Using Carbon Dioxide and Its Sulfur Analogues as Monomers in Polymer Synthesis

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Abstract: **Our recent works on the synthesis of polymers from one-carbon (C1) feedstocks are presented, including the recent advances in CO_2 copolymerization via heterogeneous catalysis of zinc-cobalt(III) double metal cyanide complex [Zn-Co(III) DMCC] catalyst, the syntheses of CO_2-based block and grafting copolymers, the COS/epoxide copolymerization, and the CS_2/epoxide copolymerization. The utilization of CO_2, COS and CS_2 as feedstocks for polymer synthesis is an alternative to sustainable chemistry.**

1. Introduction

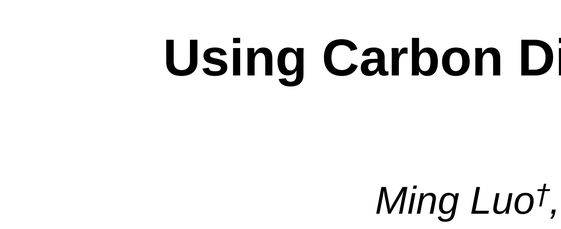

Fig. 1. The ball-and-stick models and bond length of three C1 building blocks.

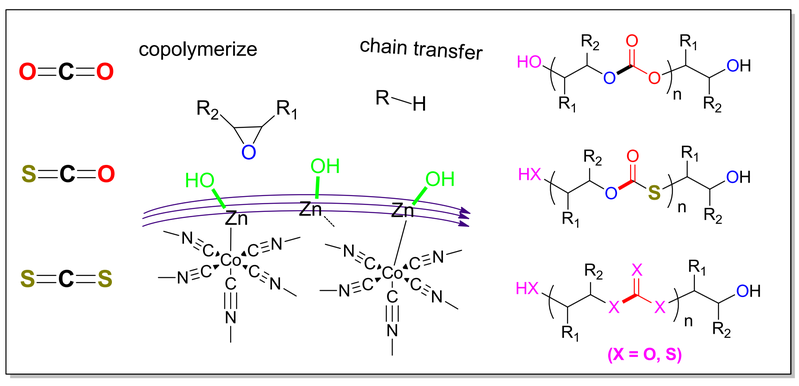

Fig. 2. C1-involved copolymerization via Zn-Co(III) DMCC catalysis. Zn-OH bond is proposed to be the initiating group of Zn-Co(III) DMCC for CO_2/epoxide copolymerization; chain transfer reaction of the propagating species to the protonic compounds (H_2O, the generated polymers with two ended hydroxyl groups, R-H), producing copolymers with various ended groups. Purple end groups (-XH and -OH) indicate that they comes from different reactants or the catalyst.

The alternating copolymerization of one-carbon (C1) building blocks including carbon dioxide (CO_2) and its sulfur analogues of carbon disulfide (CS_2) and carbonyl sulfide (COS) with epoxides afford new copolymers, namely polycarbonates and polythiocarbonates, with tailored chain structures and properties.

2. CO_2/epoxide copolymerization

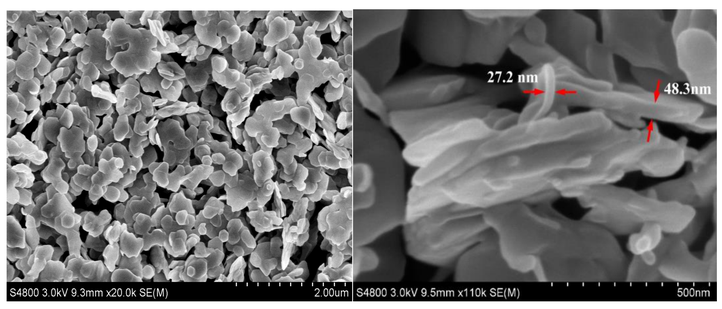

Fig. 3. SEM images of Zn-Co (III) DMCC catalyst synthesized at 75 °C.

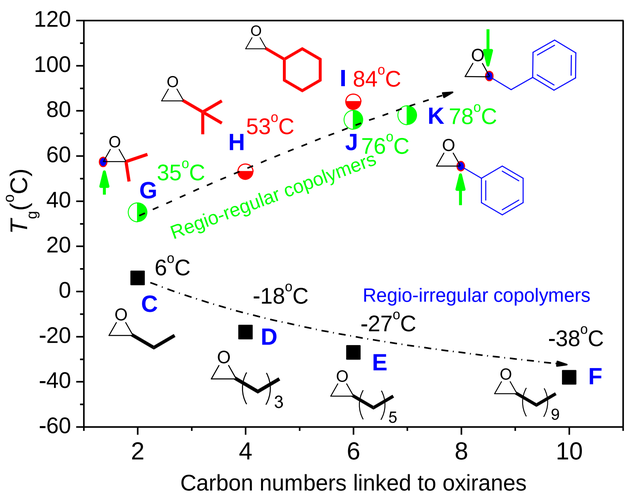

Fig. 4. Selected epoxides with alkyl and aryl groups for the copolymerization with CO_2 by using nanosized Zn-Co(III) DMCC catalyst.

The substituent effect of the epoxides on CO_2/epoxide copolymerization catalyzed by nano-sized Zn-Co(III) DMCC was intensively investigated since it can catalyze the copolymerization of CO_2 with many kinds of epoxides (Fig. 4).

3. CO_2-based polymers with various topologies

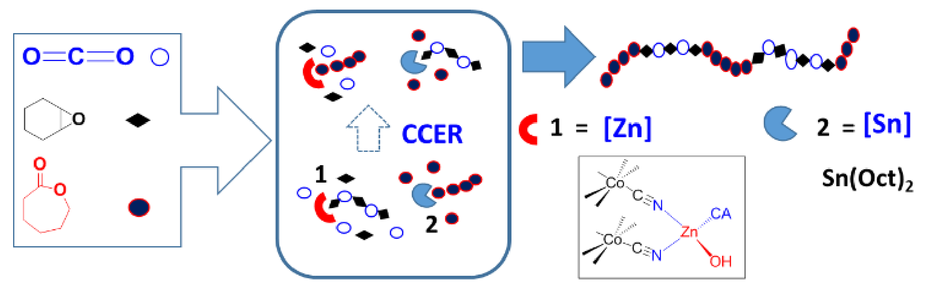

Fig. 5. Proposed cross chain exchange polymerization of CO_2, CHO and ε-CL by using Zn-Co(III) DMCC (**1**) and stannous octoate [**2**, $Sn(Oct)_2$] together.

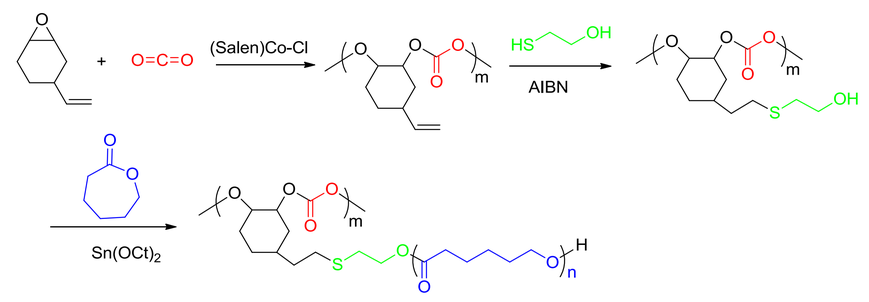

Fig. 6. Synthetic route of degradable brush copolymers with polycarbonate as backbone and PCL as side chains.

One of the main goals in polymer synthesis is to develop polymers with various topologies that presented versatile properties and functionalities. We synthesized CO_2-based multiblock and brush copolymers.

4. CS_2/epoxide copolymerization

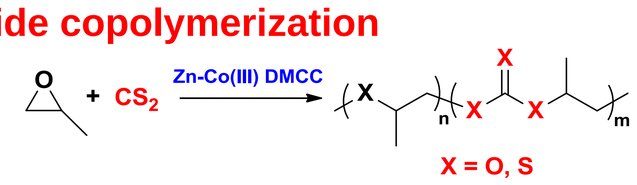

Fig. 7. The copolymerization of propylene oxide with CS_2 catalyzed by Zn-Co(III) DMCC catalyst.

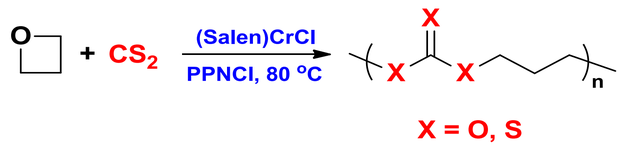

Fig. 8. The copolymerization of oxetane with CS_2.

5. COS/epoxide copolymerization

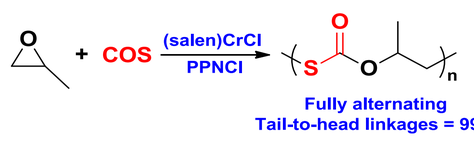

Fig. 9. The copolymerization of propylene oxide with COS.

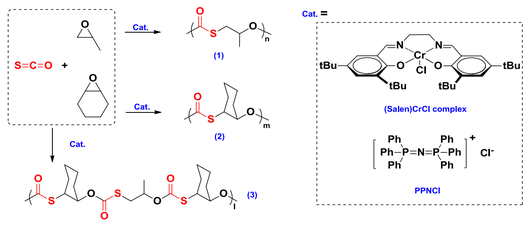

Fig. 11. The copolymerization of CHO with COS and terpolymerization of CHO/PO/COS.

The finding of oxygen-sulfur exchange reaction during COS (CS_2)/epoxide copolymerization; Polythiocarbonates with high n_d and V_d are obtained.

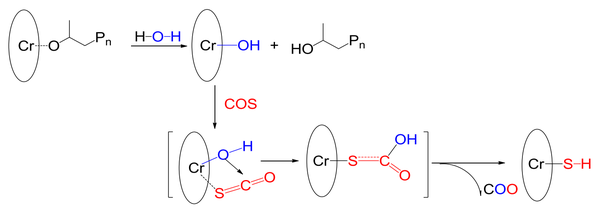

Fig. 10. The plausible mechanism for the O/S exchange reaction in the PO/COS copolymerization.

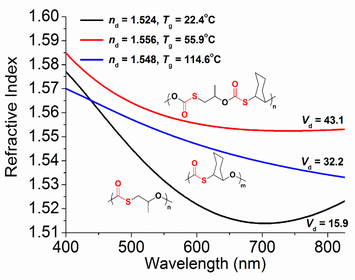

Fig. 12. The variation of the refractive indices (n) via the wavelength from 400 to 800 nm (n_d is refractive index at wavelength 587.6 nm) (Measured by Spectroscopic Ellipsometer).

Conclusions

It is still a big challenge to synthesize polymers from CO_2 and its sulfur analogues (COS and CS_2). Our ultimate goal is to develop highly active and simple catalyst that can meet the requirement of the large-scale production of CO_2-based polymeric materials, and understand the catalysis for converting C1 monomers to polymers. It is still necessary to disclose the real catalytic center of this heterogeneous catalyst and further improve its catalytic activity to a higher order of magnitude, which are the main targets of our ongoing works.

Acknowledgement

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References

[1] 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.