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]CoX complexes. [1] The catalytic activity and selectivity of Zn-Co(III) DMCC for COS/epoxide copolymerization are similar to those for CO2/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

As an analogue of carbon dioxide (CO2) and carbon disulfide (CS2), COS is a heterocumule containing C=O or C=S groups and can be regarded as an asymmetric form of CO2 and CS2. It could be an ideal one-carbon (Cl) monomer for synthesizing sulfur-containing polymers via a similar route to CO2 copolymerization. Motivated by the achievements of CO2/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/CS2/epoxides copolymerization

Since 2008, we have performed the coupling of CS2 with PO, cyclopentene oxide (CHO), cyclopentene oxide (CPO) and oxetane, by using either heterogeneous zinc-cobalt double cyanide complex [Zn-Co(III) DMCC] catalyst or homogenous [salen]CoX 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 CS2/epoxides 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 CO2/epoxide copolymerization. [salen]CoX complexes accompanied by onium salts exhibited high activity and selectivity for COS/epoxide copolymerization under mild conditions, affording copolymers with >98% 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 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.

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.

References

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