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Organocatalytic ring-opening polymerization of thionolactones: anything O can do, S can do better†

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The H-bond mediated organocatalytic ring-opening polymerizations (ROPs) of four new thionolactone monomers are discussed. The kinetic and thermodynamic behavior of the ROPs is considered in the context of the parent lactone monomers. Organocatalysts facilitate the retention of the S/O substitution as well as the synthesis of copolymers. The thionoester moieties in the polymer backbone serve as a chemical handle for a facile crosslinking reaction, and the porosity of the resulting crosslinked polymer can be tuned by altering the thioester density in the (co)polymer. The crosslinked polymers are shown to be degradable in water, and an Au³⁺ recovery application is demonstrated.

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Introduction

Over the last two decades, organocatalysts for ring-opening polymerization (ROP) have become firmly established in the synthesis community for their ability to form precision macromolecules.¹ The H-bonding class of organocatalysts are notable for their ability to effect highly controlled polymerizations.^{2–5} This class of catalysts, often an H-bond donating (thio)urea plus an H-bond accepting organic base, are believed to effect ROP by H-bond activation of a lactone monomer and alcohol chain-end/initiator.^{5,6} More recently, (thio)urea/base-mediated ROP has been found to access an alternate mechanism of enchainment whereby proton transfer from (thio)urea to the base produces a highly active (thio)imidate that is among the most active and controlled catalysts for the ROP of lactones, carbonates and other cyclic monomers.^{7–10} Of particular importance here is the highly controlled aspect of the (thio)urea/base-mediated ROP, which allows for the polymerization of functionalized and heteroatom-containing monomers while retaining polymerization control.

New catalysts and mechanisms of polymer synthesis are one means of begetting new materials. Although monomer scope has broadened recently, organocatalysts have most fre-

quently been applied to the ROP of lactones, but these same systems have also been shown to be effective for the ROP of a thiolactone and a thionolactone.^{11,12} Polythioesters have properties similar to those of their polyester analogues;^{12–14} however, the altered materials properties of polythionolactones make them an especially enticing synthetic target.¹¹ *Versus* the corresponding polyesters, the polythionoesters possess altered physical properties, degradability and novel post polymerization functionalization abilities.¹¹ In 2016, our group disclosed the H-bond-mediated ROP of thionocaprolactone (tnCL).¹¹ *Versus* earlier studies,^{15,16} the key advance with this report was that the H-bond-mediated organocatalysts facilitate the retention of the S/O substitution during the ROP. This is vital for accessing the altered materials properties of thionolactones (*versus* thiolactones), and the organocatalytic methods allow for the synthesis of copolymers.¹¹ Reported here, we believe for the first time, is the ROP of ζ-thionoheptalactone (tnHL), η-thionononalactone (tnNL), ω-thionopentadecalactone (tnPDL), thiono-ethylene brassylate (tnEB) and copolymers.

Results and discussion

Thermodynamic studies

The substitution of S for O in thionolactones causes minimal perturbation of the thermodynamics of the ROP *versus* the parent lactone monomers. A slate of lactone monomers from 7- to 17-membered rings and their thionolactones analogues were prepared according to the established methods (Fig. 1, see the ESI†),^{17,18} and their temperature-dependent [M]_{eq} were measured by ¹H NMR revealing the entropy and enthalpy of

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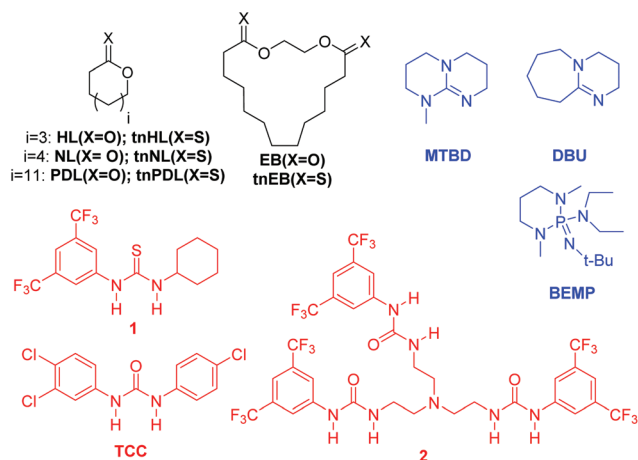


Fig. 1 Monomers and (co)catalysts used herein.

the ROP, Table 1. δ -Thionovalerolactone is known to autopolymerize at low temperature.¹⁴ The effect of the S substitution is most prominently seen in the ceiling temperature (T_{ceiling}), where tnHL and tnCL have lower T_{ceiling} versus HL and CL,

Table 1 Thermodynamics of ring-opening polymerization^a

Entry	Monomer	ΔH_p° (kcal mol ⁻¹)	ΔS_p° (cal mol ⁻¹ K)	T_{ceiling} (°C)	Ref.
1	CL	-5.90 ± 0.05	-8 ± 10	503	—
2	tnCL	-5.79 ± 0.32	-13 ± 1	156	11
3	HL	-4.60 ± 0.75	-8 ± 2	332	—
4	tnHL	-5.14 ± 0.43	-11 ± 1	193	—
5	NL	0 ± 2.5	7 ± 1	—	—
6	tnNL	0 ± 2.5	9 ± 1	—	—
7	PDL	0.7	6	—	20
8	tnPDL	0 ± 2.6	8 ± 1	—	—
9	EB	0 ± 2.6	15 ± 1	—	—
10	tnEB	0 ± 2.9	0.8 ± 1.1	—	—

^a Determined by measuring $[M]_{\text{eq}}$ versus temperature in solution, see the ESI† for full experimental details.

respectively. However, the larger (thiono)lactones (≥ 9) all possess temperature-independent equilibria, consistent with the so-called entropically controlled monomers.¹⁹ Our observations here are consistent with a previous study which showed thionylation of lactones to primarily alter the polymerization kinetics versus the thermodynamics.¹¹

Organocatalysis

Organocatalysts facilitate the ROP of strained and unstrained thionolactones with the retention of S/O substitution. A screen of polymerization conditions was conducted for the lactones and thionolactones as shown in Fig. 1, and the results are shown in Table 2. The full catalyst screen is shown in the ESI.† Our catalyst screen focused on the H-bonding class of organocatalysts because a previous study from our group demonstrated that strong base catalysts, even strong organic bases (e.g. DBU) in the absence of a H-bond-donating cocatalyst, will result in partial switching of the S/O substitution during the ROP to produce a poly(thiono-*co*-thioester).¹¹ Synthetic opportunities from this ‘liability’ can be envisaged, and this possibility is left to a future study. For all catalyst systems reported in Table 2, the retention of S/O substitution to form the polythionolactones is confirmed *via* ¹³C NMR (see the ESI†). The commercially available TCC along with MTBD or BEMP is a suitable cocatalyst system for the ROP of the all (thiono)lactones studied.²¹ The ROP of NL was sluggish with TCC, and the more active trisurea H-bond donor, 2, produces a faster and more controlled ROP. In general, the thionolactones are more labile than their lactone analogues, requiring less reaction time or a less active cocatalyst system.¹¹ The organocatalytic ROP of macro(thiono)lactones is optimally conducted at elevated temperatures, as previously established.²²

The organocatalytic ROP of thionolactones displays the characteristics of living polymerizations and is proposed to be mediated by a neutral H-bonding mechanism. Organocatalysts typically effect the ‘living’ ROP of lactone monomers: first-order consumption of monomer, linear evolution of M_n versus conversion and predictable M_n (from $[M]_0/[I]_0$).²⁰ For strained

Table 2 Organocatalytic ROP of (thiono)lactones^a

Entry	Monomer ($[M]_0$)	Cocatalysts	Solvent	$[M]_0/[I]_0$	Temp. (°C)	Time (h)	Conv. ^a (%)	M_n^b (g mol ⁻¹)	M_w/M_n^b
1	HL (2 M)	TCC/MTBD (5 mol%)	C ₆ D ₆	100	r.t.	5	90	19 200	1.02
2	tnHL (2 M)	TCC/MTBD (5 mol%)	C ₆ D ₆	100	r.t.	4	90	16 200	1.03
3	NL (2 M)	2/BEMP (1.67 mol%)	C ₆ D ₆	100	r.t.	10	90	23 200	1.30
4	tnNL (2 M)	TCC/BEMP (5 mol%)	C ₆ D ₆	100	r.t.	4	99	24 200	1.70
5	PDL (5 M)	TCC/MTBD (5 mol%)	Toluene	100	100	9.8	88	34 200	1.60
6	tnPDL (5 M)	TCC/MTBD (5 mol%)	Toluene	100	100	4.5	90	34 400	1.80
7 ^c	EB	TCC/BEMP (2 mol%)	Solvent-free	100	80	2	92	43 000	1.30
8	tnEB (2 M)	TCC/BEMP (5 mol%)	Toluene	100	80	4.5	64	10 600	1.90

^a Monomer conversion was monitored *via* ¹H NMR. ^b M_n and M_w/M_n were determined by GPC (CH₂Cl₂) versus polystyrene standards. ^c EB (2.95 mmol, 1 equiv.).

lactones (≤ 8 -membered rings), the ROPs are generally highly controlled with organocatalysts producing very narrow M_w/M_n (< 1.1). Unstrained lactones (> 9 -membered rings) typically experience post-enchaining transesterification that competes substantially with the enchainment events, producing broader M_w/M_n , but otherwise these ROPs can display the 'living' behavior.^{5,23–26} Hence, the thionolactones examined here are behaving 'normally' where the strained monomers (tnCL¹¹ and tnHL) yield narrowly dispersed polymers, and the unstrained monomers (tnNL in Fig. 2, tnPDL and tnEB) produce more broadly dispersed polymers. Metal-containing and organic catalysts have previously been shown to produce the ROP of unstrained lactones similar to what is observed here.^{3,19,22,26,27} Our thermodynamic studies corroborate previous suggestions that NL and tnNL are unstrained lactones,^{28–30} but the TCC/BEMP-cocatalyzed (0.031 mmol each) ROP of tnNL (2 M) from 1-pyrenebutanol (0.012 mmol) produces a polymer with overlapping UV and RI traces in the GPC (see the ESI[†]), further suggesting the 'living' behavior. The macrothionolactone, tnEB, displays a high equilibrium monomer concentration ($[M]_{eq} = 0.72$ M, $[2]_0$). The preponderance of evidence from our previous studies suggests that the TCC/base-mediated ROP in non-polar solvent occurs *via* a neutral H-bond-mediated mechanism. The 1/BEMP system has been shown to effect H-bond-mediated ROP, and TCC is less acidic than 1.^{7,8,10} The alternative (thio)imidate-mediated ROP mechanism available to (thio)urea/base-cocatalyzed ROP is not readily accessible in non-polar solvent with non-polar lactones (*e.g.* (tn)PDL and (tn)EB).^{6,9,10,26}

Co-polymerization

Organocatalysts facilitate the one-pot synthesis of copolymers of lactones and thionolactones. As an example, the TCC/BEMP-cocatalyzed (5 mol%, 0.0478 mmol each) copolymerization of PDL (2.5 M, 1.0 equiv.) and tnPDL (2.5 M, 1.0 equiv.) from benzyl alcohol (1 mol%, 0.0097 mmol) in toluene at 100 °C achieved full conversion to polymer in 5 h ($M_n = 34\ 100$, $M_w/M_n = 1.66$). The two monomers were observed to undergo ROP at similar rates (see the ESI[†], $k_{tnPDL}/k_{PDL} = 1.4$), suggesting

the formation of a random copolymer. Except for PtnEB, the melting points of the polythionolactones are suppressed *versus* those of the corresponding polylactones, as shown in Table 3. The full analysis of the altered materials properties of polythionolactones, including molecular weight-dependent properties, will be the subject of future work.

Oxidative crosslinking of polythionolactones

The oxidation of polythionolactones yields a degradable, cross-linked foam with controllable porosity. Sulfur is frequently used as a crosslinking handle,³³ and we sought to demonstrate the unique chemistry of thionolactones *via* an example oxidation reaction. The treatment of a CH₂Cl₂ solution (4 mL) of 200 mg of PtnCL (pre-crosslink $M_n = 20\ 600$) with 20 mL of commercial bleach solution yields a flexible, opaque, and spongy disc that is intractable in any solvent examined. This solid is swellable in organic solvents, suggesting a lightly crosslinked polymer, PtnCL-CLP. Repeating this experiment with homo-PtnHL, homo-PtnPDL and a PtnPDL-*block*-PCL copolymer revealed crosslinked polymers (CLPs) with progressively larger pores under optical microscopy, as shown in Fig. 3. The porosity and crosslink density of the several crosslinked polymers were measured with a swelling test in THF (see the ESI[†]) revealing a progressive attenuation of the crosslink density and progressive augmentation of the porosity with the

Table 3 Melting points of the poly(thiono)lactones^a

Polymer	M_n (g mol ⁻¹)	M_w/M_n	T_m (°C)	Ref.
PHL	17 100	1.02	61	—
PtnHL	14 900	1.19	19	—
PNL	25 500	1.48	70	—
PtnNL	24 200	1.70	0	—
PPDL	64 500	2.0	97	31
PtnPDL	34 400	1.80	62	—
PEB	55 100	1.50	78	32
PtnEB	10 800	1.90	72	—

^a M_n and M_w/M_n were determined by GPC (CH₂Cl₂) *versus* polystyrene standards.



Fig. 2 (Left) M_n versus conversion, and (Right) First-order evolution of [tnNL] versus time. Reaction conditions: tnNL (2 M, 0.632 mmol, 1 equiv.), benzyl alcohol (1 mol%, 0.0063 mmol) catalyzed by TCC/BEMP (5 mol%, 0.0315 mmol each) in C₆D₆.



Fig. 3 (a) Image of PtnPDL-CLP flexible polymer. (b) Images of PtnCL, PtnHL, and P(tnPDL-*b*-CL) CLPs (c) Cross sectional morphology of cross-linked polymers under optical microscopy; magnification $\times 10$.

Table 4 Calculated crosslink densities and porosity% of the CLPs^a

Crosslinked polythionolactone	Pre-crosslink M_n (M_w/M_n)	Swelling ratio	Porosity%	Crosslink density (n) (mmol cm^{-3})
PtnCL-CLP	20 600 (1.42)	4.60 ± 0.01	38.9 ± 0.1	6.47 ± 0.01
PtnHL-CLP	12 700 (1.47)	5.16 ± 0.02	47.4 ± 0.2	3.95 ± 0.02
PtnPDL-CLP	28 800 (1.68)	9.40 ± 0.03	54.6 ± 0.2	3.00 ± 0.01
P(tnPDL- <i>b</i> -CL)-CLP	31 000 (2.08)	9.72 ± 0.25	82.3 ± 0.9	0.45 ± 0.00

^a Swelling tests were carried out in THF at room temperature. Swelling ratios, porosity%, and the crosslink densities (n) were calculated as described in the ESI.

decreasing thionoester moiety content, as shown in Table 4. As expected, the PtnPDL-*block*-PCL-CLP has the largest porosity and lowest crosslink density of the studied samples, and this CLP becomes optically transparent when swollen (see the ESI).[†] In total, this suggests that the polythionolactone platform provides a means of generating crosslinked polymers with easily tunable porosity.

The crosslinked polythionolactones are degradable in aqueous solutions. The low crosslink density of the examined CLPs suggests that most of the thionolactone linkages remain unaltered from the oxidation procedures, and solid-state IR spectroscopy corroborates this suggestion (see the ESI[†]). The XPS analysis of PtnPDL-CLP at the C 1s core and S 2p core regions suggests the presence of C=S, disulfide and sulfone groups (see the ESI[†]). This suggests that some thionolactones are converted to disulfide and sulfone groups during the oxidation. This observation is reminiscent of the NaOCl-mediated oxidation/dimerization of thioketones whereby two thioketones are oxidized to the respective S oxides and undergo a [4 + 2] cycloaddition and rearrangement.³⁴ Nevertheless, previous studies from our group suggest that if the majority of the thio-

nolactone moieties were intact, the crosslinked polymers should degrade in water.¹¹ The PtnPDL-CLP samples were submerged in aqueous 0.25 M HCl, aqueous 0.25 M NaOH and deionized water and the weights of the samples monitored over days. In the basic solution, PtnPDL-CLP degraded to less than half of its original mass in 10 days. The sample was more stable (<10% mass loss in 10 days) in neutral and acidic media (see the ESI[†]), consistent with previous studies.¹¹ Despite being easily degradable *via* hydrolysis, the CLPs are thermally stable. The thermal gravimetric analysis of PtnPDL-CLP under N_2 revealed the onset of decomposition (T_d) at 421 °C. The chemical nature of the crosslink will be the subject of future studies.

Crosslinked polythionolactone as gold binding agent

Recent reports of waste gold recovery mediated by polymer-bound thiocarbonyls inspired us to apply our crosslinked polythionolactones to this challenge.³⁵ More than 25% of the annual demand for metallic gold is satisfied through recycling, especially electronic waste.^{35,36} Traditional solution-based, batch processes often employ stoichiometric reagents,^{35,37,38}

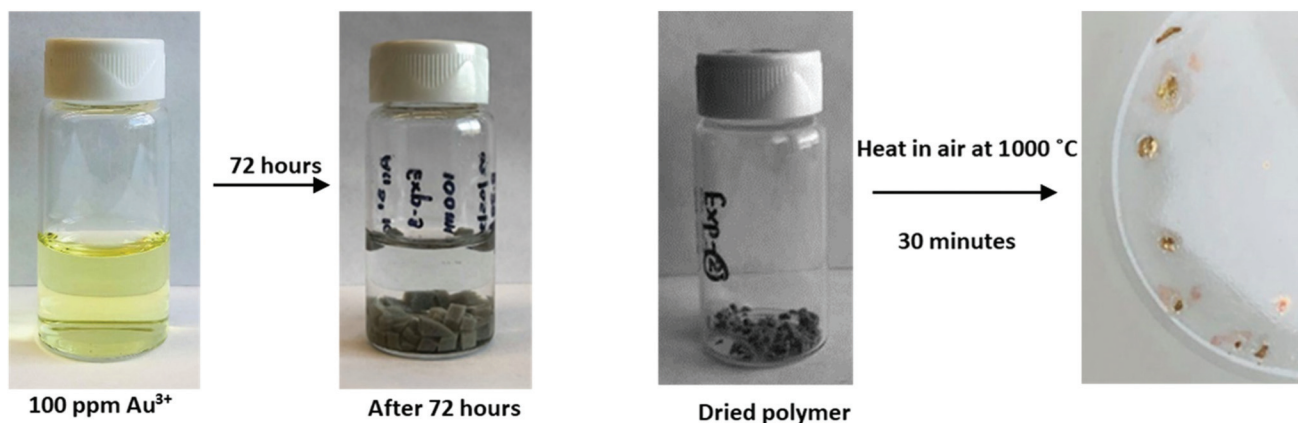


Fig. 4 Visual progress of $\text{Au}^{3+}_{(\text{aq})}$ extraction and Au^0 recovery mediated by 100 mg of PtnPDL-CLP. $[\text{Au}^{3+}]_0 = 100 \text{ ppm}$, Au^{3+} volume = 10 mL.

and the benefits of a polymer-based approach can be envisaged. PtnPDL-CLP (100 mg) was cut into small pieces (~5 mm) and added to an aqueous solution of NaAuCl_4 (100 mg L^{-1} in Au^{3+} , 10 mL), and the amount of Au^{3+} in the remaining solution over time was determined *via* UV-vis, according to established methods.^{33,35} After 3 days, the previously yellow solution turned colorless, and the UV-vis signal (Au^{3+}) was 12% as the starting intensity, suggesting 88% extraction efficiency. Isolation of the PtnPDL-CLP followed by heating in air ($1000 \text{ }^\circ\text{C}$) to remove the organic portion revealed 0.85 mg of a lustrous gold-colored metal (97% yield for Au^0), as shown in Fig. 4. A flow-through version of this batch process, including the extraction of other metals, can be envisaged. Recent studies have shown that sulfur-containing polymers are also capable of extracting toxic heavy metals.^{33,35}

Conclusion

Organocatalysts previously developed for the ROP of lactones were applied to the ROP of thionolactones. The highly controlled urea/base cocatalysts facilitated the synthesis of polythionolactones and their copolymers *via* a proposed H-bond mediated mechanism. These mild catalysts are essential to preserve the S/O substitution that renders the thionoester chemical handle in the polythionolactones. The mild and facile oxidative crosslinking of polythionolactones forms a degradable polymeric foam. Again, the highly general nature of the (thio)urea/base-mediated ROP toward cyclic monomers, broadly considered, facilitates the synthesis of a host of copolymers that allow the porosity of the subsequent crosslinked system to be tuned. Catalytic advances directly facilitate the synthesis of new materials, and fundamental, mechanistic chemistry begets new applications.

Conflicts of interest

There are no conflicts to declare.

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