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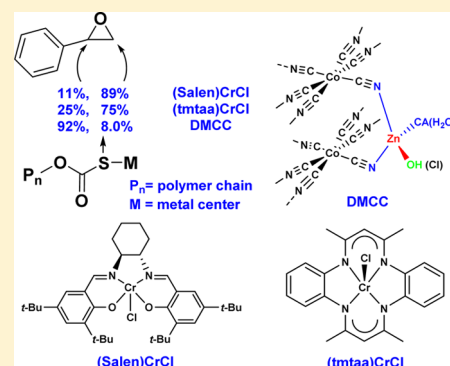
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## An Examination of the Steric and Electronic Effects in the Copolymerization of Carbonyl Sulfide and Styrene Oxide

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## S Supporting Information

**ABSTRACT:** The completely alternating copolymerization of carbonyl sulfide (COS) and styrene oxide was found to occur under mild reaction conditions (0–30 °C and 1.5 MPa) in the presence of (salen)CrCl/onium salt catalyst systems to afford high molecular weight poly(monothiocarbonates) with narrow molecular weight distributions. Ring-opening of styrene oxide was shown to be 88% selective at the methylene carbon. That is the reaction is driven by steric hindrance, where ring-opening occurs preferentially at the less congested carbon center. Similar results were found upon utilizing the tetramethyltetraazaannulene (tmtaa)CrCl/onium salt catalyst. On the other hand, upon employing a zinc–cobalt double metal cyanide (Zn–Co DMCC) catalyst, where the ligands around the active zinc site are not sterically encumbering, ring-opening of styrene oxide occurs predominantly at the methine carbon site; i.e., the reaction is electronically driven.



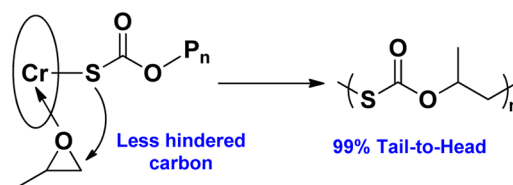
## INTRODUCTION

The catalytic copolymerization of carbon dioxide with epoxides to synthesize degradable polycarbonates has received considerable attention during the past couple of decades.<sup>1</sup> However, the analogous reaction of epoxides and carbonyl sulfide (COS) to form well-defined polythiocarbonates has received little consideration.<sup>2,3</sup> COS is an air pollutant widely released from volcanic eruptions, burning of fossil fuels, and many other chemical processes. It can cause acid rain and damage of the ozonosphere by a series of photochemical reactions.<sup>4</sup> Instead of being a toxic waste, COS can, on the other hand, be a good source of sulfur for synthesizing well-defined sulfur-containing polymers when it is employed as a monomer in copolymerization with epoxides. Meanwhile, as a carbon source, COS is more active than CO<sub>2</sub>, and the greatest difference between them is that COS is asymmetric, which makes the COS/epoxides copolymerization more complicated and interesting. Some progress has been made in the formation of polythiocarbonates from aliphatic terminal epoxides or cyclohexene oxide,<sup>2,3</sup> but the selective synthesis of polythiocarbonates from epoxides with electron-withdrawing groups such as styrene oxide still remains a challenge.

It was reported in our early research that when COS copolymerizes with aliphatic terminal epoxides, such as propylene oxide (PO), catalyzed by the binary (salen)CrCl/PPNCl catalyst, the sulfur atom from COS will bind to the chromium center and form a chromium–sulfur propagating center. Previously, it has been well-established that COS insertion into a metal–oxygen bond in low-valent metal complexes results in the formation of a metal–sulfur bond.<sup>5</sup> Subsequently, the sulfur atom in the growing polymer chain

predominantly attacks the less sterically crowded methylene carbon when PO inserts into the propagating center (Scheme 1). This regioselectivity is driven by the steric hindrance around

Scheme 1



the methine carbon center of the epoxide, resulting in a well-defined polythiocarbonate with 99% tail-to-head linkages.

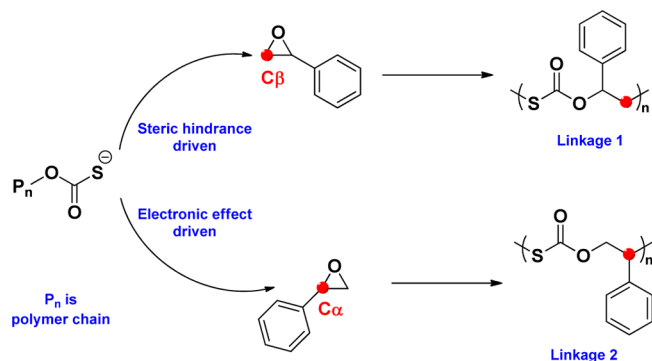
However, as a monomer, styrene oxide (SO) is quite special; the phenyl group possesses both a large steric hindrance and an electron-withdrawing ability. As shown in Scheme 2, when the sulfur propagating center attacks a styrene oxide monomer, there are two routes driven by a steric hindrance effect and an electronic effect, respectively. The steric hindrance is from the phenyl group of styrene oxide, and the anionic sulfur polymer chain end will prefer to attack the methylene carbon (C<sub>β</sub>). On the contrary, because of the strong electronic-withdrawing ability of the phenyl group, the anionic sulfur chain end would prefer to attack the electron-poor methine carbon (C<sub>α</sub>). By way of two routes, linkage 1 and linkage 2 will be produced,

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Scheme 2



respectively. Because both monomers are asymmetric, linkage 1 and linkage 2 are different linkages, and the protons of these two linkages possess different chemical shifts in the  $^1\text{H}$  NMR spectrum.

Carbon dioxide has been employed as a monomer in the copolymerization reaction with styrene oxide for decades, but only a few successful copolymerizations have been reported.<sup>6–11</sup> In general, there is lacking a detailed and comprehensive explanation concerning the mechanism of the ring-opening mode of styrene oxide. In this report, the alternating copolymerization of carbonyl sulfide and styrene oxide by a binary (salen)CrCl/onium salt catalyst is presented. Completely alternating poly(styrene monothiocarbonate) with high molecular weight is achieved. Moreover, the factors affecting the ring-opening mode of styrene oxide are investigated using various catalyst systems.

## RESULTS AND DISCUSSION

**Copolymerization of Styrene Oxide and Carbonyl Sulfide.** Because of our previous successful copolymerization of propylene oxide with carbonyl sulfide utilizing the binary (salen)CrCl/PPNCl catalyst (Figure 1), we have employed this

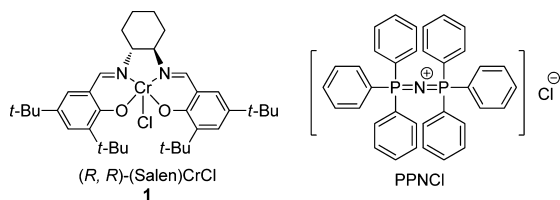


Figure 1. Structure of the binary (*R,R*)-(salen)CrCl/PPNCl catalyst.

catalyst for the copolymerization of styrene oxide (SO) and COS (Table 1, entries 1–3 and 6). At 20 °C (salen)CrCl in conjunction with an equivalent amount of PPNCl was very efficient at providing a poly(monothiocarbonate) with a high molecular weight of 77.2 kDa and narrow polydispersity ( $M_w/M_n$ ) of 1.18. The polymer selectivity was greater than 99% on the basis of the  $^1\text{H}$  NMR spectrum of the crude product (Figure S1). The isolated copolymer exhibited a bimodal molecular weight distribution, which is common for these and related processes. This represents an excellent example of the selective synthesis of a copolymer from COS and an epoxide with an electron-withdrawing group.

The main-chain sequence of the resulting copolymer was confirmed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy (Figure 1 and Figure S16) as well as MALDI-TOF mass spectrometry (Figure S25). As mentioned in Scheme 2, the protons on linkage 1 and linkage 2 possessed different chemical shifts in the  $^1\text{H}$  NMR spectrum due to their different chemical environments. In the  $^1\text{H}$  NMR spectrum (Figure 2) of the resulting copolymer in

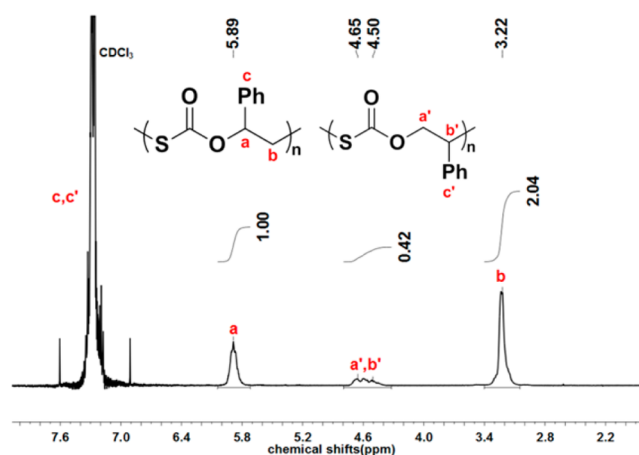


Figure 2.  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$  of the polymer product of entry 1 in Table 1 (20 °C, catalyst 1 and PPNCl employed).

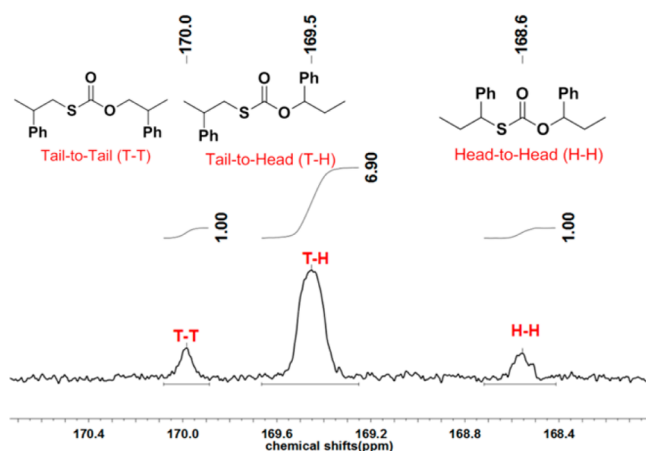
$\text{CDCl}_3$ , the resonance of methine proton in linkage 1 appeared at 5.89 ppm due to the strong electron-withdrawing effect of the phenyl group and the oxygen atom. Meanwhile, the resonance of methylene proton in linkage 1 appeared at 3.22 ppm due to the weak electron-withdrawing effect of the sulfur atom, with the integration ratio being in accord with the protons' molar ratio. For linkage 2, the peaks of the methine and methylene protons appeared at medium chemical shift of 4.65 and 4.50 ppm, respectively. No signal at  $\delta = 3.3\text{--}3.6$  ppm assignable to ether linkage units was observed in this

Table 1. Copolymerization of Styrene Oxide with COS<sup>a</sup>

entry	cocat. <sup>b</sup>	T (°C)	t (h)	conv <sup>c</sup> (%)	polymer selectivity <sup>c</sup> (%)	L1/L2 <sup>c</sup>	$M_n^d$ (kg/mol)	PDI <sup>d</sup> ( $M_w/M_n$ )
1	PPNCl	20	12	>99	>99	88/12	77.2	1.18
2	PPNCl	30	12	>99	96	87/13	40.8	1.32
3	PPNCl	0	48	61	>99	89/11	44.3	1.12
4	PPNY	20	12	>99	97	89/11	58.5	1.37
5	PPNN <sub>3</sub>	20	12	>99	>99	88/12	59.1	1.23
6	PPNCl	20	3	96	>99	88/12	48.9	1.39

<sup>a</sup>The reaction was performed in neat SO (0.3 mL, 2.64 mmol; 1.5 MPa COS was added; cat. 1 in Scheme 2 was used; catalyst/cocatalyst = 1/1; catalyst/epoxides = 1/1000, all in molar ratio) in a 10 mL autoclave. The monothiocarbonate linkage is >99%, confirmed by NMR. <sup>b</sup>Y = 2,4-dinitrophenoxy anion. <sup>c</sup>Determined by using  $^1\text{H}$  NMR spectroscopy. <sup>d</sup>Determined by gel permeation chromatography in THF, calibrated with polystyrene standards.

spectrum,<sup>10a</sup> demonstrating that the copolymer has >99% monothiocarbonate linkages. The MALDI-TOF mass spectrum (Figure S25) also confirmed the highly alternating nature of the resulting polymer. Importantly, the percentages of linkage 1 and linkage 2 can be determined by the total integral of the protons in these two linkages. For entry 1 in Table 1, the percentage of linkage 1 and linkage 2 was calculated to be 88% and 12%, respectively, indicating that ring-opening of styrene oxide during the copolymerization with COS occurs 88% at C<sub>β</sub>–O and 12% at C<sub>α</sub>–O bonds. This result demonstrates that the steric hindrance effect was dominant on the ring-opening of styrene oxide during the copolymerization with COS when the (salen)CrCl/PPNCl catalyst was used. The <sup>13</sup>C NMR spectrum (Figure 3) suggests that the resulting copolymer has a tail-to-



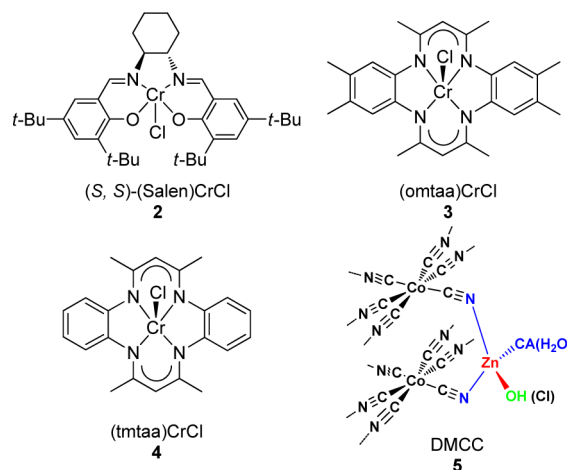
**Figure 3.** Carbonyl region of <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub> of the polymer product of entry 1 in Table 1.

head content of 78% and equivalent tail-to-tail and head-to-head content of 11%, suggesting that there was 11% of linkage 2 on the polymer backbone, which was very close to the calculated number based on <sup>1</sup>H NMR spectroscopy.

During the optimization of this reaction, lowering the temperature to 0 °C significantly reduced the reaction rate; after 48 h the conversion was only 61% (Figure S5). Also, upon increasing the temperature to 30 °C, about 4% cyclic product was produced (Figure S3). Upon precipitating the crude polymer product in methanol, the cyclic product was collected from the methanol solution and characterized by NMR, FT-IR, and GC-MS (Figures S21–S24). It was identified as 4-phenyl-1,3-dithiolan-2-one, a cyclic thiocarbonate with two sulfur atoms in the aliphatic ring. The generation of this minor product indicated that slight oxygen–sulfur scrambling occurred at this temperature. When other cocatalysts, PPNY (Y = 2,4-dinitrophenoxy) and PPNN<sub>3</sub>, were employed at 20 °C, 3% and 1% of cyclic products were observed in the <sup>1</sup>H NMR spectra, respectively. Moreover, the molecular weights were lower than that when using PPNCl as cocatalyst. All these observations suggest that using PPNCl as cocatalyst at 20 °C was the optimum reaction condition for the copolymerization. Notably, reaction temperature and cocatalyst did not affect the ring-opening mode of styrene oxide during the copolymerization with COS. As expected, the resulting polymer exhibits a relatively high glass-transition temperature of 78.4 °C (Figures S26), very close to that of poly(styrene carbonate).<sup>10a</sup>

In order to further investigate the factors dominating the ring-opening mode of styrene oxide, four alternative catalysts

possessing different structures (Figure 4) were employed in the copolymerization of styrene oxide with COS. The results are



**Figure 4.** Structures of catalysts 2–5.

shown in Table 2. First, (salen)CrCl with the salen ligand having the opposite chirality diamine backbone was employed. The activity was slightly lower than that of catalyst 1, and the percentages of linkage 1 and linkage 2 were the same as provided by catalyst 1, indicating that the chirality of the ligand did not affect the ring-opening mode of styrene oxide.

Hypothesizing that the steric hindrance of the metal center's coordination environment is an important factor in the ring-opening mode of styrene oxide, a well-studied and less sterically hindered catalyst, tetramethyltetraazaannulene (tmtaa) chromium chloride, was used in the copolymerization.<sup>12</sup> The (tmtaa)CrCl complex has been shown to be efficient at catalyzing the copolymerization of cyclohexene oxide with CO<sub>2</sub> in the presence of cocatalyst such as PPNCl by a similar mechanism to that of its (salen)CrCl counterparts.<sup>13</sup> Two different (tmtaa)CrCl (catalysts 3 and 4) in conjunction with an equivalent of PPNCl were employed in the copolymerization (entries 2 and 3 in Table 2). Catalysts 3 and 4 were demonstrated to be less active than catalyst 1. After 24 h the conversion rates of these catalyst systems were 86% and 96%, respectively. Moreover, 16% and 7% of cyclic products were observed in the crude products on the basis of <sup>1</sup>H NMR spectroscopy (Figures S10 and S12). Being different from the case of catalyst 1, oxygen/sulfur scrambling did not occur, and the cyclic products resulting from catalysts 3 and 4 were determined to be two different cyclic monothiocarbonates generated from a backbiting mechanism (Scheme 3). Importantly, as predicted, when the less bulky catalysts 3 and 4 were employed, more of linkage 2 (24%) was produced, indicating that the sulfur propagating center could more easily attack the sterically hindered C<sub>α</sub> in these instances. In addition, the electronic environment of the metal center did not affect the ring-opening mode of styrene oxide because the linkage contents were the same when employing catalysts 3 and 4. However, the electronic environment of the metal center influenced the selectivity for cyclic product formation. The metal center of catalyst 3 is more electron-rich than catalyst 4 because of the four electron-donating methyl groups on the aromatic ring, leading to more cyclic product arising from the backbiting mechanism. As indicated in Scheme 3, based on our previous studies of this process during the CO<sub>2</sub>/epoxide

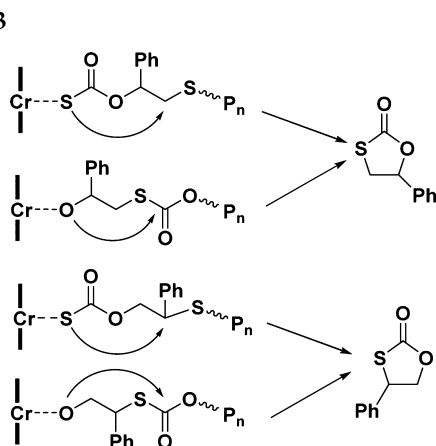


Table 2. Copolymerization of Styrene Oxide with COS Catalyzing by Catalysts 2–5<sup>a</sup>

entry	cat.	cocat.	T (°C)	t (h)	conv <sup>b</sup> (%)	polymer selectivity <sup>b</sup> (%)	L1/L2 <sup>b</sup>	M <sub>n</sub> <sup>c</sup> (kg/mol)	PDI <sup>c</sup> (M <sub>w</sub> /M <sub>n</sub> )
1	2	PPNCl	20	12	>99	>99	89/11	41.2	1.14
2	3	PPNCl	30	24	86	84	76/24	32.8	1.15
3	4	PPNCl	30	24	96	93	75/25	41.6	1.18
4	5		50	24	83	>99	8/92	11.5	2.01

<sup>a</sup>The reaction was performed in the neat SO (0.3 mL, 2.64 mmol; 1.5 MPa of COS was added; catalyst/cocatalyst = 1/1; catalyst/epoxides = 1/1000, all in molar ratio) in a 10 mL autoclave. The monothiocarbonate linkage is >99%, confirmed by NMR. <sup>b</sup>Determined by using <sup>1</sup>H NMR spectroscopy. <sup>c</sup>Determined by gel permeation chromatography in THF, calibrated with polystyrene standards.

Scheme 3



copolymerization process, backbiting is more easily achieved from a metal dissociated copolymer chain.<sup>14</sup>

Another catalyst, a zinc–cobalt double metal cyanide complex (Zn–Co (III) DMCC), was used to promote this reaction. DMCC is a highly active heterogeneous catalyst for epoxides/CO<sub>2</sub> copolymerization.<sup>11,15</sup> The structure is shown in Figure 4. It has a three-dimensional backbone in which the zinc and cobalt atoms are linked by cyanide bridges. The catalytic center of this catalyst is assumed to be a tetrahedral zinc with one OH group.<sup>15d,e</sup> We have reported the highly regioselective copolymerization of (*rac*)-SO and CO<sub>2</sub> via Zn–Co(III) DMCC providing an alternating poly(styrene carbonate) with head-to-tail contents of 96%.<sup>11</sup> Interestingly, when DMCC was used in SO/COS copolymerization (entry 4, Table 2), predominantly (92%) linkage 2 was produced, indicating that the propagating center attacked primarily at the methine carbon (C<sub>β</sub>). Therefore, this propagating process is driven by the electronic effect of aromatic ring in styrene oxide. Figure 5 provides a comparison of the linkage distribution when utilizing different catalyst systems for the copolymerization reaction.

In 1975, Inoue and co-workers concluded that ring-opening of SO predominantly (96%) takes place at the benzyl carbon (C<sub>α</sub>) in the copolymerization of (*S*)-styrene oxide with CO<sub>2</sub> catalyzed by the diethyl zinc/water system.<sup>6</sup> On the contrary, more recently, Lu and co-workers have shown in the copolymerization of (*S*)-styrene oxide (98% *ee*) with CO<sub>2</sub> using the (salen)-cobalt catalyst that only 11% ring cleavage occurred at the benzyl carbon (C<sub>α</sub>).<sup>10a</sup> Considering these two observations, it is possible to conclude that when less bulky catalysts are used, the propagating center will predominantly attack the benzyl carbon due to the strong electron-withdrawing ability of the aromatic ring on styrene oxide despite the greater steric hindrance. This is in sharp contrast with what is seen in the copolymerization of propylene oxide and COS.<sup>2</sup> When catalysts with bulky ligand are used, the steric hindrance environment around the metal center will significantly influence

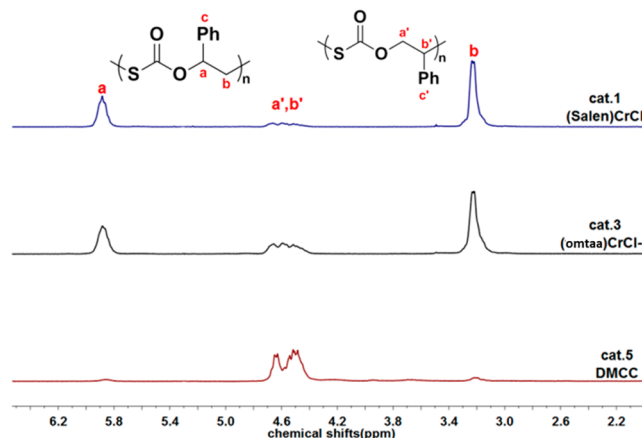


Figure 5. <sup>1</sup>H NMR spectra in CDCl<sub>3</sub> of the polymer product resulted from catalysts 1, 3, and 5.

the ring-opening mode of styrene oxide, where an uncertain amount of the ring-opening will occur at the less hindered methylene carbon depending on the ligand's steric hindrance.

The <sup>13</sup>C NMR spectra (Figure 6) of the copolymers resulting from (salen)CrCl, (tmtaa)CrCl, and DMCC catalysts exhibited

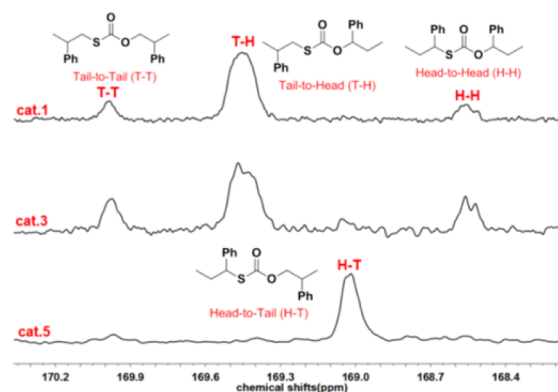
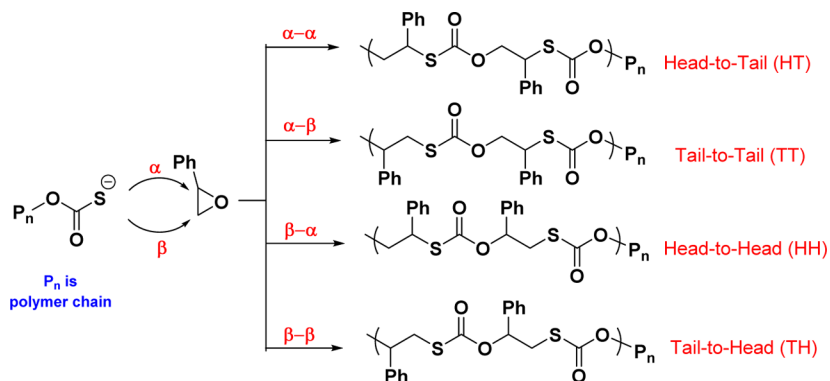


Figure 6. Carbonyl region of <sup>13</sup>C NMR spectra in CDCl<sub>3</sub> of the polymer product resulted from catalysts 1, 3, and 5.

distinctive regiochemistry in SO/COS copolymerization. As shown in Scheme 4, there are four different diad microstructures of the backbone of poly(styrene monothiocarbonate): head-to-tail (HT), head-to-head (HH), tail-to-head (TH), and tail-to-tail (TT). When (salen)CrCl was used, propagating attack predominantly occurred at the less hindered C<sub>β</sub>; thus, a large amount of the TH structure was produced by the sequential β–β attack, as shown in Figure 6. On the contrary, when DMCC was used, predominant sequential α–α attack resulted in large amounts of the HT structure. Notably, the carbonyl group in TH and HT structures possessed

Scheme 4



different chemical shifts in the  $^{13}\text{C}$  NMR spectra. After the calibration of these spectra in Figure 6 referring to the chloroform peak, TH and HT appeared at different chemical shifts. In addition, the  $^{13}\text{C}$  NMR spectrum (Figure 6) of the copolymer produced when DMCC was used as a catalyst suggests that the resulting copolymer has a HT content of 87% and equivalent tail-to-tail and head-to-head content of 6.5%, indicating that there was about 6.5% of linkage 1 on the polymer backbone, which was close to that calculated based on  $^1\text{H}$  NMR spectroscopy.

In summary, the alternating copolymerization of COS and styrene oxide to afford the corresponding poly(monothiocarbonate) with more than 99% monothiocarbonate linkages was achieved with the use of (salen)CrCl/PPNCl, (tmtaa)-CrCl/PPNCl, and DMCC catalysts. By comparing the chain structures of the copolymers resulting from these three catalysts, the ring-opening mode of styrene oxide is revealed. Further investigations aimed at examining the oxygen/sulfur scrambling process which should be enhanced at elevated temperatures are planned.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.5b01427.

Experimental and computational methods and other experimental data (PDF)

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### Notes

The authors declare no competing financial interest.

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