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Controlled Organocatalytic Ring-Opening Polymerization of ε-Thionocaprolactone

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ABSTRACT

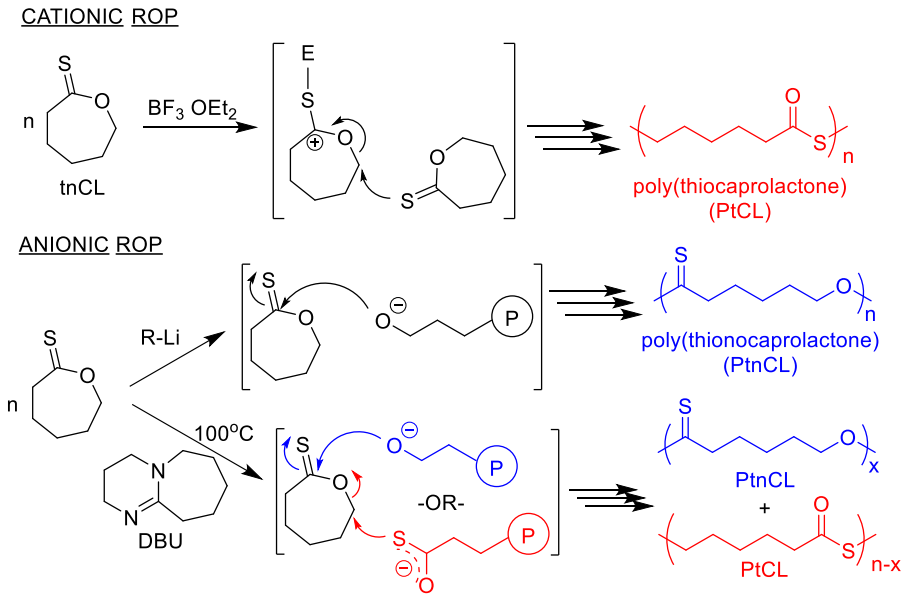
For the first time, the controlled ring-opening polymerization (ROP) of ε-thionocaprolactone (tnCL) is conducted. The organocatalytic ROP of tnCL occurs without carbonyl scrambling, leading to homo-poly(ε-thionocaprolactone) (PtnCL). The ROP by base catalysts alone is proposed to proceed via a nucleophilic mechanism, while the addition of an H-bond donating thiourea (TU) is shown to provide excellent reaction control. The increased reaction control provided by the TU occurs in the virtual absence of binding between tnCL and TU, and a mechanistic account for this observation is discussed. The monomer ring strain is measured and found to be similar to δ-valerolactone (VL). Copolymers with VL are synthesized, and the resulting analysis of the copolymer materials properties provides the only known physical characterizations of poly(thio(no)ester-co-ester)s.

INTRODUCTION

Over the last decade, developments in organocatalytic ring-opening polymerization (ROP) have demonstrated the remarkable ability of these catalysts to generate well-defined and highly functionalized polyesters and other polymers.[1–3] The H-bond mediated organocatalysts, which are a paragon of highly-controlled polymerization techniques, stand out in their ability to generate precisely tailored materials.[4–6] These catalysts are believed to operate by H-bond mediated

activation of monomer by thiourea and of growing polymer chain by base.[7,8] Given the remarkable control of these polymerization systems and the mild nature of their reactivity, the paucity of polymer backbone linkages which have been explored is surprising. The mild reactivity of organocatalysts for ROP perfectly position them for the generation of new polymer backbones and, hence, new materials and applications.

Our group recently disclosed the ROP of an S-substituted lactone, ε-*thio*caprolactone (tCL).[9] The ROP of this monomer was postulated to proceed through a classic transesterification mechanism mediated by H-bond activation of thioester by thiourea and thiol end group by base.[9] The other S-substituted caprolactone, ε-*thiono*caprolactone (tnCL, Scheme 1), has been the subject of only two published reports. [10,11] Under cationic polymerization conditions, the ROP of tnCL proceeds with quantitative inversion of substitution at the thionoester to generate the same poly(thiocaprolactone) previously reported by Overberger and our group.[9,13,14] The anionic ROP of tnCL from alkyllithium reagents retains the S-carbonyl substitution, but reaction control suffers, and this method does not allow for M_n control, copolymerization or end group selection.[10] Partial inversion of substitution occurs with weak nucleophiles, resulting in a mixed polymer backbone. Polymerization conditions which result in inversion of S/O substitution are postulated to operate via an S_n2 propagation, Scheme 1.[10] If the chain end/monomer activation mechanism of H-bond mediated ROP of tCL is correct, we reasoned that organocatalytic ROP of tnCL should allow for the retention of the S/O substitution *and* controlled-generation of homo-poly(*thiono*caprolactone).



Scheme 1. Endo's anionic and cationic ROPs of tnCL have been shown to proceed with S/O scrambling.

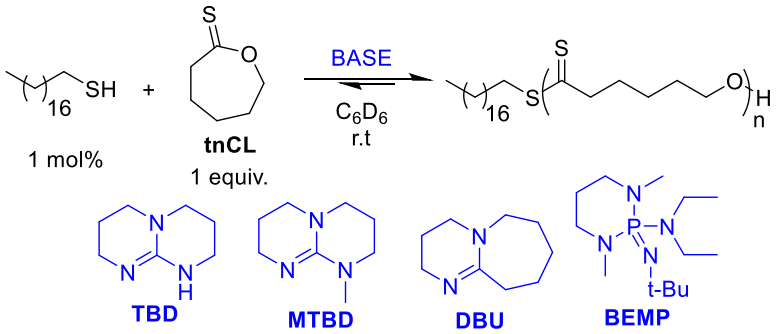
RESULTS AND DISCUSSION

Organic Base Catalyzed ROP. The organocatalytic room temperature ROP of tnCL initiated from alcohol or thiol initiators proceeds with retention of the S/O substitution. The ε-thionocaprolactone (tnCL) is generated from ε-caprolactone (CL) via a one-step reaction with P_4S_{10} (see Experimental Section); the reaction is workable on at least a 2 g scale (75% yield).[15,16] The application of DBU (5 mol%; Table 1) to a C_6D_6 solution of tnCL (2M) and octadecylthiol (1 mol%) results in 90% conversion to polymer in 25 h. ^{13}C NMR analysis of isolated tnCL suggests quantitative retention of the thiono- substitution, forming poly(ε-thionocaprolactone) (PtnCL), see Supporting Information (SI, Figure S8). The room temperature application of DBU for the ROP of tnCL from benzyl alcohol results in a linear evolution of M_n versus time and an initially narrow M_w/M_n that broadens throughout the ROP, Figure 1. The guanidine bases, MTBD and TBD, were also applied for the ROP of tnCL. MTBD exhibited a similar activity in the ROP of tnCL to that

of DBU whereas TBD effected a faster but less controlled ROP, resulting in erosion of M_w/M_n, Table 1.

PtnCL was previously only available through the application of alkyllithiums at elevated temperatures which resulted in the uncontrolled ROP of tnCL.[10] Endo's ROP of tnCL initiated from DBU at elevated temperatures was more controlled than the alkyllithium ROP but resulted in scrambling of the S/O substitution, Scheme 1.[10] ^{13}C NMR analysis of the polymer resulting from the repetition of our DBU-catalyzed ROP experiment at high temperature (1 eq. tnCL, 5 mol% DBU, toluene, 100°C) in the presence of an alcohol initiator reveals that S/O scrambling does occur (see SI, Figure S9), which suggests that the thiono/thio switching observed by Endo[10] is simply due to heating the reaction solution.

Table 1. ROP of tnCL with Base Catalysts.[a]



entry	Base	conv.[b] (%)	time (h)	M_n[c] (g/mol)	M_w/M_n[c]
1[d]	TBD	>99	0.33	17,700	1.41
2	DBU	89	25	17,200	1.30
3	MTBD	90	23	14,100	1.24
4	BEMP	0	25	--	--
5[e]	DBU	98	20	12,800	1.37
6[f]	DBU	98	19	19,700	1.20

a) Reaction conditions: 2M (0.77 mmol, 1 equiv) tnCL, 1 mol% octadecylthiol, 5 mol% base, and C_6D_6. b) Conversion to polymer obtained by ^1H NMR c) Determined by GPC (CH_2Cl_2) vs polystyrene standards. d) 1 mol% TBD. e) Initiation was from benzyl alcohol (1 mol%). f) initiation was from 1-pyrenebutanol (1 mol%).

The application of the phosphazene base, BEMP (Table 1), to a C_6D_6 solution of tnCL and benzyl alcohol does not result in ROP. The observation that the considerably more basic (vs DBU

or MTBD) but non-nucleophilic BEMP (BEMP-H^+; pK_a^{MeCN} = 27.6)[17] does not effect ROP suggests a nucleophilic mode of action for DBU (DBU-H^+; pK_a^{MeCN} = 24.3)[18] and MTBD (MTBD-H^+; pK_a^{MeCN} = 25.4)[18] in the ROP of tnCL, Scheme 2. DBU and MTBD have previously been suggested to operate as nucleophiles in ROP.[19] Conducting the DBU-catalyzed ROP of tnCL from alcoholic initiators (either benzyl alcohol or 1-pyrenebutanol) results in minimally altered M_w/M_n compared to when initiated from octadecylthiol, Table 1. This suggests no reduction in the 'living' character of the ROP due to slower initiation from alcohols vs thiols.

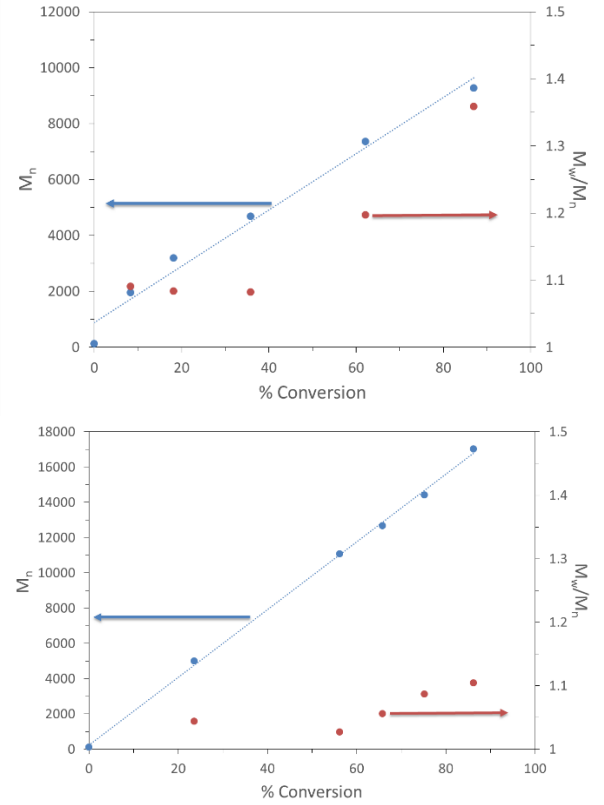
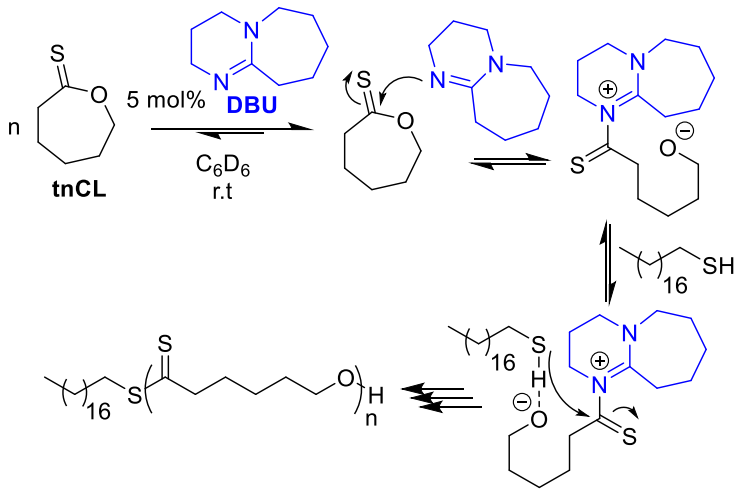


Figure 1. Evolution of M_n vs conversion for the (upper) DBU catalyzed ROP of tnCL from benzyl alcohol; (lower) **1**/BEMP (5 mol% each) catalyzed ROP of tnCL (2M, 100 mg, 1 equiv.) from benzyl alcohol (1 mol%).

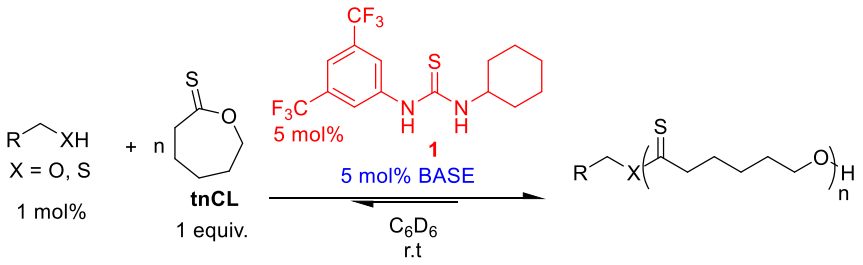


Scheme 2. Proposed mechanism for the DBU catalyzed ROP of tnCL.

Organic Base and Thiourea Catalyzed ROP. The presence of thiourea **1** (Table 2) has a distinct impact upon the base cocatalyzed ROP of tnCL. The **1**/DBU (5 mol% each) cocatalyzed ROP of tnCL from octadecylthiol in C_6D_6 lowers the reaction time and M_w/M_n versus the ROP with DBU alone. A similar effect is observed for MTBD, Table 2. The most striking results are observed with BEMP, which exhibits no activity in the absence of **1**, but the **1**/BEMP (5 mol% each) catalyzed ROP of tnCL (2M, 1 equiv.) from benzyl alcohol (1 mol%) achieves full conversion in 5 h. The reaction is highly controlled, exhibiting the characteristics of a 'living' polymerization: linear evolution of M_n vs conversion, narrow M_w/M_n (=1.10) (Figure 1), first order evolution of [tnCL] vs time (see SI, Figure S6) and a M_n that is predictable from $[M]_o/[I]_o$ (Table 2), although polymers begin to become insoluble in benzene at elevated molecular weight ($M_n \geq 22{,}000$). The ROP reaction proceeds in methylene chloride and chloroform but experiences reduced reaction control. Despite the narrow M_w/M_n, the GPC traces taken throughout the polymerization show the gradual growth of a high molecular weight tail, resulting in slight erosion of M_w/M_n, see Figure S2 (SI) and Figure 1. ^{13}C NMR analysis of the isolated polymer confirms the quantitative retention of thiono-ester moieties, and the MALDI-TOF mass spectrum is consistent with linear benzyl

alcohol terminated PtnCL, see Figure S1. When initiated from 1-pyrenebutanol, the refractive index and UV GPC traces of PtnCL overlap, including the high molecular weight tail, see Figure S2, suggesting end group fidelity. When allowed to stir past full conversion, the high weight tail on the GPC trace grows in prominence and eventually merges with the 'main' polymer peak, see SI (Figure S2). The high molecular weight tail in the GPC trace arises from an unknown post polymerization reaction.

Table 2. Thiourea Plus Base Cocatalyzed ROP of tnCL.[a]

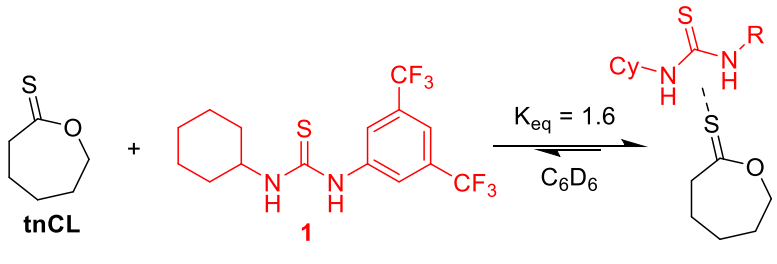


entry	initiator	Base	conv.[b] (%)	time (h)	M_n[c] (g/mol)	M_w/M_n[c]
1	octadecylthiol	DBU	93	17	22,500	1.14
2	octadecylthiol	MTBD	92	19	14,800	1.16
3	octadecylthiol	BEMP	84	5	14,600	1.25
4	1-pyrenebutanol	BEMP	89	6	15,200	1.11
5	benzyl alcohol	BEMP	91	5	12,000	1.14
6[d]	benzyl alcohol	BEMP	89	4.5	8,200	1.11
7[e]	benzyl alcohol	BEMP	90	7	20,900	1.10

a) Reaction conditions: 2M (0.77 mmol, 1 equiv) tnCL, 1 mol% octadecylthiol, C_6D_6 and given amount of catalyst. b) conversion to polymer obtained by ^{1}H NMR c) Determined by GPC (CH_2Cl_2) vs polystyrene standards. d) 2 mol% benzyl alcohol, $[M]_o/[I]_o = 50$. e) 0.5 mol% benzyl alcohol, $[M]_o/[I]_o = 200$.

Role of Thiourea in ROP. The presence of the thiocarbonyl in tnCL was expected to perturb the ability of H-bond donors to activate the monomer for ROP, yet the addition of thiourea **1** to the ROP solution clearly affects the course of the reaction. An NMR titration study[20–22] was conducted in C_6D_6 to determine the binding constant between **1** and tnCL, $K_{eq} = 1.6 \pm 0.2$ (in eq 1). The comparable binding between CL and TU was measured to be $K_{eq} = 42 \pm 5$,[7] and a similarly-dramatic perturbation from this latter strong binding value was previously measured for tCL, K_{eq}

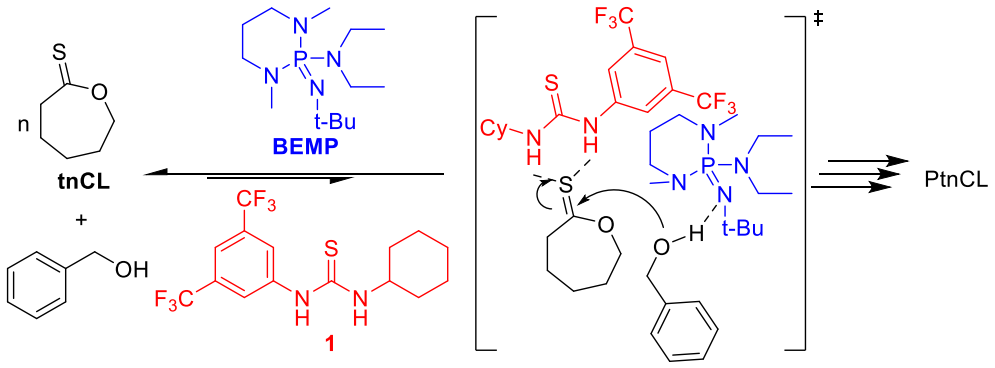
= 2.7 ± 0.5.[9] The remarkable ability of **1** to activate tnCL and tCL towards ROP despite the weak binding exhibited by **1** towards these monomers suggests an incongruity in the approximation of 'magnitude of binding' as 'extent of activation.'



(eq 1)

The clear effects of **1** upon the ROP of tnCL in the absence of strong binding suggests that **1** plays a mechanistic role that cannot be fully understood by the magnitude of a binding constant between **1** and monomer. Because **1** does not measurably bind to ethyl acetate (a surrogate for open polymer),[8] an approximation of the kinetic bias of **1** for polymerization vs depolymerization (or transesterification) is at most the magnitude of the **1**/monomer binding constant, K_{eq} = 1.6, or $\Delta\Delta G^{\neq}$ = 0.27 kcal/mol, see Figure S7. This would only be true if **1** activates *s*-cis and *s*-trans esters equally. Indeed, DFT (B3LYP/6-31G**) calculations suggest that **1** is equally effective at the activation of (i.e. increasing the electophilicity of)[10] CL, tnCL, tCL, methyl thionoacetate and methyl acetate. For these compounds, both the electrostatic charges at carbon (C=X) and polarity of the C=X bond increase by ~5-10% upon the binding of **1**, see Figure S15. The effects rendered by **1** upon ROP must then be due to interactions in the transition state that are not adequately reflected in the magnitude of the binding of **1** to monomer (vs polymer) in the reactants/products. The increased reaction control provided by **1** during the ROP of tnCL could arise from the suppression of transesterification events due to prominent secondary interactions (e.g. **1** to base cocatalyst).[5,22] These results suggest that despite minimal binding to tnCL (or tCL), the H-bond

mediated ROP of tnCL is operative by dual activation of monomer by **1** and of chain end by base, Scheme 3.

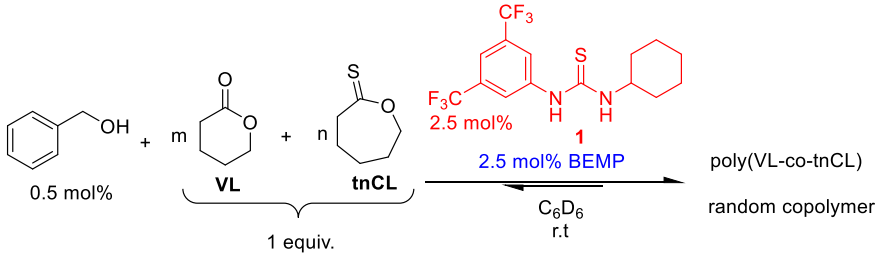


Scheme 3. Proposed mechanism for the H-bond mediated ROP of tnCL.

Thionocaprolactone vs Other Monomers. The terminal conversion of the DBU catalyzed ROP of tnCL from alcohol initiators showed a strong temperature dependence; we sought to measure the thermodynamics of ROP to energetically place tnCL among other cyclic (thio)lactone monomers. The equilibrium monomer concentration, $[tnCL]_{eq}$, of a TBD catalyzed ROP of tnCL from benzyl alcohol in C_6D_6 was monitored as a function of temperature, see Experimental Section. The resulting Van't Hoff plot allowed for the extraction of the thermodynamic parameters of ROP:[23] ΔH^o = -5.79 ± 0.32 kcal/mol (298 K); ΔS^o = -13.5 ± 1.0 cal/mol K; $[tnCL]_{eq}$ = 0.05 M at 300 K and $T_{ceiling}$ = 156°C, see Figure S3. These values suggest that tnCL is most energetically similar to VL[23]: $T_{ceiling}$ = 149 °C. For comparison, the ceiling temperatures ($T_{ceiling}$) of CL and tCL are: $T_{ceiling}$ (CL)[23] = 261°C and $T_{ceiling}$ (tCL)[9] = 7,000°C. The low ceiling temperature of tnCL accounts for the low monomer conversions which are observed when the ROP of tnCL is attempted at elevated temperatures.[10] Kinetically, tnCL is more reactive than VL. VL will not undergo ROP in the presence of MTBD or DBU alone (no **1**), and the increased reactivity of tnCL (vs VL) is attributed to the increased electophilicity of thionoesters (vs esters). In contrast, the thioester, tCL, was observed to exhibit behavior that is both more and less reactive than VL.[9]

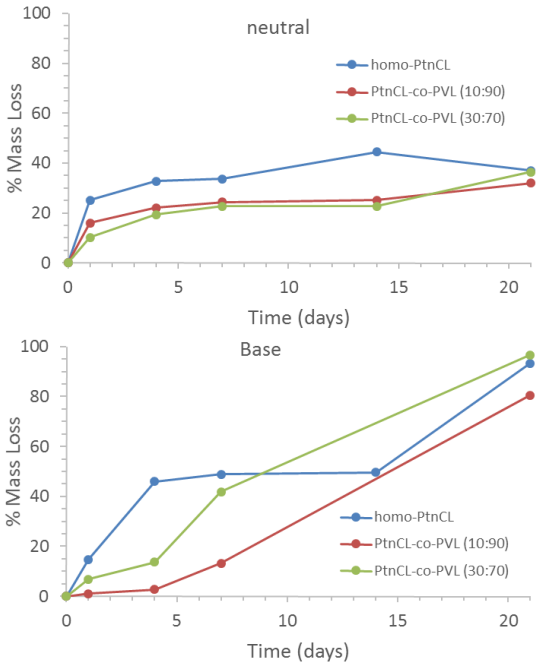
Copolymerization with δ-Valerolactone. The observation of similar ROP thermodynamics for tnCL and VL suggests that random copolymerizations of these two monomers are possible. When **1**/BEMP (5 mol% each) is added to a mixture of VL (1 M, 0.5 equiv.), tnCL (1 M, 0.5 equiv.) and benzyl alcohol (1 mol%) in C_6D_6, both monomers are observed to undergo ROP at approximately equal rates in a first order evolution of [monomer]s vs time plot (k_{tnCL}/k_{VL} = 1.07), suggesting random copolymer formation, see SI (Figure S4). ^{13}C NMR analysis of the copolymer confirms random monomer incorporation as evidenced by the equal intensities of the well-resolved tnCL-tnCL vs tnCL-VL resonances (72.15 vs 71.78 ppm), see Figure S10. The monomer feed can be adjusted to higher or lower VL/tnCL ratios to give gradient copolymers. ^{13}C NMR analyses also confirm the retention of C=S substitution in the copolymers, see SI (Figure S10). Whereas PtnCL is an oil at room temperature for all molecular weights examined in our lab (< 20 kg/mol), copolymers of tnCL and VL with greater than 70% VL are solid at room temperature. The materials properties (T_m, T_c and T_{deg}) of P(tnCL-co-VL) with varying tnCL content were analyzed by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA, under N_2). Polymers with increasing tnCL content show predictably reduced T_m, T_c and T_{deg}, Table 3. The hydrolytic stability of copolymers was measured under basic, acidic and neutral conditions by established methods,[25] Figure 2. Increased tnCL content in copolymers with VL is associated with reduced hydrolytic stability under basic conditions, increased stability towards hydrolysis under acidic conditions and minimally altered stability in neutral water. These observations are consistent with general trends of thio(no)ester stability.[12] To our knowledge, these are the only known characterizations of poly(thionoester-co-ester)s.

Table 3. Copolymers of tnCL and VL with Varying Monomer Feeds.[a]



entry	tnCL (% feed)	VL (% feed)	time (h)	% conv.[b]	M_n[c]	M_w/M_n[c]	T_m (°C)[d]	T_c (°C)[d]	T_{deg} (°C)[e]
1	0	100	5	0 : 93	12,300	1.06	53	27	380
2	5	95	4	56 : 90	19,600	1.02	49	22	440
3	10	90	5	73 : 93	19,200	1.02	43	22	360
4	20	80	4	56 : 90	19,200	1.03	40	8	340
5	30	70	5	79 : 96	18,200	1.05	31	-8	320
6	50	50	5	95 : 92	29,800	1.25	18	n/a	310
7[f]	100	0	7	89 : 0	20,900	1.10	9	n/a	260

a) Polymerization conditions: 4M ([VL] + [tnCL]) (2 mmol total), 2.5 mol% **1**/BEMP (each), 0.5 mol% benzyl alcohol in C_6D_6. b) Percent conversion to polymer obtained by ^{1}H NMR. c) Determined by GPC (CH_2Cl_2) vs polystyrene standards. d) Determined by DSC (N_2); no T_g were observed >-70°C, the limit of our DSC. e) Determined by TGA (N_2). f) Polymerization conditions: tnCL (2M, 1 mmol), 5 mol% **1**/BEMP (each), 1 mol% benzyl alcohol in C_6D_6. n/a = not observed above -70°C, the limit of our TGA.



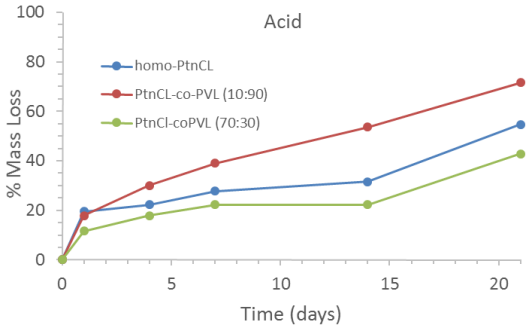


Figure 2. Percent mass loss for PtnCL and copolymers with VL in acidic (0.25 M HCl), basic (0.25 M NaOH) and neutral (distilled water) conditions vs time. The error from multiple measurements is ±5%.

CONCLUSION

The organocatalytic ROP of tnCL exhibits the characteristics of a 'living' polymerization, particularly in the presence of an H-bond donating thiourea, **1**. The marked effect of **1** upon the course of the ROP is notable because it occurs in the absence of a strong binding between the H-bond donor and monomer. The increase in reaction rate and reaction control for the ROP of tnCL in the presence of **1** cannot be accounted for by the traditional model of selectivity in the differential ability of **1** to bind to monomer or polymer, and further studies are required to elucidate the source of selectivity, presumably due to interactions in the transition state. Copolymers of tnCL with VL are, to our knowledge, the first reported and characterized copolymers of S-lactone and lactone monomers. The incorporation of tnCL to construct random (statistical), gradient or block copolymers with traditional esters offers a unique and convenient method for tuning materials properties for custom tailored applications; the multitude of possible copolymers provides a wealth of research opportunities.

EXPERIMENTAL SECTION

General Considerations: All chemicals were used as received unless stated otherwise. P_4S_{10}, hexamethyldisiloxane (HMDO) and 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-

1,3,2-diazaphosphorine (BEMP) were supplied by Acros Organics. Acetonitrile, potassium carbonate, magnesium sulfate, benzyl alcohol, benzoic acid, ethyl acetate and hexane were purchased from Fisher Scientific. ε-caprolactone (CL) and δ-valerolactone (VL) were supplied by Alfa Aesar and distilled from CaH_2 under high vacuum. Benzene-d_6 was supplied by Cambridge Isotope Laboratories and distilled from CaH_2 under a nitrogen atmosphere. Benzyl alcohol was distilled from CaH_2 under high vacuum. **1** [3,5-Bis-(trifluoromethyl)phenyl]-3-cyclohexylthiourea was synthesized and purified according to literature procedure.[7] 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) were purchased from TCI. All polymerization reactions were performed in an MBRAUN stainless steel glovebox equipped with a gas purification system under a nitrogen atmosphere using glass vials and stir bars which were baked overnight at 140°C. NMR experiments were performed on a Bruker Avance 300 MHz (proton) spectrometer. The chemical shifts for proton (^{1}H) and carbon (^{13}C) NMR were recorded in parts per million (ppm) relative to a residual solvent. Size exclusion chromatography (SEC) was performed at 30°C in dichloromethane (DCM) using an Agilent Infinity GPC system equipped with three Agilent PLGel columns 7.5 mm × 300 mm (5 μm pore sizes: 10^3, 10^4 and 10^5 Å). Molecular weight and M_w/M_n were determined versus polystyrene standards (500 g/mol–3,150 kg/mol; Polymer Laboratories). Differential scanning calorimetry (DSC) curves were obtained on a DSC Q100 (TA Instruments) under N_2 calibrated with an indium standard. The heating and cooling curves of DSC were run under a nitrogen atmosphere at a heating rate of ±10°C/min in a 40μL aluminum crucible. Thermogravimetric analysis (TGA) was performed using a TGA Q500 from TA instrument under N_2 atmosphere at a heating rate of 20°C/min from 25 to 600°C. MALDI-TOF MS analysis was performed at the University of Akron: reflectron mode with *trans*-

2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) matrix with sodium trifluoroacetate (NaTFA) salt.

Example synthesis of *ε*-thionocaprolactone (tnCL): In a dried 100 mL round-bottom flask with stir bar, P_4S_{10} (1.95 g, 4.38 mmol), *ε*-caprolactone (1.94 mL, 17.52 mmol), HMDO (6.18 mL, 29.08 mmol) and acetonitrile (17.5 mL) were added. The solution was refluxed for one hour while stirring, and the reaction was cooled to room temperature with stirring. The flask was then placed in an ice-water bath, and aqueous K_2CO_3 solution (1.26 mL of 5.3 M solution per mmol of P_4S_{10}) was added followed by distilled water (1 mL per mmol of P_4S_{10}) with stirring. Once cooled to room temperature, organics were extracted with dichloromethane and washed with brine. The organics were dried over $MgSO_4$, filtered, and removed of volatiles to obtain crude product. The crude product was purified in two stages by silica gel flash chromatography: 75:25 toluene:hexanes mobile phase and a second column with 95:5 dichloromethane:hexanes mobile phase. Kugelrohr vacuum distillation at 80°C and 200 mtorr pressure yielded tnCL, a pure yellow oil which was transferred to the glove box. Yield: 1.7 g, 75%. Characterization matched the literature.[24]

Example Ring-Opening Polymerization: In a typical polymerization, tnCL (0.100 g, 0.768 mmol) was added to a 20 mL glass vial with a stir bar. In another 20 mL glass vial with stir bar, **1** (0.0142 g, 0.0384 mmol), BEMP (11.1 μL, 0.0384 mmol), and benzyl alcohol (1.6 μL, 15.4 μmol) were added. Solvent (for C_6D_6, 0.38 mL, 2 M in tnCL) was divided equally between the two vials. After 2 minutes of stirring, the tnCL solution was transferred with a pipet to the other vial consisting of initiator and catalysts. The solution was then transferred via pipette to a NMR tube and taken out of the glovebox. Reaction conversion was monitored by ^{1}H NMR, and the reaction was quenched with benzoic acid (2 mol equiv. to base) after desired conversion had been achieved. The polymer was treated with hexanes to precipitate the polymer. After decanting the

hexanes supernatant, the polymer was removed of volatiles under reduced pressure. Yield, 85%; M_w/M_n = 1.11; $M_{n\ (GPC)}$ = 8,200; $M_{n\ (NMR)}$ = 5,200. For $[M]_o/[I]_o$ = 200, M_w/M_n = 1.10; $M_{n\ (GPC)}$ = 20,900; $M_{n\ (NMR)}$ = 15,800. ^{1}H and ^{13}C NMR spectra (see Figure S12 and S13 in SI) show resonances consistent with assignment of the polymer as quantitatively thionoester repeat unit, with the characteristic thiocarbonyl carbon peak at 224 ppm in the ^{13}C spectrum. **^{1}H NMR (300 MHz, $CDCl_3$) δ:** 7.38 (5H, aromatic); 5.48 (2H, benzylic); 4.43 (78*H*, R-C**H**2-R' of PtnCL); 2.73 (80*H*, R-C**H**2-R' of tnCL); 1.80 (159 *H*, R-C**H**2-R' of tnCL); 1.46 (88*H*, R-C**H**2-R' of PtnCL). **^{13}C NMR (75 MHz, $CDCl_3$)** (see Figure S13 in SI) δ: 224 (R-**C**=S-R'); 128 (benzyl aromatics); 72 (1*C*, Ar-**C**H_2-OR); 62 (benzylic CH_2); 47 (R-**C**H_2-O); 28 (2*C*, R-C=S-**C**H_2-**C**H_2-R'); 25 (R-C=S-CH_2-CH_2-**C**H_2-R').

Example Copolymerization of *ε*-thionocaprolactone with *δ*-valerolactone: VL (100 mg, 1 mmol) and tnCL (130 mg, 1 mmol) were added to a 20 mL glass vial with a stir bar. In another 20 mL glass vial with stir bar, **1** (0.05 mmol), BEMP (0.05 mmol) and benzyl alcohol (0.01 mmol) were added. Solvent (for C_6D_6, 0.5 mL) was added in equal proportion to both the vials. The monomer solution was transferred via pipet to the vial containing initiator after few minutes of stirring. The solution was then transferred to a NMR tube which was immediately taken out of the glovebox. Reaction progress was monitored by ^{1}H NMR, and the reaction was quenched with benzoic acid (2 mol equiv. to base). The polymer was treated with hexanes to precipitate the polymer, the supernatant was decanted and polymer was subjected to reduced pressure to remove volatiles. The polymer samples were dissolved in methylene chloride and dialyzed against methanol over 48 hours, changing the methanol solution after 24 hours. Yield, 90%; M_w/M_n = 1.25; $M_{n\ (GPC)}$ = 29,800. **^{1}H NMR (300 MHz, C_6D_6)** (see Figure S11) δ: 7.30 (5*H*, aromatic); 5.08 (2*H*, benzylic); 4.40 (164*H*, R-C**H**2-R' PVL); 4.04 (176*H*, R-C**H**2-R' PtnCL); 2.69 (164*H*, R-

C**H**2-R' PVL); 2.32 (176*H*, R-C**H**2-R' PtnCL); 1.85-1.53 (m, 680*H*, R-C**H**2-R' PtnCL and PVL); 1.40 (176*H*, R-C**H**2-R' PtnCL). **^{13}C NMR (75 MHz, $CDCl_3$)** (see Figure S10) δ: 224 (1*C*, R-**C**=S-R'); 173 (1*C*, R-**C**=O-R'); 128 (6*C*, aromatic **C**'s); 72.15 & 71.78 (ε-CH_2, tnCL-tnCL & tnCL-VL); 64.21 & 63.90 (δ-CH_2, VL-VL & tnCL-VL); 53.5 (α-CH_2, VL); 46.6 (α-CH_2, tnCL); 33.7 (γ-CH_2, VL); 28.32, 28.07, 27.80, 27.57 (γ-CH_2 & δ-CH_2, tnCL-tnCL & tnCL-VL); 25.2 (β-CH_2, tnCL); 21.4 (β-CH_2, VL).

Determination of Binding Constant (K_{eq}) between tnCL and 1: Binding constant (K_{eq}) between **1** and tnCL was determined in benzene-d_6 by the titration method and curve fitting as previously described.[20–22] The K_{eq} values were determined by fitting the binding curve to the quadratic form of the binding equation with K_{eq} and Δδ as variables: $\delta_{obs} = \delta_H - (\Delta\delta/2[H]_o)\{[H]_o + [G]_o + 1/K - (([H]_o + [G]_o + 1/K)^2 - 4[H]_o[G]_o)^{1/2}\}$; Δδ is the difference in the chemical shift of host and complex; δ_{obs} is the observed chemical shift of the TU in the presence of monomer; δ_H is the chemical shift of free TU in the absence of monomer.

Determination of Thermodynamic Parameters: A sample of tnCL (100 mg, 0.77 mmol), TBD (5.3mg, 0.038 mmol) and benzyl alcohol (0.80 μL, 0.0077 mmol) in C_6D_6 (2M in monomer) was heated in a variable temperature NMR probe, and ^{1}H NMR spectra were acquired at temperatures from 290 to 330 K. Data points were taken in duplicate, during heating and cooling. The heating and cooling $[M]_{eq}$ values were within error, heating values shown in SI (Figure S3). The thermodynamic values of tnCL ROP were determined from a Van't Hoff plot of the data and error was calculated from linear regression at 95% confidence interval, see Figure S3 in SI.

Polymer Hydrolysis: Polymer samples (approximately 10 mg each) were loaded into empty 20 mL scintillation vials. The polymers were then dissolved in dichloromethane to evenly distribute the polymer on the bottom of the vial, and the dichloromethane was subsequently removed under

vacuum. Each vial was charged with 10 mL of aqueous 0.25M HCl, aqueous 0.25M NaOH solution or distilled water. Each hydrolysis medium was tested in quadruplicate. All vials were shaken on a rotary shaker for the duration of the study. To take a data point, the solutions were removed via syringe, and the polymer samples were rinsed with minimal distilled water (~1 mL). After removing the distilled water via syringe, the vials were put in a vacuum oven overnight (60°C, 30 inches Hg vacuum). The vials were cooled and weighed. Percent mass loss is given by $mass_o$-$mass_i$/$mass_o$. The same steps were repeated over a three-week period at different intervals.

Computational Methods: Computational experiments using Endo's methods[10] were performed in Spartan '14 (Windows 7). Structures were geometry optimized at the DFT B3LYP/6-31G* level of theory in the gas phase. Energies and electrostatic charges in toluene solvent were calculated as Single Point energies (DFT B3LYP/6-31G**) from the DFT-optimized structures. Energies, electrostatic charges, computed structures and coordinates of optimized structures are given in the SI (Figure S15).

ASSOCIATED CONTENT

Supporting Information. Experimental details, MALDI-TOF, kinetic plots, M_n vs conv, GPC traces, binding isotherm, thermodynamic data, ^1H and ^{13}C NMR spectra, computed structures, energies and coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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Table of Contents Graphic

“Controlled Organocatalytic Ring-Opening Polymerization of ε-Thionocaprolactone”

by Partha P. Datta and Matthew K. Kiesewetter*