ROP of tCL. The addition of 5 mol % (to monomer) base catalyst to a $CDCl_3$ solution of tCL (1 M) and octadecylthiol (2 mol %) resulted in ROP only for amidine bases. MTBD (7-

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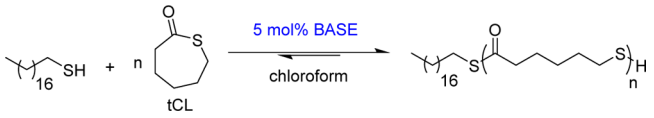
Table 1. Catalyst Screen for the Ring-Opening Polymerization of tCL[a]



entry	catalyst	$[M]_o/[I]_o$	time (min)	% convn (NMR)	M_n (GPC)	M_w/M_n (GPC)
1	DMAP	50	24 h	0	N/A	N/A
2	Me_6TREN	50	24 h	0	N/A	N/A
3	TBD	50	0.5	97	6000	1.70
4	BEMP	50	24 h	0	N/A	N/A
5	DBU	50	240	89	9000	1.67
6	MTBD	50	80	88	10 000	1.63
7	MTBD	100	1440	92	25 000	1.40
8	MTBD	200	1440	89	32 000	1.51

[a]Reaction conditions: 100 mg (0.77 mmol, 1M) tCL; 0.015 mmol octadecylthiol, 0.038 mmol base catalyst in $CHCl_3$ (BEMP reaction was attempted in both $CDCl_3$ and C_6D_6).

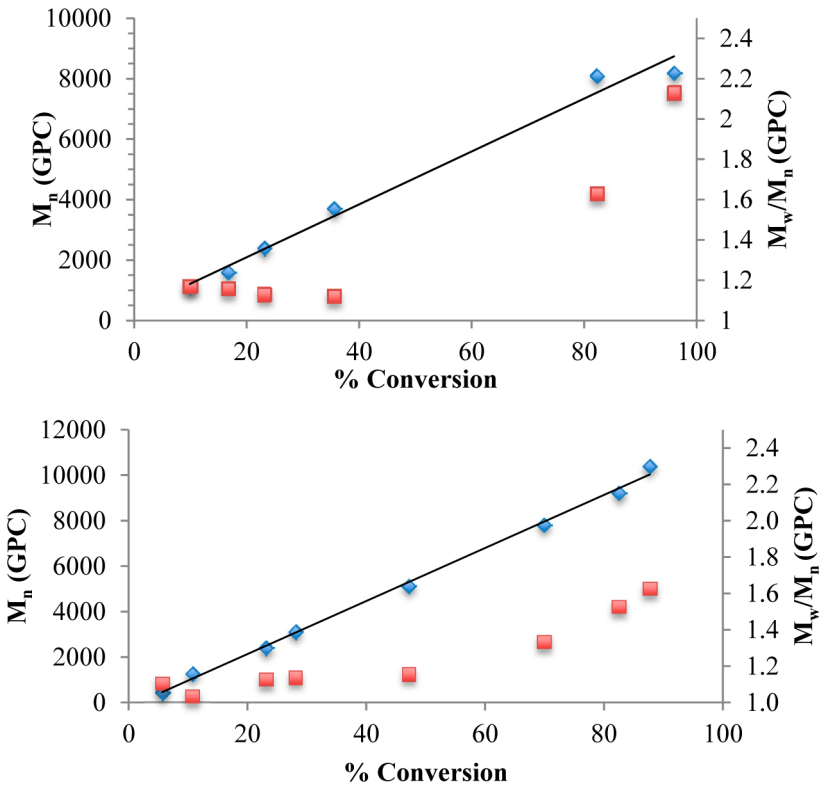


Figure 1. Evolution of percent conversion vs M_n and M_w/M_n for the ROP of tCL (1M) from octadecylthiol (0.02 M) in chloroform catalyzed by (upper) 0.05 M MTBD; and (lower) 0.05 M MTBD and 0.05 M **1**. Conversion determined by NMR.

methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene; MTBD-H^+ pK_a^{MeCN} = 25.4)[18] and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene; DBU-$H^+pK_a^{MeCN}$ = 24.3)[18] resulted in full consumption of monomer in a reasonable time scale, while tris[2-(dimethylamino)ethyl]-amine (Me_6TREN), BEMP (2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine; BEMP−H^+ pK_a^{MeCN} = 27.6)[19] and DMAP (4-(dimethylamino)pyridine; DMAP−H^+pK_a = 18.2)[20] resulted in no observable conversion to polymer, Table 1. Poly(thiocaprolactone) exhibits good solubility in chlorinated solvents but is minimally soluble in THF.

The high activity of DBU and MTBD for the ROP of tCL combined with the observation that the considerably more basic but non-nucleophilic BEMP did not form polymer suggests a nucleophilic ROP mechanism. As shown in Table 1, both amidine bases provided rapid but controllable ROP and moderate M_w/M_n (DBU, M_w/M_n = 1.67; MTBD, M_w/M_n = 1.63). For the MTBD and DBU catalyzed ROPs, the evolution of M_n versus conversion was linear (Figure 1), M_w/M_n remained low but broadened with increased reaction time, and M_n is predictable from $[M]_o/[I]_o$, Table 1 entries 6−8. Poly tCL becomes insoluble in chlorinated solvents at high degree of polymerization (DP ≥ 200). Kinetic analyses reveal first order consumption of monomer versus time for the MTBD or DBU catalyzed ROPs (see Supporting Information). These data suggest that MTBD and DBU exhibit the characteristics of a "living" polymerization while the relatively high M_w/M_n (vs polyesters) may be attributable to the increased nucleophilicity of thiols versus alcohols. The surprising observation that the strongest and bulkiest Brønsted

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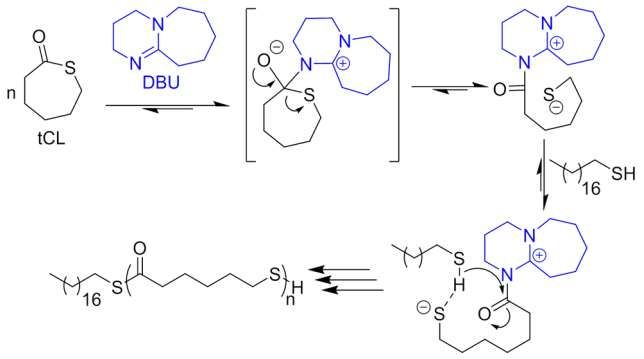
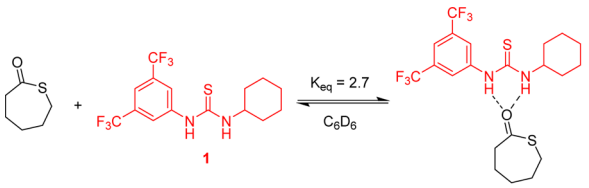
base examined (BEMP) is inoperative for ROP suggests that DBU and MTBD are not acting as general bases but rather are effecting ROP via nucleophilic attack at the thioester moiety, Scheme 1. Under basic conditions, thioesters are expected to be

Scheme 1. Nucleophilic Mechanism for the ROP of tCL with DBU



better electrophiles than esters,[5] which may account for the different reactivity vs organocatalytic ROP of esters, but nucleophilic modes of action have previously been suggested for these amidine bases.[21]

Effect of Thiourea upon Catalysis. The perturbation to ring geometry that occurs upon the change from caprolactone to thiocaprolactone was expected to render thiourea H-bond donors ineffective for the activation of tCL. An NMR titration study in C_6D_6 was conducted to determine the binding constant between **1** (in eq 1) and tCL, eq 1, K_{eq} = 2.7 ± 0.5.



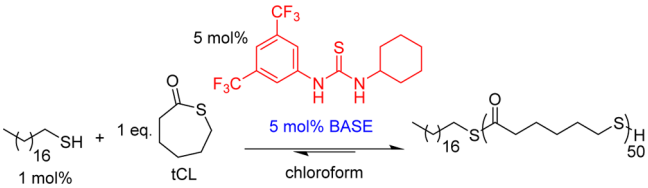
(eq 1)

The analogous binding constant between CL and **1** was reported to be K_{eq} = 42.[16] DFT-predicted geometries for CL and tCL (see Supporting Information) support the NMR binding studies. The dipole of CL, which is activated by **1**,[16] is aligned with the carbonyl whereas that of tCL is offset, which corroborates the observed minimal activation of tCL by **1**.

Despite the small binding constant between tCL and **1**, the H-bond donor exhibits a marked effect upon the ROP. The addition of an equimolar amount of **1** (to base) in the DBU catalyzed ROP of tCL from octadecylthiol decreases the reaction time (240 min versus 120 min) and lowers M_w/M_n (1.67 versus 1.47). For the analogous MTBD catalyzed experiment, the addition of TU has no effect on the rate, but the M_w/M_n is lower in the presence of **1** (1.83 versus 1.63). These results corroborate a previous report from our laboratory which suggested that the selectivity of **1**/base cocatalyzed ROP is due, in part, to favorable interactions between base and **1**.[22] The increased rate of the DBU experiment in the presence of **1** suggests that some monomer activation by TU may be operative despite the low binding constant, eq 1. The evolution of M_n vs conversion plots for the MTBD or DBU plus **1** catalyzed ROP of tCL are linear which suggests a "living" ROP, Figure 1 and Supporting Information, respectively. The M_w/M_n versus conversion plots demonstrate that transesterification at high conversion (especially past 50% conversion) leads to broadened M_w/M_n, but this broadening is suppressed versus those ROPs in the absence of TU (see Supporting Information). When initiated from pyrenebutanol (2 mol %), the ROP of tCL (1 M) catalyzed by MTBD/**1** (5 mol % each) in $CHCl_3$ exhibits similar ring-opening kinetics as when initiated from octadecylthiol, and the resulting polymer exhibits overlapping RI and UV GPC traces (M_n = 21 000 g/mol; M_w/M_n = 2.11), see Supporting Information. These observations suggest end group fidelity and "living" ROP behavior.

The mechanism of ROP (Table 2) is altered in the presence of **1**. Though inactive when alone, BEMP is observed to

Table 2. Base Catalyzed ROP of tCL in the Presence of Thiourea 1[a]



entry	cocatalyst	time (min)	% convn (NMR)	M_n (GPC)	M_w/M_n (GPC)
1[b]	DMAP	1440	0	N/A	N/A
2[b]	Me_6TREN	1440	0	N/A	N/A
3	BEMP	960	100	10 000	1.45
4	DBU	120	88	9000	1.47
5	MTBD	80	88	10 000	1.63

[a]Reaction conditions: 100 mg (0.77 mmol, 1 M) of tCL, 0.015 mmol of octadecylthiol, 0.038 mmol of base, 0.038 mmol of **1** in $CHCl_3$. [b]Reaction did not convert at 24 h.

cocatalyze the formation of polymer when applied with **1** in the ROP of tCL. Concentration dependent ^{1}H NMR spectra of BEMP and octadecylthiol implicate a chain-end activating role for BEMP in a bifunctional BEMP/**1** catalyzed ROP of tCL. In an equimolar mixture of BEMP and octadecylthiol (10 mM each) in C_6D_6, the chemical shifts of all resonances are negligibly altered in the presence vs absence of the other species, which suggests that quantitative deprotonation of the thiol is not occurring despite the strong basicity of BEMP. However, concentrating the mixture results in thiol proton exchange as evidenced by the broadening of the thiol H and α-methylene resonances due to increased decoherence of this coupling constant at high concentration. The J^3_{HH} coupling between those protons is eventually lost at 100 mM in each species. The same phenomena are observed when MTBD or DBU are used instead of BEMP, but this phenomenon is not observed in a solution of octadecylthiol alone. Thiols are generally weaker H-bond donors than alcohols,[23] and while BEMP cannot be observed to H-bond to the thiol (no chemical shift), its presence is sufficient to cause rapid chemical exchange. These observations are consistent with a chain-end activation mode of action where BEMP is activating the thiol proton for nucleophilic attack, Scheme 2. This is in contrast to traditional poly(ester) organocatalysis wherein the chain-end is activated through strong H-bonding.

Thiocaprolactone vs Lactone Monomers. The kinetic behavior of tCL is unusual vis-à-vis ester monomers which demonstrate relative ring-opening kinetics: $k_{LA} > k_{VL} \gg k_{CL}$, where LA is lactide. Typically, those monomers which are kinetically reluctant to open (CL) require strong bases (higher

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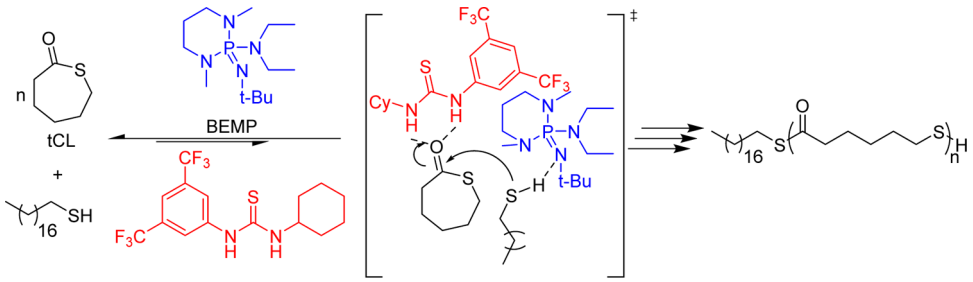
Scheme 2. Proposed Bifunctional Mechanism for the ROP of tCL by BEMP/1 Cocatalysts



pK_a) in conjunction with an H-bond donor (**1**) to effect ROP.[1,2,16] Kinetically facile ROPs (like those with LA) will require only strong bases (MTBD, DBU, TBD, etc.), but these ROPs are generally far more controlled upon the application of a weak base (e.g., Me_6TREN) in conjunction with **1**.[24,25] In this broader context of ester monomers, tCL occupies an unusual space in that it demonstrates ROP behavior that is both more and less reactive than VL. The thiolactone is more reactive in that it opens upon the application of strong base (i.e., DBU, MTBD) alone, which may be attributed to the increased nucleophilicity of thiols vs alcohols. It is less reactive in that upon the application of strong base and **1**, its rate of ROP is slower when compared to the same reaction with VL.[22] This observation could be due to the decreased ability of **1** to activate thioesters vs esters or the reduced electrophilicity of the thioester moiety.

CONCLUSION

The organocatalytic ROP of tCL exhibits the characteristics of a "living" polymerization. Typical ester organocatalytic ROP results in extremely narrow M_w/M_n which is eroded in the case of the ROP of tCL late in the reaction. This phenomenon may be attributable to the increased nucleophilicity of thiols (versus alcohols). The extremely rapid rate of the TBD-catalyzed ROP and the rate acceleration observed upon the addition of H-bond donor **1** to the base (DBU, MTBD or BEMP) catalyzed ROP suggest that thioester activation of tCL may contribute to the accelerated ROP of tCL. If this is the case, the binding between tCL and **1** would be among the weakest observed to effect catalysis. The suppression of M_w/M_n broadening upon the addition of TU may be attributable to the strong interaction of **1** and amine base catalysts, as previously described.[22] The decreased H-bonding ability of thiols (vs alcohols) and the altered electrophilicity of thioesters (vs esters) dominates the ROP of poly(thiocaprolactone), but the collective effects of extraordinarily weak bifunctional activation by **1** and strong base serve to effect the ROP of tCL. We expect that the incorporation of this new polymer backbone into the lexicon of organocatalytic ROP will facilitate the generation of new materials and applications.

EXPERIMENTAL SECTION

General Considerations. All chemicals were purchased from Fisher Scientific except where indicated: 6-Bromohexanoic acid (Chem-Impex International, Inc.), sodium hydrosulfide monohydrate (Sigma-Aldrich), 1-octadecanethiol (Sigma-Aldrich). All chemicals were used as received except where indicated. HPLC grade methylene chloride (DCM) and tetrahydrofuran (THF) were dried on an Innovative Technology solvent system featuring alumina columns. Chloroform and chloroform-d (Cambridge Isotopes) were distilled from calcium hydride (CaH_2) under vacuum (10 mTorr), stored over 4 Å molecular sieves, and passed through a plug of activated basic alumina just before use. Benzene-d_6 (Cambridge) was distilled from CaH_2 under nitrogen atmosphere and stored over 3 Å sieves. 1-[3,5-Bis(trifluoromethyl)phenyl]-3-cyclohexylthiourea (**1**) was prepared according to literature procedures.[16] All reactions were performed in a glovebox or by standard Schlenk techniques under N_2 atmosphere and at room temperature, unless stated otherwise. ^{1}H and ^{13}C NMR spectra were obtained utilizing a Bruker Avance III 300 instrument at 300 and 75 MHz, respectively. Gel permeation chromatography (GPC) was performed in DCM utilizing an Agilent Technologies 1260 Infinity fitted with three 5 μm Agilent analytical columns connected in series with increasing pore size (10^5, 10^4, 10^3 Å), an Agilent Infinity 1260 refractive index detector, and an Agilent Infinity 1260 UV/vis detector (250 and 300 nm), calibrated with polystyrene standards. DFT calculations were run with Spartan '14 at the DFT B3LYP/6-31G* level of theory, gas phase.

Preparation of 6-Mercaptohexanoic Acid. A 1 L round-bottom flask was charged with 6-bromohexanioc acid (10 g, 51.3 mmol), MeOH (500 mL), and a magnetic stir bar. After the 6-bromohexanoic acid dissolved, sodium hydrosulfide monohydrate (11.4 g, 154 mmol) was added, placed onto a hot/stir plate, and refluxed under a stream of N_2 for 24 h. After 24 h, the reaction was removed from the heat and cooled to room temperature under N_2. The reaction mixture was then acidified with H_2SO_4 (pH = 5). Next, DI water was added to mixture (~50 mL) and extracted three times with DCM. Organics were dried with $MgSO_4$, and all volatiles were removed *in vacuo* to yield a colorless oil (6.67 g, 88% yield). Crude material was carried forward without purification; characterization matched the literature.[26] ^{1}H NMR ($CDCl_3$): δ = 2.57−2.49 (q, 2H; $-CH_2SH$), 2.39−2.34 (t, 2H; $-CH_2COOH$), 1.70−1.59 (m, 2H; $-CH_2CH_2SH$), 1.50−1.42 (m, 2H; CH_2CH_2COOH), 1.37−1.31 (m, 2H; $-CH_2(CH_2)2SH$).

Preparation of ε-tCL. A dried 25 mL round-bottom flask was charged with 6-mercaptohexanoic acid (7.00 g, 0.0472 mmol), phosphorus pentoxide (4.022 g, 0.0283 mmol), and a stir bar. The flask was attached to a short path distillation head fitted with a receiving flask which had both been baked overnight at 140 °C, and the apparatus was allowed to cool under N_2 for approximately 20 min. Once cooled, the apparatus was subjected to high active vacuum. After 5 min, the pressure had reached 10 mmHg, and the distilling flask was heated to 200 °C. The receiving flask was placed into an ice bath. After approximately 1 h, the distillation head was at room temperature, and the temperature of the reaction flask was increased (210 °C) and left to react until the distillation head was again at room temperature. This process was repeated once more at 220 °C. The apparatus was removed from the heat and allowed to cool under N_2 until it reached room temperature. The yellow-orange oil was then purified via silica gel column chromatography (90:10 hexanes:ethyl acetate) and further purified via Kugelrohr distillation (50 °C, 200 mTorr) which yielded a colorless, odorless oil (1.5 g). The characterization matched the literature (see Supporting Information).[9] ^{1}H NMR ($CDCl_3$): δ = 3.05−3.01 (t, 2H; $-CH_2SC(=O)-$), 2.88−2.84 (t, 2H; $-CH_2C(=O)S-$), 2.16−2.09 (m, 2H; $-CH_2CH_2S-$), 1.88−1.74 (m, 4H; $-CH_2)_2CH_2C(=O)-$). ^{13}CNMR ($CDCl_3$): δ = 207.11 (s, 1C, $-SC(=O)CH_2-$), 45.87 (s, 1C, $-C(=O)CH_2$) 31.76 (s, 1C, $-SCH_2-$), 31.50 (s, 1C, $-SCH_2CH_2-$), 30.90 (s, 1C, $-C(=$

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O)$CH_2CH_2CH_2$−), 23.42 (s, 1C, −C(=O)CH_2CH_2−). GC−MS (electron ionization): m/z = 130.1 g/mol; mass = 130.05 g/mol.

Representative Polymerization of ε-tCL with DBU and 1. ε-tCL (100 mg, 0.768 mmol, [1M]) was dissolved in half of the total $CHCl_3$ (0.77 mL) used in the reaction and added to a solution of 1-octadecanethiol (4.4 mg, 0.015 mmol), **1** (14.2 mg, 0.038 mmol), and DBU (5.9 mg, 0.038 mmol) made with the remaining $CHCl_3$. The reaction was left to stir for 180 min, quenched with benzoic acid (3.0 mg), and solvent removed *in vacuo* to yield a white film. Conversion was determined by NMR and polymer purified by precipitation from DCM with hexanes. ^{1}H NMR ($CDCl_3$): δ = 3.53−3.49 (t, 2H; $(CH_2)_{16}CH_2S$), 2.87−2.82 (t, ∼66H; PB CH_2S), 2.55−2.50 (t, ∼58H; PB C(=O)CH_2), 1.71−1.52 (m, ∼128H; PB CH_2), 1.43−1.33 (m, ∼61H; PB CH_2), 0.89−0.85 (t, 3H; CH_3CH_2). ^{13}C NMR ($CDCl_3$): δ = 199.29 (s, 50C, C(=O)CH_2−), 43.86 (s, 50C, -C(=O)CH_2) 29.29 (s, 50C, −SCH_2−), 28.53 (s, 50C, −SCH_2CH_2−), 28.11 (s, 50C, −C(=O)$CH_2CH_2CH_2$−), 25.12 (s, 50C, −C(=O)CH_2CH_2−). GPC (UV−vis): M_n(M_w/M_n) = 8300 g mol^{-1} (1.8). 80% yield.

Representative Polymerization of ε-tCL with MTBD. ε-tCL (100 mg, 0.768 mmol, [1M]) was dissolved in half of the total $CHCl_3$ (0.77 mL) used in the reaction and added to a solution of 1-octadecanethiol (4.4 mg, 0.015 mmol) and MTBD (5.9 mg, 0.039) made with the remaining $CHCl_3$. Reaction was left to stir for 80 min, quenched with benzoic acid (3.0 mg), and solvent removed *in vacuo* to yield a white film. Conversion was determined by NMR and purified by precipitation from DCM with hexanes. ^{1}H NMR ($CDCl_3$): δ = 3.53−3.49 (t, 2H; $(CH_2)_{16}CH_2S$), 2.87−2.82 (t, ∼66H; PB CH_2S), 2.55−2.50 (t, ∼58H; PB C(=O)CH_2), 1.71−1.52 (m, ∼128H; PB CH_2), 1.43−1.33 (m, ∼61H; PB CH_2), 0.89−0.85 (t, 3H; CH_3CH_2). GPC (UV−vis): M_n (M_w/M_n) = 8400 g mol^{-1} (1.62). 85% yield.

Binding Study Procedure. The titration method and the linear forms of the binding equations were used as previously described.[22] Briefly, two stock solutions were made for this experiment: solution A was 533.3 mM ε-tCL (78.12 mg, 0.6 mmol) dissolved in C_6D_6 (1.5 mL, 16.93 mmol). Solution B was 20 mM **1** (7.4 mg, 0.20 mmol) dissolved in C_6D_6 (1.0 mL, 11.29 mmol). Several NMR samples were made from the above solutions using a calibrated volumetric pipet and dried NMR tubes. The binding constant was determined by monitoring the chemical shift of the *ortho*-aromatic protons of the thiourea and error was determined by linear regression at the 95% confidence interval. Plot of the data using the Lineweaver−Burke form of the binding equation is given in the Supporting Information.[27−29]

Determining Thermodynamics of tCL ROP. In a variable temperature NMR probe, a sample of 100 mg (0.77 mmol) of ε-tCL was reacted with 0.015 mmol initiator and 0.19 mmol TBD and the concentration of monomer was determined at multiple temperatures from 293 to 333 K. The concentrations were recorded twice, once upon heating and once upon cooling; the values at each temperature were within error of each other. These concentrations are the equilibrium monomer concentration ($[M]_{eq}$ = $1/K_{eq}$)[17] at each temperature. The thermodynamic values were extracted from a van't Hoff plot of the data, see Supporting Information, and error was determined by linear regression at the 95% confidence interval.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.5b01463.

Binding data, two views of a calculated equilibrium geometry, thermodynamic plots, kinetic plots, NMR data, and M_n vs conversion plots (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*(M.K.K.) E-mail: mkiesewetter@chm.uri.edu.

Notes

The authors declare no competing financial interest.

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