# Modulating Polymerization Thermodynamics of Thiolactones Through Substituent and Heteroatom Incorporation

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(mol·K)) of polymerization allows for a monomer whose equilibrium polymerization conversion is very sensitive to temperature.

**E** ach year, more than 300 million tons of plastic waste are produced worldwide.<sup>1</sup> The majority of this plastic waste is either landfilled, combusted, or polluted into the environment, leaving only a small fraction that is recycled.<sup>2</sup> Of the plastic waste that is recycled, most is converted into lower quality materials.<sup>3</sup> An emerging approach that seeks to address this issue is chemical recycling to monomer (CRM).<sup>2,4–13</sup> In CRM, the polymer is depolymerized back to its monomeric starting material, which can then be used to remake the polymer with no loss in material properties.

Monomers with ceiling temperatures  $(T_c)$  near ambient temperatures (and below) are good candidates for chemical recycling. The  $T_{\rm c}$  of a monomer is defined as the temperature at which the rates of polymerization and depolymerization are equal, which occurs when the Gibbs free energy of polymerization  $(\Delta G_p)$  is zero. The  $T_c$  is thus determined by both the enthalpy  $(\Delta H_p^o)$  and entropy  $(\Delta S_p^o)$  of polymerization,<sup>14</sup> and low- $T_c$  monomers can be targeted by identifying systems that have the proper balance of enthalpic and entropic contributions to the polymerization reaction. For a polymerization equilibrium to be temperature-dependent in a manner that allows for practical depolymerization, the entropic contribution (favoring depolymerization) must be able to overcome the exothermicity of monomer addition (favoring polymerization) at reasonable temperatures (Figure 1A). Thus, polymers made from low- $T_c$  monomers can be reprocessed at temperatures mild enough to minimize chemical side reactions and energy consumption. While T<sub>c</sub> is an important parameter often used to qualify monomers for CRM, it is important to consider the ratio of the individual  $\Delta H_p^o$  and  $\Delta S_p^o$  values, as this determines how sensitive the polymerization equilibrium is to temperature. A monomer that is ideally suited for CRM would display a narrow and near-ambient temperature range in which it can be fully polymerized and depolymerized.

A variety of monomers have been explored for the use of low  $T_c$  polymers in CRM, including lactones,<sup>15–28</sup> phthalaldehydes,<sup>29,30</sup> carbonates,<sup>31–36</sup> cyclic acetals,<sup>37</sup> and others.<sup>38,39</sup> Early efforts largely focused on lactones,<sup>40</sup> but the rates of polymerization and depolymerization are prohibitively slow for many applications. This has led to an increased interest in thiolactones, which polymerize and depolymerize more rapidly due to rapid thiol-thioester exchange reactions.<sup>41,42</sup> The first thiolactone ring-opening polymerization was reported by Overberger in 1968 for the synthesis of poly-(thiocaprolactone).<sup>43</sup> After receiving minimal attention in the literature since that time, thiolactones have seen renewed interest in the field and a number of groups have recently revisited this monomer class (Figure 1B) and thioester-based materials in general.<sup>44–56</sup> Ghadiri and Bowman explored polythioester systems to create abiotic mimics of polypeptides

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C. This Work: Design evolution of six-membered thiolactone monomers



More negative  $\Delta H_p$  and more negative  $\Delta S_p$ Substitution induced conformational change

**Figure 1.** (A) Thermodynamics of ceiling temperature  $(T_c)$ . (B) Recently reported thiolactone monomers. (C) This work: Design evolution of six-membered thiolactones via sulfur substitution and methylation; gray, C; white, H; red, O; yellow, S.

and polynucleic acids, respectively, that could undergo dynamic reorganization of the polymer sequence via thiolthioester exchange. More recent studies by the Lu, Chen, and Tao groups have each focused on developing low  $T_c$  thiolactones for applications in chemical recycling. Lu has developed a number of thiolactone systems that can be polymerized to yield high molecular weight polymers with narrow dispersities.<sup>46</sup> Chen has built upon Lu's [2.2.1] bicyclic framework to yield stereodisordered polythioesters with high crystallinity and chemical recyclability.<sup>47</sup> Most recently, Tao has investigated alkylated dithiolactones, and shown them to possess high polymerizability, chemical recyclability, and crystallinity.<sup>49</sup> While these reports have contributed to the understanding of thiolactone polymerizations, there is still much to learn with regard to how changes to ring size, substituents, and heteroatomic substitution impact polymerization thermodynamics.

In this work, the synthesis and polymerization behavior of a series of six-membered thiolactone derivatives is reported, augmented by insights from computational studies (Figure 1C). Through systematic heteroatom substitution and methylation, the monomer-polymer equilibria can be significantly modulated through surprising changes to the ground state monomer conformation. From this study, an improved understanding of how sulfur atoms affect the conformations of thiolactone monomers is gained and leads to a nonintuitive approach for modulating polymerization thermodynamics.

Interest in six-membered thiolactone derivatives was prompted by Overberger's early attempts to polymerize thiovalerolactone (TVL, 1).<sup>43</sup> In these studies, low molecular weight polymers were obtained at high temperatures, suggesting that TVL may have a low ceiling temperature. To test this hypothesis, a series of six-membered thiolactone monomers were designed to investigate polymerization behavior at reduced temperatures (Figure 2). Based on the Thorpe–Ingold effect,<sup>57</sup> the introduction of methyl groups to the monomers was expected to accelerate the rate of cyclization, thereby favoring depolymerization and lowering the  $T_c$ . Two series of monomers were synthesized that varied in methylation and sulfur substitution: TVLs (1-5) and 1,4dithianones (DTNs; 6-9). For both series, methyl groups were introduced at different positions to study the effect of alkyl substitution on polymerizability. All monomers were prepared through two general strategies. TVLs 1-5 were prepared following Scanlan's protocol involving thiol-ene reaction, hydrolysis, and Steglich cyclization.58 The DTN monomers (6-9) were prepared based on Lenoir's reaction of ethane dithiol with the appropriate haloacetyl halides (see SI3-SI8 for synthetic details).<sup>59</sup> Monomers were all prepared in 31-61% yields from commercially available materials and were readily scaled for production of sufficient quantities to evaluate polymerization behavior (500 mg to 12 g).

Initial polymerization studies on this collection of thiolactone monomers were performed to identify reaction conditions to produce polymeric material. Anionic polymerizations were performed in either CDCl<sub>3</sub> or THF using 1dodecanethiol as the initiator and 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU) as the base. Depending on the monomer, concentrations ranged from 3 M to bulk and temperatures from room temperature to -33 °C (Table 1). All polymerizations were found to be rapid and reached equilibrium after 30 min, after which time they were quenched with trifluoroacetic acid (TFA). Polymers that showed conversion were isolated by precipitation, then characterized by size-exclusion chromatography (SEC), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The results of the polymerizations are summarized in Table 1. The molecular weights of the polymers ranged from 3.7 to 18.7 kDa, and generally correlated with the overall conversion of the monomers. High dispersities were observed for all polymers, likely due to chain transfer events derived from transthioesterification of the polymer backbone, as indicated by GPC (Figures S9-S15). Semicrystalline materials were observed by DSC with monomers that lacked side chains (1 and 6) and amorphous polymers were obtained from monomers containing side chains (2, 3, and 7-9). Glass transition temperatures for all systems were generally low (-40)to 19 °C) but could be increased by the introduction of methyl



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Figure 2. Synthesis of TVL and DTN monomers.

Table 1. Polymerizations of Thiolactone Monomers

		<b>X</b> =	= CH <sub>2</sub> or S H, Me, or P	R Ph	200 eq.	1 eq. 1 e th	C <sub>12</sub> H <sub>25</sub> SH eq. DBU	► C <sub>12</sub> H <sub>25</sub>		s) <sub>n</sub>		
Entry	Monomer	Т (°С)	Conc. (M)	Conv. <sup>a</sup>	Mn <sup>b</sup> (kDa)	$\mathbb{D}^{b}$	$\Delta H_{calc}^{c}$ (kJ/mol)	ΔH <sup>o</sup> p (kJ/mol)	ΔS <sup>o</sup> p (J/(mol·K))	Tc <sup>d</sup> (°C)	Td, 5% (°C)	T <sub>g</sub> (°C)
1 <sup>e</sup>	o s	rt	5	46%	14.3	2.1	-2.3	-4.9	-23.7	-66	245	Not observed $(T_m = 123)$
2	Me	0	5	35%	15.2	1.7	-2.0	-4.5	-26.2	-101	265	-40
3 <sup>f</sup>	Me S	-33	7.3 (bulk)	16%	5.6	1.3	-5.7	-	-	-	223	-34
4	Me	-20	8.5 (bulk)	0%	-	-	-5.4	-	-	-	-	-
5	Me Me	-20	7.1 (bulk)	0%	-	-	-18.3	-	-	-	-	-
6 <sup>e</sup>	s s	rt	5	87%	15.8	1.6	-10.7	-9.5	-30.8	34	184	-34 (T <sub>m</sub> = 88)
7	Me S S	rt	8.2 (bulk)	70%	18.7	2.2	-5.4	-10.2	-39.9	-18	218	-25
8		0	3	91%	18.1	2.1	-18.3	-19.3	-58.4	58	239	-12
9 <sup>g</sup>	Ph S	0	3	36%	3.7	1.9	-7.2	-	-	-	242	19

<sup>*a*</sup>Conversion determined by <sup>1</sup>H NMR in CDCl<sub>3</sub>. <sup>*b*</sup>Determined by CHCl<sub>3</sub> size-exclusion chromatography (SEC) calibrated using polystyrene standards. <sup>*c*</sup>Calculated as described in ref 61. <sup>*d*</sup> $T_c$  expressed at 1 M conditions. <sup>*e*</sup>THF was used instead of CDCl<sub>3</sub> for the polymerization of these monomers. <sup>*f*</sup>Experimental thermodynamic values not obtainable due to low equilibrium polymerization conversion. <sup>*g*</sup>Experimental thermodynamic values not obtainable due to polymer insolubility at low temperature.

and phenyl substituents that inhibit rotation of the polymer backbone.

As expected, the monomer conversion of these polymerizations was highly dependent on the monomer structure. Using a 5 M monomer concentration at room temperature, TVL (1) achieved 46% conversion at equilibrium (Table 1, entry 1). Attempts to increase the monomer concentration as a means to increase conversion were prevented by the insolubility of the polymer product in all solvents explored. The introduction of the methyl substituent in  $\alpha$ -methyl TVL

(2) yielded a more soluble polymer, but also led to a decrease in the equilibrium polymer conversion to 35% at 5 M monomer concentration (Table 1, entry 2). This was anticipated according to the Thorpe-Ingold effect, as discussed above. The substitution effect was heightened in the polymerization of  $\alpha_{,\alpha}$ -dimethyl TVL (3) and displayed only 16% conversion to polymer when performed in the bulk (Table 1, entry 3). Surprisingly, introducing one or two methyl substituents at the  $\beta$ -position led to complete inhibition of polymerization in the bulk at temperatures as low as -20 °C (Table 1, entries 4 and 5), possibly due to a conformational impact of the ring-opened state.48 The parent DTN (6) monomer displayed a much higher equilibrium polymer conversion (87%) compared to the parent TVL monomer (1) under the same reaction conditions. While the introduction of one methyl group in  $\alpha$ -methyl DTN (7) led to a decrease in polymer conversion (70%, in the bulk), addition of the second methyl in  $\alpha$ , $\alpha$ -dimethyl DTN (8) led to a significant increase in conversion (91%) even at lower concentrations (3 M). Further experiments were performed to better understand this counterintuitive result and elucidate the relative roles of ring-strain and entropy in each of these systems.

To gain insight into the underlying thermodynamics of these systems, variable temperature NMR (VT-NMR) experiments were performed to measure the change in monomer equilibrium as a function of temperature. This enabled the experimental determination of  $\Delta H_p^{\circ}$  and  $\Delta S_p^{\circ}$  through van't Hoff analysis. Applying the Dainton equation, the  $T_c$  could also be obtained. A general procedure for the van't Hoff analysis and corresponding plots is included in the SI (Figures S30– S34). Given the different solubilities and polymerizabilities of these monomers, the entropy of polymerization and ceiling temperature ( $T_c$ ) values in Table 1 are normalized to 1 M. VT-NMR data were not obtained for monomers 3, 4, and 5 due to insufficient conversion at the concentration used for the experiments.

The thermodynamic trends observed during VT-NMR were in general agreement with the conversion results discussed above. Specifically, an increased enthalpy and decreased entropy of polymerization was observed upon methylation of 1 ( $\Delta H_p^o = -4.9 \text{ kJ/mol}$  and  $\Delta S_p^o = -23.7 \text{ J/(mol·K)}$ ) to 2 ( $\Delta H_p^o = -4.5 \text{ kJ/mol}$  and  $\Delta S_p^o = -26.2 \text{ J/(mol·K)}$ ), leading to a decrease in  $T_c$  from -66 to -101 °C. As observed during the initial polymerization studies, the DTN monomer series 6-8 did not follow trends expected from the Thorpe-Ingold effect. Table 1 shows how addition of one methyl substituent leads to a slightly more exothermic polymerization of 7 ( $\Delta H_p^o = -10.2$ kJ/mol) and a  $T_c$  of -18 °C was measured. However, introduction of the second methyl group in 8 significantly decreased the  $\Delta H_p^o$  (-19.3 kJ/mol) and the  $\Delta S_p^o$  (-58.4 J/ (mol·K)), leading to a  $T_c$  of 58 °C. To highlight the different polymerization behaviors of DTNs 6-8, a graph of the conversions at different temperatures predicted by the Dainton equation was plotted for these monomers using the thermodynamic values obtained (Figure 3). At first consideration, it would seem that a lower ceiling temperature would lead to a more easily recyclable material. This plot demonstrates that this assumption can be misleading. The more exothermic and exoentropic ring-opening of DTN 8 allows it to reach high conversions at near-ambient temperatures, while still maintaining a relatively low  $T_c$ . In addition, the larger magnitude of  $\Delta S_{\rm p}^{\rm o}$  in 8 gives an equilibrium



**Figure 3.** Predicted polymer conversion at different temperatures. Plotted at 1 M using the van't Hoff equation and experimental values of  $\Delta H_p^{\circ}$  and  $\Delta S_p^{\circ}$ .

monomer conversion that is much more sensitive to changes in temperature. This allows the monomer to shift from a highly polymerized to fully depolymerized state with a relatively small change in temperature. To demonstrate this behavior on an isolated polymer sample, a 0.5 M solution of  $poly(\alpha,\alpha-dimethyl DTN)$  in THF was treated with substoichiometric quantities of DBU and dodecanethiol (1 mol % relative to each repeating unit). After heating the reaction at 80 °C for 1 h, <sup>1</sup>H NMR and SEC (Figures S37 and S38) showed 90% conversion back to monomer.

Due to the insolubility of the  $\alpha$ -phenyl homopolymer (9), VT-NMR analysis could not be carried out. However, monomer 9 was still viable for copolymerization experiments to explore how monomers that are not easily homopolymerized can be kinetically trapped in a copolymer product and modify the thermal properties. A first experiment was performed using a 4:1 ratio of 8:9 and resulted in a polymer composed of 88% monomer 8 and 12% monomer 9 (Table S10, entry 1). A second experiment was conducted using a 3:1 ratio of 8:9 and resulted in 83% incorporation of monomer 8 and 17% monomer 9 (Table S10, entry 2). The thermal properties of these copolymers were also tested, which revealed two distinct glass transition temperatures (Table S10 and Figures S39 and S40). The presence of two  $T_{gs}$  could suggest phase separation from block-like incorporation of 8 into the polymer backbone.<sup>60</sup>

To better understand the unexpectedly high exothermicity in the ring-opening of monomer 8, we have developed a firstprinciples based computational strategy to compute  $\Delta H$ .<sup>61</sup> By adequately incorporating conformational sampling through ab initio molecular dynamics and extrapolating schemes to access behavior at large length-scales, this important quantity can now be computed accurately for a large and chemically diverse set of ring-opening polymers. This capability is separately described and validated against a diverse benchmark set of



Figure 4. Energy-minimized configurations of DTN (6),  $\alpha$ -methyl DTN (7),  $\alpha$ , $\alpha$ -dimethyl DTN (8), and  $\alpha$ -phenyl DTN (9); gray, C; white, H; red, O; yellow, S.

polymers produced using ring-opening polymerization. In the present contribution, this procedure is adopted to calculate enthalpies of polymerization  $\Delta H_{calc}$  for polymers considered here, and the  $\Delta H_{\text{calc}}$  results are shown in Table 1. As can be seen,  $\Delta H_{calc}$  correlates well with available experimentally determined  $\Delta H_p^o$  for monomers, including low  $\Delta H_{calc}$  values for 4 and 5 that were completely resistant to polymerization. While the  $\Delta H_{calc}$  of 8 was in good agreement with the experimental results, further insights into the origins of this change were seen in the ground state monomer conformations obtained in the DFT calculations. TVL monomers 1-3consistently featured half-chairlike conformations (Figure S42) that followed the expected polymerization trends. Interestingly, the introduction of a second sulfur atom caused the DTN monomers 6 and 7 to adopt a boat conformation (Figure 4), which was further supported by the crystal structure obtained for  $\alpha$ -phenyl-DTN (9). A similar boat conformation was recently observed by Tao and co-workers for analogous dithiolactone monomers.<sup>49</sup> As seen in Figure 4, the boat conformation causes two hydrogen atoms to point internally toward each other, which increases ring strain through transannular interactions and explains why DTN 6 possesses a higher  $\Delta H_p^o$  than TVL 1. Substitution of both  $\alpha$ -hydrogens for two methyl groups in DTN 8 would lead to severe transannular strain between the methyl and hydrogen substituents in the boat configuration. This prompts a conformational change to a flattened structure with increased ring strain as observed in the more negative  $\Delta H_p^o$  (Figure 4).

In summary, the effect of methyl substitution and sulfur incorporation on the polymerization thermodynamics of a series of thiolactone monomers was investigated. Polymerization and VT-NMR experiments revealed that addition of methyl substituents to the TVL monomers favors depolymerization and lowers the T<sub>c</sub>. First-principles computations and crystallographic data showed how the addition of a sulfur heteroatom in the DTN series alters the ground state conformation and polymerization thermodynamics in nonintuitive ways. DTNs were observed to preferentially adopt a boat structure, but the addition of bulky substituents in 8 further disrupts the monomer geometry to give increased monomer strain and exoentropicity. This highlights the importance of the magnitude of  $\Delta H_{\rm p}^{\rm o}$  and  $\Delta S_{\rm p}^{\rm o}$  values in designing low ceiling-temperature monomers with efficient recyclability. With insufficiently small  $\Delta S_p^o$  values, a monomer with a low  $T_{\rm c}$  may still require large changes in temperature to reach reasonable conversions. Having the appropriate combination of thermodynamic values can give rise to systems capable of high conversion at modest temperatures, while still retaining polymerization equilibria highly sensitive to temperature. It is anticipated these findings will further the rational development of low ceiling temperature thiolactone monomers

and encourage the exploration of heterocyclic systems that have nontraditional ground-state conformations.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmacrolett.2c00319.

X-ray crystallographic data for **9** (CIF) Experimental details and characterization data (PDF)

#### **Accession Codes**

CCDC 2174022 contains supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_ request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; Fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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