Organocatalytic Ring-opening Polymerization of Thionolactones: Anything O Can Do, S Can Do Better

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Organocatalytic Ring-opening Polymerization of Thionolactones: Anything O Can Do, S Can Do Better

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ABSTRACT

The H-bond mediated organocatalytic ring-opening polymerizations (ROPs) of four new thionolactones monomers is discussed. The kinetic and thermodynamic behavior of the ROPs are 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 Au^{3+} recovery application is demonstrated.

INTRODUCTION

Over the last two decades, organocatalysts for ring-opening polymerization (ROP) have become firmly established in the community for their ability to synthesize 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 activating a lactone monomer and alcohol chain-end/initiator.[5,6] More recently, (thio)urea/base mediated ROP have been found to access an alternate mechanism of enchainment whereby proton transfer from (thio)urea to 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 (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 frequently been applied to the ROP of lactones, but these same systems have been shown to be effective for the ROP of a thiolactone and a thionolactone.[11,12] Polythioesters have similar properties to their polyester analogues;[12–14] however, the altered materials properties of polythionolactones make them an especially enticing synthetic target.[11] Versus the corresponding polyesters, polythionoesters feature 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 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-thiononalactone (tnNL), ω-thionopentadecalactone (tnPDL), thiono-ethylene brassylate (tnEB) and copolymers.

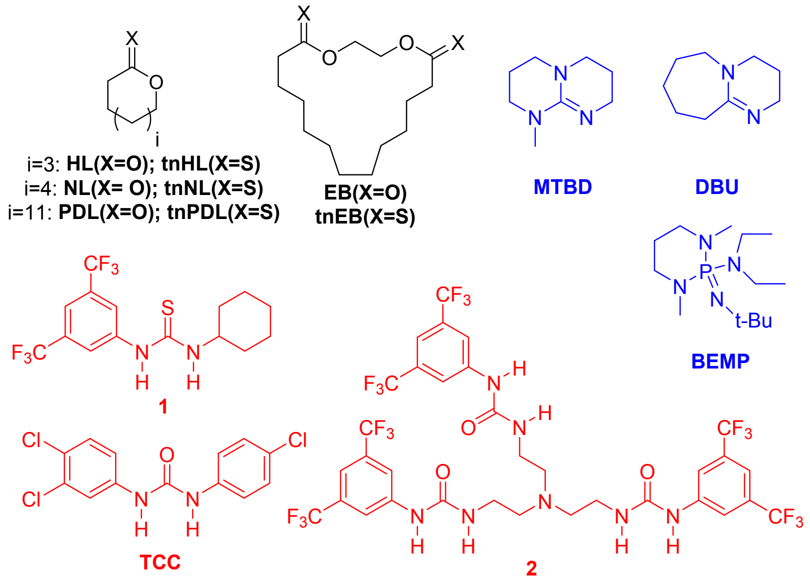


Figure 1. Monomers and (co)catalysts used herein.

RESULTS AND DISCUSSION

Thermodynamic Studies. The substitution of S for O in thionolactones provides minimal perturbation to the thermodynamics of ROP versus the parent lactone monomers. A slate of lactone monomers from seven to seventeen membered rings and their thionolactones analogues were prepared according to established methods (Figure 1, see SI),[17,18] and their temperature dependent $[M]_{eq}$ were measured by ^{1}H NMR revealing the entropy and enthalpy of 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, 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 polymerization kinetics versus thermodynamics.[11]

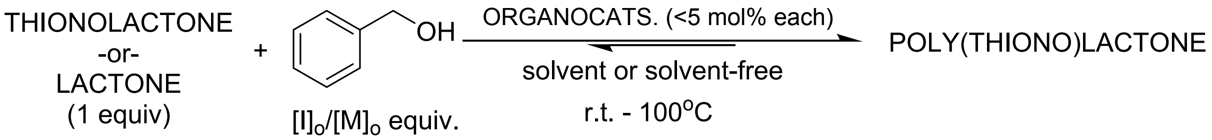
Table 1. Thermodynamics of Ring-Opening Polymerization[a]

entry	monomer	ΔH°_p (kcal/mol)	ΔS°_p (cal/mol 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 $[M]_{eq}$ versus temperature in solution, see SI for full experimental details.

Organocatalysis. Organocatalysts facilitate the ROP of strained and unstrained thionolactones with retention of S/O substitution. A screen of polymerization conditions was conducted for the lactones and thionolactones shown in Figure 1, and the results are shown in Table 2. The full catalyst screen is shown in the SI. 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 an 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 ^{13}C NMR (see SI). The commercially available TCC plus MTBD or BEMP is a suitable cocatalyst system for the ROP of 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 less active cocatalyst system.[11] The organocatalytic ROP of macro(thiono)lactones is optimally conducted at elevated temperatures, as previously established.[22]

Table 2. Organocatalytic ROP of (thiono)lactones[a]



entry	monomer ($[M]_o$)	cocatalysts	solvent	$[M]_o/[I]_o$	temp. (°C)	Time (h)	conv. (%)[a]	M_n[b] (g/mol)	M_w/M_n[b]
1	HL (2 M)	TCC/MTBD (5 mol%)	C_6D_6	100	r.t	5	90	19,200	1.02
2	tnHL (2 M)	TCC/MTBD (5 mol%)	C_6D_6	100	r.t	4	90	16,200	1.03
3	NL (2 M)	**2**/BEMP (1.67 mol%)	C_6D_6	100	r.t	10	90	23,200	1.30
4	tnNL (2 M)	TCC/BEMP (5 mol%)	C_6D_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 (CH_2Cl_2) versus polystyrene standards. c. EB (2.95 mmol, 1 equiv).

The organocatalytic ROP of thionolactones display the characteristics of living polymerizations and are proposed to be mediated by a neutral H-bonding mechanism. Organocatalysts typically effect 'living' ROPs of lactone monomers: first order consumption of monomer, linear evolution of M_n versus conversion and predictable M_n (from $[M]_o/[I]_o$).[20] For strained lactones ($\leq$ 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-enchainment transesterification that competes substantially with enchainment events, producing broader M_w/M_n, but otherwise these ROP can display 'living' behavior.[5,23–26] Hence, the thionolactones examined here are behaving 'normally' where the strained monomers (tnCL[11] and tnHL) yield narrowly dispersed polymers, and the unstrained monomers (tnNL in Figure 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 (0.031 mmol each) cocatalyzed ROP of tnNL (2 M) from 1-pyrenebutanol (0.012 mmol) produces a polymer with overlapping UV and RI traces in the GPC (see SI), further suggesting 'living' behavior. The macrothionolactone, tnEB, displays a high equilibrium monomer concentration ($[M]_{eq}$ = 0.72 M, $[2]_o$). The preponderance of evidence from our previous studies suggests that 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 alternate (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]

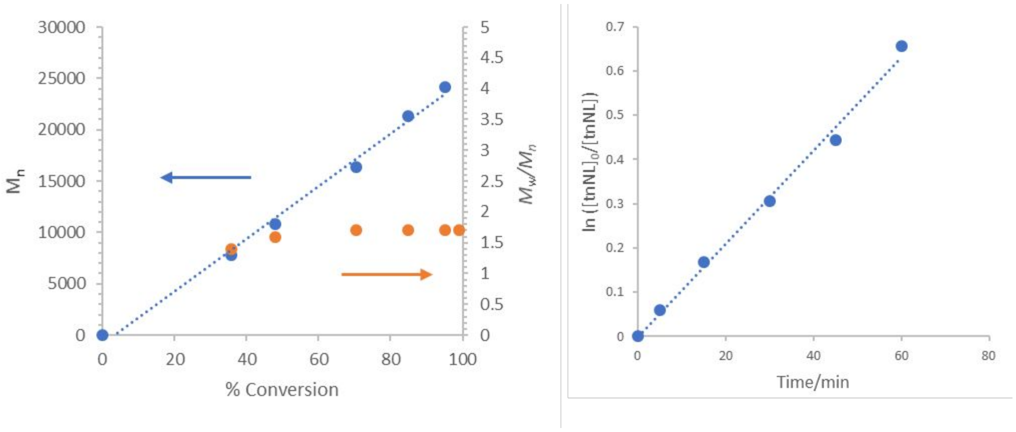


Figure 2. (Left) M_n versus conversion, and (Right) First order evolution of [tnNL] versus time. Reaction conditions: tnNL (2 M, 0.632 mmol, 1 equiv), benzyl alcohol (1 mol%, 0.0063 mmol) catalyzed by TCC/BEMP (5 mol%, 0.0315 mmol each) in C_6D_6.

*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 SI, k_{tnPDL}/k_{PDL} = 1.4), suggesting formation of a random copolymer. Except for PtnEB, the melting points of the polythionolactones are suppressed versus the corresponding polylactones, Table 3. Full analysis of the altered materials properties of polythionolactones, including molecular weight dependent properties, will be the subject of future work.

Table 3. Melting Points of the Poly(thiono)lactones[a]

Polymer	**M_n (g/mol)**	**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 (CH_2Cl_2) versus polystyrene standards.

Oxidative Crosslinking of Polythionolactones. The oxidation of polythionolactones yields a degradable, crosslinked foam with controllable porosity. Sulfur is frequently employed as a crosslinking handle,[33] and we sought to demonstrate the unique chemistry of thionolactones via an example oxidation reaction. Treatment of a CH_2Cl_2 solution (4 mL) of 200 mg of PtnCL (pre-crosslink M_n = 20,600) with 20 mL commercial bleach solution (20 mL) yields a flexible, opaque, spongy disk 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, Figure 3. The porosity and crosslink density of the several crosslinked polymers was measured with a swelling test in THF (see SI) revealing a progressive attenuation of the crosslink density and progressive augmentation of the porosity with decreasing thionoester moiety content, 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 SI. In total, this suggests that the polythionolactone platform provides a means of generating crosslinked polymers with easily tunable porosity.

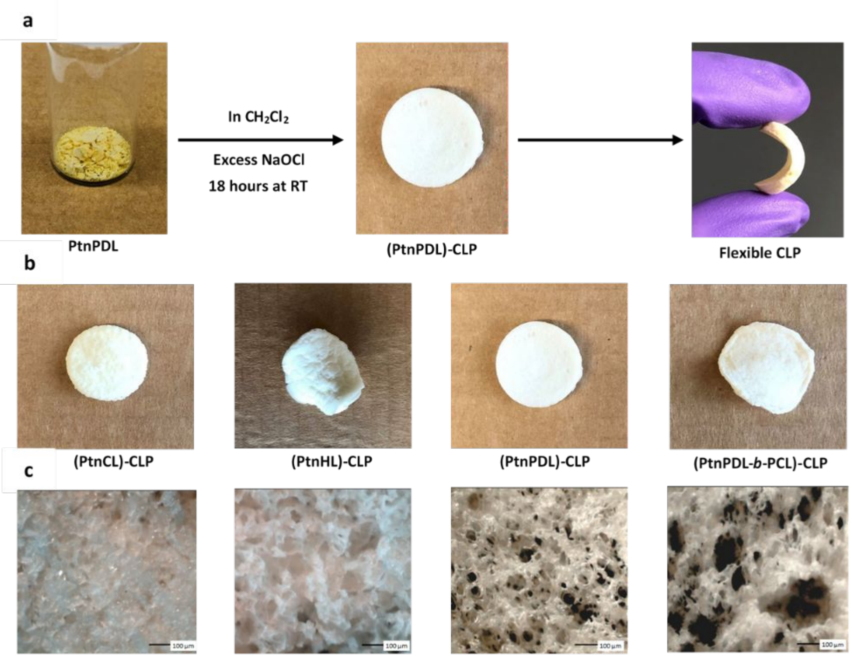


Figure 3. (a) Image of PtnPDL-CLP flexible polymer. (b) Images of PtnCL, PtnHL, and P(tnPDL-*b*-CL) CLPs (c) cross sectional morphology of crosslinked polymers with optical microscopic; magnification X 10.

Table 4. Calculated crosslinked densities and porosity% of the CLPs[a]

Crosslinked polythionolactone	Pre-crosslink M_n (M_w/M_n)	swelling ratio	porosity%	crosslinked 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-*b*-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 crosslinked densities (***n***) were calculated using equation (1), (2), and (4), respectively.

The crosslinked polythionolactones are degradable in aqueous solutions. The low crosslink density of the examined CLPs suggests that most of the thionolactones linkages remain unaltered from the oxidation procedures, and solid-state IR spectroscopy corroborates this suggestion (see SI). 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 SI). 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] Regardless, previous studies from our group suggest that if the majority of the thionolactones moieties were intact, the crosslinked polymers should degrade in water.[11] PtnPDL-CLP samples were submerged in aqueous 0.25 M HCl, aqueous 0.25 M NaOH and deionized water, and the weight 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 SI), consistent with previous studies.[11] Despite being easily degradable via hydrolysis, the CLPs are thermally stable. Thermal gravimetric analysis of PtnPDL-CLP under N_2 revealed 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.[36,35] Traditional solution-based, batch processes, methods often employ stoichiometric reagents,[35,37,38] and benefits to 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 in Au^{3+}, 10 mL), and the amount of Au^{3+} in remaining solution over time was determined via UV-vis, according to established methods.[33,35] After 3 days, the once yellow solution appeared colorless, and the UV-vis signal (Au^{3+}) was 12% the starting intensity, suggesting 88% extraction efficiency. Isolation of the PtnPDL-CLP followed by heating in air (1000°C) to remove the organic portion revealed 0.85 mg of a lustrous gold-colored metal (97% yield for Au^0), Figure 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]

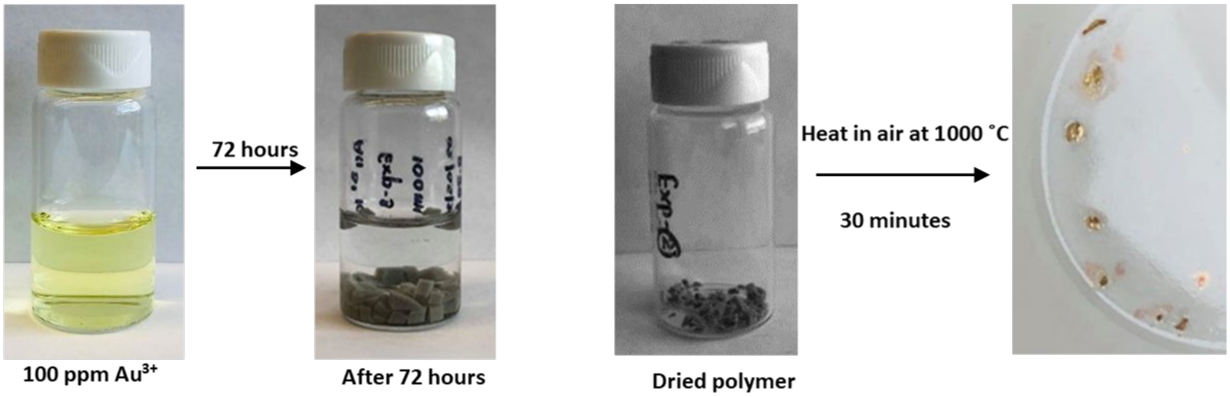


Figure 4. Visual progress of $Au^{3+}_{(aq)}$ extraction and Au^o recovery mediated by 100 mg of PtnPDL-CLP. $[Au^{3+}]_o$ = 100 ppm, Au^{3+} volume = 10 mL.

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 which 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 (thio)urea/base mediated ROP toward cyclic monomers, broadly considered, facilitates the synthesis of a host of copolymers which renders tunable the porosity of the subsequent crosslinked system. Catalytic advances directly facilitate the synthesis of new materials; fundamental, mechanistic chemistry begets new applications.

AUTHOR INFORMATION

Conflicts of Interest

There are no conflicts to declare.

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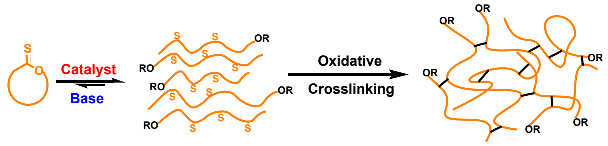
TOC Graphic:



Organocatalysts facilitate the synthesis of polythionolactones; oxidative crosslinking yields a degradable polymer foam.