CJC Chinese Journal of Chemistry
中国化学 - An International Journal

Title: An Investigation on the Production of Random Copolymer with Monothiocarbonate and Trithiocarbonate Units over Cyclic Thiocarbonate via Metal-free Catalysis

Authors: Jia-Liang Yang, Lan-Fang Hu, Xiao-Han Cao, Ying Wang, and Xing-Hong Zhang*

This work may now be cited as: *Chin. J. Chem.* **2020**, *38,* 10.1002/cjoc.201900522.

WILEY-VCH SIOC CCS

ISSN 1001-604X • CN 31-1547/O6
mc.manuscriptcentral.com/cjoc
www.cjc.wiley-vch.de

An Investigation on the Production of Random Copolymer with Monothiocarbonate and Trithiocarbonate Units over Cyclic Thiocarbonate via Metal-free Catalysis

Jia-Liang Yang,[a] Lan-Fang Hu,[a] Xiao-Han Cao,[a] Ying Wang,[a] and Xing-Hong Zhang *,[a]

[a] *MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China*

Summary of main observation and conclusion Synthesis of poly(thiocarbonate)s from the copolymerization of epoxides and carbon disulfide (CS_2) remains a tough challenge, due to inevitable oxygen-sulfur atom scrambling process. In this work, we utilized the oxygen-sulfur exchange reaction (O-S ER) to synthesize a random copolymer with monothiocarbonate and trithiocarbonate units from CS_2 and phenyl glycidyl ether (PGE) via metal-free Lewis pairs. The copolymers contained monothiocarbonate and trithiocarbonate units of which the molar fraction could be tuned by varying either the types of Lewis pairs or the reaction temperature. Keeping track on the intermediate provided an insight in the process of O-S ER and thus gave a hint to control the product structure. Production and consumption of phenyl thioglycidyl ether was the key process to regulate the chain structure. Remarkably, the oxygen atoms of PGE could be excluded out of the chain, resulting in the nearly complete production of poly(trithiocarbonate)s. Correspondingly, the refractive index of this kind of copolymer could be regulated in a wide range of 1.73-1.79 (at 590 nm).

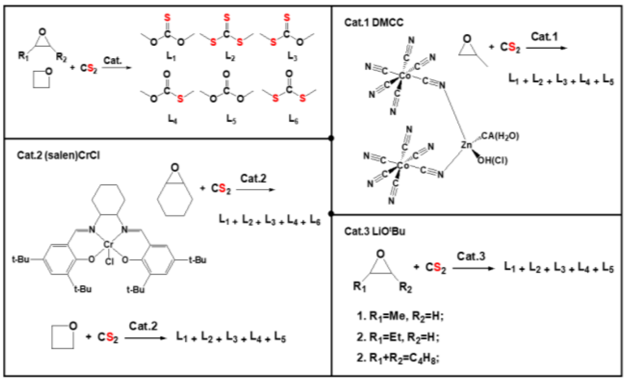
Background and Originality Content

(Main Text Paragraphs. **Note**: Poly(thiocarbonate)s with tunable structure and high refractive index (RI) were successfully synthesized from CS_2 and phenyl glycidyl ether. This work provided a new method to harness O-S ER in the copolymerization of CS_2 with epoxides that are low-cost commercially available chemicals)

Copolymerization of carbon dioxide has got a rapid development in the past decades[1-5], while the coupling of its sulfur containing analogue CS_2 hasn't been treated equally. The utilization of CS_2 as a C1 monomer could potentially relieve the pressure of petroleum resources crisis and introduce sulfur atoms into the polymers by a "green" route simultaneously[6]. In 2007, Nozaki and co-workers conducted the copolymerization of propylene sulfide and CS_2 to yield poly(propylene trithiocarbonate) with high refractive index (RI) of 1.78[1]. During 2008-2009, various structures produced by Oxygen-Sulfur Exchange Reaction (O-S ER) in both the polymer and cyclic byproducts were confirmed by Zhang[8] and Darensbourg[9] respectively. This process can generate CO_2, carbonyl sulfide (COS) and episulfide that mixing in the reaction system and mutually copolymerize with CS_2 and epoxide, resulting in the copolymers with randomly distributed thiocarbonates [-SC(=O)O-, -OC(=S)O-, -SC(=S)S-], carbonate [-OC(=O)O-] or even (thio)ether units. As an important scrambling intermediate, carbonyl sulfide (COS), was firstly identified by GC-MS in Zhang's work when investigating the copolymerization of CS_2 with propylene oxide (PO). Since then, utilization of COS as a C1 monomer in copolymerization has got widely concerned and made rapid progress in a short time[10-18], while investigations on CS_2 copolymerization is standstill. The greatest challenge for studying CS_2 copolymerization lies in the O-S ER process which will interrupt the coupling reaction, as a result, complicated linkages will be generated in the polymer chain.

To figure out the mechanism of O-S ER, we have investigated the pathways for O-S ER process by using oxetane, a symmetric monomer, to copolymerize with CS_2 in the catalyzing of (salen)CrCl/(onium salts) binary system[19]. As a result, five different polymer linkages and two cyclic products were revealed by ^{1}H and ^{13}C NMR spectroscopy, and a plausible mechanism on a tetrahedral intermediate was presented based on the result of in situ infrared spectroscopic monitoring of the polymerization process. After that, Werner and his coworkers used metal alkoxide as catalyst to mediate the reaction of CS_2 with different epoxides[20-21], similar mechanism was proposed for O-S ER process. In particular, catalyst loading was found to have decisive effect in the product constitute for this catalyst system. Lower concentration of metal alkoxide (0.125-0.5%) leaded to highly regioregular and alternating polythiocarbonates composed of five different linkages, while at higher loadings the reaction pathway switched in favor to the formation of cyclic dithiocarbonates. Of all these works, the formation of copolymers was always accompanied by the O-S ER process, therefore, the copolymerization always results in complicated chain structures.

Scheme 1 O-S ER products of CS_2 with cyclic ethers from different catalysts, Cat. 1: Zinc-Cobalt(III) double-metal cyanide complexes (DMCC), Cat. 2: (salen)CrCl/oniumsalts), Cat. 3: Lithium t-butoxide.



Since O-S ER was inevitable in the copolymerization of CS_2 with cyclic ethers, so we wondered the possibility of harnessing it.

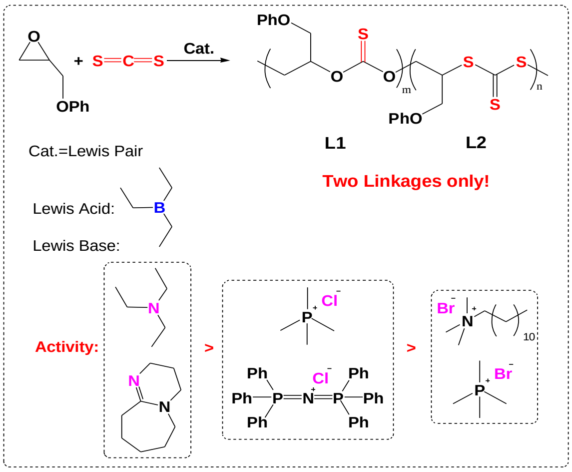
---

*E-mail: xhzhang@zju.edu.cn

Varying the tendency of O-S ER[22] might be used as an effective method to tune the sulfur content in the polymer chain. Meanwhile introduction of sulfur atom in the polymer chain is benefit for increasing refractive index (RI) of the resulted copolymer[21-23]. The thusly formed high RI polymer is an important class of materials that has been widely developed in recent years for optical components due to their lightweight, high impact resistance, low cost and easy processing[26-29]. Remarkably, polymerization with elemental sulfur (S_8) is the universal way to provide sulfur-rich polymers with high RI, and these polymers performed well in Li-S batteries, metal ion detection, IR imaging technology and self-healing materials[30]. Here we propose that O-S ER could be utilized as an atom redistribution process, by which we could synthesize poly(thiocarbonate)s from CS_2 with precise structure and easily tunable sulfur content, thus to produce sulfur containing polymers with high RI.

Catalyst design is usually the core of meditating a polymerization process[31-33]. Confined by the difficulty in intricate design and multiple synthesis steps of metal catalyst, modifying of the polymer by varying catalyst structure faces great troubles. Worse still, metal residue of the catalyst imposed much restrictions on the application of the resulted polymer materials[13]. Recently, development in organic Lewis pairs (LP)s catalysts provided an alternative route[33-35]. Organic LPs were proved to be effective in catalyzing the copolymerization of CO_2/COS with different epoxides[13,36], providing various polycarbonates and poly(monothiocarbonate)s without metal residues. It is convenient to tune the synergy between Lewis acid (LA) and Lewis base (LB) for particular polymerization situation since their simple structures and easily accessible characters. Another notable factor is that phenyl glycidyl ether (PGE) showed lower activity when copolymerize with COS by LPs[13], comparing with the same copolymerization catalyzed by metal catalyst[17]. Since COS is a confirmed intermediate of O-S ER, so we considered that, using LPs as catalysts for the copolymerization of CS_2 and PGE could result in much simpler mainchain structure for the bluntness of PGE to COS[27]. Except for this, introduction of aromatic rings is also benefit for increasing RI of a polymer material. We supposed that, organic Lewis pairs could be utilized to catalyze the copolymerization of CS_2 and PGE, providing poly(thiocarbonate)s with precise chain structure, tunable sulfur content, high RI and free of metal residue.

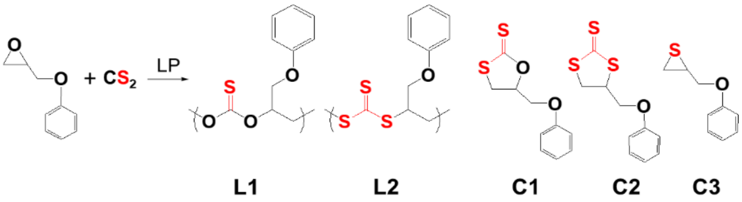
Scheme 2 Copolymerization of CS_2 with PGE catalyzed by organic Lewis pairs.



Results and Discussion

Copolymerization of Carbon Disulfide and Phenyl Glycidyl Ether (PGE)

Table 1 Copolymerization of CS_2 with PGE catalyzed by different Lewis pairs composed of TEB and Lewis bases [a]



Entry	LB	TOF (h^{-1})[b]	Copolymer Selectivity (%)[c]	M_n (kg/mol)[d]	$Đ$ (M_w/M_n)[d]	L1:L2 (%)[c]	C1:C2:C3 (%)[c]
1	TEA	63	35	7.4	1.5	68:32	88:8:4
2	DBU	63	40	5.8	1.4	69:31	83:17:0
3	PPNCl	63	41	11.1	1.5	76:24	88:12:0
4	PPh_4Cl	63	40	12.6	1.7	75:25	86:10:4
5	PPh_4Br	46	41	9.7	1.6	83:17	93:0:7
6	DTMeAB	30	35	11.6	1.4	82:18	95:0:5
7	TBD	60	0	-	-	-	96:4:0
8	DMAP	0	-	-	-	-	-

[a] (The reactions were performed in bulk ([TEB]:[LB]: [PGE]: [CS_2] = 1:1:500:750, molar ratio) in a 10 ml autoclave at 40 °C for 8 h. TEB: Triethyl borane, TEA: Triethyl amine, DBU: 1,8-Diazabicyclo[5.4.0]undec-7-ene, [PPN]Cl: Bis(triphenylphosphine)iminium chloride, PPh_4Cl: Tetraphenyl phosphonium chloride, PPh_4Br: Tetraphenyl phosphonium bromide, DTMeAB: Dodecyltrimethylammonium bromide, TBD: 1,5,7-Triazabicyclododecene, DMAP: 4-dimethylaminopyridine.) [b] ((Mol epoxide consumed)/(mol TEB h), determined by using ^1H NMR spectroscopy of crude product.) [c] (Determined by using ^1H NMR spectroscopy of crude product. Polymer selectivity is the molar ratio of the copolymer to all the cyclic product.) [d] (Determined by using gel permeation chromatography (GPC) in THF, calibrated with polystyrene standards.)

As summarized in Table 1, copolymerization of CS_2 and PGE was successfully catalyzed by organic Lewis pairs composed of TEB as LA and various LBs at 40 °C. In most cases, conversion of PGE accomplished in 8 h resulting in TOF values around 63 h^{-1}. Rather than a couple of complicated linkages as previously reported in metal catalyst systems[8-9,21-22] (Scheme 1), all of the resulted copolymers had only two kinds of alternating linkages, monothiocarbonate [-O(C=S)O-] (**L1**) and trithiocarbonate linkages [-S(C=S)S-] (**L2**), confirmed by ^1H NMR and ^1H-^{13}C HSQC spectra (Figure 1, Figures S1-S7). As expected, COS was still an intermediate in this copolymerization, confirmed by GC-MS (Figure S8). Bluntness of PGE to COS in forming copolymer might be the major reason for the absence of other linkages, and the resulted copolymers with only two kinds of linkages is very convenient for further structure optimizing. Molecule weights of the produced copolymers ranged from 5.8-12.6 kg/mol with cyclic thiocarbonates produced in a proportion of around 60 %. There was no dithiocarbonate linkages [-S(C=S)O-] in the backbone, indicating that the copolymer was totally formed by O-S ER process. The ratio of **L1**/**L2** linkages was decided by the tendency of O-S ER and finally reflected sulfur content in the copolymer. Since **L2** is "sulfur-rich" compared with **L1**, high concentration of L2 in the backbone is in favor of increasing sulfur content and high RI of the copolymer.

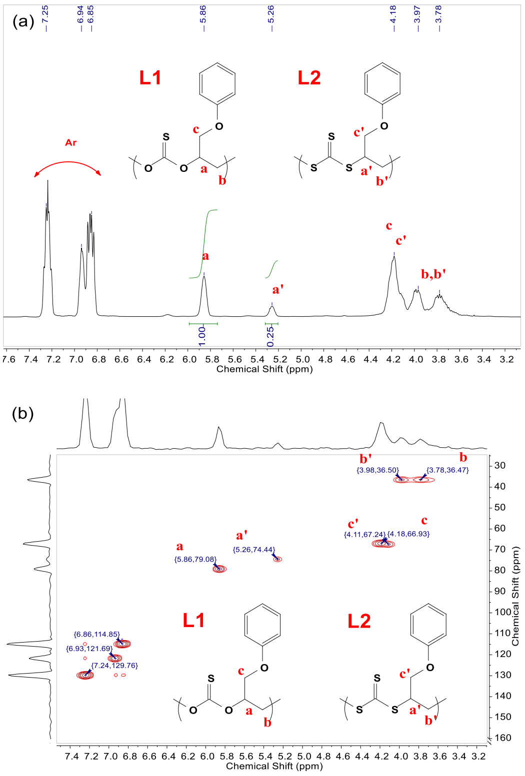
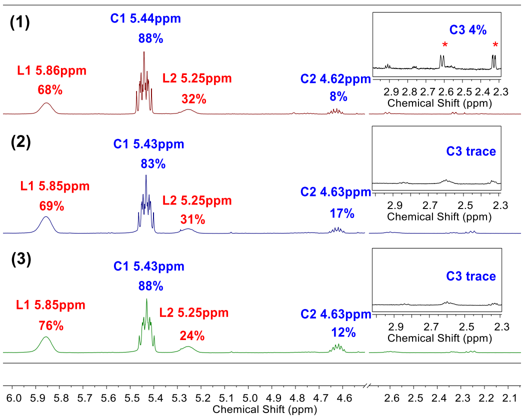


Figure 1 (a) ^1H NMR spectrum of purified product (entry 6, Table1); (b) ^1H-^{13}C HSQC spectrum of purified product showing ^1J correlation peaks of hydrogen atom and carbon atom in the same methyne and methylene (entry 6, Table1).

Nature of the Lewis base has a strong impact on the activity, selectivity and molecule weight. When the feeding ratio of [TEB]: [LB]: [PGE]: [CS_2] was 1: 1: 500: 750 (molar ratio), other than DMAP, most of the LBs could catalyze the copolymerization of CS_2 and PGE resulted in a copolymer chain composed of **L1** and **L2** at 40°C (entries 1-6, Table 1). Based on activity, these LBs could be divided into three groups. TEA and DBU showed relatively high activity when coupled with TEB at 40 °C, TOF value of 63 h^{-1} was observed, and **L2** content were over 30 % (entry 1, 32 %, entry 2, 31 %, Table1). Chlorine anion of PPNCl and PPh_4Cl led to a lower **L2** content of 24-25 % (entries 3-4, Table1), with similar TOF values. While PPh_4Br and DTMeAB with bromine anion showed relatively low activity, not all the monomers accomplished conversion in 8 h, and the TOF were 46 h^{-1} and 30 h^{-1} respectively. Meanwhile, the corresponding polymer chains had low **L2** content (entry 5, 17%, entry 6, 18 %, Table 1). Variation in the content of product is revealed in Figure 2. The special case was when TBD served as LB, no polymer was produced and the selectivity of C1 was very high (96 %, entry 7, Table1). However, changes in molecule weight of the resulted copolymer was irregular, because the molecule weight was determined by a series factors including initiator efficiency, conversion and copolymer selectivity[13]. With similar TOF value and copolymer selectivity, molecule weights of poly(thiocarbonate)s obtained from chlorine anion (11.4, 12.6kg/mol, entries 3, 4, Table 1) were larger than that of TEA and DBU (7.4 and 5.8 kg/mol entries 1, 2, Table 1), which means the initiator efficiency of quaternary ammonium salts was lower than that of organic LB. And the initiator efficiency of bromine anion was even lower (entries 5, 6, Table 1), for the size of bromine is larger which hindered its combination with TEB in the chain initiation stage[13].



---

[a] *Department, Institution, Address 1*
E-mail:

[b] *Department, Institution, Address 2*
E-mail:

[c] *Department, Institution, Address 3*
E-mail:

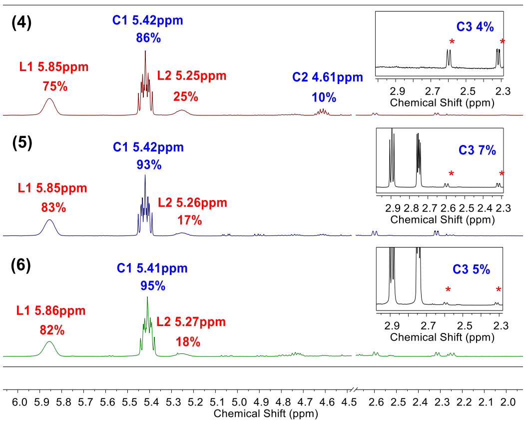


Figure 2 Effect of Lewis base on the result of CS_2/PGE copolymerization, corresponding content of linkages in the polymer chain (red color) and composition of cyclic products (blue color) are marked respectively. (1) entry 1 in Table 1, TEA served as LB, (2) entry 2 in Table 1, DBU served as LB, (3) entry 3 in Table 1, PPNCl served as LB, (4) entry 4 in Table 1, PPh_4Cl served as LB, (5) entry 5 in Table 1, PPh_4Br served as LB, (6) entry 6 in Table 1, DTMeAB served as LB.

Other than linear copolymer, cyclic product was another pivotal factor that worth noticing. Ratio of cyclic product to the copolymer and constituent of cyclic product indicated the distribution of oxygen and sulfur element between linear and cyclic products. If the cyclic product is sulfur-rich, then the copolymer should be oxygen-rich, vice-versa. And this distribution was totally determined by the tendency of O-S ER. What is important is that, other than two common five member cyclic products 5-(phenoxymethyl)-1,3-oxathiolane-2-thione (**C1**) and 4-(phenoxymethyl)-1,3-dithiolane-2-thione (**C2**)[20], phenyl thioglycidyl ether (**C3**) was observed in the ^{1}H NMR spectra of crude product (Figures S3, S5, S6). Usually thiiranes are taken as the byproduct in the coupling of CS_2 with epoxides[37], while we think it may serve as an intermediate of O-S ER just like COS, and its participation in the copolymerization process resulted in inequality of **L1** and **L2**[21]. As a whole, the tendency of oxygen/sulfur ratio in cyclic product was ought to be in accordance with the constitution change in copolymers. However, when oxygen-rich content **L1** increased from 68 % to 82 % in the backbone (entries 1 and 6, Table 1), decrease of dithiocarbonate in cyclic product was unobvious (Figure 2). Reasonable speculation is that, oxygen-rich intermediate COS and CO_2 were produced and excluded from the polymerization process[13]. Rather than **L3**, linkages of **L1** and **L2** were produced by the interaction of CS_2 and PGE through a tetrahedral intermediate[19,21], on the other hand, direct copolymerization of CS_2 with C3 would also resulted to the formation of **L2**.

Tuning the O-S ER process by the influencing factors

Table 2 Copolymerization of CS_2 with PGE at different temperature by three kinds of LPs. [a]

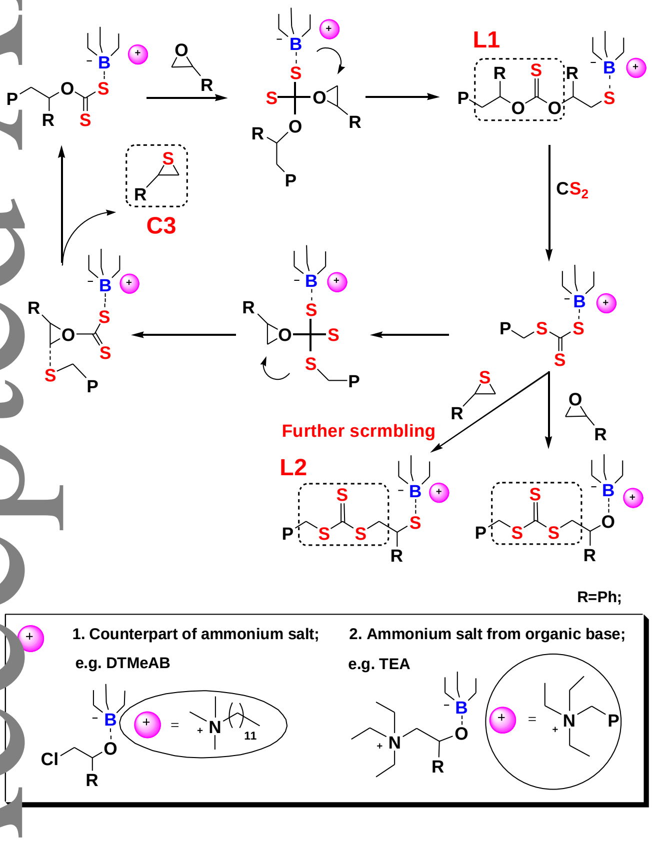
Entry	Temp [°C]	LB	TOF [h^{-1}][b]	Copolymer selectivity (%)[c]	M_n [kg/mol][d]	Đ [M_w/M_n][d]	L1: L2 %[c]	C1: C2: C3 %[c]
1	25	TEA	45	34	7.5	1.7	82:18	94:0:6
2	30	TEA	53	30	7.8	1.5	75:25	89:4:7
3	60	TEA	63	27	6.2	1.5	38:62	85:15:0
4	80	TEA	63	14	2.9	1.3	0:100	82:18:0
5	25	PPh_4Cl	13	35	3.1	1.5	91:9	100:0:0
6	30	PPh_4Cl	54	42	10.5	1.5	85:15	89:5:6
7	60	PPh_4Cl	63	26	7.4	1.6	38:62	80:20:0
8	80	PPh_4Cl	63	18	5.7	1.7	0:100	78:22:0
9	25	DTMeAB	9	30	2.3	1.4	84:16	100:0:0
10	30	DTMeAB	11	34	2.6	1.4	83:17	100:0:0
11	60	DTMeAB	58	34	12.4	1.5	54:46	83:7:10
12	80	DTMeAB	63	27	4.6	1.7	38:62	81:19:0

[a] (The reactions were performed in bulk ([TEB]:[LB]: [PGE]: [CS_2] = 1:1:500:750, molar ratio) in a 10 ml autoclave for 8 h.) [b] ((Mol epoxide consumed)/(mol TEB h), determined by using ^{1}H NMR spectroscopy of crude product.) [c] (Determined by using ^{1}H NMR spectroscopy of crude product. Polymer selectivity is the molar ratio of the copolymer to all the cyclic product.) [d] (Determined by using gel permeation chromatography (GPC) in THF, calibrated with polystyrene standards.)

We further investigated the influential factors of O-S ER and their effect on the distribution of sulfur atoms between poly(thiocarbonate)s and cyclic product. TEA, PPh_4Cl and DTMeAB differed from each other in activity, were chose to couple with TEB to catalyze the copolymerization of CS_2 and PGE at different temperatures, the results were summarized in Table 2 (Figures S10-21). Caused by the rising of temperature, increasing in activity and sacrifice of copolymer selectivity were observed in all the three LPs, which is conform to the previous reported results of LP catalysts[13]. For all the LPs, sulfur atoms preferred to concentrate in linear polymer when the reaction temperature increased (entries 1-12, Table 2). For TEA and PPh_4Cl, copolymers composed of fully **L2** linkages were produced when the reaction temperature was raised to 80°C. While high temperature also resulted in inferior copolymer selectivity, thus molecule weights of the resulted copolymers were low (2.9kg/mol, entry 4, Table 2; 5.7kg/mol, entry 8, Table 2). As for TEB/DTMeAB pair, since its low activity, the highest **L2** content was 62% in 80°C (entry 12, Table 2). On the other hand, low reaction temperature was in favor of forming C1. When TOF value was less than 13h^{-1}, only C1 was produced as cyclic product (entries 5, 9, 10, Table 2). To draw a conclusion, temperature and the activity of LPs are two powerful factors which could be utilized to regulate the sulfur/oxygen distribution between the linear polymer and cyclic product.

What is important in deciding the copolymerization result is the appearance and vanishing of C3. As the polymerization intermediate, C3 was produced in accompany with COS from CS_2 and PGE in the presence of equivalent TEB and TEA, confirmed by ^{1}H NMR spectrum and GC-MS (Figures S8, S9). However, C3 didn't always appear in all of the copolymerization crude product and it experienced prominent variation with the change of temperature. When TEA was used as LB, C3 was only tracked in reaction temperature below 40°C (entry 1, Table1, entries 1 and 2, Table2), and disappeared when the temperature was above 60°C (entries 3 and 4, Table2). Correspondingly, with the consumption of C3, content of **L2** in the polymer chain increased from 18 to 100% (entries 1-4, Table2). Similar trend of cyclic product constitution was observed when using PPh_4Cl and DTMeAB as Lewis base. Appearance of C3 at relative low reaction temperature and disappearing with rising of temperature was observed for these two LBs (Figure 3), while the demarcation point for each LB was different. Appearance and ceiling temperature for the existence of C3 increased with the diminishing of LP activity (25-40°C for TEA, 30-40°C for PPh_4Cl, 40-60°C for DTMeAB). We supposed that, the activation energy for consummation of C3 is higher than that of producing it, so this reaction intermediate only exist in a particular temperature range, and the range goes up with the decreasing activity of Lewis base. As a result, high temperature and LP with stronger activity inclined to produce sulfur concentrated polythiocarbonates (**L2** linkage in this work).

Scheme 3 Plausible mechanism of CS_2/PGE copolymerization.



Based on these observations, we proposed a plausible mechanism for the copolymerization process, and the pathways were shown in Scheme 3. PGE is initially ring-opened by LPs followed with a facile CS_2 insertion. Actually, similar to the copolymerization process involving oxetane and CS_2, this is still anticipated to be the rate determining step here[19]. An alternative reaction pathway could involve anion attack at the carbon center of the −O(C=S)S− propagating unit to form a tetrahedral intermediate. Following rearrangement at the carbon center of the tetrahedral intermediate, the anion is regenerated with concomitant formation of the −O(C=S)O− linkages (**L1**) ended with sulfur anion. Successional insertion of CS_2 leads to a structure of −S(C=S)S− linkages (**L2**). In this view, the content of **L1** and **L2** should be equal with each other, however, ether **L1** > **L2** or **L2** > **L1** were observed in the above mentioned results. Loss of **L2** may be caused by another rearrangement process involving −S(C=S)S- and epoxide monomer. This process converts a **L2** linkage to **L1** with the production C3 as byproduct, which might be one of the routes to form C3. And this rearrangement of course reduces the content of **L2** in the polymer chain. On the other hand, C3 could also serve as a monomer to participate in the alternating insertion competing with PGE. Insertion of C3 will increase the content of **L2**, apparently increasing temperature and enhancing the activity of LPs were apparently benefit for this reaction. As a result, high concentration (even fully) **L2** linkages were observed at above 60°C when using TEA or PPh_4Cl as Lewis base.

High Refractive Index copolymers from CS2 and PGE

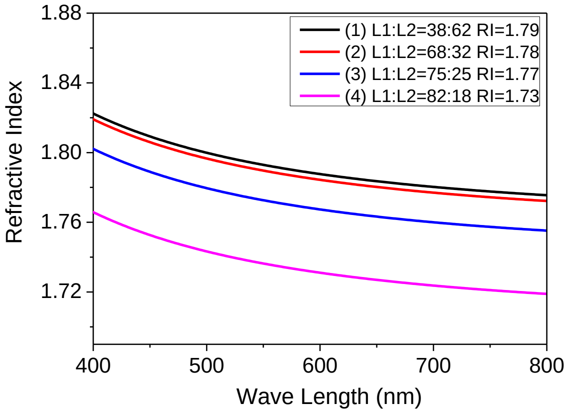


Figure 3 Variation of refractive index ((1)entry 7, Table 2; (2)entry 1, Table 1; (3)entry 2, Table 2; (4)entry 1, Table 2;) via the wavelength of 400-800nm, RI is referred to the refractive index at 590nm.

As we can see, regulation of O-S ER process is an effective way to adjust sulfur content of the produced poly(thiocarbonate)s with varying RI. Converting PGE to C3 and consumption of C3 in the copolymerization process would raise the content of sulfur in the polymer chain. When the content of **L2** is more than 50% in the polymer chain, ratio of sulfur atom to oxygen atom will exceed 2:1, which is the original ratio of sulfur and oxygen in the monomer (two sulfur atoms in CS_2 and one oxygen atom in PGE). By mediating the tendency of O-S ER, ratio of **L2** ranging from 9% (entry 5, Table2) to 100% (entries 4 and 8, Table2) was achieved. We chose poly(thiocarbonate)s of molecule weight around 7.5kg/mol with gradually varied **L2** content to test their RI by spectroscopic ellipsometry (Figure 3). As expected, RI of the copolymer went up with the increasing of **L2** content. Value of RI at 590nm were 1.73, 1.77, 1.78, 1.79 respectively for copolymers with **L2** content of 18%, 25%, 32%, 62%. When the ratio of **L2** linkage was 62%, polythiocarbonate with RI of 1.79 was produced, which is even higher than that of fully alternating poly(ethylene trithiocarbonate)s[7] for the introduction of aromatic rings.

Conclusions

We have described here the synthesis of high refractive index poly(thiocarbonate)s from CS_2 and phenyl glycidyl ether (PGE) employing metal-free Lewis pairs as catalyst. Polythiocarbonates with only two kinds of linkages were produced with tunable content. Phenyl thioglycidyl ether (C3) and COS were monitored as the intermediate of Oxygen-Sulfur Exchange Reaction, and provided an insight of O-S ER. O-S ER process and constituent of the product could be easily tuned by varying the reaction temperature or activity of Lewis base. In virtue of O-S ER, distribution of oxygen and sulfur element in polymer chain and cyclic product could be changed in a large range, thus the resulted poly(thiocarbonate)s would be oxygen-rich (RI=1.73) or sulfur-rich (RI=1.79). Our ongoing efforts are to seek more biological monomers to copolymerize with CS_2 to produce high refractive index polymer materials.

Experimental

Copolymerization of CS_2 with PGE catalyzed by Lewis pairs, experimental details

A 10ml autoclave with magnetic stirrer was first dried in an oven at 120 °C overnight, then immediately placed into the glove box chamber. After keeping under vacuum for 2-3 hours, the reaction vessel was moved into the glovebox with nitrogen atmosphere. The copolymerization of CS_2 with PGE described below is taken from Entry 1 in Table 1 as an example. Triethyl amine (TEA, 2.5ul, 0.018 mmol) was firstly added into the reactor and dissolved in 0.8 mL of CS_2. PGE (1.2 mL, 9 mmol) was carefully added into the vessel after the introduction of an appropriate amount of TEB (18 µL, 0.018 mmol). The reactor was sealed and taken out from the glovebox and put into oil bath. The copolymerization was carried out at 40°C for 8h. The reactor was then cooled in ice-water bath, and an aliquot was then taken from the resulting crude product for the determination of constituent of the product by ^{1}H NMR spectrum. The crude product was quenched with acetic acid in ethyl alcohol (1 mol/L), and it divided into two parts, solid part and liquid part. The solid part was dissolved with CH_2Cl_2 and then precipitated by ethyl alcohol, then the copolymer was collected by centrifugation and dried in vacuum at 40 °C overnight. The cyclic product in liquid part was collected by centrifugation.

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.2018xxxxx.

Acknowledgement

X.-H. Zhang gratefully acknowledge the financial support of the Distinguished Young Investigator Fund of Zhejiang Province (LR16[illegible]040001) and the National Science Foundation of the People's Republic of China (no. 21774108).

References

[1] Wang, Y.; Darensbourg, D. J. Carbon dioxide-based functional polycarbonates: Metal catalyzed copolymerization of CO_2 and epoxides. *Coord. Chem. Rev.* **2018,** *372*, 85-100.

[2] Thevenon, A.; Cyriac, A.; Myers, D.; White, A. J. P.; Durr, C. B.; Williams, C. K. Indium catalysts for low-pressure CO_2/epoxide ring-opening copolymerization: evidence for a mononuclear mechanism? *J. Am. Chem. Soc.* **2018,** *140*, 6893-6903.

[3] Zhang, Y. Y.; Yang, G. W.; Wu, G. P. A bifunctional β-Diiminate zinc catalyst with CO_2/epoxides copolymerization and RAFT polymerization capacities for versatile block copolymers construction. *Macromolecules* **2018,** *51*, 3640-3646.

[4] Xu, Y. H.; Lin, L. M.; Meng, Y. Z. Synthesis and properties of CO_2-based plastics: environmentally-friendly, energy-saving and biomedical polymeric materials. *Prog. Polym. Sci.* **2018,** *80*, 163-182.

[5] Zhu, Y.; Romain, C.; Williams, C. K. Sustainable polymers from renewable resources. *Nature* **2016,** *540*, 354-362.

[6] Luo, M.; Li, Y.; Zhang, Y. Y.; Zhang, X. H. Using carbon dioxide and its sulfur analogues as monomers in polymer synthesis. *Polymer* **2016,** *82*, 406-431.

[7] Nakano, K.; Tatsumi, G.; Nozaki, K. Synthesis of sulfur-rich polymers: copolymerization of episulfide with carbon disulfide by using [PPN]Cl/(salph)Cr(III)Cl system. *J. Am. Chem. Soc.* **2007,** *129*, 15116-15117.

[8] Zhang, X. H.; Liu, F.; Sun, X. K.; Chen, S.; Du, B. Y.; Qi, G. R.; Wan, K. M. Atom-exchange coordination polymerization of carbon disulfide and propylene oxide by a highly effective double-metal cyanide complex. *Macromolecules* **2008,** *41*, 1587-1590.

[9] Kaminsky, W.; Funck, A.; Hahnsen, H., New application for metallocene catalysts in olefin polymerization. *Dalton Trans.* **2009,** 41, 8891-8899.

[10] Wang, X. H.; Wan, X. H., Metal-free access to precise synthesis of sulfur-containing polymers. Acta Polym. 2018, 7, 1-3.

[11] Zhang, C. J.; Yang, J. L.; Hu, L. F.; Zhang, X. H., Anionic copolymerization of carbonyl sulfide with epoxides via alkali metal alkoxides. Chin. J. Chem. 2018, 36, 625-629.

[12] Zhang, C. J.; Zhang, X. H., Recent progress on COS-derived polymers. Chin. J. Polym. Sci. 2019, 37, 951-958.

[13] Yang, J. L.; Wu, H. L.; Li, Y.; Zhang, X. H.; Darensbourg, D. J. Perfectly alternating and regioselective copolymerization of carbonyl sulfide and epoxides by metal-free Lewis pairs. *Angew. Chem. Int. Ed.* **2017,** *56*, 5774-5779.

[14] Luo, M.; Zhang, X. H.; Darensbourg, D. J. Poly(monothiocarbonate)s from the alternating and regioselective copolymerization of carbonyl sulfide with epoxides. *Acc. Chem. Res.* **2016,** *49*, 2209-2219**.**

[15] Wu, H. L.; Yang, J. L.; Luo, M.; Wang, R. Y.; Xu, J. T.; Du, B. Y.; Zhang, X. H.; Darensbourg, D. J. Poly(trimethylene monothiocarbonate) from the alternating copolymerization of COS and oxetane: a semicrystalline copolymer. *Macromolecules* **2016,** *49*, 8863-8868.

[16] Luo, M.; Zhang, X. H.; Du, B. Y.; Wang, Q.; Fan, Z. Q. Well-defined high refractive index poly(monothiocarbonate) with tunable Abbe's numbers and glass-transition temperatures via terpolymerization. *Polym. Chem.* **2015,** *6*, 4978-4983.

[17] Luo, M.; Zhang, X. H.; Darensbourg, D. J. Highly regioselective and alternating copolymerization of carbonyl sulfide with phenyl glycidyl ether. *Polym. Chem.* **2015,** *6*, 6955-6958.

[18] Luo, M.; Zhang, X. H.; Du, B. Y.; Wang, Q.; Fan, Z. Q. Regioselective and alternating copolymerization of carbonyl sulfide with racemic propylene oxide. *Macromolecules* **2013,** *46*, 5899-5904.

[19] Luo, M.; Zhang, X. H.; Darensbourg, D. J. An investigation of the pathways for oxygen/sulfur scramblings during the copolymerization of carbon disulfide and oxetane. *Macromolecules* **2015,** *48*, 5526-5532.

[20] Diebler, J.; Spannenberg, A.; Werner, T. Atom economical synthesis of di- and trithiocarbonates by the lithium tert-butoxide catalyzed addition of carbon disulfide to epoxides and thiiranes. *Org. Biomol. Chem.* **2016,** *14*, 7480-7489.

[21] Diebler, J.; Komber, H.; Häußler, L.; Lederer, A.; Werner, T. Alkoxide-Initiated regioselective coupling of carbon disulfide and terminal epoxides for the synthesis of strongly alternating copolymers. *Macromolecules* **2016,** *49*, 4723-4731.

[22] Darensbourg, D. J.; Wilson, S. J.; Yeung, A. D. Oxygen/sulfur scrambling during the copolymerization of cyclopentene oxide and carbon disulfide: selectivity for copolymer vs cyclic [Thio]carbonates. *Macromolecules* **2013,** *46*, 8102-8110.

[23] Sun, Z.; Huang, H.; Li, L.; Liu, L.; Chen, Y. Polythioamides of high refractive index by direct polymerization of aliphatic primary diamines in the presence of elemental sulfur. *Macromolecules* **2017,** *50*, 8505-8511.

[24] Anderson, L. E.; Kleine, T. S.; Zhang, Y.; Phan, D. D.; Namnabat, S.; LaVilla, E. A.; Konopka, K. M.; Ruiz Diaz, L.; Manchester, M. S.; Schwiegerling, J.; Glass, R. S.; Mackay, M. E.; Char, K.; Norwood, R. A.; Pyun, J., Chalcogenide hybrid inorganic/organic polymers: ultrahigh refractive index polymers for infrared imaging. *ACS Macro Lett.* **2017,** *6*, 500-504.

[25] Nakabayashi, K.; Imai, T.; Fu, M.-C.; Ando, S.; Higashihara, T.; Ueda, M. Poly(phenylene thioether)s with fluorene-based cardo structure toward high transparency, high refractive index, and low birefringence. *Macromolecules* **2016,** *49*, 5849-5856.

[26] Li, M.; Tao, Y.; Tang, J.; Wang, Y.; Zhang, X.; Tao, Y.; Wang, X. Synergetic organocatalysis for eliminating epimerization in ring-opening polymerizations enables synthesis of stereoregular Isotactic polyester. *J. Am. Chem. Soc.* **2018,** *141*, 281-289.

[27] Tang, Y.; Pina-Hernandez, C.; Niu, Q.; Nie, J.; Cabrini, S. A novel high-refractive index episulfide-thiol polymer for nanoimprinting optical elements. *J. Mater. Chem. C.* **2018,** *6*, 8823-8831.

[28] Kleine, T. S.; Diaz, L. R.; Konopka, K. M.; Anderson, L. E.; Pavlopolous, N. G.; Lyons, N. P.; Kim, E. T.; Kim, Y.; Glass, R. S.; Char, K.; Norwood, R. A.; Pyun, J. One dimensional photonic crystals using ultrahigh refractive index chalcogenide hybrid inorganic/organic polymers. *ACS Macro Lett.* **2018,** *7*, 875-880.

[29] Higashihara, T.; Ueda, M. Recent progress in high refractive index polymers. *Macromolecules* **2015,** *48*, 1915-1929.

[30] Boyd, D. A. Sulfur and its role in modern materials science. *Angew. Chem. Int. Ed.* **2016,** *55*, 15486-15502.

[31] Lu, X. B.; Darensbourg, D. J. Cobalt catalysts for the coupling of CO_2 and epoxides to provide polycarbonates and cyclic carbonates. *Chem. Soc. Rev.* **2012,** *41*, 1462-1484.

[32] Trott, G.; Saini, P. K.; Williams, C. K. Catalysts for CO_2/epoxide ring-opening copolymerization. *Philos. Trans. R. Soc. London, Ser. A* **2016,** *374* (2061).

[33] Hong, M.; Chen, J.; Chen, E. Y. Polymerization of polar monomers mediated by main-group Lewis acid-base pairs. *Chem. Rev.* **2018**. *118*, 10551-10616.

[34] Zhang, Y.; Miyake, G. M.; Chen, E. Y. Alane-based classical and frustrated Lewis pairs in polymer synthesis: rapid polymerization of MMA and naturally renewable methylene butyrolactones into high-molecular-weight polymers. *Angew. Chem., Int. Ed.* **2010,** *49*, 10158-10162.

[35] Xu, T.; Chen, E. Y. Probing site cooperativity of frustrated phosphine_borane Lewis pairs by a polymerization study. *J. Am. Chem. Soc.* **2014,** *136*, 1774-1777.

[36] Zhang, D.; Boopathi, S. K.; Hadjichristidis, N.; Gnanou, Y.; Feng, X. Metal-free alternating copolymerization of CO_2 with epoxides: fulfilling "green" synthesis and activity. *J. Am. Chem. Soc.* **2016,** *138*, 11117-11120.

[37] Clegg, W.; Harrington, R. W.; North, M.; Villuendas, P. A bimetallic aluminum(salen) complex for the synthesis of 1,3-oxathiolane-2-thiones and 1,3-dithiolane-2-thiones. *J. Org. Chem.* **2010,** *75*, 6201-6207.

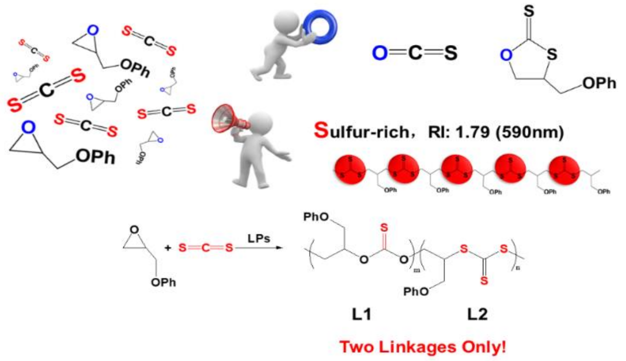
(The following will be filled in by the editorial staff)
Manuscript received: XXXX, 2019
Manuscript revised: XXXX, 2019
Manuscript accepted: XXXX, 2019
Accepted manuscript online: XXXX, 2019
Version of record online: XXXX, 2019

Entry for the Table of Contents

Page No.

Title: An Investigation on the Production of Random Copolymer with Monothiocarbonate and Trithiocarbonate Units over Cyclic Thiocarbonate via Metal-free Catalysis

Max. Table height 6 cm



Ji Liang Yang, Lan-Fang Hu, Xiao-Han Cao, and
ing-Hong Zhang *

---

[a] *Department, Institution, Address 1*
E-mail:

[b] *Department, Institution, Address 2*
E-mail:

[c] *Department, Institution, Address 3*
E-mail: