Poly(monothiocarbonate)s from the Alternating and Regioselective Copolymerization of COS with Epoxides

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Abstract: This poster describes our efforts on the discovery of the selective formation of poly(monothiocarbonate)s from COS with epoxides via heterogeneous zinc-cobalt double metal cyanide complex (Zn-Co(III) DMCC) and homogenous (salen)CrX complexes. [1] The catalytic activity and selectivity of Zn-Co(III) DMCC for COS/epoxide copolymerization are similar to those for CO_2/epoxide copolymerization. COS-based copolymers are highly transparent sulfur-containing polymers with excellent optical properties, such as high refractive index and Abbe number. Very recently, crystalline COS-based polymers with or without chiral carbon have been synthesized, which may further expand the scope of application of these new materials.

Introduction

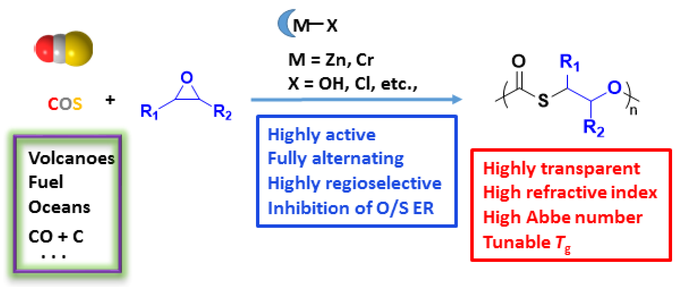

Fig. 1. Synthesis of poly(monothiocarbonate)s from COS/epoxide copolymerization (R_1 and R_2 represent substituted groups).

As an analogue of carbon dioxide (CO_2) and carbon disulfide (CS_2), COS is a heterocumulene containing C=O or C=S groups and can be regarded as an asymmetric form of CO_2 and CS_2. It could be an ideal one-carbon (C1) monomer for synthesizing sulfur-containing polymers via a similar route to CO_2 copolymerization. Motivated by the achievements of CO_2/epoxide copolymerization in the past decade, we have undertaken the research on the COS/epoxide copolymerization for synthesizing poly(monothiocarbonate) (Fig.1).

Catalysts for COS(CS_2)/epoxides copolymerization

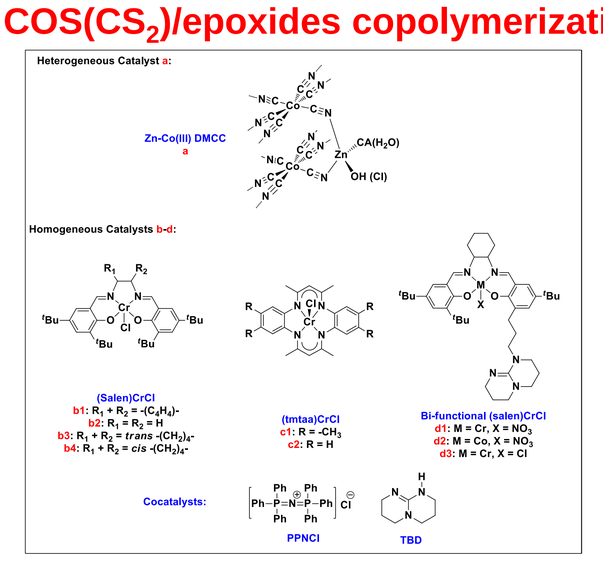

Fig.2 The catalysts and cocatalysts reported for COS/epoxide copolymerization. (The ground state of the catalytic center of a was proposed as a tetrahedral zinc ion with one Zn-OH bond (or Zn-Cl bond), CA is a complexing agent). Cat.d1-d3 were reported by Ren and Lu group.(*Macromolecules* **2015**, *48*, 8445-8450)

Since 2008, we have performed the coupling of CS_2 with PO, cyclohexene oxide (CHO), cyclopentene oxide (CPO) and oxetane, by using either heterogeneous zinc-cobalt double cyanide complex [Zn-Co(III) DMCC] catalyst or homogenous (salen)CrCl complex (Fig.2). Oxygen-sulfur exchange reaction (O/S ER) was observed in both the polymeric and cyclic products resulting in irregular polymer chain structure and poor selectivity.

The observation of COS intermediate during CS_2/epoixdes copolymerization intrigued us to explore COS/epoxides copolymerization. The catalytic activity and selectivity of Zn-Co(III) DMCC for COS/epoxide copolymerization are similar to those for CO_2/epoxide copolymerization. (Salen)CrX complexes accompanied by onium salts exhibited high activity and selectivity for COS/epoxide copolymerization under mild conditions, affording copolymers with >99% monothiocarbonate units and a high tail-to-head content up to 99%. The specialty of COS polymerization that are the unit selectivity caused by O/S ER and regioselectivity induced by the asymmetrical structure of COS. Of importance, COS can copolymerize with numerous epoxides, whether they contain electron-donating or electron-withdrawing groups, displaying high catalytic activities and regioselectivity in a well-controlled process carried out under mild conditions.

Mechanistic aspects of the COS/epoxide copolymerization

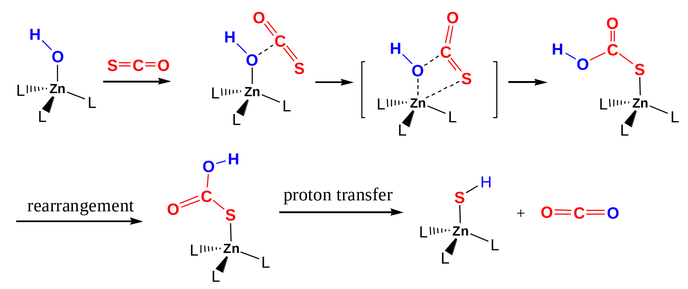

Fig. 3. Metal-OH catalysis for O/S ER. Similar to the mechanism of fixation of COS by the CA compound $[L_3ZnOH]^+$, L is histidine (CA center structure) or ligand (generally, amine, CA models).

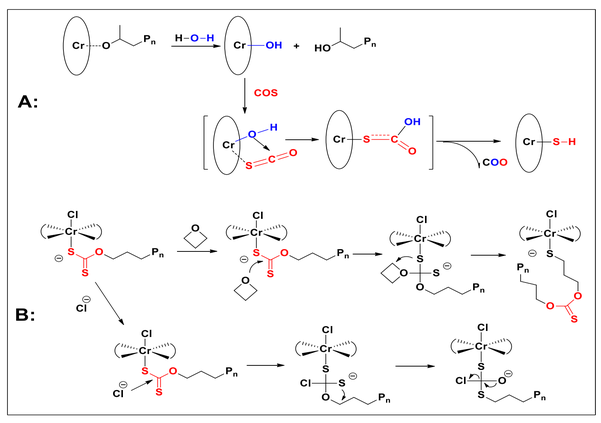

Fig. 4. Proposed O/S ER mechanism for COS/epoxide and CS_2/oxetane copolymerization. (A) Metal-OH catalysis, (B) **Rearrangement of tetrahedral intermediate** (Take Cr^{3+} as an example).

Properties of COS/epoxide copolymer

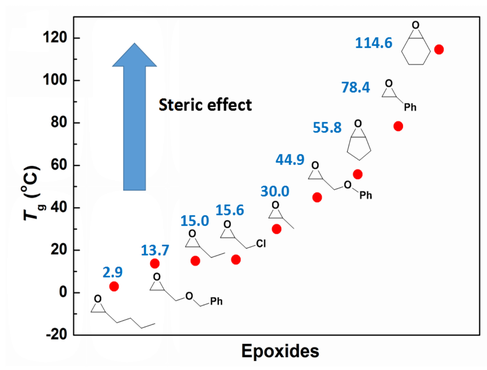

Fig. 5. T_gs of the poly(monothiocarbonate)s from COS/epoxides copolymerization.

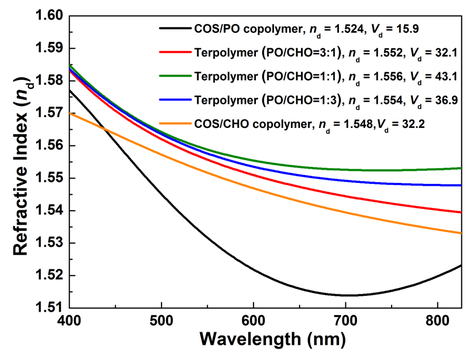

Fig. 6. The refractive indices (n) of COS/CHO/PO terpolymers *via* the wavelength from 400 to 800 nm (n_d is refractive index at wavelength 587.6 nm).

Crystalline COS/oxetane copolymer

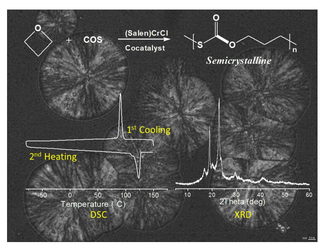

Fig.7 A semicrystalline poly(trimethylene monothiocarbonate) (PTMMTC) was firstly synthesized via the selective and alternating copolymerization of COS with oxetane. It presents similar crystallization behavior to high-density polyethylene (HDPE), i.e., being spherulite and possesses melting temperature (T_m) of up to 127.5°C and degree of crystallinity (X_c) of up to 71%.[2]

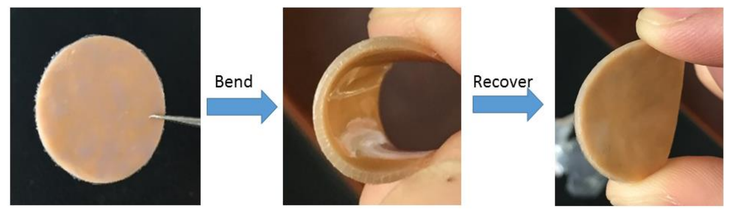

Fig.8 PTMMTC could be hot pressed at 150°C for 8 min and then cool pressed at room temperature for 8 min. It is flexible and tough.

Conclusions

The production of sulfur-containing polymers from the copolymerization of COS and epoxides represents an atom-economical and significantly "greener" route to these thermoplastics. Our efforts on the COS/epoxides copolymerization disclosed the specialty of COS polymerization that are the unit selectivity caused by O/S ER and regioselectivity induced by the asymmetrical structure of COS. With regard to future directions for synthesizing COS-based copolymers, we hope to broaden the scope of catalysts capable of catalyzing COS with epoxides, affording various poly(monothiocarbonate)s, as well as their block copolymers and crystalline polymers.

Acknowledgement

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References

[1] Luo, M.; Zhang, X. H.; Darensbourg, D. J. Poly(monothiocarbonate)s from the Alternating and Regioselective Copolymerization of COS with Epoxides. (Accepted)

[2] 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 Alternating Copolymerization of COS and Oxetane: A Semicrystalline Copolymer. (Submitted)