# Macromolecules

## Oxygen/Sulfur Scrambling During the Copolymerization of Cyclopentene Oxide and Carbon Disulfide: Selectivity for Copolymer vs Cyclic [Thio]carbonates

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**S** Supporting Information

**ABSTRACT:** The catalytic coupling of cyclopentene oxide with carbon disulfide has been investigated utilizing (salen)-CrCl in the presence of added onium salts. Both polymeric and cyclic materials were produced, with oxygen/sulfur atom scrambling observed in both instances. This atom redistribution process was found to require (salen)CrCl and excess epoxide, though an increase in the rate of atom scrambling was noted upon the addition of the onium salt. Cyclopentene sulfide was observed as a side product of the coupling reaction



and was found to be unreactive toward both  $CS_2$  and  $CO_2$ , instead undergoing desulfurization to cyclopentene under the conditions of the reaction. Of the 12 cyclic cyclopentene [thio]carbonates possibly produced by this coupling reaction, eight were observed, and the crystal structure of *trans*-cyclopentene trithiocarbonate is reported herein. Computational studies reveal that the *cis*- cyclic materials are more stable than their *trans*-counterparts by >5 kcal/mol of enthalpy, and there is a 10–25 kcal/mol preference for the formation of a C=O vs C=S double bond. When *trans*-cyclohexene trithiocarbonate was exposed to the catalyst system in the presence of excess cyclopentene oxide, mixed-species scrambling was observed, whereby cyclic [thio]carbonate compounds displaying both cyclopentyl and cyclohexyl backbones were produced. A proposed mechanistic pathway for atom scrambling involves nucleophilic alkoxide attack at a [thio]carbonyl center to induce oxygen/sulfur atom exchange.

### ■ INTRODUCTION

While the coupling of epoxides and carbon dioxide to form polycarbonates has garnered widespread attention, the analogous reaction of epoxides and carbon disulfide, CS2, to form polythiocarbonates has received little consideration.<sup>1</sup> However, there are reports of the selective coupling of epoxides and CS<sub>2</sub> to afford cyclic trithiocarbonate and thiocarbonate materials that have applications in materials science and biologically active systems.<sup>2</sup> Notable among these studies is that by North and co-workers utilizing bimetallic aluminum (salen) complexes along with tetrabutylammonium bromide (n-Bu<sub>4</sub>NBr) as effective catalysts for this process.<sup>3</sup> Previously, this system has been demonstrated to be very active for the coupling of CO<sub>2</sub> and epoxides to cyclic carbonates, under both academic and industrial laboratory settings.<sup>4,5</sup> In 2007, Nozaki and co-workers investigated the coupling of propylene sulfide with CS<sub>2</sub> to yield poly(propylene trithiocarbonate) and cyclic propylene trithiocarbonate.<sup>6</sup> This process was optimized to provide a high molecular weight copolymer with 92% selectivity. Importantly, the poly(propylene trithiocarbonate) was found to be completely alternating with a high refractive index, a desirable property for plastic lenses.

In 2008, Qi and co-workers investigated the coupling of propylene oxide and  $CS_2$  using a heterogeneous cobalt/iron double metal cyanide (DMC) catalyst with the aim of synthesizing copolymers.<sup>7</sup> This catalyst system afforded a

polymer product which displayed a mix of different backbone repeat units, instead of only the expected -O-(C=S)-S- dithiocarbonate repeat unit (Scheme 1). Oxygen and sulfur

Scheme 1. General Catalytic Coupling of Epoxides and CS<sub>2</sub> Displaying O/S Scrambling



scrambling was also noted in the cyclic carbonate byproducts. The presence of scrambled COS produced in the process was detected by GC–MS, though no trace of propylene sulfide was observed. It was hypothesized that propylene sulfide was quickly consumed in reactions with available  $CS_2$ , COS, or CO<sub>2</sub> within the system. The poly[thio]carbonates produced in this process displayed broad molecular weight distributions, with PDI varying between 1.24 and 3.50.

Although the structure of the DMC could be surmised with some degree of merit, the detailed nature of the specific modes

Received: July 22, 2013 Revised: September 20, 2013 of reaction of these catalytic materials is poorly defined.<sup>8</sup> Hence, more recently our group described the analogous copolymerization reaction between cyclohexene oxide and CS<sub>2</sub> utilizing the well-characterized (salen)CrCl/PPNCl system in hope of elucidating the mechanistic aspects of this process with more clarity.<sup>9</sup> In this instance, oxygen/sulfur atom scrambling was observed as well in both the polymeric and cyclic carbonate products, with the copolymer being oxygen enriched and the cyclic carbonate being sulfur enriched. Nevertheless, the pathway for O/S scrambling was inadequately understood.<sup>10</sup>

In this report, we have investigated the catalytic coupling of carbon disulfide with an alternative alicyclic epoxide, cyclopentene oxide, employing (salen)CrCl in the presence of onium salts. It is noteworthy that these two alicyclic epoxide monomers, cyclopentene and cyclohexene oxides, have been shown to exhibit grossly different reactivity patterns with  $CO_2$  under the influence of these catalyst systems.<sup>11</sup> This behavior is anticipated to lead to additional and more definitive information with regard to the mechanistic details of the observed oxygen/sulfur atom scrambling process. Because sulfur-containing copolymer and cyclic materials are projected to possess attractive properties, this atom exchange process can provide a convenient route to these products, avoiding the need for expensive and generally commercially unavailable thiiranes. The reactivity of cyclopentene sulfide with both  $CO_2$  and  $CS_2$ was also examined in an effort to provide a more comprehensive analysis of these processes.

#### RESULTS AND DISCUSSION

Coupling of Cyclopentene Oxide and Carbon Disulfide Utilizing PPNN<sub>3</sub>. Azide,  $N_3^-$ , is often used as an initiator in the copolymerizations of epoxides and CO<sub>2</sub> due to its distinct  $\nu_{N_1}$  bond stretching patterns that can be monitored by infrared spectroscopy. Clear shifts in the azide stretch can be observed depending on the chemical environment. Because of this valuable spectroscopic trace, bis(triphenylphosphine)iminium azide, PPNN<sub>3</sub>, was originally chosen as the cocatalyst for this investigation. Following the aforementioned coupling of CPO with  $CS_2$  utilizing (salen)CrCl and PPNN<sub>3</sub>, a wide array of polymeric and cyclic [thio]carbonate materials were produced. Scrambling of the oxygen and sulfur atoms is observed in both the reactants and the products. In an effort to quickly identify the various materials produced during the coupling process, basic information including mass of produced polymer versus [thio]cyclic carbonate was not collected for these reactions. Regardless, both polymer and cyclic carbonates were produced in each case, and differences in scrambling products can be noted. These reactions were monitored utilizing ATR-FTIR, and three-dimensional stack plots and reaction profiles can be found in the Supporting Information. Because of the overlapping nature of the <sup>1</sup>H and FT-IR of these species, spectral assignments were difficult.

In general, peak production of the -O-(C=O)-Spolymer peak<sup>9</sup> at 1712 cm<sup>-1</sup> is maximized after ~4 h, after which it decays away, presumably because of backbiting or rearrangement reactions. The spectral region from 1000 to 1400 cm<sup>-1</sup> is difficult to assign, as many different peaks are overlapping. CS<sub>2</sub> can be observed as the strong band at 1514 cm<sup>-1</sup>. The unchanging absorbance in the early stages of the reaction is caused by the saturation of CS<sub>2</sub> within the solution. Only after sufficient consumption of CS<sub>2</sub> can the absorbance change be observed. CO<sub>2</sub> production can be seen at 2338 cm<sup>-1</sup>, particularly when a limiting amount of  $CS_2$  is employed in the reaction. When  $CO_2$  is added to the reaction, production of *cis*-cyclopentene carbonate is achieved very quickly.

Elemental analysis was performed on the purified polymer samples in order to better determine the chemical makeup (Table 1). The hydrogen atoms were set at 8.00/repeat unit

Table 1. Reaction of Cyclopentene Oxide with  $CS_2$  with (salen)CrCl and PPNN<sub>3</sub> in a 300 mL Stainless Steel Parr Reactor<sup>*a*</sup>

entry	equiv of PPNN <sub>3</sub>	equiv of CS <sub>2</sub>	P <sub>CO₂</sub> , MPa	polymer repeat unit <sup>b</sup>	$T_{g'}^{c} \circ C$
1	2	1500	0	$C_{5.69}H_8S_{1.56}O_{0.76}$	14.4
2	1	1500	0	$C_{5.58}H_8S_{1.15}O_{0.88}$	9.6
3	2	750	0	$C_{5.22}H_8S_{0.80}O_{1.22}$	-17.6
4	2	750	0.7	$C_{5,81}H_8S_{1,08}O_{1,81}$	32.3

<sup>*a*</sup>Reaction conditions 9.64 g of cyclopentene oxide (10.0 mL, 115 mmol, 1500 equiv), 0.0483 g of (salen)CrCl (0.076 mmol, 1 equiv), and the appropriate amounts of PPNN<sub>3</sub>, CS<sub>2</sub>, and CO<sub>2</sub> pressure, where applicable. 80 °C, 24 h. <sup>*b*</sup>H set at 8.00, and other elements were calculated from elemental analysis of the purified polymer sample. <sup>*c*</sup>Midpoint  $T_g$  from the second heating cycle utilizing Differential Scanning Calorimetry.

because this value is consistent for both poly[thio]carbonate and poly[thio]ether linkages (Figure 1). In each case, the



**Figure 1.** Repeat units for [thio]carbonate and [thio]ether linkages. X = O or S.

carbon content is significantly below the expected 6.0 for [thio]carbonate linkages, indicating a large amount of ether or thioether linkages in the polymer backbone. Indeed, when a limiting amount of CS<sub>2</sub> was employed, only 5.22 carbons exist in the idealized repeat unit, indicating that the polymer contains mostly [thio]ether linkages (entry 3). The decrease of [thio]carbonate content is mirrored by a decrease in  $T_g$ , from +14.4 to -17 °C. Upon the addition of 0.7 MPa CO<sub>2</sub>, both the [thio]carbonate content and  $T_g$  greatly increase, with 5.81 carbons/repeat unit and  $T_g = 32.3$  °C.

Notably, <sup>1</sup>H and <sup>13</sup>C NMRs (CDCl<sub>3</sub>) of the crude reaction mixtures each clearly display the production of cyclopentene sulfide (peaks at 3.28, 30.0 ppm, respectively) and cyclopentene (peaks at 5.76, 32.4 ppm, respectively). At the end of the 24 h reaction period, the cyclopentene oxide has been either completely or almost completely consumed, as evident by the disappearance of the peaks at 3.39 and 27.1 ppm in the <sup>1</sup>H and <sup>13</sup>C NMRs, respectively.

**Reaction of N<sub>3</sub><sup>-</sup> with CS<sub>2</sub>.** Though we were unaware prior to the start of this project, the facile reaction of azide with CS<sub>2</sub> to form the 5-membered heterocyclic anion azidodithiocarbonate, CS<sub>2</sub>N<sub>3</sub><sup>-</sup>, is well-defined in the literature (Scheme 2).<sup>12</sup> Caution! Azidodithiocarbonate salts and derivatives are potentially explosive, and appropriate safety precautions should be taken. Only small quantities of the azidodithiocarbonate compounds were Scheme 2. Reaction of Azide with Carbon Disulfide To Yield the Azodithiocarbonate Anion $^a$ 

$$\stackrel{\oplus}{\xrightarrow{}}_{N}^{N} \stackrel{O}{\longrightarrow} \stackrel{CS_{2}}{\longrightarrow} \stackrel{N=S}{\underset{N}{\longrightarrow}} \stackrel{heat}{\longrightarrow} N_{2} + SCN^{-} + 1/_{8}S_{8}$$

 $^a{\rm Upon}$  heating, this anionic heterocycle will breakdown to dinitrogen, thiocyanate, and elemental sulfur.

generated in these experiments, and they were normally generated *in situ* inside of a stainless steel reactor.

As a test to confirm the presence of the  $CS_2N_3^-$  anionic heterocycle, tetrabutylammonium azide, n-Bu<sub>4</sub>NN<sub>3</sub>, was dissolved in toluene at ambient temperature, and the characteristic free  $N_3^-$  peak was observed at 2000 cm<sup>-1</sup>.<sup>13</sup> Upon addition of 5 equiv of CS2, the N3- peak immediately disappeared, and no distinct peaks were visible, consistent with reports that  $CS_2N_3^$ complexes have only weak infrared stretching patterns.<sup>14</sup>  $CS_2N_3^-$  salts and compounds are known to be thermally unstable,<sup>15</sup> and so the reaction was heated to the typical reaction temperature, 80 °C, to observe any potential decomposition. Indeed, almost immediately upon heating a sharp peak appeared at 2055 cm<sup>-1</sup> which indicates the formation of *n*-Bu<sub>4</sub>NSCN (Figure 2).<sup>16</sup> As such, the  $CS_2N_3^$ heterocycle is not long-lived in the reaction medium, instead decomposing to thiocyanate, SCN<sup>-</sup>. It is unclear at this time if  $CS_2N_3^-$  is able to initiate polymer growth prior to this decomposition.

Coupling of Cyclopentene Oxide and Carbon Disulfide Utilizing PPNCI. Because of the unclear  $N_3^-/CS_2N_3^-/SCN^-$  nature of the cocatalyst in the previous studies, it was desirable to investigate this system with the well-defined PPNCl cocatalyst. Initial ATR-FTIR monitoring of a reaction between cyclopentene oxide and  $CS_2$  revealed that peak -O-(C=O)-S- polymer production at 1712 cm<sup>-1</sup> was achieved after 6 h, after which it drops off quickly, presumably due to depolymerization (Figure 3). Thus, all subsequent reactions were monitored for this amount of time to maximize the amount of copolymerization (Table 2).<sup>17</sup>



**Figure 3.** Trace of the -O-(C=O)-S- monothiocarbonate polymer at 1712 cm<sup>-1</sup> displaying peak growth after 6 h. Reaction loading is (salen)CrCl:PPNCl:cyclopentene oxide:CS<sub>2</sub> = 1:2:1500:3000.

As previously stated, the reaction time for those experiments with PPNCl cocatalyst was reduced to 6 h in order to maximize the growth of the known -O-(C=O)-S- monothiocarbonate polymer product at 1712 cm<sup>-1</sup>. The largest amount of polymer and greatest polymer selectivity occurred when equal parts cyclopentene oxide and CS<sub>2</sub> were employed (Table 2,



**Figure 2.** At left, three-dimensional stack plot of the reaction of azide (2000 cm<sup>-1</sup>) with CS<sub>2</sub>. CS<sub>2</sub> was added after 3 min. After ~2 h, the reaction was heated to 80 °C, and the growth of thiocyanate was observed at 2055 cm<sup>-1</sup>. At top right, traces of the disappearance and growth peaks of free  $N_3^-$  (red), and SCN<sup>-</sup> (blue). Bottom right, zoomed in view from 0 to 2.75 h reaction time.

Table 2. Reaction of Cyclopentene Oxide with  $CS_2$  with (salen)CrCl and PPNCl in a 25 mL Stainless Steel Parr Reactor<sup>*a*</sup>

entry	equiv of $CS_2^b$	mass polymer, <sup>c</sup> g	mass cyclic carbonates, g	polymer repeat unit <sup>d</sup>
1	2.5	0.20	0.22	n.d. <sup>e</sup>
2	2.0	1.11	0.91	$C_{5.92}H_8S_{1.70}O_{1.43}$
3	1.5	1.27	1.26	$C_{5.97}H_8S_{1.65}O_{1.24}$
4	1.0	2.04	0.83	$C_{5.96}H_8S_{1.64}O_{1.32}$
5	0.5	trace	0.49	n.d.
6 <sup><i>f</i></sup>	1.0	0.17	1.50	n.d.

<sup>*a*</sup>Reaction conditions: 24.2 mg (salen)CrCl (1 equiv), 43.9 mg PPNCl (2 equiv), 5.0 mL cyclopentene oxide (1500 equiv), 80 °C, 6 h in a 25 mL stainless steel reactor. <sup>*b*</sup>Relative to cyclopentene oxide. <sup>*c*</sup>Mass of purified polymer sample. <sup>*d*</sup>H set at 8.00 and other elements were calculated from elemental analysis of the purified polymer sample. <sup>*e*</sup>Not determined. <sup>*f*</sup>0.7 MPa CO<sub>2</sub> added.

entry 4). When the amount of  $CS_2$  was limiting, only trace amounts of polymer and cyclic [thio] carbonates were produced (entry 5). Similarly, polymer and cyclic production were inhibited by large excesses of  $CS_2$ , presumably due to dilution of the reaction (entry 1). The addition of 0.7 MPa  $CO_2$ prevented significant polymer growth, though a relatively large amount (1.50 g) of cyclic material was produced (entry 6). Though other mixed O/S [thio] carbonates were produced, NMR and GC–MS confirmed that *cis*-cyclopentene carbonate formed from the coupling of cyclopentene oxide and  $CO_2$  was the major product for this reaction, highlighting the large difference in reactivity for cyclopentene oxide with  $CO_2$  and  $CS_2$ .

Elemental analysis of multiple polymers give a consistent repeat unit of  $C_6H_8S_{1,6}O_{1,3}$ , indicating that there is very little [thio]ether content in the backbone of the polymer (Table 2, entries 2 and 4). The polymer is therefore oxygen-enriched from the expected  $(C_6H_8S_2O)_n$  repeat unit. We believe that the increased time for the 24 h PPNN<sub>3</sub> reactions led to backbiting reactions, the loss of CS<sub>2</sub>, CO<sub>2</sub>, and COS, and corresponding increase in ether and thioether linkages in the polymer backbone. Similar observations have been made for the decomposition of polycarbonates.<sup>18</sup> Additionally, no transcyclopentene trithiocarbonate was observable in any of the produced cyclic materials by GC-MS, which is starkly different than the 24-h PPNN<sub>3</sub> reactions in which trans-cyclopentene trithiocarbonate was typically the major cyclic product. This indicates that trans-cyclopentene trithiocarbonate likely forms from late-stage polymer backbiting reactions after CS<sub>2</sub> has been largely consumed.

The produced poly(cyclopentene [thio]carbonate)s are semicrystalline with  $T_g$  near 50 °C and  $T_m$  near 125 °C.<sup>19</sup> Cyclopentene sulfide and cyclopentene are again observed in the <sup>1</sup>H and <sup>13</sup>C NMRs of the crude reaction mixtures, though significant amounts of unreacted cyclopentene oxide also exist in each case. Notably, <sup>13</sup>C NMR revealed that the major [thio]carbonate component is actually at 211 ppm, caused by the unscrambled -S-(C=S)-O- polymeric product (Figure 4).<sup>9</sup> The infrared spectrum of the corresponding polymer shows several large peaks in the 1000–1400 cm<sup>-1</sup> range expected for thiones, but overlapping from the various thiocarbonates as well as C–O and C–S single bond stretches has prevented absolute assignment of peaks (Figure 5). The next largest contributor to the polymeric backbone is -O-(C=O)–S–, with corresponding to peaks at 169 ppm and



**Figure 4.** Carbonate region of the <sup>13</sup>C NMR of poly[thio]carbonate from Table 2, entry 2. CDCl<sub>3</sub>, 125 MHz.



Figure 5. FT-IR of poly[thio]carbonate from Table 2, entry 2.  $CH_2Cl_2$  solvent.

1712 cm<sup>-1</sup> in the <sup>13</sup>C NMR and FT-IR, respectively. Notably, a small amount of the all-oxygen polycarbonate can be seen both in the NMR (~153 ppm) and IR spectra (1750 cm<sup>-1</sup>), and other minor contributions from the trithiocarbonate (~220 ppm) and dithiocarbonate (~193 ppm) can be observed by NMR.

**Coupling of Cyclopentene Sulfide with CS<sub>2</sub> and CO<sub>2</sub>.** Since the generation of cyclopentene sulfide has clearly been observed, it is believable that cyclopentene sulfide is also being consumed during the reaction. It is therefore desirable to independently determine the relative reactivity of cyclopentene sulfide with  $CS_2$  and  $CO_2$ .

Several attempts were made to synthesize cyclopentene sulfide according to recent literature reports through the reaction of cyclopentene oxide with thiourea,<sup>20</sup> potassium thiocyanate,<sup>20</sup> and ammonium thiocyanate<sup>21</sup> as sulfur sources, though none were successful. A 1951 report from van Tamelen states that thiocyanate is not effective for the synthesis of cyclopentene sulfide, though identical conditions are quite effective at the synthesis of cyclohexene sulfide in a 73% yield from cyclohexene oxide (Scheme 3).<sup>22</sup> Indeed, the reaction between cyclopentene oxide and SCN<sup>-</sup> does not proceed beyond the first equilibrium step, and cyclopentene oxide is the only recovered material. This is significant, as the SCN<sup>-</sup> produced by the decomposition of  $CS_2N_3^-$  will therefore not directly react with cyclopentene oxide to form the episulfide.

An alternative, 15 day stepwise synthesis of cyclopentene sulfide by Harding and Owen<sup>23</sup> and Goodman, Benitez, and Baker<sup>24</sup> was instead followed (Scheme 4). The foul-smelling

Scheme 3. Thiocyanate, SCN<sup>-</sup>, Is Able To Convert Cyclohexene Oxide to Cyclohexene Sulfide with a 73% Yield, though this Same Process Is Not Effective for Cyclopentene Oxide to Cyclopentene Sulfide<sup>22</sup>



product was distilled over  $CaH_2$  under reduced pressure to yield pure cyclopentene sulfide as a clear, colorless liquid.

Scheme 4. Three Step Synthesis of Cyclopentene Sulfide



Several coupling studies of cyclopentene sulfide with CS<sub>2</sub> were performed (Table 3). At 80 °C, the same temperature used for the coupling of cyclopentene oxide and  $CS_2$ , the reactivity of cyclopentene sulfide can be observed to be very poor, with only limited formation of *cis*-cyclopentene trithiocarbonate (entries 1-3). A trace amount of the desulfurization product, cyclopentene, is also observed. This desulfurization is undoubtedly the source of cyclopentene within the coupling reactions, as similar tests with cyclopentene oxide were unsuccessful. By increasing the temperature and reaction time to 110 °C and 24 h, respectively, ~20% conversion to *cis*-cyclopentene trithiocarbonate and ~40% conversion to cyclopentene is observed (entries 4-5). Cyclopentene is the major product (36%) when only (salen)CrCl is employed, though 7% coupling products are observed (entry 6). In the absence of both catalyst and cocatalyst, 4% desulfurization is observed with no noticeable coupling product (entry 8). Similarly, cyclopentene sulfide remains relatively unreactive with CO<sub>2</sub> with both Cl<sup>-</sup> and N<sub>3</sub><sup>-</sup> cocatalysts (Table 4). It is thus apparent that cyclopentene sulfide formation is a thermodynamic sink within this reaction

Table 3. Co	oupling Reactions	of Cyclopentene	Sulfide with	$CS_2^a$

Table 4. Coupling Reactions of Cyclopentene Sulfide with  $\text{CO}_2^{\ a}$ 

entry	cocatalyst	cyclopentene sulfide, <sup>b</sup> %	cyclic, <sup>b,c</sup> %	cyclopentene, <sup>b</sup> %
1	PPNCl	98.1	1.3	0.6
2	n-Bu <sub>4</sub> NN <sub>3</sub>	99.4	0.3	0.3
-				

<sup>*a*</sup>All reactions performed in 10 mL stainless steel reactors. 0.250 g cyclopentene sulfide (2.5 mmol, 250 equiv), 1.0 mL toluene- $d_8$ , 6.3 mg (salen)CrCl (0.01 mmol, 1 equiv), 2 equiv of the appropriate cocatalyst, and 3.4 MPa CO<sub>2</sub> at 80 °C for 24 h. <sup>*b*</sup>Relative product yield from crude <sup>1</sup>H NMR. <sup>*c*</sup>Unidentified coupling products.

process. Cyclopentene sulfide is synthesized *in situ*, but it has limited further reactivity after it is generated. This lack of reactivity for the episulfide appears to be unique to the cyclopentyl derivative, as both cyclohexene sulfide<sup>9</sup> and propylene sulfide<sup>6</sup> will effectively couple with  $CS_2$  to yield poly(trithiocarbonate) and cyclic trithiocarbonate materials utilizing chromium catalysts.

**Cyclic [Thio]carbonates.** In the crude <sup>13</sup>C NMR of cyclic materials, three distinct compounds were consistently noted as the major cyclic products. Peaks at 234.7, 228.3, and 197.6 ppm (CDCl<sub>3</sub>) have been assigned to *trans*-cyclopentene trithiocarbonate, *cis*-cyclopentene trithiocarbonate, and *cis*-cyclopentene dithiocarbonate (-S-(C=O)-S- connectivity), respectively. Following purification by column chromatography, single crystals of *trans*-cyclopentene trithiocarbonate were grown and analyzed by X-ray crystallography (Figure 6). The *trans*-



**Figure 6.** Thermal ellipsoid representation of *trans*-cyclopentene trithiocarbonate with ellipsoids at 50% probability surfaces. Inset image is looking down the S1–C4 plane to show torsion caused by the *trans*-configuration. S2–C2–C2′–S2′ angle =  $46.44^{\circ}$ .

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entry	reaction loading $^{b}$	cocat.	temp, °C	<i>t,</i> h	cyclopentene sulfide, <sup>c</sup> %	<i>cis</i> -cyclopentene trithiocarbonate, <sup>c</sup> %	cyclopentene, <sup>c</sup> %
1	1:2:500:1000	PPNCl	80	6	98.8	0.9	0.3
2	1:2:500:1000	PPNN <sub>3</sub>	80	6	99.1	0.8	0.1
$3^d$	1:2:500:1000	n-Bu <sub>4</sub> NN <sub>3</sub>	80	12	99.1	0.4	0.5
$4^d$	1:2:250:500	PPNCl	110	24	39	19	42
$5^d$	1:2:250:1000	PPNCl	110	24	39	21	39
$6^d$	1:0:250:1000	_	110	24	56	$0.7 \ (6.3^e)$	36
$7^d$	0:2:250:1000	PPNCl	110	24	86	8	6
$8^d$	0:0:250:500	PPNCl	110	24	96	-	4

<sup>*a*</sup>All reactions performed in 10 mL stainless steel reactors. <sup>*b*</sup>Reaction loading refers to the relative equivalents of (salen)CrCl:cocatalyst:cyclopentene sulfide:  $CS_2$  loaded into the reactor. <sup>*c*</sup>Relative product yield from crude <sup>1</sup>H NMR. <sup>*d*</sup>Toluene solvent employed; total volume of  $CS_2$  + toluene = 1.0 mL. <sup>*c*</sup>Unidentified coupling products.

assignment is consistent with a previous literature report.<sup>25</sup> Attempts were made to separate *cis*-cyclopentene trithiocarbonate and the -S-(C=O)-S- *cis*-cyclopentene dithiocarbonate by physical and chemical means, but these experiments were unsuccessful. When a limiting amount of CS<sub>2</sub> or added CO<sub>2</sub> was employed, *cis*-cyclopentene carbonate formation could also be clearly observed at 155.6 ppm.

Gas chromatography-mass spectrometry (GC-MS) proved a useful tool for the identification of the identities of the cyclic [thio]carbonate materials, as the GC was able to separate out the various cyclic materials by their different elution times, and then mass spectrometry could be employed to identify the molecular weight of the cyclic materials. Additional information regarding the identity and spectral data of the various cyclic [thio]carbonate materials can be found in the Supporting Information. GC-MS analysis showed that eight of the possible 12 cyclic [thio] carbonates are produced from the coupling of CS<sub>2</sub> and cyclopentene oxide. Cis-cyclopentene carbonate, both isomers of cyclopentene trithiocarbonate, and cis-cyclopentene dithiocarbonate (-S-(C=O)-S- connectivity) were each positively identified by matching traces from pure samples. Only one isomer of cyclopentene monothiocarbonate was observed. All four structural and geometric isomers of cyclopentene dithiocarbonate were observed, though only the cis-(-S-(C=O)-S-) connectivity was isolated. Without calibrating for the GC-MS response factor, relative concentrations of the individual cyclic carbonates were unable to be determined.

In order to better hypothesize the identity of each material, the relative enthalpies of each of the possible cyclopentene [thio]carbonate species were calculated. Slight (1-2 kcal/mol) energy differences can be observed between the *cis*-boat and *cis*-chair conformations of the cyclic systems (Figure 7). Generally,



**Figure 7.** Calculated local minima for cyclopentene carbonate (OOO) species: *cis*-boat, *cis*-chair, and *trans*-.

the *cis*-systems are lower in energy than their *trans*-counterparts (Table 5; see also Supporting Information). For cyclopentene carbonate, the difference is stark at ~20 kcal/mol.<sup>11a</sup> This is understandable, given that only cis-cyclopentene carbonate has ever been isolated, and all attempts to make trans-cyclopentene carbonate have failed. The enthalpy difference is much smaller for cyclopentene trithiocarbonate, ~5 kcal/mol, as the larger sulfur atoms allow for less-strain in the fused 5-membered rings. The mixed O/S species also show ~10 kcal/mol preference for the *cis*-isomers over *trans*-. Notably, there is also a large (10-25)kcal/mol) preference for the formation of the carbon-oxygen double bond over the carbon-sulfur double bond. C=O is known to be a stronger bond than C=S, but this preference may also be due to the greater ability of the large sulfur atoms to relax the molecule and therefore reduce the strain caused by the fused 5-membered rings.

Table 5. Calculated Relative Enthalpies of Cyclic [Thio] carbonates $^{a,b}$ 

Cyclic [Thio]carbonate	<b>x</b> a	Calculated Relative	
Family	Isomer	Enthalpy, kcal/mol <sup>b</sup>	
0	cis-boat	0.0	
	cis-chair	2.5	
$\left\langle \right\rangle$	trans-	19.2	
0	cis-boat	0.0	
o, j	cis-chair	1.0	
$\left\langle \right\rangle$	trans-	10.3	
S	cis-boat	14.7	
	cis-chair	17.5	
$\left\langle \right\rangle$	trans-	34.7	
S II	cis-boat	11.7	
o j	cis-chair	12.8	
$\left\langle \right\rangle$	trans-	22.9	
0	cis-boat	0.0	
s j	cis-chair	0.3	
$\sum$	trans-	4.1	
S	cis-boat	0.0	
s j	cis-chair	0.1	
$\square$	trans-	5.0	
<sup><i>a</i></sup> As defined in Figure 7. <sup><i>b</i></sup>	CBS-QB3, gas pha	se.	

Scrambling Mechanism. Scrambling of the oxygen and sulfur atoms has been observed in both the polymer and cyclic [thio]carbonate samples. In the literature, several similar mechanisms involving the ring-opening of preformed cyclic carbonates have been proposed. In Endo's 2001 investigation of cyclic trithiocarbonate formation utilizing a titanium catalyst, scrambling was observed in the presence of excess CS<sub>2</sub>.<sup>2d</sup> In our 2009 report, the Darensbourg group proposed that the insertion of  $CO_2$ , COS, and  $CS_2$  is reversible, and it is this reversibility that brings about the scrambling.<sup>9</sup> A similar mechanism has been proposed by North for the coupling of propylene oxide and CS<sub>2</sub> in which propylene sulfide is first eliminated and then reenters the mechanism as a new reagent.<sup>3a</sup> Tetrahedral spiro intermediates have been proposed and isolated by Barbero et al. for propylene oxide/sulfide scrambling systems utilizing HBF<sub>4</sub>·Et<sub>2</sub>O,<sup>26</sup> but these were not directly observable by NMR or FT-IR in this investigation.

Several test reactions were run in order to determine the conditions necessary to induce scrambling for reactions involving cyclopentene oxide, (salen)CrCl, and an onium salt cocatalyst (Table 6). In three separate reactions, toluene solutions containing a mix of cyclic cyclopentene [thio]carbonates were heated to 80 °C with (salen)CrCl and n- $Bu_4NCl$  in the presence of  $CO_2$ ,  $CS_2$ , and a control with no other added reagents. After 48 h, no scrambling was observed by <sup>1</sup>H NMR or GC-MS for any of the cases (entries 1-3). Conversely, a solution of the same cyclic [thio]carbonates, catalyst, and cocatalyst heated to 80 °C in the presence of cyclopentene oxide displayed distinct changes in composition, indicating scrambling had taken place (entry 4). Further investigations revealed that the presence of (salen)CrCl catalyst was necessary to induce scrambling, though added n-Bu<sub>4</sub>NCl cocatalyst increased the activity (Table 7). Thus, the catalyst is required to activate and ring-open the epoxide, and the more nucleophilic alkoxide then attacks the [thio]carbonyl to induce

Table 6. Conditions Needed for O/S Scrambling Utilizing a Purified Mix of Cyclic [Thio]carbonate Materials Utilizing (salen)CrCl and *n*-Bu<sub>4</sub>NCl

entry	added reagent <sup>a</sup>	time, h	scrambling observed?
1	none <sup>c</sup>	48	no
2	100 psi CO <sub>2</sub> <sup>c</sup>	48	no
3	1 equiv of CS <sub>2</sub> <sup>c</sup>	48	no
4	1 equiv of cyclopentene oxide <sup>d</sup>	16	yes

<sup>*a*</sup>Average MW of cyclic materials arbitrarily assigned to be 160 g/mol for calculations. Catalyst loading held at (salen)CrCl:*n*-Bu<sub>4</sub>NCl:cyclic mix =1:2:50. 80 °C. <sup>*b*</sup>Scrambling observed by changes in the <sup>1</sup>H NMR and GC–MS traces of the starting material and reaction products. <sup>*c*</sup>0.875 M solution in toluene. <sup>*d*</sup>1.4 M solution.

Table 7. Conditions Needed for O/S Scrambling Utilizing *trans*-Cyclohexene Trithiocarbonate and Cyclohexene Oxide

Entry	catalyst	cocatalyst	scrambling observed? <sup>a</sup>
1	_	-	no
2	(salen)CrCl	-	yes, slight
3	_	<i>n</i> -Bu <sub>4</sub> NCl	no
4	(salen)CrCl	<i>n</i> -Bu <sub>4</sub> NCl	yes

<sup>*a*</sup>Analyzed by *in situ* ATR-FTIR spectroscopy, with scrambling being assigned by the growth of cyclohexene carbonate at 1809  $cm^{-1}$ .

scrambling (Figure 8). The trithiocarbonate species can be produced from the coupling of the ring-opened thiirane produced during the scrambling process and  $CS_2$ . In addition to the pathways outlined in Figure 8, it is possible that cyclopentene sulfide is produced via the elimination of the RO-(C=S)-O anion from (RO-(C=S)-O)C<sub>5</sub>H<sub>8</sub>-S<sup>-</sup>. It is unlikely that cyclopentene sulfide will be separately ring-opened to undergo coupling. The possibility of spiro intermediates has not yet been ruled out at this time.

**NMR Scrambling Studies.** In addition to being studied by ATR-FTIR, it was desirable to monitor the scrambling reactions by NMR. Figure 9 shows the time lapsed <sup>13</sup>C NMRs for the reaction of four equivalents cyclopentene oxide with one equivalent *trans*-cyclopentene trithiocarbonate utilizing (salen)CrCl and *n*-Bu<sub>4</sub>NCl at 80 °C in toluene- $d_8$ . After 15 h, the growth of cyclopentene sulfide is clearly visible with peaks at 41.1, 29.0, and 18.3 ppm. Growth of *cis*-cyclopentene carbonate can also be clearly observed by 22.5 h. After 48 h,



**Figure 9.** Time lapsed <sup>13</sup>C NMR of the reaction between 4 equiv of cyclopentene oxide (red) and 1 equiv *trans*-cyclopentene trithiocarbonate (purple) to produce cyclopentene sulfide (green) and *cis*-cyclopentene carbonate (blue) in toluene- $d_8$ . Broadening of cyclopentene oxide's carbon at 56.3 ppm is likely due to ring-opening and ring-closing of the epoxide.

faint traces of cyclopentene can be observed at 130.7 ppm. Notably, cyclopentene oxide's signal at 56.3 ppm broadens during the course of the reaction, likely because the epoxide is undergoing reversible ring-opening and ring-closing processes. Other coupling products are visible but have not been identified. Continued experiments to identify these compounds are underway in our laboratory.

For completeness, the reaction of cyclopentene sulfide with *cis*-cyclopentene carbonate at 80  $^{\circ}$ C was also monitored by  $^{13}$ C NMR (Figure 10). The desulfurization product cyclopentene (32.7, 23.2 ppm) is the only observable product after 48 h reaction time, indicating that either the catalyst is incapable of ring-opening the episulfide or that the thiolate is not a strong enough nucleophile to attack the carbonate. A proposed mechanism for these observed epoxide/cyclic scramblings can be seen in Figure 11. It is expected that a mixture of the mechanisms proposed in Figures 8 and 11 are both operational during the course of the reaction.



Figure 8. Proposed mechanism for scrambling in the coupling of cyclopentene oxide and CS<sub>2</sub>.



**Figure 10.** Time-lapsed <sup>13</sup>C NMR of the reaction between 4 equiv of cyclopentene sulfide (green) and 1 equiv *cis*-cyclopentene carbonate (blue) in toluene- $d_8$ . Cyclopentene (orange) is the first observable product.

**Mixed Species Scrambling.** O/S scrambling is not limited to epoxides and episulfides of the same backbone connectivity. Indeed, when *trans*-cyclohexene trithiocarbonate was reacted with cyclopentene oxide, (salen)CrCl, and *n*-Bu<sub>4</sub>NCl at 80 °C, six cyclic [thio]carbonate materials were observed by <sup>13</sup>C NMR and GC–MS including *cis*-cyclopentene carbonate and residual *trans*-cyclohexene trithiocarbonate. Mixed species cyclopentene thiocarbonate (SO<sub>2</sub>), cyclohexene thiocarbonate (SO<sub>2</sub>), and cyclohexene dithiocarbonate (S<sub>2</sub>O) were observed, though their exact connectivity cannot be commented on. Cyclohexene sulfide was also clearly produced during the course of the reaction. The reaction mixture was concentrated *in vacuo* prior to GC–MS and NMR analysis, so it is unclear whether cyclopentene sulfide was also generated. However, production of this thermodynamic sink is likely to have occurred.

#### CONCLUSION

The catalytic coupling of cyclopentene oxide with carbon disulfide has been examined utilizing (salen)CrCl and onium salt cocatalyts. Scrambling of the oxygen and sulfur atoms is observable in both the polymer and cyclic carbonate products. When PPNN<sub>3</sub> is employed as cocatalyst, the temperaturesensitive five membered heterocyclic anion  $CS_2N_3^-$  is formed. It is unclear at this time whether this pseudohalogen is able to initiate the coupling reaction before decomposing to thiocyanate, SCN<sup>-</sup>. Under certain conditions, cyclopentene sulfide is actually produced during the coupling of cyclopentene oxide and  $CS_2$ , and it is thus regarded as a thermodynamic sink for this process. The coupling of cyclopentene sulfide and both  $CO_2$  and  $CS_2$  was examined, but it was determined that cyclopentene sulfide is highly unreactive under the conditions studied in this report. Cyclopentene production can be observed from the desulfurization of cyclopentene sulfide.

The  $T_g$  of the polymers is highly dependent on the [thio]carbonate content of the polymer backbone. When a large percentage of [thio]ether is observed, the  $T_g$  drops significantly. [Thio]ether content is believed to increase with increasing reaction time, as backbiting reactions lead to the loss of CS<sub>2</sub>, COS, and CO<sub>2</sub>. The largest amount of [thio]carbonate copolymer is produced utilizing (salen)CrCl and PPNCl at 80 °C for 6 h. The major repeating units of the polymer backbone are dithiocarbonate -S-(C=S)-O- and monothiocarbonate -S-(C=O)-O-.

A wide range of cyclic [thio]carbonate materials are produced, and they have been identified utilizing NMR and GC-MS. Single crystals capable of X-ray diffraction were grown of *trans*-cyclopentene trithiocarbonate, and the S-C-C-S carbonate dihedral angle displays 46.44° of torsion. Computational analysis of the cyclic [thio]carbonates determined that, in general, the *cis*-isomers are more stable than their *trans*- counterparts by >5 kcal/mol, and there is a 10–25 kcal/ mol preference for the formation of a C=O double bond rather than C=S.

Investigations into the mechanism of O/S scrambling were also performed. It was determined that scrambling requires the presence of excess epoxide and catalyst. Added cocatalyst will greatly increase the rate of the reaction, but it is not a requirement. Two mechanisms have been proposed for the observed scrambling processes, though some aspects still remain poorly understood.



Figure 11. Proposed mechanism for observed scrambling between cyclopentene oxide and trans-cyclopentene trithiocarbonate.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

Experimental and computational methods, other experimental data, and the .cif crystallographic data file for *trans*-cyclopentene trithiocarbonate. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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