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Zhang Cheng-Jian, Zhang Xing-Hong

Cite this article as:

Zhang Cheng-Jian, Zhang Xing-Hong. Recent Progress on COS-derived Polymers[J]. *Chinese J. Polym. Sci.*, 2019, 37(10): 951-958. doi: 10.1007/s10118-019-2288-y

View online: <https://doi.org/10.1007/s10118-019-2288-y>

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Recent Progress on COS-derived Polymers

Cheng-Jian Zhang and Xing-Hong Zhang*

Key Laboratory of Macromolecular Synthesis and Functionalization (Ministry of Education), Department of Polymer Science & Engineering, Zhejiang University, Hangzhou 310027, China

Abstract The synthesis of sulfur-containing polymer, a very promising functional material, has made a great progress in the past several years. This review is focused on the very recent advances in poly(monothiocarbonate)s derived from carbonyl sulfide (COS) and epoxides including biomass-derived epoxides. Of significance, metal-free catalyst systems, including triethyl borane/Lewis base pair and thiourea/Lewis base pair are developed for the alternating copolymerization of COS with epoxides. Thereof, the thiourea/Lewis base pair is highly active to the copolymerization of COS with epoxide in a living manner. Moreover, a series of crystalline poly(monothiocarbonate)s are presented, including the copolymers derived from COS with oxetane, ethylene oxide, enantiopure epichlorohydrin, and achiral *meso*-epoxides *via* enantioselective copolymerization. Based on these COS/epoxide copolymerization process, a variety of COS-based block copolymers with well-defined structure are presented.

Keywords Carbonyl sulfide; Epoxide; Copolymerization; Poly(monothiocarbonate)

Citation: Zhang, C. J.; Zhang, X. H. Recent progress on COS-derived polymers. *Chinese J. Polym. Sci.* 2019, 37, 951–958.

INTRODUCTION

The fascinating and wide-ranging properties of polymers have made them pervaded through modern life and indispensable to burgeoning technologies.^[1,2] Extending and diversifying polymer performance present great challenges and tremendous opportunities to produce improved materials, new products, and innovative technologies.^[3–5] In general, introduction of sulfur atom into the polymer architecture can endow the counterpart polymers with superior properties, *e.g.* higher melting temperature, greater heat stability, and lower solubility in various organic solvents.^[6] Actually, sulfur-containing polymer is a very promising material and has attracted much scientific attentions and industrial interests.^[7–14] For example, the well-known poly(phenylene sulfide) (PPS) derivatives are among the earliest commercially produced sulfur-containing polymers. They are super engineering plastics possessing excellent comprehensive performance. Nowadays, sulfur-containing polymers are very promising in many functionalized applications including rechargeable batteries, optical materials, biological materials, *etc.*^[15–18]

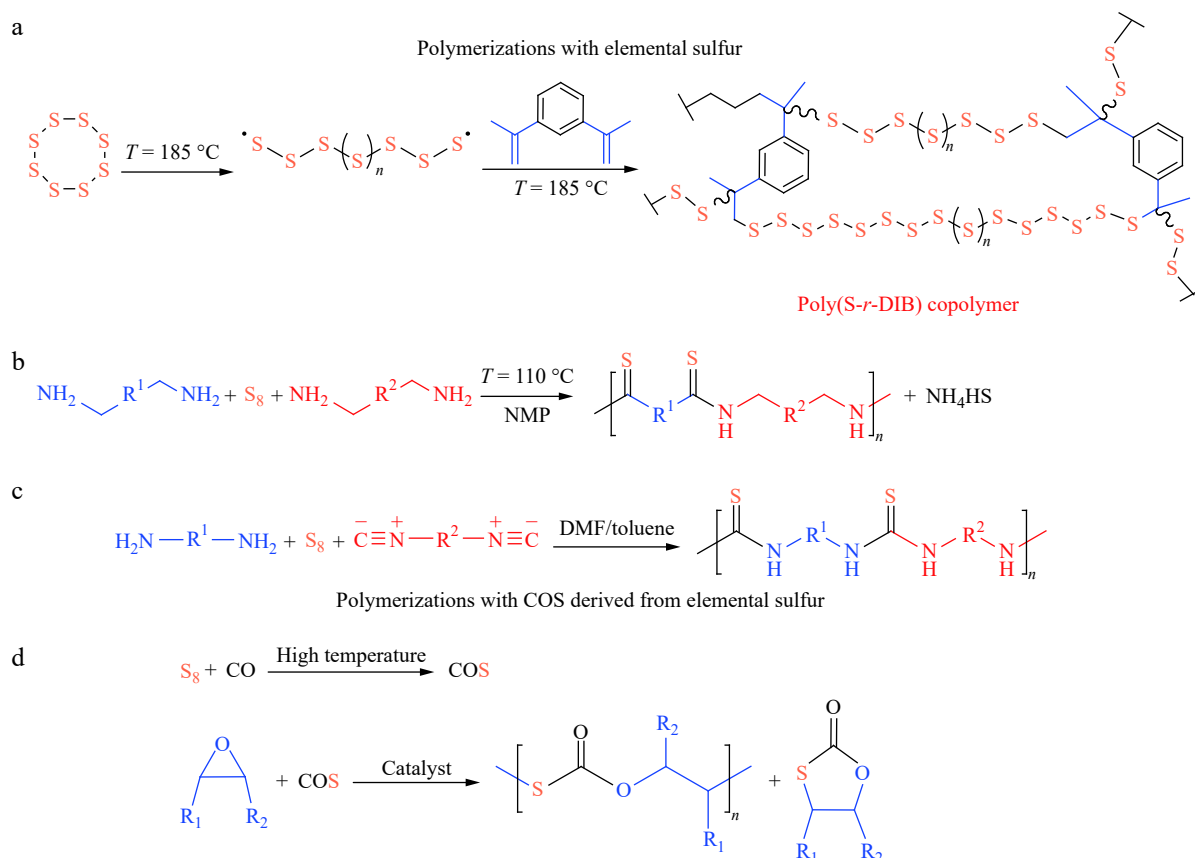
The last decade has witnessed significant progress in the synthesis of a great diversity of sulfur-containing polymers. A very recent advance is that a sustainable poly(thioester) was achieved *via* metal-free catalytic ring-opening polymerization (ROP) process by Lu *et al.*^[11] This unique sulfur-con-

taining polymer is completely recyclable and can be facilely functionalized. Back to a longer period of time, the primary progress is the strategy of direct utilization of elemental sulfur (S_8) as a chemical feedstock.^[19–21] Sulfur is a by-product of the petroleum industry, and more than 60 million tons of elemental sulfur are produced annually. Converting sulfur into useful polymers and related materials is an extraordinary progress in waste valorization. In 2013, Pyun and co-workers reported a process that they termed as “inverse vulcanization” (Scheme 1a).^[21] In the process, S_8 was used as the backbone material, and aromatic carbon comonomer, 1,3-diisopropenyl benzene (DIB), was bound to sulfur chains to form stable polymer complexes. This method took advantage of ring-opening of S_8 and enchainment at elevated temperatures by binding divinyl molecules to the sulfur radicals. Successively, a mass of vinyl molecules were utilized as comonomers with S_8 to make polymers with improved properties.^[20] In short, the unique method points toward a very cheap and environmentally beneficial means by which to produce sulfur-containing polymers and utilize the large stockpiles of elemental sulfur. Chen *et al.* demonstrated a direct polymerization of aliphatic primary diamines with elemental sulfur (Scheme 1b).^[22] The generated poly(thioamide)s possess high refractive indexes as high as 1.7. It is a promising polymerization technique with outstanding features such as catalyst-free, low-cost and versatile monomer, and atom economy. Moreover, Hu, Tang, and co-workers described the room temperature conversion from sulfur to functional poly(thiourea)s through a catalyst-free multi-component polymerization of sulfur, aliphatic diamines, and diisocyanides in air (Scheme 1c).^[23,24] The polymerization process exhibits quick kinetics and wide monomer scope, affording a

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

Invited review for special issue of “The 100th Anniversary of the Birth of Prof. Shi-Lin Yang”

Received March 28, 2019; Accepted April 29, 2019; Published online July 1, 2019



Scheme 1 Illustration of the syntheses of sulfur-containing polymers: (a–c) direct utilization of elemental sulfur as a monomer; (d) indirect way of utilizing sulfur through COS that is generated from the reaction of sulfur with CO

variety of poly(thiourea)s with precise structures and high molecular weights.

Recently, the alternating copolymerization of epoxide with carbonyl sulfide (COS) has been successfully developed to produce poly(monothiocarbonate)s (Scheme 1d).^[9,25] COS is an important intermediate of the sulfur cycle in atmosphere, which comes up as a product of volcano eruptions and the decomposition of sulfur compounds in nature.^[26] More recently, COS is considerably released from oil refinery and the consumption of fossil fuels. In industry, COS can be produced by a direct reaction of CO with S₈.^[27] Therefore, the fixation and utilization of COS is of great significance to environmental governance and emission reduction, and also a fascinating approach to utilize the elemental sulfur. On the other hand, COS is a heterocumulene and structural analog of CO₂, so it could be an ideal one-carbon (C1) monomer for producing poly(thiocarbonate)s with epoxides, similar to the CO₂/epoxide copolymerization.^[28–30] Since the alternating copolymerization of COS with propylene oxide (PO) was disclosed in 2013,^[31] a series of works of using COS as feedstock to synthesize sulfur-containing polymers have been reported, and reviewed in 2016.^[25] This manuscript mainly highlights the very recent advances of COS/epoxide copolymerization, including metal-free copolymerization, crystalline poly(monothiocarbonate)s, COS-based block copolymers, and corresponding methods for precisely structural control.

SYNTHESIS OF COS-DERIVED POLYMERS

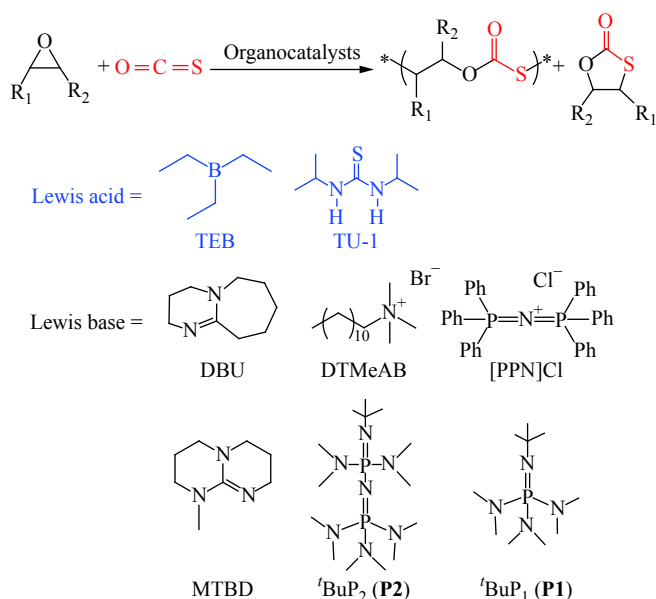
Organocatalytic Copolymerization of COS with Epoxide

A variety of homogeneous (salen)MX (onium salts) (M = Co, Cr, Fe)^[31–37] and heterogeneous zinc-cobalt (III) double metal cyanide complexes^[38] have been developed for the alternating copolymerization of COS and epoxides. Of interest, commercially available alkali metal alkoxides have been found able to catalyze (initiate) the copolymerization of COS and epoxides with an anionic polymerization mechanism.^[39] The resultant poly(monothiocarbonate)s possess alternating degree and regioselectivity over 99%, high number-average molecular weights (*M_n*s) of up to 90.3 kg/mol, and narrow dispersity (1.05–1.31). Nevertheless, the primary disadvantages of metal catalysts include the multiple-step preparation process for some metal catalysts and the metal residues in the final products that limits their applications in optical and electric materials. As a potential alternative, organocatalyst, which feature extraordinary characteristics including inexpensiveness, simpler preparation, lower air-sensitivity, and lower toxicity, has been utilized in polymer synthesis in recent years.^[40–46] Recent works have witnessed the success of organocatalysts for alternating copolymerization of COS with epoxides.

Organic Lewis pair-catalyzed copolymerization of COS with epoxide was developed (Scheme 2) by the collaboration of the author's group and Darensbourg's group.^[47] The

Lewis pair was composed of Lewis bases (LBs: amidine, guanidine, or quaternary onium salts) and Lewis acid (triethyl borane, TEB). Colorless and highly transparent copolymers were successfully obtained (Fig. 1). The applicable epoxides included PO, cyclohexane oxide (CHO), and phenyl glycidyl ether (PGE). The produced poly(monothiocarbonate)s had over 99% tail-to-head (T-H) diad content (different to H-T diad because two monomers are asymmetrical) and high M_n s of up to 92.5 kg/mol. It was proposed that the coordinative bonds between these Lewis pairs allowed for the insertion of COS and epoxide.

Unfortunately, the TEB/LB Lewis pair-catalyzed COS/epoxide copolymerization shows a poor controllability and



Scheme 2 Illustration of the metal-free Lewis pairs for copolymerization of COS and epoxides

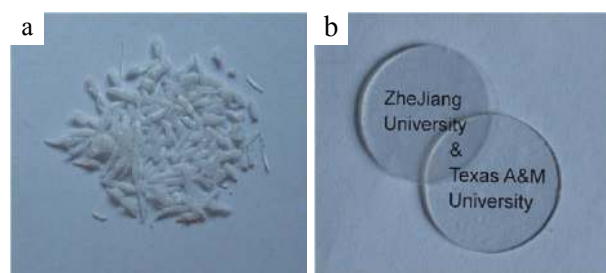


Fig. 1 (a) The purified COS/PO copolymer from metal-free Lewis pair catalyzed process; (b) Wafers of COS/PO copolymer made by hot press (25 mm in diameter and 1.0 mm in thickness) (Reprinted with permission from Ref. [47]; Copyright (2017) Wiley)

affords products with broad polydispersity. Further, TEB is a hazardous chemical, which is toxic and spontaneously combustible in air. Subsequently, we developed a living copolymerization of COS with epoxide using dual organocatalysts composed of thioureas as hydrogen-bond donors and LBs (e.g. phosphazene, amidine, and guanidine) (Scheme 2).^[48] The produced poly(monothiocarbonate)s had well-defined structures, alternating degrees higher than 99%, controllable molecular weights of up to 98.4 kg/mol, and narrow molecular weight distributions. These dual organocatalysts exhibited high activity with the turnover frequency (TOF) of up to 112 h⁻¹ at room temperature. Mechanistically thinking, thioureas and LBs have cooperative effect on the copolymerization by undergoing a non-covalent mode to activate the monomer and stabilize the propagating anionic species.

The thiourea/LB dual organocatalysts can provide fully alternating COS/epoxide copolymers with well-defined microstructure. For example, using BnOH as an initiator for the copolymerization of COS with PO, single distribution of [BnO + (PO + COS)_n + H] was obtained, as revealed by MALDI-TOF MS spectroscopy (Fig. 2). Moreover, the living feature of this process was clearly confirmed by the linear time-de-

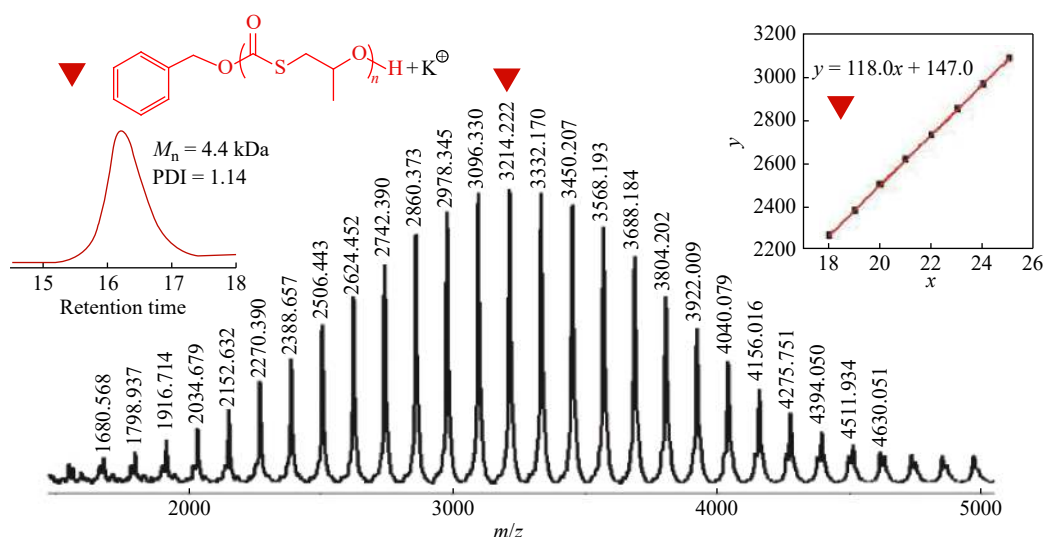


Fig. 2 Analysis of PPTMCs by MALDI-TOF MS spectra. GPC curves, the chemical structure of PPTMCs and the plot of M_n versus repeated unit number are inserted. PPTMC was synthesized with BnOH, which afforded α -OBn, ω -OH copolymer-terminated [BnO + (PO + COS)_n + H + K⁺] (M_n : 4.4 kg/mol; PDI: 1.14). Reaction conditions: PO/DBU/diisopropyl thiourea/BnOH = 100/1/1/1 (molar ratio), 25 °C, 3.5 h (Reprinted with permission from Ref. [48]; Copyright (2018) Springer Nature)

pendent conversion plots, linear increase of molecular weight with monomer conversion, narrow polydispersity to high monomer conversion, and the chain extension reaction.

Synthesis of Crystalline Poly(monothiocarbonate)s

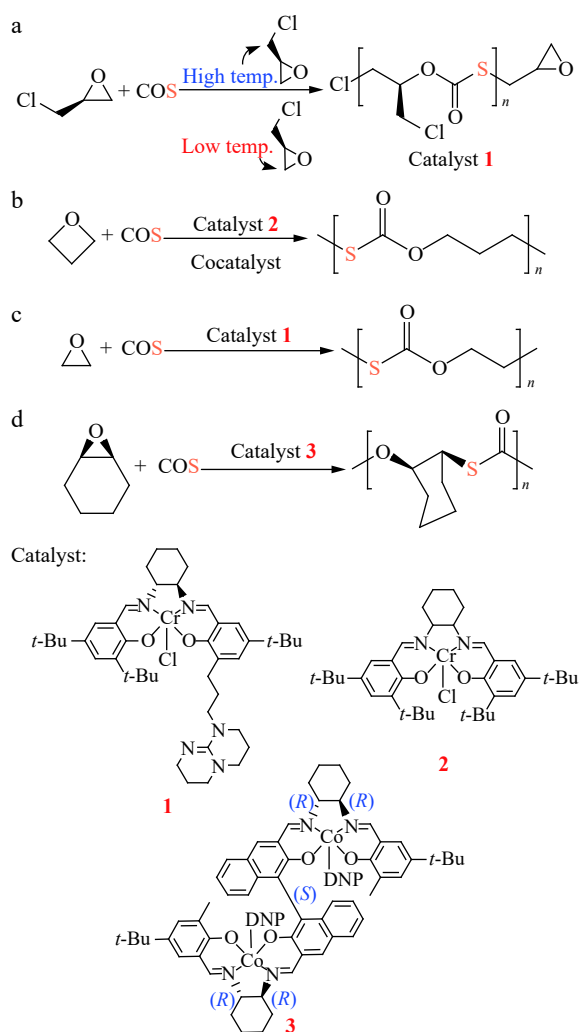
Most of the COS-derived copolymers reported are amorphous. Ren and co-workers published the first example of semicrystalline COS-based copolymer from the regioselective copolymerization of COS and enantiopure epichlorohydrin (ECH) (Scheme 3a) using a bifunctional Cr(III)-salen catalyst (catalyst **1** in Scheme 3).^[49] The copolymerization showed excellent regioselectivity for ECH ring-opening at the methylene carbon at reduced temperature. Therefore, isotactic poly(monothiocarbonate)s were obtained with this catalyst. It was revealed that the reaction temperatures played significant roles in the crystallization behavior of the ECH-COS copolymers. The resultant copolymer was semicrystalline with a glass transition temperature (T_g) of 15.6 °C and a melting point (T_m) of 96.7 °C. At ambient temperature, the propagating monothiocarboxylate species favored the nucleophilic attack at the chloromethylene of ECH, releasing chloride ion as a new initiator. Due to the fast chain transfer reaction to ECH, M_n of the resultant polymer reached merely

3.1 kg/mol even at –25 °C. The synthesis of high molecular weight ECH-COS copolymers remains a challenge.

Our group reported the first example of semicrystalline poly(trimethylene monothiocarbonate) (PTMMTC) depending on the chain folding mechanism, from the copolymerization of COS and oxetane (Scheme 3b).^[25,50] The copolymerization was catalyzed by (salen)CrCl complex (catalyst **2** in Scheme 3) with the presence of cocatalyst. The reaction could be efficiently performed at high reaction temperatures (100–130 °C) without the occurrence of oxygen/sulfur atom exchange, which could generate CO₂ (or COS) and episulfide mixed in the system, leading to the produced polymers with randomly distributed thiocarbonate, carbonate, and even thioether units.^[51] M_n s of the produced PTMMTCs were as high as 55.7 kg/mol. These semicrystalline copolymers presented T_m s of up to 127.5 °C, similar to that of HDPE, and had a suitable processing temperature window of ca. 100 °C. Furthermore, the copolymerization of COS and ethylene oxide (EO) was reported to produce semicrystalline poly(ethylene monothiocarbonate) (PEMTC) with a T_m of up to 128.2 °C (Scheme 3c), using catalyst **1** (Scheme 3).^[52] Note that the semicrystalline copolymers can also be synthesized by using TEB/LB Lewis pairs.^[53]

It is of interest that the poly(carbonate) analogues of PTMMTC and PEMTC are amorphous (or crystallize only upon tensile loading)^[54] and often decompose during the melt processing. Hence, we recently studied their crystallization behaviors. Both PTMMTC and PEMTC exhibited spherulite morphology^[53] and possessed double melting peaks after the isothermal crystallization. The equilibrium melting temperature (T_m^0) of PTMMTC, an important crystallization parameter, was determined to be 147.9 °C by the high temperature melting peaks, as shown in Fig. 3(a). And T_m^0 of PEMTC was calculated to be 134.6 °C by the lower temperature melting peaks (Fig. 3b). Small-angle X-ray scattering (SAXS) pattern showed that more amorphous phases were included into the spherulites of PTMMTC, leading to a larger long period and a thicker amorphous layer. Intriguingly, PTMMTC carrying a longer alkane segment (CH₂CH₂CH₂) in the main chain exhibited a larger free energy of the folding surface than that of PEMTC, which could be attributed to the stronger interchain interactions of PTMMTC.

Very recently, Ren and co-workers reported an elegant work that described the synthesis of chiral sulfur-containing polymers by asymmetric alternating copolymerization of COS and achiral *meso*-epoxides (Scheme 3d).^[55] The binaphthol-linked bimetallic complex having a *R,R,R,R,R* conformer (catalyst **3** in Scheme 3) was employed to the asymmetric transformation under mild reaction conditions, producing a series of isotactic poly(monothiocarbonate)s with more than 99% isotacticity. The monomer scope included CHO, cyclopentene oxide (CPO), 4,4-dimethyl-3,5,8-trioxabicyclo-[5.1.0] octane (CXO), and 3,4-epoxytetrahydrofuran (COPO). The stereoregular copolymers derived from COS and COPO presented the highest T_m of 232 °C. The as-produced sulfur-containing polymers also showed good optical properties with Abbe's numbers up to 43 and refractive indices of up to 1.56.



Scheme 3 Illustration of the synthetic routes to crystalline poly(monothiocarbonate)s from COS and epoxides

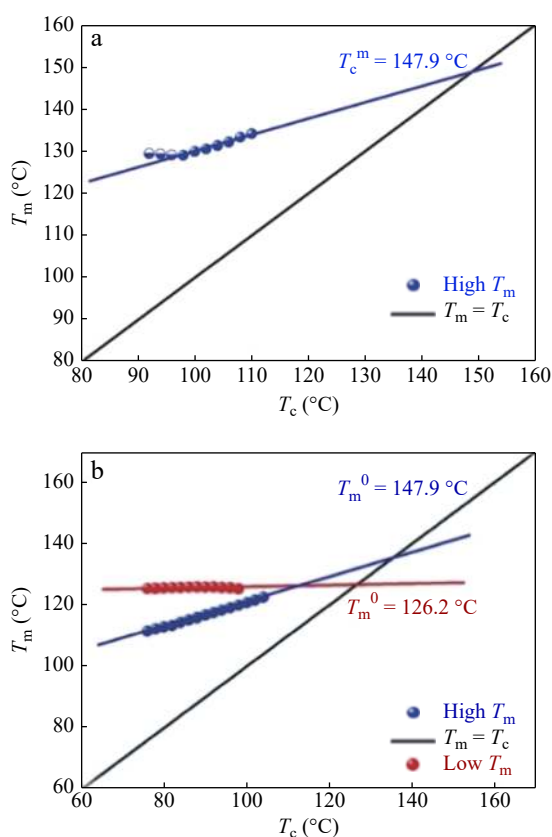


Fig. 3 Hoffman-Weeks plots for (a) PTMTC and (b) PEMTC (Reprinted with permission from Ref. [53]; Copyright (2019) Elsevier)

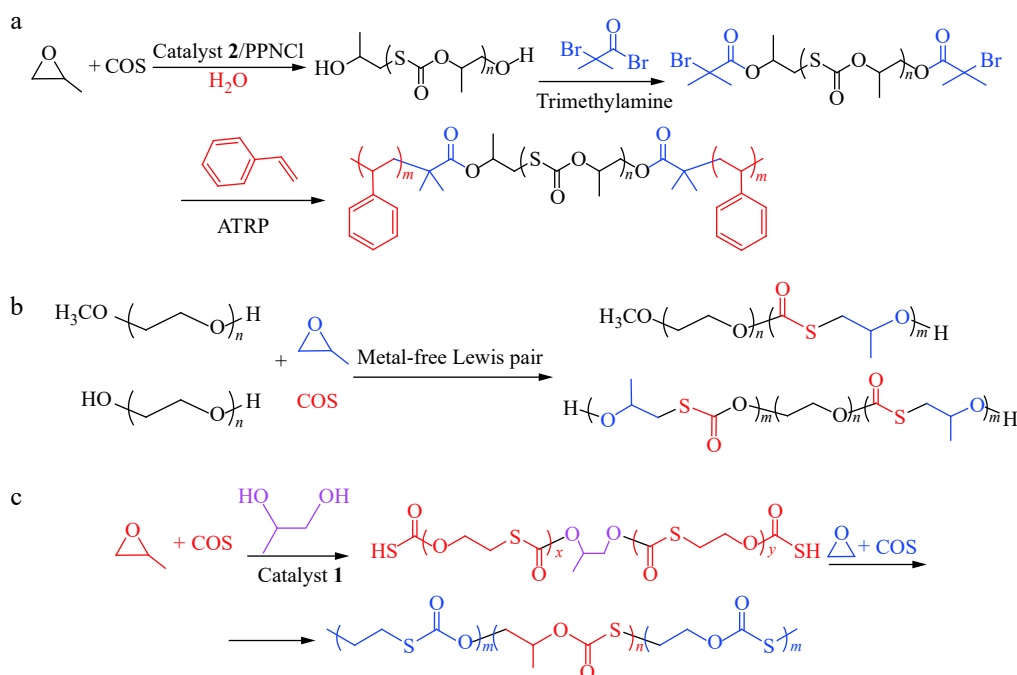
Synthesis of COS-based Block Copolymers

Block copolymers provide an extraordinary and fascinating approach to modify and enrich the performance of polymeric materials.^[56] A series of COS-based block copolymers have

been developed recently. We synthesized a triblock copolymer containing poly(monothiocarbonate) block, *i.e.*, polystyrene-block-poly(propylene monothiocarbonate)-block-polystyrene (PS-*b*-PPMTC-*b*-PS).^[57] The α -OH, ω -OH PPMTC (M_n : 3.7 kg/mol; PDI: 1.06) was initially prepared using binary (salen)CrCl/[PPN]Cl as the catalyst and water as the chain transfer agent (Scheme 4a). Note that the α -OH, ω -OH PPMTC was a fully alternating and regioregular copolymer with a tiny amount of tail-to-tail (T-T) diad and dithiocarbonate[–S(C=O)S–] units that were defined as the regio-defects.^[57] Then, esterification of the PPMTC diol was completely performed by the reaction with 2-bromoisobutyryl bromide, leading to the brominated PPTMC. Finally, the PS-*b*-PPMTC-*b*-PS triblock with M_n of 10.8 kg/mol and PDI of 1.08 was prepared *via* the atom transfer radical polymerization (ATRP) of styrene. This triblock copolymer showed a single glass transition temperature (T_g) of 61.9 °C, indicating the potential compatibility of PPMTC and PS blocks. Therefore, the blocks are very promising to the application of transparent optical materials.

We have also developed a one-pot synthesis of COS-based block copolymers using metal-free TEB/LB pairs (Scheme 4b).^[58] The block copolymers of PPMTC-*b*-PEG and PPMTC-*b*-PEG-*b*-PPMTC with narrow dispersities (1.1–1.3) were obtained by the copolymerization of COS and PO, using poly(ethylene glycol) (PEG) with one or two –OH end groups as the macroinitiators. The initiating efficiency of these PEGs could be up to 100%. The molecular weights of the produced block copolymers can be regulated by varying the amount of PEGs. Both copolymers displayed a single T_g without the crystallization point of PEG block, suggesting a good compatibility between the blocks of PPMTC and PEG.

Ren and co-workers reported a triblock PEMTC-*b*-PPMTC-*b*-PEMTC copolymer, which was synthesized by



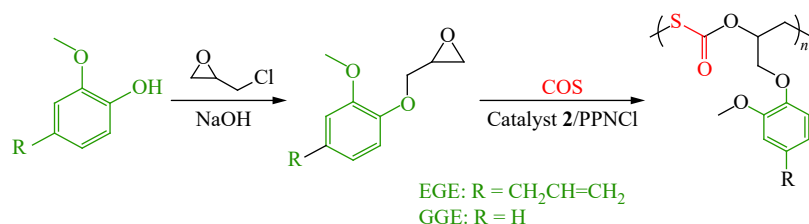
Scheme 4 Illustration of synthetic method to COS-based block copolymers

using 1,2-propanediol as a chain transfer agent and stepwise addition of epoxides (Scheme 4c).^[52] The amorphous PPMTC block was firstly formed and used as the soft segment, while the crystalline PEMTC block was used as the hard segment. The resultant triblock copolymer had an ultimate tensile strength of (11.2 ± 0.1) MPa and a strain to failure of $(575 \pm 52)\%$, indicating the potential of this block as a thermoplastic elastomer. These discussed strategies in Scheme 4 are all effective for the synthesis of sulfur-containing block copolymers, while developing a novel, versatile, and convenient method for synthesizing COS-based block copolymers is still highly desired.

Copolymerization of COS with Biomass-derived Epoxides

Oil/gas-based polymers are currently the majority of commercial polymeric materials, while the synthetic polymers

from biomass have received considerable attention in recent years.^[59] We have successfully prepared biomass- and COS-derived copolymers by the copolymerization of biomass-derived epoxides with COS using the binary (salen)CrCl/[PPN]Cl catalyst system (Scheme 5).^[60] Two epoxides, eugenol-based glycidyl ether (EGE) and guaiacol-based glycidyl ether (GGE), were synthesized from eugenol and guaiacol, respectively, which are lignin-derived monomers. The copolymerization exhibited high activity with TOF of up to 12000 h^{-1} at 40°C . The copolymers possessed perfectly alternating degrees of 100%, regioregularity with a T-H diad content over 99%, and high M_n s up to 62.2 kg/mol. Moreover, the produced copolymers exhibited high refractive index of larger than 1.58 and suitable Abbe's numbers (32.5–40.4), representing a new promising optical polymer.



Scheme 5 The synthetic route to COS and biomass-derived copolymers from guaiacol and eugenol. EGE: eugenol-based glycidyl ether; GGE: guaiacol-based glycidyl ether

CONCLUSIONS AND OUTLOOK

We highlighted the recent advances in the synthesis of poly(monothiocarbonate)s derived from COS and epoxides. Organocatalyst provides several advantages, such as no need for costly removal of metal impurities, commercial availability or readily synthesis in few steps, and enhanced stability with respect to trace impurities that enables simple storage. It is still a brand challenge to develop new, robust, and effective organocatalysts, and even chiral organocatalysts to control the stereoselectivity of the copolymerization. The application of currently developed catalysts for COS-derived copolymers has been extended to the synthesis of sulfur-containing block copolymers and crystalline copolymers. These copolymers displayed fantastic structures and properties, as compared with their poly(carbonate) counterparts. Further studies will hopefully broaden the epoxide scope of this copolymerization process such as the biomass epoxides to enhance the utility and performance of sulfur-containing polymers produced, and to develop effective catalysts as well as the large-scale production of these sulfur-containing polymers and their applications.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (No. 21774108) and the Distinguished Young Investigator Fund of Zhejiang Province (No. LR16B040001).

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