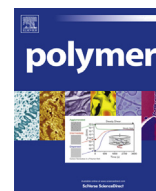




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Feature article

Using carbon dioxide and its sulfur analogues as monomers in polymer synthesis

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ABSTRACT

The alternating copolymerization of one-carbon (C1) building blocks including carbon dioxide (CO₂) and its sulfur analogues of carbon disulfide (CS₂) and carbonyl sulfide (COS) with epoxides afford new copolymers, namely polycarbonates and polythiocarbonates, with tailored chain structures and properties. This review mainly focuses on the recent advances in C1-involved copolymerization via heterogeneous catalysis of zinc-cobalt(III) double metal cyanide complex [Zn–Co(III) DMCC] catalyst. The chemistry of zinc-hydroxyl bond of Zn–Co(III) DMCC is responsible to the copolymerization of these C1 monomers with epoxides through the formation of C–O (S) bond. The syntheses of CO₂-based copolymers with various topologies are also reviewed in detail. The utilization of CO₂, COS and CS₂ as monomers for polymer synthesis have significant contributions to the sustainable use of renewable resources.

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1. Introduction

Nowadays, the vast majority of commodity polymers are obtained from fossil fuels [1]. With the possible depletion of fossil fuels in near future [2], it is an urgent need to develop polymers via a sustainable manner from abundant renewable resources. Polymers from non-petrochemical feedstocks is gaining a lot of attention from academia in recent decades [3–14]. Many biomass-originated monomers, such as oxygen-rich (e.g. carboxylic acids, polyols, dianhydroalditols and furans), hydrocarbon-rich (e.g. vegetable oils, fatty acids, terpenes, terpenoids and resin acids), hydrocarbon monomers (e.g. bio-olefins) and non-hydrocarbon monomers (carbon dioxide, carbon monoxide) have been investigated for synthesizing various polymers [5,8]. In this review, we discuss the methods for synthesizing one carbon (C1)-based polymers from an important non-hydrocarbon monomer, carbon dioxide (CO_2) and its sulfur analogues of carbon disulfide (CS_2) and carbonyl sulfide (COS).

CO_2 in the atmosphere is mostly released from the combustion of fossil fuels, respiration of living organisms and decomposition of sugar-containing vegetation. CO_2 is the most important part of the carbon cycle in the natural environment, and the concentration of CO_2 in the atmosphere has been kept in a balance before human-activities intervened. Burning of carbon-based fuels since the industrial revolution has rapidly increased its concentration in the atmosphere, leading to global warming because it absorbs heat from the sunlight. It is also a major cause of ocean acidification since it dissolves in water to form carbonic acid [15–17]. However, in view of chemistry, CO_2 is a naturally abundant, low cost, nontoxic and nonflammable C1 feedstock. Therefore, the chemical fixation of CO_2 into a useful material has been a meaningful and pragmatic subject in both chemistry and environment science [18–22]. A great deal of researches have been done on the fixation of CO_2 as a C1 building block and the corresponding chemistry [23–33].

CO_2 , as a symmetrical heterocumulene exhibiting special reactivity, which inherently comprise both electron-donating and electron-withdrawing sites, as shown in Fig. 1. However, activation of CO_2 for polymerization is still challenging because the carbon atom is highly oxidized and CO_2 is thermodynamically stable and/or kinetically inert in many targeted chemical transformations [31,32]. The catalytic copolymerization of CO_2 with epoxides to produce polycarbonates has drawn significant attention in the field of polymer chemistry over the past decades [23–29]. Such process is closely involved with the formation of carbon-oxygen bond as a key step. The research on the formation of carbon-carbon bond

with CO_2 for producing polymer is rather limited and rarely reported [33].

As a sulfur analogue of CO_2 , carbon disulfide (CS_2) can be produced through the reaction of charcoal (from plant) and sulfur (from natural ore and desulfurization from crude oil), and thus is considered as a sustainable and low-cost monomer. CS_2 is widely used as a non-polar organic solvent, and has long been used as a sulfur source in organic chemistry. The carbon of CS_2 is more electrophilic than that of CO_2 because of the weaker π donor-ability of the sulfide atom (Fig. 1). However, up to date, the polymerization of CS_2 with other monomers is still rarely reported [34–37]. In addition, another sulfur analogue of CO_2 , carbonyl sulfide (COS), is an air pollutant widely released from volcanic eruptions, burning of fossil fuels and many other chemical processes. It can cause acid rain and damage of the ozonosphere by a series of photochemical reactions [38]. Instead of a toxic waste, COS can be a good sulfur source to synthesize well-defined sulfur-containing polymers when it is employed as a monomer in copolymerization [39–42]. Meanwhile, as a C1 source, COS is more active than CO_2 in some catalytic processes due to its asymmetric structure (Fig. 1), which makes COS-involved copolymerization more interesting, which will be demonstrated in detail.

This review will provide a comprehensive chronicle of the synthesis of polymers with CO_2 , CS_2 and COS as C1 building blocks. Thereof, we emphasis on the *heterogeneous catalysis* of CO_2 into polycarbonates including the catalyst preparation, catalytic copolymerization and related mechanism study, which were rarely reviewed in the past [29,43]. The synthetic methods for CO_2 -based polymers with various topologies [44–54], which emerges as new directions in C1 copolymerization field, will be presented based on recently published works for their potential applications. Cyclic carbonates, which could be prepared from the coupling reaction of CO_2 with epoxides (and epoxy resins), are important intermediates for synthesizing poly(hydroxyl urethane)s [55–61]. It is a new non-isocyanate route to make new polyurethanes and will be discussed with recent progress. Moreover, CS_2 - and COS-involved copolymerizations are comprehensively reviewed with the detail discussion on the finding of the oxygen-sulfur exchange reaction and its influence on the related copolymerizations.

2. CO_2 /epoxide copolymerization

Nearly all the reported pathways for CO_2 copolymerization are to couple it with energy-rich substrates such as epoxides by using various catalyst system [23–29]. The main criteria for assessing the catalyst performance for CO_2 /epoxide copolymerization includes:

- 1) Activity, turnover frequency (TOF) is often given by mole epoxide converted to product per mole metal per hour, and turnover number (TON) is generally given by mole epoxide converted to product per mole metal. Meanwhile, gram copolymer per gram catalyst (or metal) can also be used to represent productivity in the cases of catalysts without well-defined structures. The level for the activity of a catalyst system is often defined on the basis of TOF as follows: low ($<5 \text{ h}^{-1}$), moderate ($5\text{--}200 \text{ h}^{-1}$), and high ($>200 \text{ h}^{-1}$) [25]. Note that the

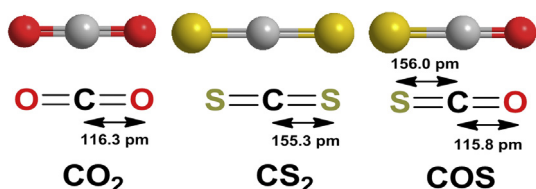


Fig. 1. The ball-and-stick models and bond length of three C1 building blocks.

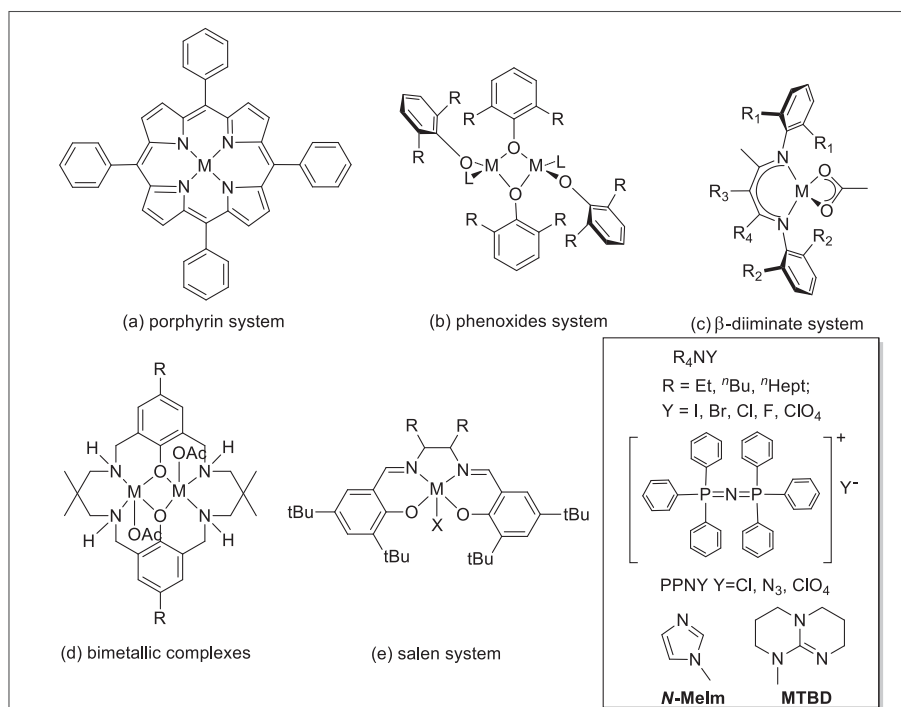


Fig. 2. Representative homogeneous metal catalysts for copolymerization of CO₂ with epoxides. (M = Mg, Co, Zn, Cr, Al, R, R₁–R₄ = alkyl group or aryl group, etc., X = halogen, N₃ or NO₃, etc.).

reaction conditions should be provided when the TOF, TON and the productivity of different kinds of catalysts are compared.

- 2) Selectivity, the polymer selectivity refers to the molar or weight ratios of polymer to the byproduct cyclic carbonate, and alternating degree (F_{CO_2}) that represents the molar ratio of carbonate unit to the all units of the resulting copolymer, generally based on the proton Nuclear Magnetic Resonance (¹H NMR) spectroscopy.

Regioselectivity, enantioselectivity and stereoselectivity are often used for the polymerizations with subtle control of the chain microstructures and have been intensively reviewed by Lu's group recently [26]. Herein, we briefly summarize some important homogeneous catalysts for CO₂ copolymerization with nice contributions in this field.

2.1. Homogeneous catalyst for CO₂ copolymerization

Since the landmark discovery of the diethyl zinc (ZnEt₂)/H₂O system for CO₂/propylene oxide (PO) copolymerization by Inoue et al., in 1969 [23], much progress has been made in developing different catalyst systems for the copolymerization of CO₂ with various epoxides [25–29]. Initially, numerous heterogeneous zinc-based catalysts were developed for higher activity and selectivity [29]. However, the polycarbonate selectivity of heterogeneous catalysts were usually low, and the relating mechanism study was put in a tight spot because the characterization of these heterogeneous catalyst was limited, thus the understanding of the heterogeneous catalysis for fixing CO₂ into polymers was somewhat limited. The development of homogeneous organic metal catalysts for CO₂ copolymerization brought several breakthroughs in recent decades, as well as intensive understanding on CO₂ copolymerization, as a consequence, many kinds of CO₂-based copolymers with precisely well-defined structures were developed and reported by several research groups [28].

In 1978, the first homogeneous catalyst based on the aluminium tetraphenylporphyrin (tpp) complex was reported by Takeda and Inoue [62]. This catalyst could catalyze the copolymerization of PO with CO₂ under 0.8 MPa (Note that 1 atm = 0.1 MPa = 1.01 bar = 14.7 psi = 760 mmHg) at 20 °C, providing poly (propylene carbonate) (PPC) with a M_n of 3.9 kg/mol, a polydispersity (PDI) of 1.15 and 40% carbonate linkages. However, pretty long reaction time was needed for fully conversion of PO (19 days). (tpp)AlCl and (tpp)AlOMe (Fig. 2a) were found to be “living” initiators for the ring-opening polymerization (ROP) of PO, lactones and the copolymerization of CO₂ with epoxides [63,64]. Following these results, Kruper and Dellar investigated the activity of (tpp)CrX (X = Cl, Br, OAc) complexes which predominantly yielded copolymer for CO₂/cyclohexene oxide (CHO) copolymerization, yet only cyclic carbonate in CO₂/PO system [65,66]. Wang and co-workers have shown through a series of experiments that the (tpp)CoCl/cocatalyst system is indeed active in the PO/CO₂ copolymerization. A TOF of 188 h^{−1} was achieved within 5 h, and the byproduct PPC was lowered to <1%, where the obtained PPC showed a M_n of 48 kg/mol, head-to-tail (H-T) content of 93%, and alternating degree of >99%, i.e., nearly fully alternating structure [67].

The development of discrete zinc bis-phenoxide complex as a kind of well-defined zinc complex was a keystone event in the field of CO₂ copolymerization. A zinc(II) bis (2,6-diphenylphenoxide) initiator (Fig. 2b) for the copolymerization of CO₂ and epoxides was reported by Darensbourg and Holtcamp in 1995 [68]. The well-characterized mononuclear zinc catalysts exhibited high productivity, i.e. >350 g polymer/g zinc over a 69 h period, for CO₂/epoxide copolymerization, however, it produced polymers with quite broad PDIs and high proportions of ether linkages [69,70].

The next major breakthrough was reported by Coates and co-workers in 1998 [71], who discovered a series of highly active zinc β-diimine complex for the synthesis of highly alternating and mono dispersed CO₂/epoxide copolymers with high molecular weights. This kind of zinc complex was the most active reported

catalyst for CO₂/CHO copolymerization then, which exhibited extremely high TOF up to 247 h⁻¹ even under substantially mild conditions (20–80 °C, 0.7 MPa). Furthermore, the produced polymers possessed high M_n of 19.1–31.0 kg/mol with a narrow PDI of 1.07–1.17, which is consistent with a “living” polymerization style. The effect of a variety of substituents and initiating groups of zinc β-diimine complexes on the activity of copolymerization were closely correlated (Fig. 2c) [72].

In 2005, Lee and co-workers reported a series of bimetallic anilido-alimine zinc complexes which exhibited extremely high TON up to 2980 for producing poly(cyclohexene carbonate) (PCHC) with high M_n up to 284.0 kg/mol and F_{CO2} ranged from 85 to 96% as a common feature of zinc catalysts [73]. It was the first discrete complexes to yield copolymers with quite high molecular weights and TONs, as the extremely dilute condition such as a zinc/monomer ratio of 1/16800 could be operated. A series of di-zinc complexes coordinated by a macrocyclic ancillary ligand (Fig. 2d), which showed remarkable activity for CO₂/CHO copolymerization was reported by Williams group in 2008 [74]. It is impressive that such di-zinc catalyst showed moderate activity of 140 h⁻¹ at CO₂ pressure of 0.1 MPa.

In 2001, Darensbourg group, inspired by the work of Jacobsen on asymmetric ring opening of epoxides [75,76] as well as the success of the chromium(III) porphyrin derivatives catalysts reports of Kruper [66] and Holmes [77], developed an air-stable chromium salen (salicylalimine) catalysts (Fig. 2e) which showed moderate activity, high stereoselectivity. TON and TOF were 683 and 28.5 h⁻¹, respectively, for CO₂/CHO copolymerization [78] carried out at 80 °C and 5.9 MPa CO₂ pressure. The resulting polycarbonate contained >99% carbonate linkages and had a M_n of 8.9 kg/mol with a PDI of 1.2. The early-stage studies of metal salen catalysts were comprehensively reviewed by Darensbourg in 2007 [79].

The most significant development involving the use of (salen)Co(III)X (Fig. 2) catalysts was first disclosed in 2003 by Coates and co-workers [80], in the copolymerization of CO₂ with PO. This cobalt catalyst provided >99% polymer selectivity, and 99% carbonate linkages with a TOF of 70 h⁻¹, when albeit at high catalyst loadings (Cat./monomer = 1/200–1/500). The results showed that the substitution of chromium for cobalt in salen catalysts increased both the activity and selectivity for copolymer formation.

Since 2004, Lu and co-workers studied a series of chiral

tetradentate Schiff base cobalt complex [(salen)Co(III)X] for catalyzing CO₂/PO copolymerization, investigating a number of different ligand substitutions, initiating groups (such as Cl, Br, NO₃, ClO₄), and a variety of different cocatalysts such as organic ammonium salts or sterically hindered strong organic bases (R₄NX, [PPN]X, MeIm, MTBD) (Fig. 2e) [81,82]. The results showed that a bulky chiral cyclohexene diimine backbone complex with an axial X group of poor leaving ability as the electrophile, combined with a bulky nucleophile with poor leaving ability and low coordination ability, is an ideal binary catalyst system for the copolymerization of CO₂ and racemic aliphatic epoxides to selectively produce polycarbonates with relatively high enantioselectivity, >95% head-to-tail content, and >99% carbonate linkages. Note that (salen)Co(III)X alone as catalyst for CO₂/epoxide copolymerization only performed at high CO₂ pressure and room temperature, while the enhancement of reaction temperature, the decrease of CO₂ pressure, or the use of low catalyst loading led to a quite low activity even no activity. On the contrary, the presence of a nucleophilic cocatalyst such as quaternary ammonium salt not only improved both catalytic activity and product selectivity significantly, but also performed at very mild conditions, such as low CO₂ pressures and low catalyst loading. Furthermore, they also reported a highly active and thermally stable cobalt based catalyst with 1,5,7-triabicyclo[4.4.0] dec-5-ene anchored on the ligand frame work and bi-functional catalyst bearing a quaternary ammonium salt (**1** in Fig. 3). These catalysts showed high activities for the copolymerization of CO₂ with both aliphatic epoxides and CHO at high temperatures and low catalyst loading, or/and low CO₂ pressures [83,84]. After the above landmark works, Lu group designed a series of multi-chiral (S,S,S)–Co(III) catalysts (**2** in Fig. 3) [85,86] for precisely controlling the chain microstructure of the resulting CO₂-based copolymers. Recently, they reported a chiral catalyst system based on an enantiopure dinuclear Co(III) complexes (**3** in Fig. 3) with a rigid bridging biphenyl linker, which exhibited high activity, unprecedented enantioselectivity, and molecular-weight control for the alternating copolymerization of CO₂ with *meso*-epoxides under mild reaction conditions [87]. Meanwhile, their further study illustrated that this kind of enantiopure and dinuclear catalyst was very efficient to synthesize crystalline isotactic polycarbonates via the copolymerization of CO₂ with *meso*-epoxides. Remarkably, crystalline stereocomplexed polycarbonates with enhanced

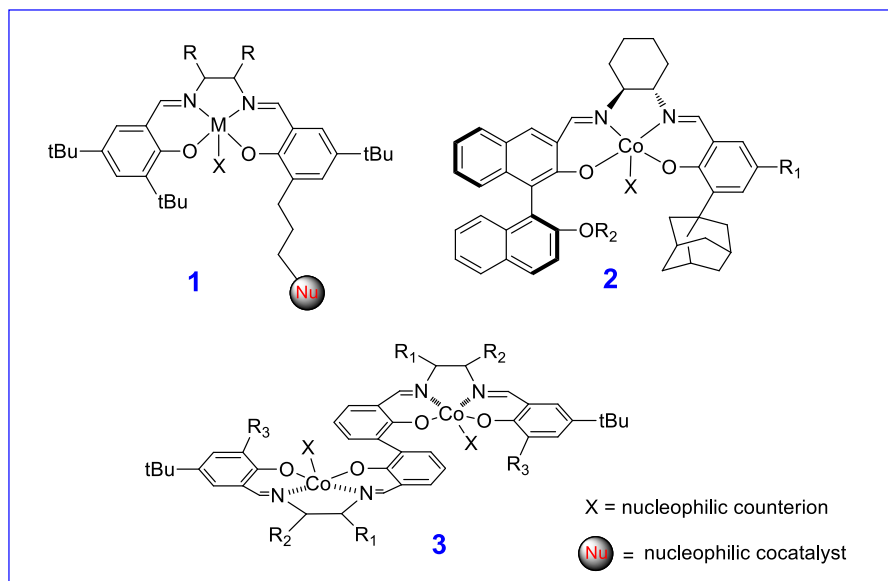


Fig. 3. Bi-functional and chiral catalytic system based on enantio-pure di-nuclear Co(III) complexes. (M = Co, Cr, R = alkyl group or aryl group, etc., X = halogen, N₃ or NO₃, etc.).

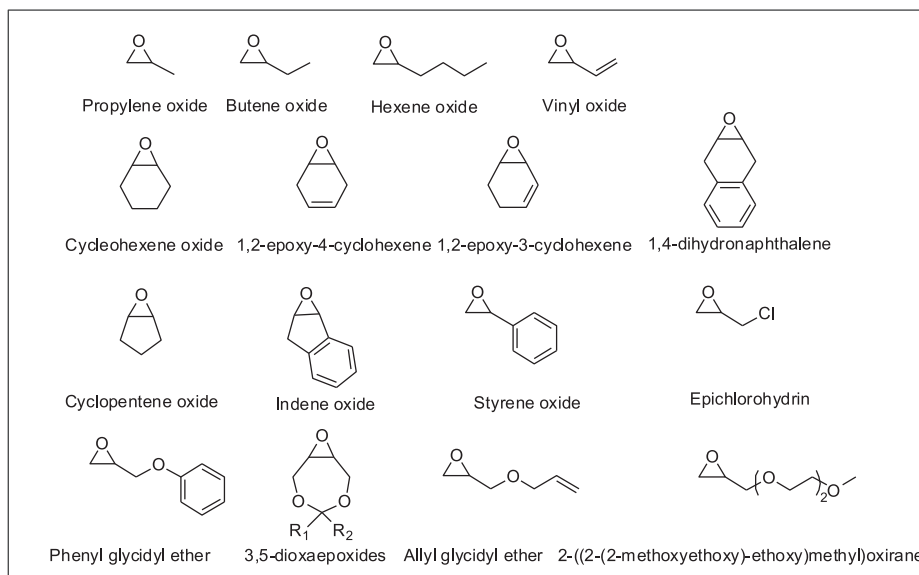


Fig. 4. Epoxides with various substituents could be copolymerized with CO₂ by using salen metal complexes catalysts.

thermal properties could be achieved by mixing equivalent opposite chiral isotactic polycarbonates [88,89].

Nozaki and co-workers investigated the copolymerization of PO with CO₂ by using dinuclear (salen)Co(III)X complexes with a series of di-cobalt salen complexes contained different linker distance in 2010 [90]. The complex showed a TOF of 180 h⁻¹, 84% carbonate linkages and a molecular weight of 36.7 kg/mol (5.3 MPa, [PO]:[Co] = 3000:1, 20 °C). Nozaki group compared the catalytic performances of these dinuclear (salen)Co(III)X complexes with their mononuclear counterpart, and disclosed that the chain propagation was indicated to proceed via a mono-metallic mechanism in the presence of onium salts even when using a dinuclear cobalt(III)X complex. Lee and co-workers synthesized an unusual binding mode of a cobalt(III) complex prepared from salen-type ligands bearing four quaternary ammonium salt units, which showed a TOF exceeding 10 000 h⁻¹ and produced a strictly alternating copolymer with a high molecular weight (*M_n*) of up to 300 kg/mol and a high selectivity (>99%) for CO₂/PO copolymerization ([PO]/[Cat] = 1 × 10⁵, 2.0–1.7 MPa, 70–75 °C, 1 h) [91,92].

Very recently, a novel trivalent titanium complex combining salen ligand [(salen)Ti(III)Cl] was reported by Wang group [93]. In combination with onium salt PPNCI (Fig. 2), (salen)Ti(III)Cl showed impressive high activity (TOF of 557 h⁻¹) and selectivity for CO₂/CHO copolymerization at 120 °C, yielding completely alternating copolymer without the formation of cyclohexene carbonate. It deserves to highlight because Ti is a non-toxic metal in compared with Co and Cr and this catalyst showed perfect selectivity and activity at relative high temperatures.

The substituents of the epoxides have a big impact on CO₂/epoxide copolymerization catalyzed by the above catalyst systems. Although considerable amounts of homogeneous catalyst systems have been developed to synthesize polycarbonates, few of them were capable of catalyzing the copolymerization of CO₂ with epoxides with different substituents, presumably due to the limitation of the structural matching of the catalysts and the epoxides with respect to the steric/electronic effects. For example, as reported, dinuclear (Zn, Co, Fe) catalysts were specifically active to CO₂/CHO copolymerization [29]. It is good to see that binary and bifunctional (salen)M (M = Co, Cr) complex/cocatalysts that are highly active to the perfectly alternating copolymerization of CO₂

with many kinds of epoxides, as shown in Fig. 4, affording various CO₂-based copolymers.

The above homogeneous catalysts have nearly the same coordination structure, totally, which are basically multi-dentate metal complexes with N₄-, O₂-, N₂- and N₂O₂-chelating ligands and showed tetrahedral or octahedral coordination structures. These homogeneous catalysts show some advantages for CO₂/epoxide copolymerization, including:

- 1) The copolymerization is well-controlled and the chain structure of the resulting copolymer is well-defined. By delicately changing the molecular structure of the catalyst and selecting the cocatalysts, the polymer selectivity, regioselectivity, enantioselectivity and stereoselectivity could be purposely tuned,

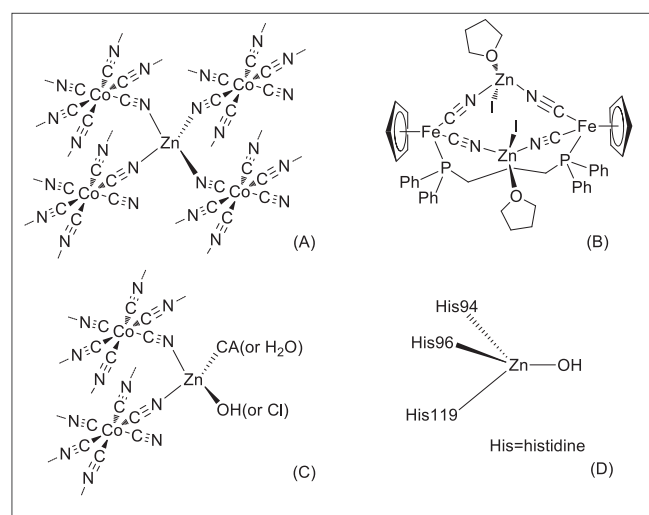


Fig. 5. (A) Bulk structure of ZHCC [111]; (B) well-defined soluble Zn–Fe(II) DMCC [112]; (C) the proposed initiating group of Zn–Co(III) DMCC [113]. Herein, two CN⁻ groups are shared by Zn²⁺ and Co³⁺ ions. They contain one negative charge in one tetrahedral Zn²⁺ structure. Such structure meets the electroneutrality principle because of the existence of OH⁻ (and Cl⁻). CA is the complexing agent (generally *tert*-butyl alcohol, *t*-BuOH) (D) carbonic anhydride zinc enzyme.

and thus CO₂-based copolymers with new properties can be synthesized.

- 2) The copolymerization kinetic is generally controlled by the diffusion of the monomers to the catalyst because the catalyst is soluble in the substrates and the copolymerization occurs in the liquid phase. Thereof, (salen)CoX complexes are deserved to underline again because it presents “immortal” propagation in a well-controlled pathway, in which the “dead” chains can be activated by chain transfer reaction with a protic compound and rapidly re-propagate [94]. Thus, block or grafted copolymers can be synthesized through “immortal” copolymerization by introducing macromolecule chain transfer agents [95–97].

Unfortunately, in most instances, low reaction temperatures are required in copolymerization process in order to avoid the production of cyclic carbonates. In view of energy-saving production process, relative high temperature for the copolymerization is welcomed in industrial production [98]. Moreover, the homogeneous catalyst systems are often synthesized through complicated multiple-steps process, and numbers of catalysts are required an organic base or organic salt as the cocatalysts, such as salen-type metal complexes. In addition, since the anions (such as axis anions) in these catalysts initiated the copolymerization, the resultants often contain the copolymers with one end of hydroxyl group and one end group from axis anions.

The strategy of binary (or bifunctional) catalysts for tuning the polymerization is to subtle balance several mutual factors, such as, the electronic and steric structures of CO₂, epoxide, the catalyst and the cocatalyst, as well as the copolymerization conditions. To date, the success of homogeneous catalysis for CO₂/epoxide copolymerization is huge and impressive. The related studies provided clear and intensive understandings on CO₂ copolymerization, which is very helpful to design heterogeneous catalysts.

2.2. Heterogeneous catalyst for CO₂ copolymerization

Heterogeneous catalysts, though they often contain multiple active sites that result in polymers with broad PDIs and irregular composition distributions, are more suitable to industrial processes as they are easy to prepare and handle with, low-toxic and economically viable. Typical heterogeneous catalysts include ZnEt₂/protonic compounds [23,99–101], zinc dicarboxylates [102–105], rare earth metals (including Y and La) in combination with other metals (e.g. zinc) [106,107], and double metal cyanide complexes

[65,108,109]. The catalytic activities of the heterogeneous catalysts for CO₂/epoxide copolymerization are often not as high as their homogeneous counterparts, however, some heterogeneous catalysts exhibited high copolymer selectivity and the resulting copolymers showed very high molecular weights. A serial of comprehensive reviews of the earlier studies on this topic have been published [25,28,29,79,110]. Herein, we mainly focus on zinc-cobalt(III) double metal cyanide complex [Zn–Co(III) DMCC] catalyst for C1 copolymerization on the basis of our research in recent years.

2.2.1. Introduction of Zn–Co(III) DMCC

As shown in Fig. 5, DMCC is an inorganic coordinated complex with three-dimensional network, in which the inner metal M^{II} is linked with the external metal M^I by several cyano-bridges (M^{II} - C≡N - M^I, generally, M^I = divalent metal ions such as Zn²⁺, Fe²⁺, Co²⁺, Ni²⁺, etc., M^{II} = transition metal ions such as Fe²⁺, Fe³⁺, Co²⁺, Co³⁺, Ni²⁺, etc.). The external metal M^I on the surface of the catalyst is generally considered to be the active site for the polymerizations due to its unsaturated coordinated structure. The bulky structure of Zn–Co(III) DMCC is proposed as Fig. 5A, in which zinc is a tetrahedral coordinated structure with four cyano anions. Note that this catalyst is often abbreviated to be DMC (double metal cyanide). Since it is structurally a metal-cyanide complex with typical coordination structure and shows coordinated anion mechanism for C1 and epoxide-involved copolymerizations, we suggest that DMCC (double metal cyanide complex) is a more suitable abbreviation for this catalyst.

Up to date, DMCC has been reported to use as the catalysts for various reactions, such as epoxide-involved polymerizations and C1-involved reactions as next discussion, hydroamination (the direct addition of an amine to a carbon–carbon unsaturated bond) [114], the inter-esterification of cyclic carbonate and alcohol to synthesize dimethyl carbonate [115], the hydrolysis or alcoholysis of the plant oil to obtain biodiesel [116,117] and the condensation reaction between alcohol and acid [118]. Moreover, DMCC can also be applied as the materials for separating CO₂ from CH₄ [119], and H₂ storage [120]. DMCC is indeed a powerful catalyst in synthesis and also a useful material for gas separation and storage.

Zn–Co(III) DMCC was early discovered to be an efficient catalyst for ROP of epoxides, especially PO [43,121,122]. It is still industrially used to produce poly (propylene oxide) polyols with moderate and high molecular weights and low unsaturation degrees, which are widely used for making soft polyurethanes. In 1985, Kruper et al.

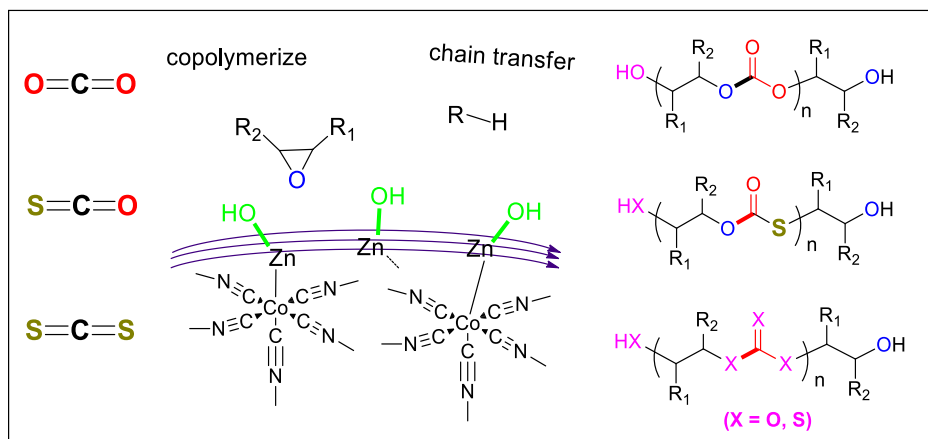


Fig. 6. C1-involved copolymerization via Zn–Co(III) DMCC catalysis. Zn–OH bond is proposed to be the initiating group of Zn–Co(III) DMCC for CO₂/epoxide copolymerization; chain transfer reaction of propagating species to the protonic compounds (H₂O, the generated polymers with two ended hydroxyl groups, R–H), producing copolymers with various ended groups. Purple end groups (–XH and –OH) indicate that they comes from different reactants or the catalyst.

applied Zn–Fe (III) DMCC to CO₂/epoxide copolymerization for the first time [65]. Then, many other research groups studied the preparation and application of Zn–Co(III) DMCC for synthesizing CO₂-based copolymers [108,123–125]. Now, it has been developed to be a promising class of effective heterogeneous catalyst for C1-involved copolymerization, such as CO₂/epoxide copolymerization [43], epoxide/CS₂ copolymerization [36] and epoxide/COS copolymerization [39–42] (Fig. 6).

For DMCC-catalyzed CO₂/epoxide copolymerizations, most of the published works focused on the improvement of its activity by altering the preparation process, such as changing the catalyst precursors [126–128], complexing agent [108,129,130] and using mechanochemistry method [131]. Chen [130] reported the CO₂/CHO copolymerization by a Zn–Co(III) DMCC prepared with different complexing agents. Among them, Zn–Co(III) DMCC prepared by *tert*-butyl alcohol (*t*-BuOH) as electron-donating complexing agent showed high catalytic activity of 1670 h^{−1} at 100 °C, 3.8 MPa. Besides, changes in either the cobalt ion or zinc ion, for example, Zn[Ni(CN)₄] [132,133], Co[Ni(CN)₄] [134] and substitution of one of the cyanide ions resulted in a dramatic change of the catalytic activity and polycarbonate selectivity [132]. However, up to date, Zn–Co(III) DMCC prepared using *t*-BuOH as a complexing agent was still the best one for C1-involved polymerizations [43].

As a heterogeneous catalyst, the morphology of DMCC catalyst have a big impact on its catalytic activity. Kim [126] synthesized a variety of catalysts with low crystallinity using ZnX₂ (X = F, Cl, Br, I) together with *t*-BuOH and poly(tetramethylene ether glycol) as complexing reagents, these catalysts showed improved productivity for CO₂/epoxide polymerizations. Our studies [111,113] indicated that Zn–Co(III) DMCC with low crystallinity was more active to CO₂/epoxide polymerizations.

The preparation of the aforementioned Zn–Co(III) DMCC was often operated at room temperatures via precipitation reaction of excess ZnCl₂ and K₃Co(CN)₆ in water/*t*-BuOH mixed solution [135]. The resultant catalyst presented irregular lumps with several to dozens of micrometers and showed moderate productivity and low polycarbonate selectivity towards CO₂/epoxide copolymerization. The empirical formula of this catalyst was traditionally denoted as Zn₃[Co(CN)₆]₂·xZnCl₂·yCA·zH₂O (CA is the complexing agent), which was considered to be non-stoichiometric because x, y and z varied with the methods and batches of the preparation. Moreover, because the complexity of the surface structure of this catalyst, the catalytic center had not yet clearly characterized and disclosed. To illuminate the origination of the activity of this kind of catalyst, Darensbourg et al. had reported a related homogeneous complex (Fig. 5B) [112], which had a tetrahedral zinc structure and could catalyze the coupling of CHO and CO₂ for producing cyclic *cis*-

cyclohexene carbonate with a small percentage of low molecular weight polycarbonate. It seems that the tetrahedral zinc structure could effectively function to the copolymerization.

2.2.2. Nano-sized Zn–Co(III) DMCC

Because Zn–Co(III) DMCC is not soluble in the substrate, the resulting polymer and solvent in the reaction system, it is a typical heterogeneous catalyst for C1 copolymerization. Hence, increasing the surface area of Zn–Co(III) DMCC is an effective method to improve the productivity. In 2008, our group reported the first example of a highly active SiO₂/Zn–Co(III) DMCC hybrid catalyst for CO₂/epoxide copolymerization [111]. A hydrothermal method was employed to synthesize such hybrid catalyst at an elevated temperature of 25 °C. The obtained catalyst was thermal-stable, non-sensitive to air and moisture. The synthesis of such nano-sized Zn–Co(III) DMCC is simple and repeatable. It possesses unique nano-lamellar structure (Fig. 7) with nano-sized pores, and thus presents high surface area >500 m²/g determined from N₂ adsorption–desorption isotherm. This nano-sized structure could accommodate more catalytic sites on the surface of the catalyst and thus improved the catalytic activity for CO₂/epoxide copolymerization [111]. A TON of 11444, TOF of 3815 h^{−1}, and productivity of 24.0 kg polymer/g zinc were achieved at 3.8 MPa and 100 °C for CO₂/CHO copolymerization. The resulting PCHC had an alternating degree of >90%, without the observation of cyclic carbonate.

The nano-lamellar structure of the SiO₂/Zn–Co(III) DMCC hybrid catalyst was directly resulted from the crystallization of Zn–Co(III) DMCC, rather than the formation of nano-sized SiO₂ because nano-lamellar Zn–Co(III) DMCC could be synthesized via the same hydrothermal method. The zinc/cobalt molar ratio of such nano-lamellar Zn–Co(III) DMCC was ca. 2.0 and unvaried [111,113,136]. The molar ratio of Zn²⁺: Co³⁺: CN[−] in the catalyst was 2: 1: 6 based on the elemental analysis result. Moreover, since Cl[−] was observed by elemental analysis and the existence of OH[−] was confirmed by Infrared (FT-IR) spectroscopy of Zn–Co(III) DMCC without complexing agent and water (removed by heat treatment) [137], the structure of Zn–Co(III) DMCC was supposed to be Zn₂[Co(CN)₆](OH)_aCl_b·yCA·zH₂O (a+b = 1) for meeting the electro-neutrality principle (Fig. 5C).

2.2.3. Zinc-hydroxyl (Zn–OH) structure of Zn–Co(III) DMCC

On the basis of nano-sized Zn–Co(III) DMCC catalyst with certain composition, we proposed that the zinc-hydroxyl (Zn–OH) bond in Zn–Co(III) DMCC catalyst (Fig. 5C) was the initiating site for CO₂ copolymerization. Indeed, the structure of the carbonic anhydride zinc enzyme that contained one Zn–OH bond (Fig. 5D) inspired us to make such a proposal because carbonic anhydride

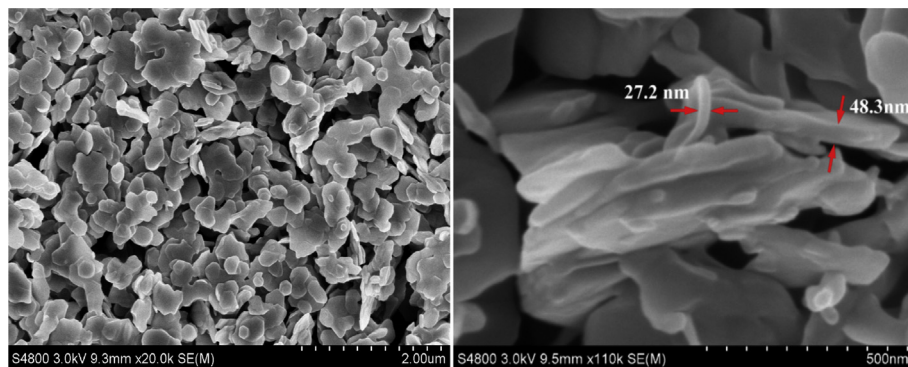


Fig. 7. SEM images of Zn–Co (III) DMCC catalyst synthesized at 75 °C [113]. Reprinted from Polymer, 52, Xing-Hong Zhang*, Ren-Jian Wei, Xue-Ke Sun, Jiang-Feng Zhang, Bin-Yang Du, Zhi-Qiang Fan, Guo-Rong Qi, Selective copolymerization of carbon dioxide with propylene oxide catalyzed by a nanolamellar double metal cyanide complex catalyst at low polymerization temperatures, 5494–5502., Copyright (2011), with permission from Elsevier.

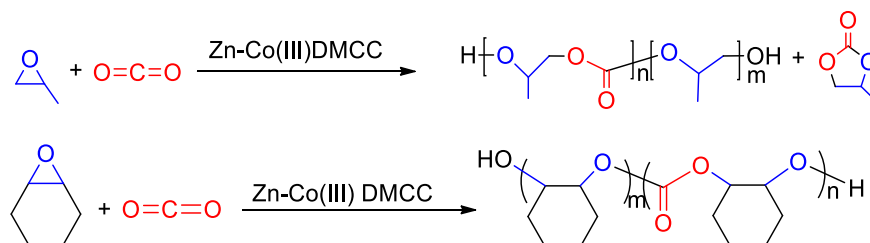


Fig. 8. Zn–Co (III) DMCC-catalyzed CO₂/PO and CO₂/CHO copolymerization and chain structure of the resulting copolymers [113,137].

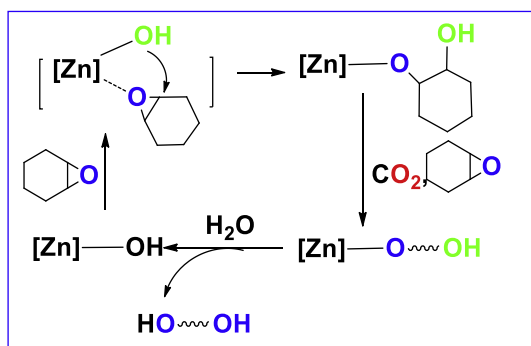


Fig. 9. The proposed catalytic cycle with Zn–OH initiation for Zn–Co(III) DMCC (Take CO₂/CHO copolymerization as an example).

zinc enzyme exists widely in nature and is highly active to the hydration reaction of CO₂. In 2011, we reported the CO₂/PO copolymerization catalyzed by this nano-lamellar Zn–Co(III) DMCC (Fig. 8). The results indicated that nano-lamellar Zn–Co(III) DMCC could catalyze CO₂/PO copolymerization with high productivity of 2050–6460 g polymer/g Zinc at 40–80 °C. The obtaining poly (ether-*co*-carbonate) had a M_n up to 36.5 kg/mol and high F_{CO_2} of 74.2% [113]. Of importance, the influences of adding water content on CO₂/PO copolymerization were quantitatively investigated. It was proposed that trace amount of water in the reaction system not only acted as an efficient chain transfer agent, which decreased the molecular weight of the resulting copolymer, but also strongly interacted with zinc site of the catalyst, which led to low productivity of PPC and more amount of cyclic PPC. As a chain transfer agent, one water molecule could interact with zinc site and produce a Zn–OH bond, which might initiate a new polymerization. Therefore, a closed catalytic cycle for Zn–OH was finished, and one initiating site could generate many polymer chains, which ensured high productivity of the catalyst. Since such poly (ether-*co*-carbonate) with random chain structure has two end –OH group, it

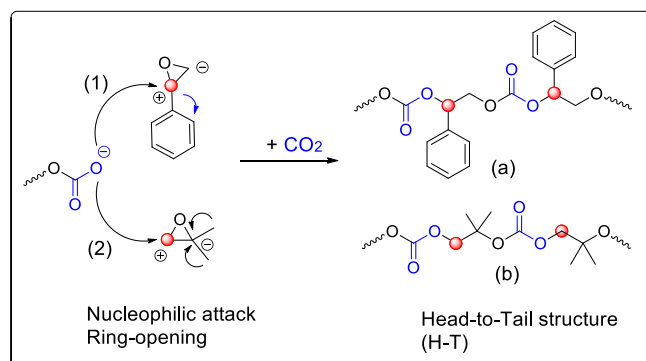


Fig. 11. Proposed mechanism for regioselective CO₂/styrene oxide and CO₂/isobutene oxide copolymerization via Zn–Co (III) DMCC catalysis. Red dot in the backbone represents the site that was proposed to be attacked by the carbonate anion [138]. Reproduced with permission from Ref. [138]. Copyright (2015) American Chemical Society. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

could be used as promising precursor for making new poly-urethanes. The method for producing copolymers with two end –OH groups via adding water could lead to the synthesis of CO₂-based block copolymers, which will be discussed later.

In order to further confirm the Zn–OH initiation mechanism, and understand the chain composition variation of the CO₂/epoxide copolymers, a model copolymerization, CO₂/CHO copolymerization via nano-sized Zn–Co(III) DMCC catalysis was performed by detail kinetic study. The end groups of the resulting PCHC with low molecular weight were accurately determined by electrospray ionization mass spectrometry (ESI-MS). It was disclosed that the short ether units were mainly generated at the early stage of the copolymerization, and hence in the “head” of the copolymer, i.e., Zn–OH initiated ring-opening reaction of CHO was the initiation step (Fig. 9). All observed copolymers in ESI-MS spectrum presented two ended hydroxyl groups. One came from the initiation of Zn–OH

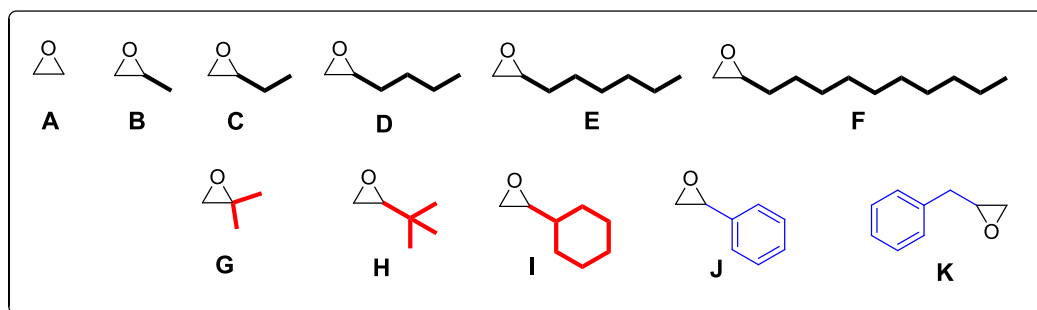


Fig. 10. Selected epoxides with alkyl and aryl groups for the copolymerization with CO₂ by using nanosized Zn–Co(III) DMCC catalyst. A: ethylene oxide, B: propylene oxide, C: 2-ethyloxirane (1,2-butene oxide), D: 2-butyloxirane (1,2-hexeneoxide), E: 2-hexyloxirane (1,2-octeneoxide), F: 2-decyloxirane (1,2-epoxydodecane), G: isobutene oxide, H: 2-(*tert*-butyl)oxirane, I: 2-cyclohexyloxirane, J: styrene oxide, K: 2-benzyloxirane [138]. Reproduced with permission from Ref. [138]. Copyright (2015) American Chemical Society.

bond of the catalyst and the other one was produced by the chain transfer process from propagating chain to water (or free copolymer), and thus it is an “immortal” polymerization [137]. Such “immortal” polymerization behaviors led to the creation of a method for synthesizing CO₂-based multiblock copolymers later.

Zn–OH bond of Zn–Co(III) DMCC can be regarded as a Lewis acid–base pair, which is able to activate the epoxide and CO₂ collaboratively [137]. The proposed ground state of the active site of the catalyst is shown in Fig. 5C. The chain initiation, propagation and transfer reaction for Zn–Co(III) DMCC-catalyzed CO₂/CHO copolymerization are shown in Fig. 9 [137]. Therefore, a closed catalytic cycle for regenerating Zn–OH bond is achieved, and Zn–Co(III) DMCC is in fact a catalyst for CO₂/epoxide copolymerization. Note that Zn₂[Co(CN)₆]OH [119] and Zn₂[Co(CN)₆]Cl had no catalytic activity towards CO₂/epoxide copolymerization, which demonstrated that the activity of this catalyst might be closely related to Zn₂[Co(CN)₆](OH)_aCl_b (*a*+*b* = 1), although its real structure still needs further investigation [138].

2.2.4. Structural effect of epoxides on CO₂/epoxide copolymerization

The substituent effect of the epoxides on CO₂/epoxide copolymerization catalyzed by nano-sized Zn–Co(III) DMCC was intensively investigated since it can catalyze the copolymerization of CO₂ with many kinds of epoxides. Epoxides with various substituents (Fig. 10) were successfully copolymerized with CO₂ by using nano-sized Zn–Co(III) DMCC [138]. In Fig. 10B, C, D, E and F are the epoxides containing pendant linear alkyl groups with carbon numbers of 1, 2, 4, 6 and 10, respectively. J and K are the epoxides with the pendant electron-withdrawing aryl groups. G, H and I are the epoxides with branched alkyl groups with carbon numbers of 2, 4 and 6, respectively. Zn–Co(III) DMCC succeeded in catalyzing the copolymerization of CO₂ with these epoxides with alkyl or aryl groups at 50–60 °C within 15 h, providing various CO₂/epoxide copolymers with high epoxide's conversion up to 100%. *F*_{CO₂} of the resulting copolymer was solely decided by the steric hindrance of the substituents of the epoxides, whatever the substituents exhibited electron-donating or withdrawing properties. The substituents with large steric hindrance (2, 2-dimethyl, *tert*-butyl, cyclohexyl, decyl and benzyl) led to highly alternating degree (up to 100%).

The regioselective copolymerization of CO₂/epoxide copolymerization via Zn–Co(III) DMCC catalysis was studied because most of the copolymers had highly alternating degrees of 94.2%–>99%. In this circumstance, the carbonate anion (–OOCO[–]) was the

main nucleophilic species to attack the methylene (CH₂) or methine (CH) sites of epoxide for ring-opening (Fig. 11). It was observed that the electron induction effect of the substituent dominated the regioselective copolymerization. Electron-withdrawing substituent, such as phenyl and benzyl induced regioselective ring-opening at the methine site of the epoxide. For example, when CO₂ copolymerized with styrene oxide (J), the nucleophilic attack of propagating species to styrene oxide would occur predominantly at the methine bond (CH–O) (route 1 in Fig. 11) rather than the methylene bond (CH₂–O) [136]. Moreover, when referring the result by Inoue [139], in which ZnEt₂/water system was employed in the copolymerization of CO₂ with *rac*-styrene oxide, the ring-opening of styrene oxide predominantly occurred at methine carbon (96%), similar to the result from Zn–Co(III) DMCC catalysis.

For the CO₂/isobutene oxide copolymerization, regioselective reaction occurred at the methylene site of isobutene oxide because of the strong electron-donating ability and steric hindrance of two methyl groups of isobutene oxide (route 2 in Fig. 11). Linear alkyl groups of the epoxides (B, C, D, E, F) could not induce the regioselective reaction and the head-to-tail content of these copolymers was roughly estimated to be ca. 52%.

The substituents of the epoxides had a strong impact on glass transition temperatures (*T*_gs) of the resultant CO₂/epoxide copolymers (Fig. 12). *T*_gs of the resulting copolymers were ranged from –44 °C [47] to 109 °C [137], depending on the substituent groups of the epoxide. Fig. 12 shows that *T*_gs of the copolymers with side linear groups decreased from 6 °C to –38 °C with increasing the length of the side chain from two carbons to ten carbons because the longer side linear alkyl group caused stronger plasticizing effect and regioirregular microstructure. We reported the first example of a polycarbonate with the lowest *T*_g of –44 °C that from CO₂ and a biorenewable monomer of epoxy methyl 10-undecenoate (Fig. 13) [47]. The resulting polycarbonate was fully alternating and had two hydroxyl end groups, which could be used as a macroinitiator to initiate ROP of lactide via metal-free catalytic route (Fig. 13), or react with isocyanate to afford polyurethanes.

For the copolymers with side branched alkyl group and aryl groups, *T*_gs increased from 35 °C to 84 °C with increasing the steric hindrance of the substituents, which could effectively inhibit the free rotation of the backbone. Moreover, CO₂/styrene oxide and CO₂/2-benzylloxirane (Fig. 12) with regio-regular microstructures favored the improvement of *T*_gs [136]. The copolymers with branched side groups presented higher *T*_gs than their linear counterparts, as compared CO₂/2-ethyloxirane copolymer (6 °C) with CO₂/isobutene oxide copolymer (35 °C), CO₂/2-butyloxirane copolymer (–18 °C) with CO₂/2-*tert*-butyl oxirane copolymer (53 °C), CO₂/2-hexyloxirane copolymer (–27 °C) with CO₂/2-cyclohexyloxirane (84 °C) copolymer [138]. Thus, through Zn–Co(III) DMCC catalysis, various CO₂/epoxide copolymers with a wide-range *T*_g from –44 °C to 109 °C could be synthesized and applied as elastomers or plastics.

Zn–Co(III) DMCC is also effective to the copolymerization of CO₂ with some common and low-cost epoxides with electron-withdrawing substituents [47,140]. Epichlorohydrin, as a cheap raw chemical material, is an ideal monomer for producing biodegradable polycarbonates. However, few of catalysts have been reported for the alternating CO₂/epichlorohydrin copolymerization [140,141]. Nano-lamellar Zn–Co (III) DMCC was proved to be an effective catalyst for CO₂/epichlorohydrin copolymerization, affording a poly (carbonate–*co*–ether) with *F*_{CO₂} up to 70.7% at low temperatures (Fig. 14). Remarkably, the cyclic carbonate contents in the product were 5.0%–11.3% at 25–60 °C, better than those from homogeneous catalysis [141]. Moreover, the copolymer with 70.7% carbonate content presents high thermal decomposition temperature of 250 °C and relatively high *T*_g of 31.2 °C. Although we

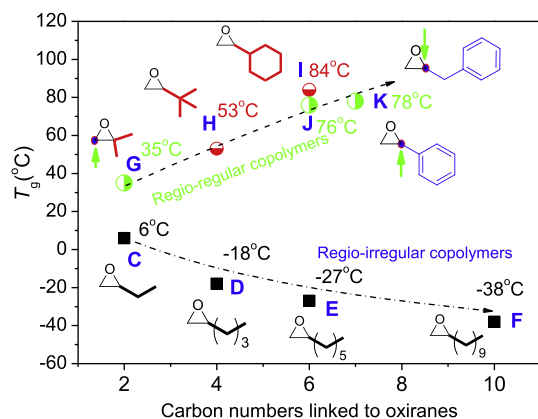


Fig. 12. The substituent effect of selected epoxides on the glass transition temperatures (*T*_gs) of the resulting CO₂/epoxide copolymers (*F*_{CO₂} = 91.5–99%; *M*_n: 6.6–93.2 kg/mol) [138]. Reproduced with permission from Ref. [138]. Copyright (2015) American Chemical Society.

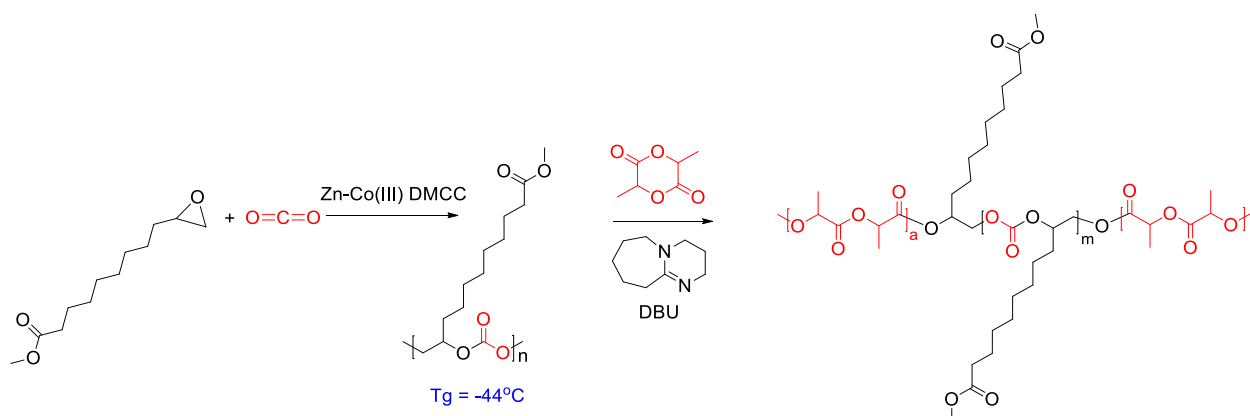


Fig. 13. Alternating copolymerization of epoxy methyl 10-undecenoate and CO_2 via Zn–Co (III) DMCC catalysis and corresponding triblock copolymer from ring opening polymerization of L-lactide at 25 °C [47].

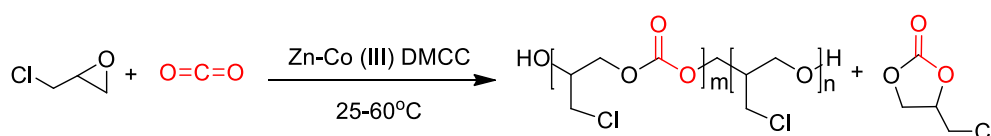


Fig. 14. The CO_2 /epichlorohydrin copolymerization catalyzed by Zn–Co (III) DMCC catalyst at 25–60 °C.

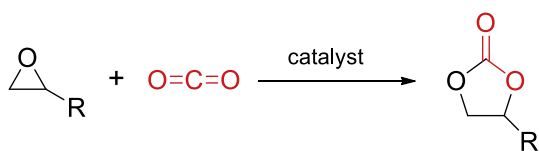


Fig. 15. Epoxide/ CO_2 cycloaddition reaction.

observed that Zn–Co(III) DMCC was a regioselective catalyst for ROP of epichlorohydrin on the site of methine group [142], we had no direct evidence for supporting the regioselective CO_2 /epichlorohydrin copolymerization.

Terpolymerization of two epoxides with CO_2 could also be performed well by Zn–Co(III) DMCC catalyst, affording terpolymers with tunable T_g s [143]. The terpolymerization of CO_2 , styrene oxide and 1, 2-epoxydodecane with electron-donating dodecane group was successfully performed by using Zn–Co(III) DMCC catalyst, resulting in a new random terpolymer with single T_g s in a wide range of 3–56 °C.

In addition, Zn–Co(III) DMCC is also an efficient catalyst for the terpolymerization of CO_2 , CHO and maleic anhydride, as we reported in 2010 [144]. A convenient and highly efficient one-pot synthesis for terpolymerization of CO_2 , CHO and maleic anhydride by using Zn–Co(III) DMCC afforded a random poly (ester-carbonate). The result of the terpolymerization kinetic analysis suggests that polyester production was faster than polycarbonate production in the early stage. The ester unit and carbonate unit of the resulting terpolymer was not evenly distributed along the chain.

As discussed above, Zn–Co(III) DMCC is an effective catalyst for CO_2 /epoxide copolymerization. In compared with its homogenous counterparts, the real structure of active center and catalytic mechanism of Zn–Co(III) DMCC are still unclear, which limit the improvement of its catalytic performance. On the other hand, the effort for precisely controlling the chain structure of copolymer via under Zn–Co(III) DMCC catalysis is still needed. Despite these disadvantages, Zn–Co(III) DMCC is a promising catalyst for CO_2 copolymerization in large-scale production, because the following advantages: 1) One-step preparation using water and alcohol as the solvent, and the process was low-toxic; 2) Nano-sized particles and white fine powder, it can be broken to be smaller particles during copolymerization, and thus the crude product is highly transparent. Of importance, Co^{3+} in Zn–Co(III) DMCC is tightly coordinated by six CN^- , thus it is thermally stable and has no influence on the color of the final polymers, so it is not leaked out during copolymerization and the process of the resulting copolymers. 3) High productivity, satisfied polycarbonate selectivity and regioselectivity. 4) Function well for many epoxides, and other two C1 monomers of COS and CS_2 .

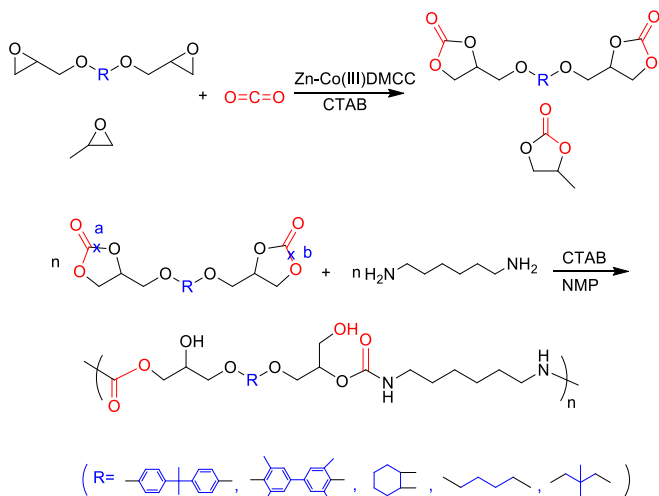


Fig. 16. The one-pot coupling reaction of PO, bis-epoxide and CO_2 catalyzed by Zn–Co(III) DMCC/CTAB binary catalyst system and polyaddition of bis(cyclic carbonate)s and 1, 6-hexamethylenediamine. Note that two pathways (a and b) to the ring opening of the cyclic carbonate occur randomly during reaction, leading to the formation of the secondary and primary hydroxyl groups [60].

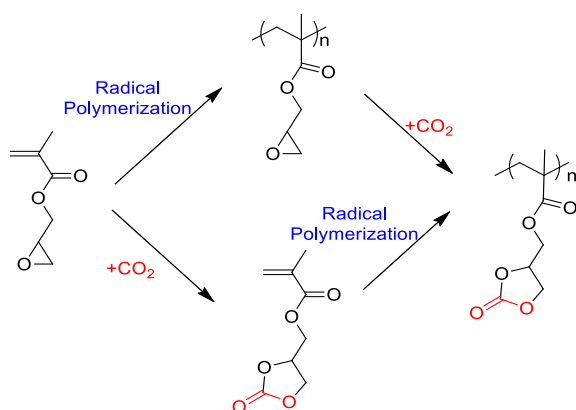


Fig. 17. Two methods for carbon dioxide fixation through the combination of free radical polymerization and coupling reaction.

3. Bi- and polyfunctional cyclic carbonates via Zn–Co(III) DMCC

The coupling reaction of CO₂ with epoxides to afford cyclic carbonates is an atom economic pathway for CO₂ fixation (Fig. 15). Numerous catalyst systems with significant advances have been discovered for CO₂/epoxide coupling reaction in recent decades. Heterogeneous catalysts such as metal oxides [55–57], zeolite and its supported catalysts [58,59,145,146] were utilized to catalyze CO₂/epoxide coupling reaction. Homogeneous catalysts such as amines and phosphines [147,148], alkali metal halides [149], metal-salen complexes [150,151], metal porphyrins [152,153], and transition metal complexes [154–156] were also extensively investigated. Inspired by the observation that ammonium salt could increase the content of cyclic carbonate in DMCC-catalyzed CO₂/PO coupling copolymerization, the nano-sized Zn–Co(III) DMCC with cetyltrimethyl ammonium bromide (CTAB) as the cocatalyst was screened out for effectively catalyzing the coupling reaction of CO₂ with hydrous PO, producing PPC with nearly 100% productivity and 100% selectivity (Fig. 16) [61]. The virtue of our binary catalyst systems for CO₂/PO reaction is that small amounts of water have minimized influence on the reaction and thus commercial epoxides

could be used directly.

Based on the above discovery, by the coupling reaction of CO₂ with epoxides containing two or more oxirane groups and epoxy resin, bi- or polyfunctional cyclic carbonates could be obtained, then they can react with bi- and polyfunctional primary alkyl amines, leading to polyurethanes with massive hydroxyl groups, which might be an alternative and attractive green route for synthesizing polyurethane materials without using toxic isocyanates or phosgene. Our group reported an efficient one-pot coupling reaction of CO₂, PO and bisepoxides without the addition of external organic solvents by using a binary nanolamellar Zn–Co(III) DMCC/CTAB system [60]. PPC and bis(cyclic carbonate)s were obtained at the same time with high monomer conversions (PO: 93.6%, bisepoxides: 82.9%). The *in situ* produced PPC acted as a good solvent for the coupling reaction of CO₂ with bisepoxides. Two products could be easily separated by distillation or precipitation. What's more, the obtained bis(cyclic-carbonate)s could be used to prepare poly(-hydroxylurethane)s with massive side hydroxyl groups via the polyaddition reaction with diamines, such as 1,6-hexamethylenediamine.

Radical polymerization of the cyclic carbonates with vinyl groups can give the corresponding poly(methacrylate)s with pendant cyclic carbonate [157–159]. These five-membered cyclic carbonates with vinyl group [157,160] could be directly prepared from CO₂. Normally, both glycidyl acrylate [161,162] and glycidyl methacrylate [163] were used to transform into the corresponding methacrylate monomers bearing a cyclic carbonate moiety. These vinyl monomers with cyclic carbonate moiety have high reactivity [161–163]. On the other hand, direct coupling reactions of the oxirane group in polymers with CO₂ have also provided polymers with pendant cyclic carbonate groups. (Fig. 17) Typical examples are the conversion of poly(glycidyl acrylate) and poly(glycidyl methacrylate) to poly(1,3-dioxolan-2-one-ylmethyl acrylate) and poly(1,3-dioxolan-2-one-4-ylmethyl methacrylate), respectively [164–171]. Lots of works have been done and a precedent review described about this topic in detail was reported by the Endo group [170]. Recently, our group reported an example that the side oxirane group of poly(glycidyl methacrylate) were completely converted to the cyclic carbonate groups by coupling reaction with CO₂ by using Zn–Co(III) DMCC/CTAB catalyst system. The resulting poly(1,3-dioxolan-2-one-4-ylmethyl methacrylate) had a weight

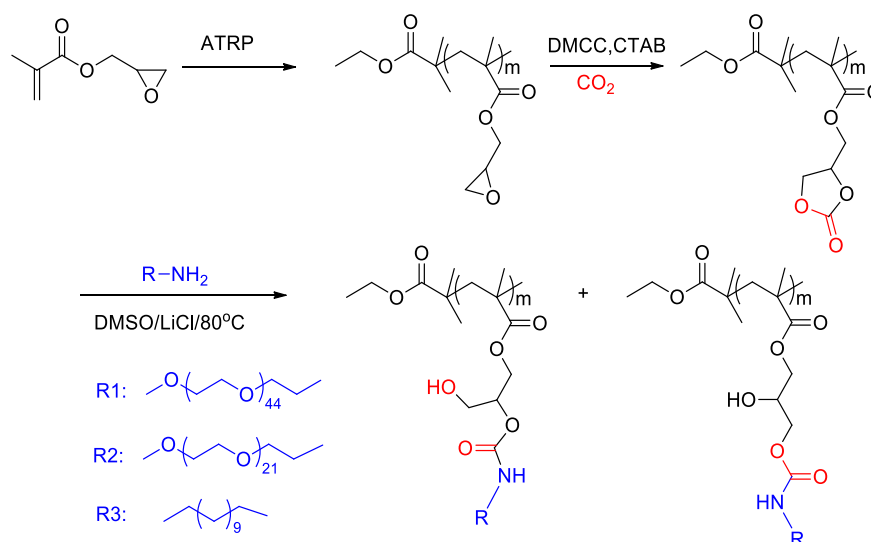


Fig. 18. Synthetic route of brush copolymers poly(glycidyl methacrylate)-graft-polyethylene glycol (PGMA-g-PEG) and poly(glycidyl methacrylate)-graft-dodecylamine (PGMA-g-DDA) [171].

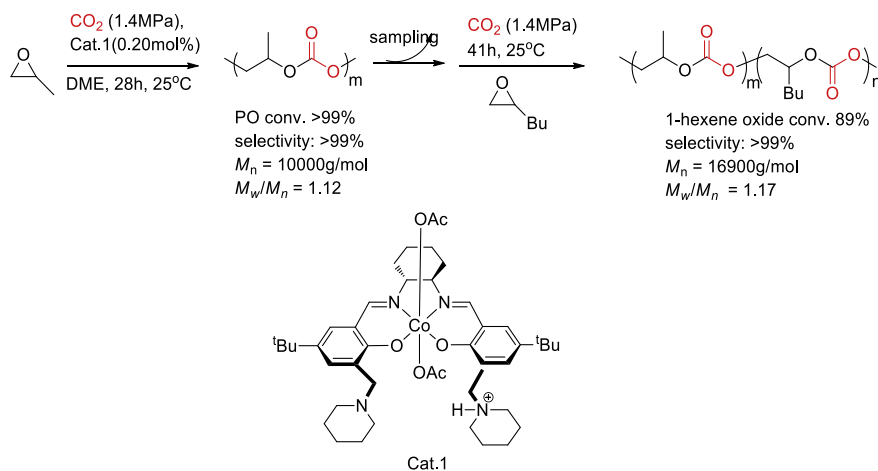


Fig. 19. Synthesis of a block terpolymer reported by Nozaki group [172].

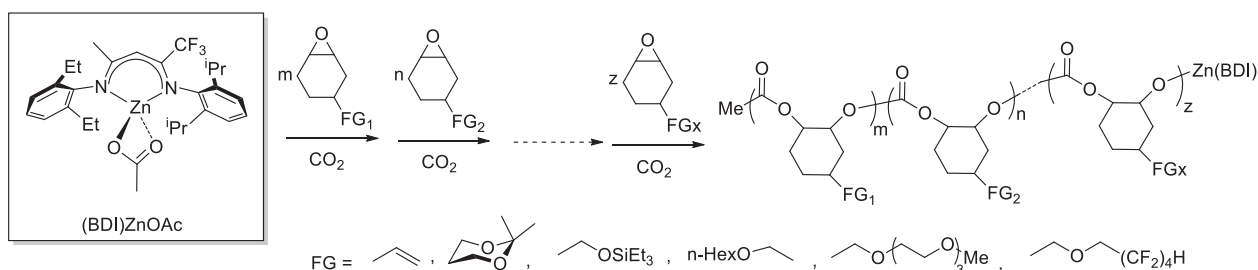


Fig. 20. Preparation of cyclohexene carbonate multiblock copolymers [44].

percentage of CO_2 of 24 wt% as well as a high T_g of 141.4 °C which could be comparable with some commercial engineering plastics. Moreover, a new amphiphilic brush copolymer poly(glycidyl methacrylate)-*graft*-polyethylene glycol (PGMA-*g*-PEG) with high grafting densities of 97–98% was obtained through “grafting onto” method via cyclic carbonate-primary amine addition reaction (Fig. 18) [171]. In some extent, cyclic carbonate-primary amine

addition reaction could be regarded as a “click” reaction due to its high reactivity. In unique, the resulting brush copolymer contains hydroxyurethane structures as the junction sites between the poly(glycidyl methacrylate) (PGMA) backbone and polyethylene glycol (PEG) side chain, which can be used for further modification.

4. CO_2 -based polymers with various topologies

One of the main goals in polymer synthesis is to develop polymers with various topologies that presented versatile properties and functionalities. However, to date, CO_2 -based polymers with different topologies, such as block copolymers [44–49], grafted (brush) copolymers [50–52] and star copolymers [53,54], etc. are rarely reported.

4.1. Block copolymers

Based on the operation steps for synthesizing block copolymers, two methods could be classified for the synthesis of CO_2 -based block copolymers.

One involves multiple operations. In 2006, Nozaki and co-workers reported the copolymerization of CO_2 with two terminal epoxides via two-step operations by using a bi-functional (salen) CoOAc complex with a piperidinium arm (Cat. 1 in Fig. 19) that could consume PO added at first completely, without producing cyclic carbonate, then continued to catalyze the copolymerization of CO_2 with 1-hexene oxide after the consumption of PO, producing a diblock copolymer [172].

Sequential living polymerization is one-pot reaction but needs multiple injections during reaction and a useful tool for preparing block copolymers based on the same chain propagation manner. Coates reported a method for the living multiblock

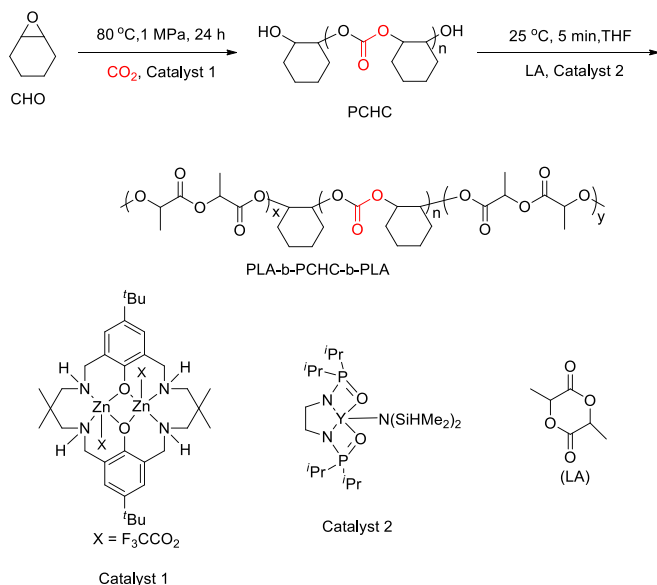


Fig. 21. Copolymerization of CHO and subsequent block copolymerization with lactide [46].

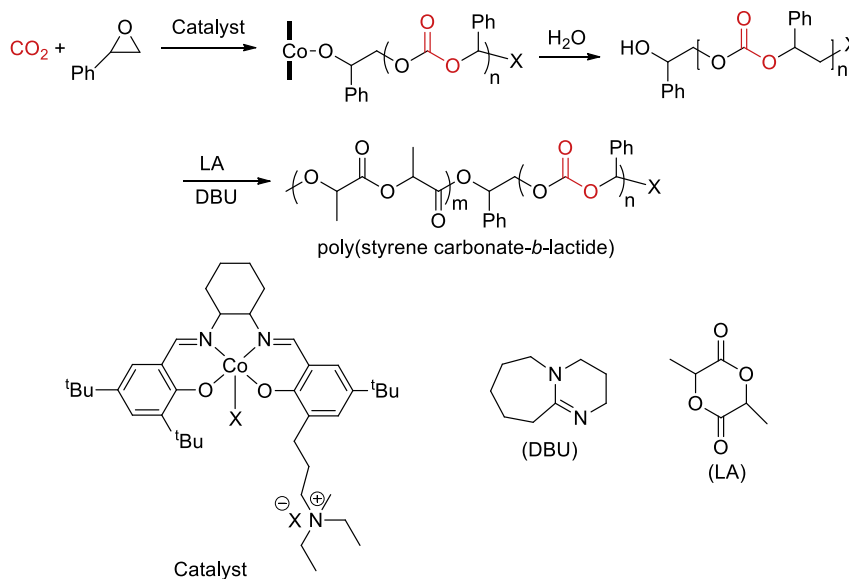


Fig. 22. Tandem strategy for the synthesis of CO₂-based model A-B diblock copolymer and the related catalyst system. X = 2, 4-dinitrophenoxide [173].

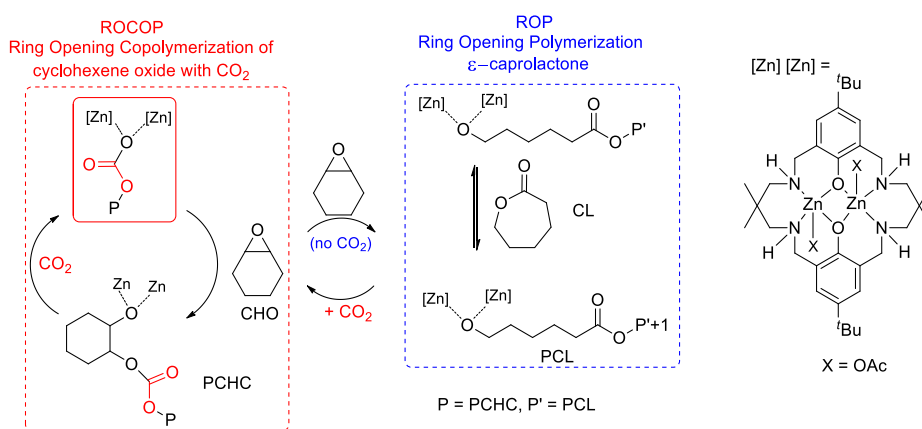


Fig. 23. Ring opening polymerization and ring opening copolymerization catalyzed by a di-zinc catalyst, CO₂ could either react with CHO or depress the ring opening reaction of caprolactone [174].

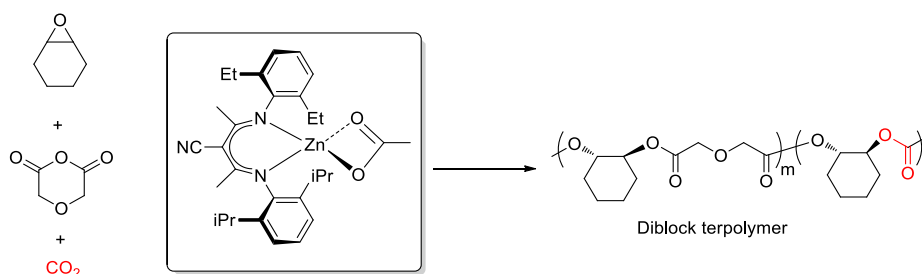


Fig. 24. Terpolymerization of CHO, DGA and CO₂ to a diblock copolymer via one-pot reaction [48].

copolymerization of functionalized cyclohexene oxides and CO₂ by sequentially adding CHO derivatives containing different substituents (Fig. 20) [44]. The success of this method depends on the living polymerization character and the high activity of the catalyst that could consume the previous epoxide completely before the next one added.

Tandem method is a two-step operation which involves the first synthesis of a polycarbonate with hydroxyl end group, which can

be used as a macromolecular transfer agent for ROP of lactone in the next step. By using this method, CO₂-based block copolymers with different blocks could be achieved by combination of two polymerization modes. Williams et al. prepared a di-hydroxyl terminated PCHC through a di-zinc catalyst, which was used as a macroinitiator in ROP of lactide to yield ABA-type triblock copolymers in the presence of an yttrium co-initiator (Fig. 21) [46]. Darendbourg reported the syntheses of di- and tri-block

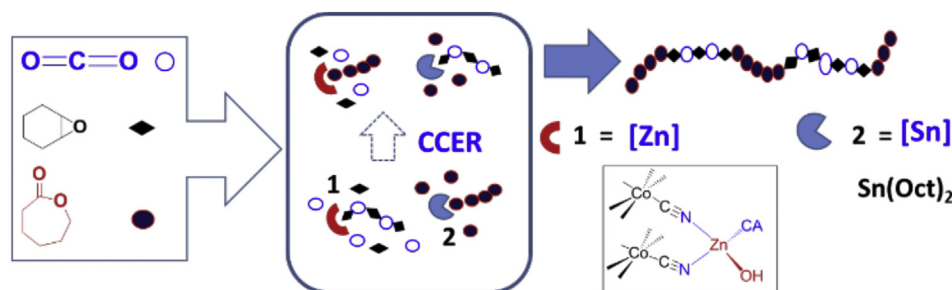


Fig. 25. Proposed cross chain exchange polymerization of CO_2 , CHO and $\epsilon\text{-CL}$ by using Zn–Co(III) DMCC (**1**) and stannous octoate [**2**, $\text{Sn}(\text{Oct})_2$] together [49]. Reproduced from Ref. [49] with permission from the Royal Society of Chemistry.

copolymers from CO_2 , epoxide and lactone via macroinitiator intermediate by tandem using a $(\text{salen})\text{Co}(\text{III})$ complex plus an organic base 1,8-diazabicyclo[5.4.0]undec-7-ene [45,173]. Water was used as the chain transfer and/or chain termination agent, which was added in the CO_2 /epoxide copolymerization to *in situ* generate the copolymers with two hydroxyl end groups (Fig. 22), which then initiated ROP of lactone. The success of this method depends on the fully utilizing chain transfer reaction to water and polycarbonates with hydroxyl end groups. Note that, the precondition of tandem method is that the polycarbonate with “pure”-hydroxyl end groups should be synthesized, as our initial report on the synthesis of polycarbonate diols by introducing water [113]. Recently, we reported the synthesis of a CO_2 -based triblock copolymer by using a low- T_g copolymer from Zn–Co(III) DMCC catalysis as macroinitiator and ROP of lactone by 1,8-diazabicyclo[5.4.0]undec-7-ene in tandem (Fig. 13) [47].

Recently, Williams et al. reported an interesting method to synthesize a CO_2 -based diblock copolymer from epoxide, CO_2 and ϵ -caprolactone ($\epsilon\text{-CL}$) by using a di-zinc catalyst through venting CO_2 from the system, hence, the copolymerization could be reversibly switched from a polycarbonate catalyst to a polyester catalyst (Fig. 23). The success of this method is that CO_2 is either a reactant for forming polycarbonate or the switching agent for changing the catalytic centers [174].

The other involves one-step operation. A pioneering work, reported by Coates group, described a pre-rate determining process for making diblock copolymer involving the transfer of one propagating center to another [48]. In this protocol, poly(ester-block-carbonate)s were obtained through a simple one-step, one-pot procedure with a zinc β -diiminate catalyst for epoxides, cyclic acid anhydrides, and CO_2 (Fig. 24) [48,175]. The success of this method depends on the addition of a monomer that copolymerizes with epoxides at a much faster rate than CO_2 . Such one-pot terpolymerization reaction of epoxides, cyclic acid anhydrides and CO_2 to synthesize polyester-block-polycarbonate polymers have been prepared by using a variety of catalysts (such as chromium

tetraphenylprophyrinato (TPPCrCl), $(\text{salen})\text{CrCl}$ /onium salt catalysts) [176,177].

As we all know, it is a long-standing challenge to combine mixed monomers into multiblock copolymer in a one-pot/one-step polymerization manner. Very recently, our group reported the first example of multiblock copolymer with alternating polycarbonate and polyester blocks from highly efficient one-pot/one-step polymerization of CHO, CO_2 and $\epsilon\text{-CL}$ in the presence of Zn–Co(III) DMCC and stannous octoate (Fig. 25) [49]. This method involves the cross-chain exchange reaction based on the difference of catalytic activity towards the monomers. In this protocol, two cross-chain exchange reactions occurred at dual catalysts respectively and connected two independent chain propagation procedures (i.e., polycarbonate formation and polyester formation) simultaneously in a *block-by-block* manner, affording multiblock copolymers. M_n s of the obtained multiblock copolymers increased from 9.7 to 35.2 kg/mol with decreasing the $[\text{benzyl alcohol}]/[\epsilon\text{-CL}]$ molar ratios from 1: 40 to 0. The structure of multiblock copolymers was supported by the apparent kinetic study of the terpolymerization, and fully evidenced by the differential scanning calorimetry (DSC) and small-angle X-ray scattering (SAXS) profiles that presented a clear restricted crystallization behavior of PCL blocks in multiblock copolymers. Due to the multiblock structure, the terpolymer showed improved elongation at break of 22.8% relative to those of PCHC (3.3%) [178] and PCHC/PCL blend (1.8%), which meant that multiblock copolymer was tougher than the pure PCHC and PCHC/PCL blend. Note that only a few examples of multiblock copolymer synthesized by using two catalysts via one-pot procedure [179,180]. In the previous methods, two catalysts of the same type were used to catalyze two monomers with same functionality (e.g., double bond) [179] or one monomer with *R* and *S* enantiomers [180]. This example provided a cross-chain exchange reaction route between two independent chain propagation processes catalyzed by two different types of catalysts for three monomers with different functionalities in a one-pot/one-step way.

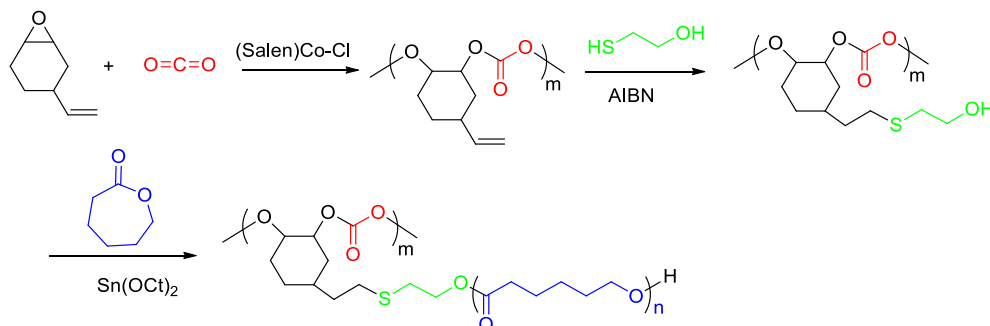


Fig. 26. Synthetic route of degradable brush copolymers with polycarbonate as backbone and PCL as side chains [50].

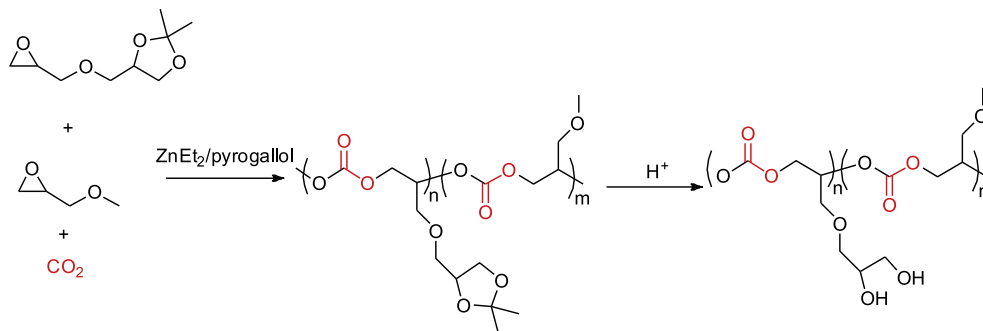


Fig. 27. Synthesis of poly[(isopropylidene glycerylglycidyl ether)-co-(glycidyl methyl ether) carbonate] and subsequent acidic deprotection [51].

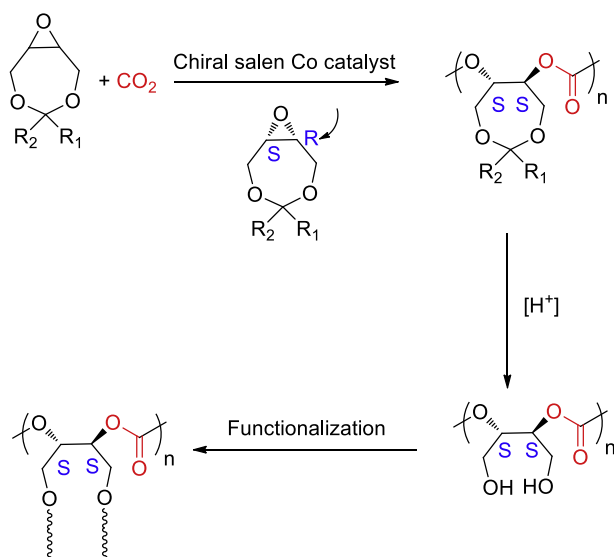


Fig. 28. The alternating copolymerization of CO₂ with 3,5-dioxapoxides and the polycarbonate functionalization [183].

4.2. Brush and star copolymers

In 2011, our group reported the synthesis of a polycarbonate with hydroxyl side groups, which was used as a precursor for synthesizing brush copolymers with well-defined structure and nearly 100% grafting density through “grafting from” method. Firstly, alternating copolymerization of CO₂/4-vinyl-cyclohexene-1, 2-epoxide was catalyzed by (salen)Co(III)Cl complex without using any cocatalysts, then thiol-ene click reaction was applied for converting side vinyl group to hydroxyl group which could initiate ring

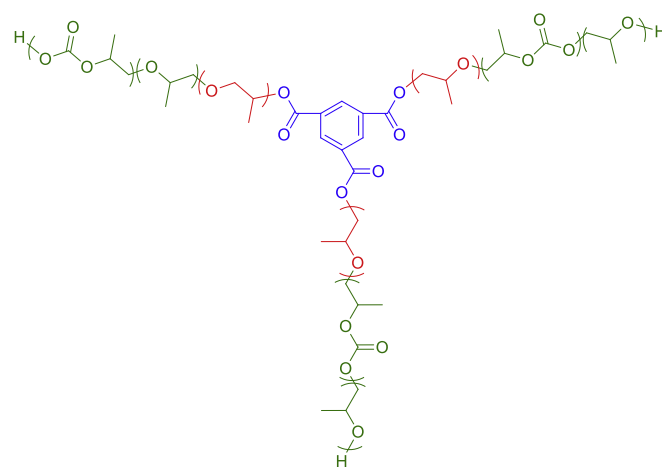


Fig. 30. The structure of oligo(carbonate-ether) triol [53]. Reproduced from Ref. [53] with permission from the Royal Society of Chemistry.

opening polymerization of ϵ -CL to afford a PCL side chain (Fig. 26) [50].

Later, a series of polycarbonates with hydroxyl side groups were reported by using various methods [51,54,181–184]. Frey et al. synthesized a series of functional polycarbonates [51,54,181,182,185,186], for example, poly[(isopropylidene glycerylglycidyl ether)-co-(glycidyl methyl ether) carbonate] random copolymers with different fractions of 1,2-isopropylidene glycerylglycidyl ether units [181] was synthesized and followed by treating with acid, the pending acetal protected groups was hydrolyzed, and a new type of functional polycarbonate prepared directly from CO₂ and glycerol was obtained (Fig. 27). Besides, novel functional, linear aliphatic polycarbonate random copolymers from CO₂, glycidyl methyl ether, and a protected

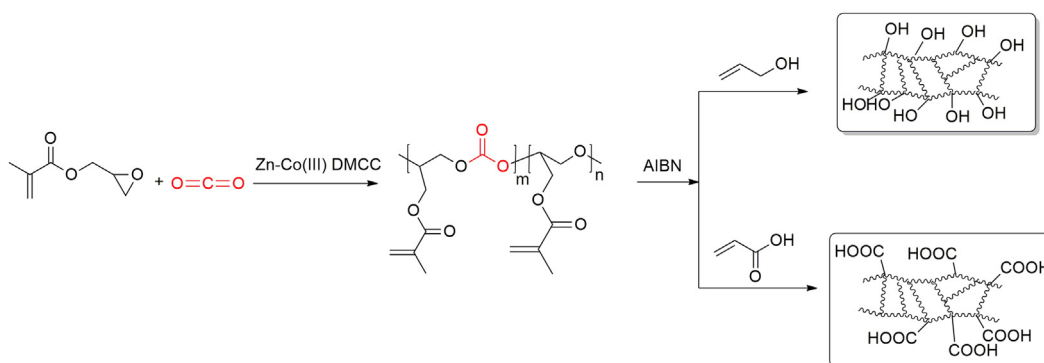


Fig. 29. The curing reaction of CO₂/glycidyl methacrylate copolymer with allyl alcohol or acrylic acid via free radical polymerization [52].

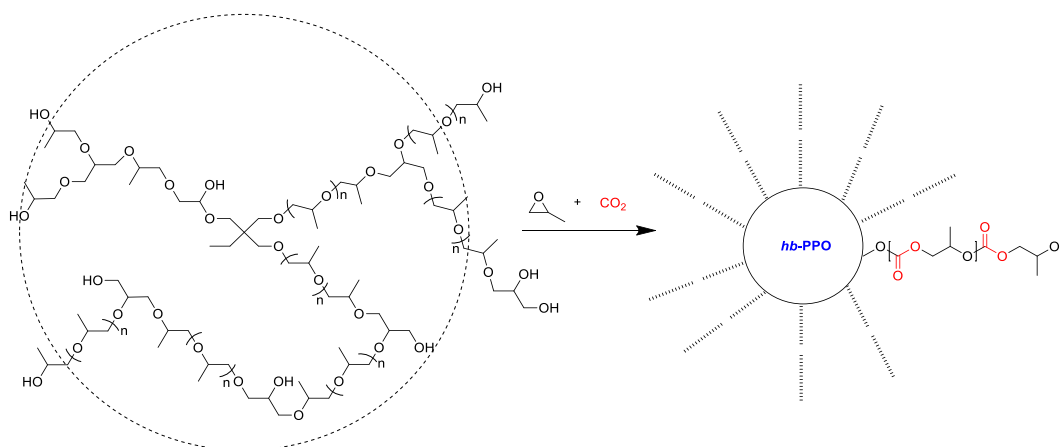


Fig. 31. Two-step synthesis of hyper branched PPC multi-arm star copolymers with *hb*-PG-co-PPO core (left); branching points are generated from glycidol in the first step [147].

glycidyl ether derivative (benzyl glycidyl ether) have been synthesized by Frey group [182]. Via catalytic hydrogenation of the benzyl protected groups the hydroxyl groups were released and functional polycarbonates with tailored functionality were obtained. Lu group reported the selective synthesis of highly isotactic copolymers from perfectly alternating copolymerization of CO_2 with *meso*-3,5-dioxapoxides catalyzed by an enantiopure dinuclear (salen)Co(III)X complex catalyst (Fig. 28) [183]. The acid hydrolysis of this highly isotactic copolymer led to a stereoregular poly (1,2-bis(hydroxymethyl) ethylene carbonate) which contained two hydroxyl groups in each carbonate unit. Recently, this group [184] reported fully degradable brush polymers with polycarbonate backbones and polylactide side chains through a “grafting-from” method via the terpolymerization of CHO, benzyl glycidyl ether (BGE) and CO_2 , deprotection of the benzyl groups by hydrogenation, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)-mediated ROP of lactide initiated by the $-\text{OH}$ groups on the polycarbonate backbone.

On the other way, the side double bond could be used for crosslinking to prepare CO_2 -based thermosets [52]. A poly (carbonate-co-ether) with massive pendant acrylate groups was synthesized from the copolymerization of glycidyl methacrylate with CO_2 by using Zn–Co(III) DMCC catalyst, then new thermosets with high T_g s (105 and 120 $^\circ\text{C}$) and massive carbonate units as well as hydroxyl (or carboxylic) groups were prepared by the curing reaction of CO_2 /glycidyl methacrylate copolymer with allyl alcohol or acrylic acid (Fig. 29).

CO_2 -based multi-arm star polycarbonates could be synthesized via chain transfer reactions. Wang's group [53] reported a one-pot synthesis of oligo(carbonate-ether) triol from CO_2 /PO copolymerization by using a Zn–Co(III) DMCC catalyst in the presence of 1,3,5-benzenetricarboxylic (trimesic) acid as a chain transfer agent (Fig. 30). By using a hyper-branched poly(propylene oxide) polyol as the chain transfer agent, multi-arm star copolymers could be synthesized via two steps from PO, a small amount of glycidol and

CO_2 . The PPC arms were prepared via CO_2 /PO copolymerization, using poly(propylene oxide) polyol as a multifunctional macro-initiator and the (*R,R*)-(salen)CoOBzF₅ as catalyst reported by Frey's group (Fig. 31) [54].

5. Carbon disulfide polymerization

5.1. Carbon disulfide (CS_2) is an analogue of CO_2

CS_2 is also an abundant and widely used C1 heterocumulene. Being a sulfur-containing C1 resource, CS_2 has also been employed as a sulfur resource to synthesize sulfur-containing polymers. Introducing sulfur atoms into polymer backbone, depending on the kind of functional groups, can impart some special properties, such as electrical, absorption and optical properties, and then adhesion to metals, resistance to heat, chemicals, radiation, and bacteria, biocompatibility, etc. As a result, sulfur-containing polymers can be used as high performance engineering plastics, chemically stable ion-exchange membranes in electro membrane processes, proton-conducting electrolytes, as well as optical, optoelectronic, and photochemical materials [34,170,187]. In this part, the synthesis of polymers with CS_2 as a starting material is reviewed.

5.2. Homopolymerization of carbon disulfide

Since the first synthesis of a black solid from CS_2 by Bridgman [188], many researchers have synthesized and characterized polymers from CS_2 [188–197]. CS_2 can homopolymerize on the condition of high pressure [188–190], ultrasonic treatment [196], gamma ray irradiation [197], plasma [191,195,198], and photoirradiation [194]. The resulting polymers have nearly the same structure as Bridgman's black solid product (Fig. 32). The CS_2 homopolymers are demonstrated to comprise a linear main chain of dithioester and trithiocarbonate structures, by head-to-head and head-to-tail polymerizations, respectively, along with the disulfide linkages produced by coupling two thiocarbonyl groups [194].

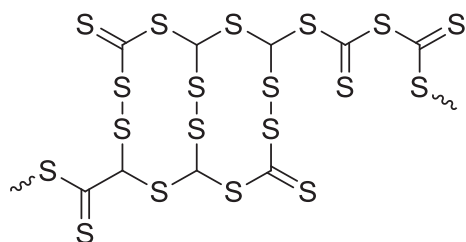


Fig. 32. The homopolymerization of carbon disulfide.

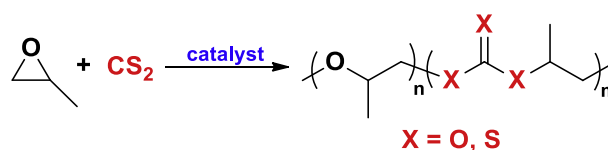


Fig. 33. The copolymerization of propylene oxide with carbon disulfide catalyzed by diethyl zinc combined with bases.

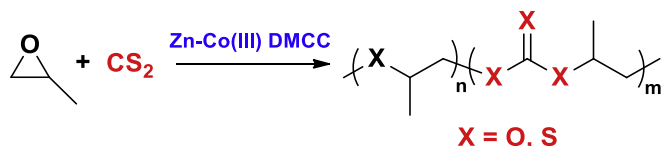


Fig. 34. The copolymerization of propylene oxide with CS_2 catalyzed by Zn–Co(III) DMCC catalyst.

5.3. Carbon disulfide/epoxide copolymerization

Since CS_2 is structurally similar to CO_2 , it is expected to copolymerize with epoxides like CO_2 . Indeed, by copolymerizing with epoxides, CS_2 could be converted to poly(thiocarbonate)s.

5.3.1. Heterogeneous catalysis

Studies on the copolymerization of CS_2 with epoxides began with the target to synthesize poly(thiocarbonate)s. After a short conference report of Inoue et al., in 1968 [199], Adashi et al. published a study of copolymerization of PO and CS_2 in 1977 [200]. Diethyl zinc in combination with various bases was used as the catalysts. As shown in Fig. 33, the resulting copolymers were observed by IR spectroscopy to contain different thiocarbonate linkages, as well as large percentage of ether linkages. Yet, with the analytical methods of that time, a full elucidation of the chain composition and sequences was infeasible. Meanwhile, long reaction time was required for these reactions, and the molecular weight of the obtained poly(thiocarbonate) was rather low, e.g., only 560 g/mol.

In 2008, we reported the use of the aforementioned highly effective Zn–Co(III) DMCC catalyst to achieve a one-pot polymerization of CS_2 with PO (Fig. 34) [36]. A poly(thiocarbonate) with a complex structure was produced. The molecular weight of the copolymer was determined by GPC to be in the range 1.2–5.4 kg/mol, with a PDI of 1.24–3.50. However, the polymerization selectivity was poor, different cyclic products and complicated linkages including ether, thioether, carbonate and thiocarbonate were determined by the method of Nuclear Magnetic Resonance (NMR) and Fourier Transform Infrared (FT-IR) spectroscopy. Irregular unit structure meant a complex polymerization mechanism. With the help of gas chromatography-mass spectrometry (GC–MS) technique, the intermediates of COS and CO_2 were detected during the reaction process, five species, i.e., CS_2 , PO, COS, propylene sulfide [because of the generation of small portion of poly(propylene sulfide) segment], and CO_2 , were coexistent. Their random copolymerization in the reaction system then resulted in a copolymer with complex unit sequences. It was observed that oxygen atoms are much more easily incorporated into the main chain of the copolymer. Seven five-membered cyclic compounds were also simultaneously generated in the reaction. Thus a concept of oxygen/sulfur exchange reaction was proposed to explain the observed oxygen/sulfur scrambling result. In this instance, Zn–Co(III) DMCC could either catalyze the copolymerization or act as exchange sites

for producing intermediates. However, the precise mechanism of the oxygen/sulfur exchange reaction was not revealed. This is the first success for directly synthesizing polythiocarbonate with high molecular weight and high productivity from CS_2 .

5.3.2. Homogeneous catalysis

In 2009, the copolymerization of CHO with CS_2 was investigated by Darensbourg group by utilizing a well-defined (salen)CrCl/PPNCl system (Fig. 35) [201] and our group by Zn–Co(III) DMCC [202]. O/S scrambling phenomenon was observed as well in the polymer and cyclic products in both systems, with the copolymer being oxygen enriched and the cyclic carbonate being sulfur enriched. Nevertheless, the pathway for O/S scrambling was inadequately understood.

Very recently, the copolymerization of CS_2 with CHO was also investigated by using a homogeneous zinc catalyst with an asymmetric bis-Schiff-base ligand accompanied with PPNCl [203], similar to the previous works [36,201], intense O/S exchanging reaction occurred, thus poly(thiocarbonate) with mixed units was achieved with high M_n up to 19 kg/mol. In this example, the main byproduct was cyclic trithiocarbonate. However, the mechanism was not disclosed.

In 2013, the catalytic coupling reaction of cyclopentene oxide with CS_2 was studied by Darensbourg group by utilizing (salen)CrCl in the presence of onium salts [204]. As shown in Fig. 36. Both polymeric material and cyclic compounds were produced, with O/S scrambling observed in both instances. (salen)CrCl was shown to be necessary for the scrambling process, and onium salts impacted this process. Mix-species scrambling resulted in very complicated products and the proposed mechanism for scrambling was somewhat better assessed.

In all the aforementioned examples, the chain structure of the produced polythiocarbonates was not well-defined, and the mechanism of O/S scrambling still remained questionable. More recently, Darensbourg group cooperated with us to investigate the copolymerization of CS_2 with oxetane catalyzing by binary (salen)CrCl/onium salt catalyst (Fig. 37) [205]. Oxetane is an analogue of PO, but it is symmetric and such binary symmetric copolymerization provided informative results. Molar ratios of various thiocarbonate linkages and cyclic products are precisely determined for the first time, providing reliable reference to test the factors effecting the O/S scrambling. The coupling of oxetane and CS_2 was selective for copolymer formation over a wide range of reaction conditions. When CS_2 /oxetane loading was increased, the scrambling of oxygen and sulfur atoms was slightly modulated, enhancing the linkages containing the less stable moiety ($\text{C}=\text{S}$ bond). Reaction temperature has a significant effect on the variation of the linkages in the resulting copolymers, with increasing temperature promoted O/S exchange rate during copolymerization, as illustrated in Fig. 38. When using (salen)CrCl in the absence of an added onium salt, the reaction is as expected, very slow and the numbers of the units are reduced. Hence, the onium salt cocatalysts not only accelerate the reaction, but also promote O/S scrambling process. The pathway of the O/S exchange process was proposed as Fig. 39. By investigating the CS_2 /oxetane copolymerization, a more suitable proposal for interpenetrating the O/S exchange process is disclosed.

5.4. Copolymerization of carbon disulfide with other monomers

CS_2 can also couple with other monomers for its higher chemical reactivity than CO_2 . Fritze et al. reported an approach to use CS_2 as a starting material to prepare ϵ -thiocaprolactone and its polyester in his three U.S. patents [206–208]. Heating of ϵ -CL with CS_2 in the presence of NaOH at 200 °C yielded a low molecular weight polythioester, however, the thermal depolymerization in turn resulted

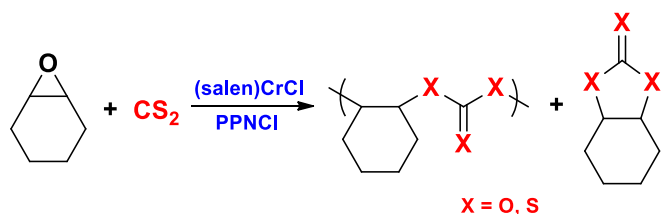


Fig. 35. The copolymerization of CHO with CS_2 catalyzed by (salen)CrCl/PPNCl catalyst.

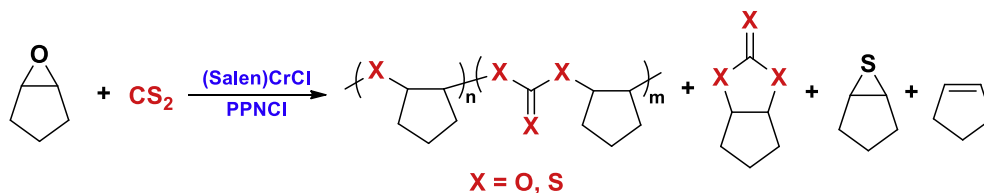


Fig. 36. The coupling reaction of cyclopentene oxide with CS_2 catalyzed by (salen)CrCl/PPNCl catalyst.

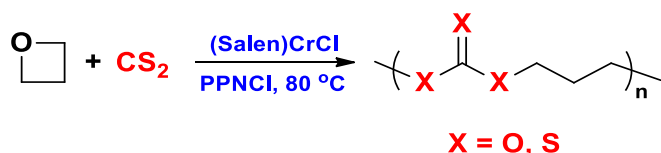


Fig. 37. The copolymerization of oxetane with CS_2 .

in monomeric ϵ -thiocaprolactone, which was then self-polymerized or copolymerized with ϵ -CL in the presence of manganese (II) benzoate (Fig. 40).

Another approach was described by a Japanese group [209,210] who studied the copolymerization of ethylene sulfide and propylene sulfide with CS_2 (Fig. 41). $Cd(C_2H_5)_2$, $ZnCl_2$ and $Hg(SC_4H_9)_2$ served as the catalysts. Low molecular weight homopolymers and copolymers (containing oligoethylene sulfide blocks) were obtained. In 2007, Nozaki and co-workers [40] investigated the coupling of propylene sulfide with CS_2 to yield a well-defined poly(propylene trithiocarbonate) and cyclic propylene trithiocarbonate. This process was optimized to provide a high molecular weight copolymer with 92% selectivity. Since no oxygen-containing monomer existed in the reaction, O/S scrambling was not an issue, and this polymer was completely alternating. Because of the high sulfur content of the copolymer, it possessed a very high refractive index of 1.78 (measured by Abbe's refractometer, cast film, 20 °C), which could be classified into the highest values among those of the reported sulfur-containing polymers [211].

The preparation of aliphatic and aromatic poly(trithiocarbonate)s is also reported by "polyalkylation" of the trithiocarbonate ion (from CS_2 and Na_2S) with the α , ω -dibromoalkanes (Fig. 42) or bischloromethyl benzenes (Fig. 43) [212–214]. These syntheses were conducted by an interfacial polycondensation using excess CS_2 as organic phase and tetra-alkyl ammonium salts as phase

transfer catalysts. But the molecular weight of the resulting polymers was rather low. End group analysis result showed two halogen end groups, suggesting no production of cyclic intermediates or oligomers during polymerization.

Ketene cyclic N, O-acetals were also reported to copolymerize with CS_2 spontaneously with ring-opening (Fig. 44) [215]. This copolymerization completed nearly instantaneously at ambient temperature, or within 1 h at -50 °C. The intermediates of the copolymerization were zwitter-ionic adducts of the monomers, the dithiocarboxylate in which attacks the β -carbon atom in the oxazolinium ring of the other zwitter ion. CS_2 was copolymerized with 2-methylene-3-methyl-1,3-oxazolidine, only an oligomer produced due to the termination reaction by the transfer of a proton from the α -carbon of the oxazolinium ring to the dithiocarboxylate, however, when CS_2 reacted with 2-isopropylidene-3-methyl-1,3-oxazolidine, a polymer with high M_n of 260–300 kg/mol was effectively produced.

Olefins can also copolymerize with CS_2 . Attempts to copolymerize CS_2 and methyl acrylate or acrolein in gas phase resulted in separate polymerization of each monomer and aerosol particles of the mixture [216,217]. On the other hand, copolymerization of CS_2 with ethylene has been reported recently [218]. The copolymerization of a gaseous mixture of CS_2 and ethylene could be induced by UV-irradiation (193 nm), resulting in deposition of a copolymer as illustrated in Fig. 45. The resulting polymer was almost insoluble in chloroform. The polymer structure was elucidated to contain different linkages and moieties by the analysis of X-ray photoelectron and FT-IR spectroscopy.

CS_2 could be employed as a starting material to synthesize poly(thiocarbonate) through a two-step method. Firstly, cyclic monothiocarbonates or dithiocarbonates (such as 1,3-oxathiolan-2-one, 1,3-dioxolane-2-thiones, 1,3-oxathiolane-2-thiones) were prepared through the reaction of CS_2 with epoxides. And then poly(thiocarbonate)s were synthesized through ROP of these cyclic

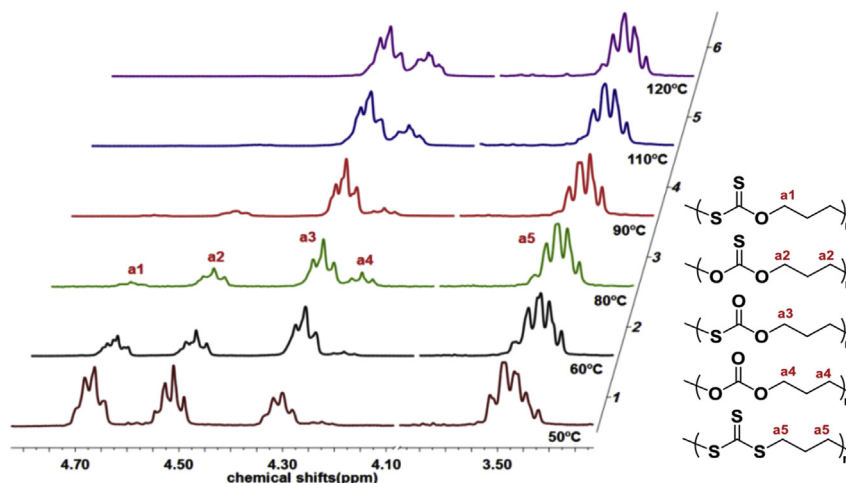


Fig. 38. The trends of the 1H NMR spectra of entries from different temperatures. Reproduced with permission from Ref. [205]. Copyright (2015) American Chemical Society.

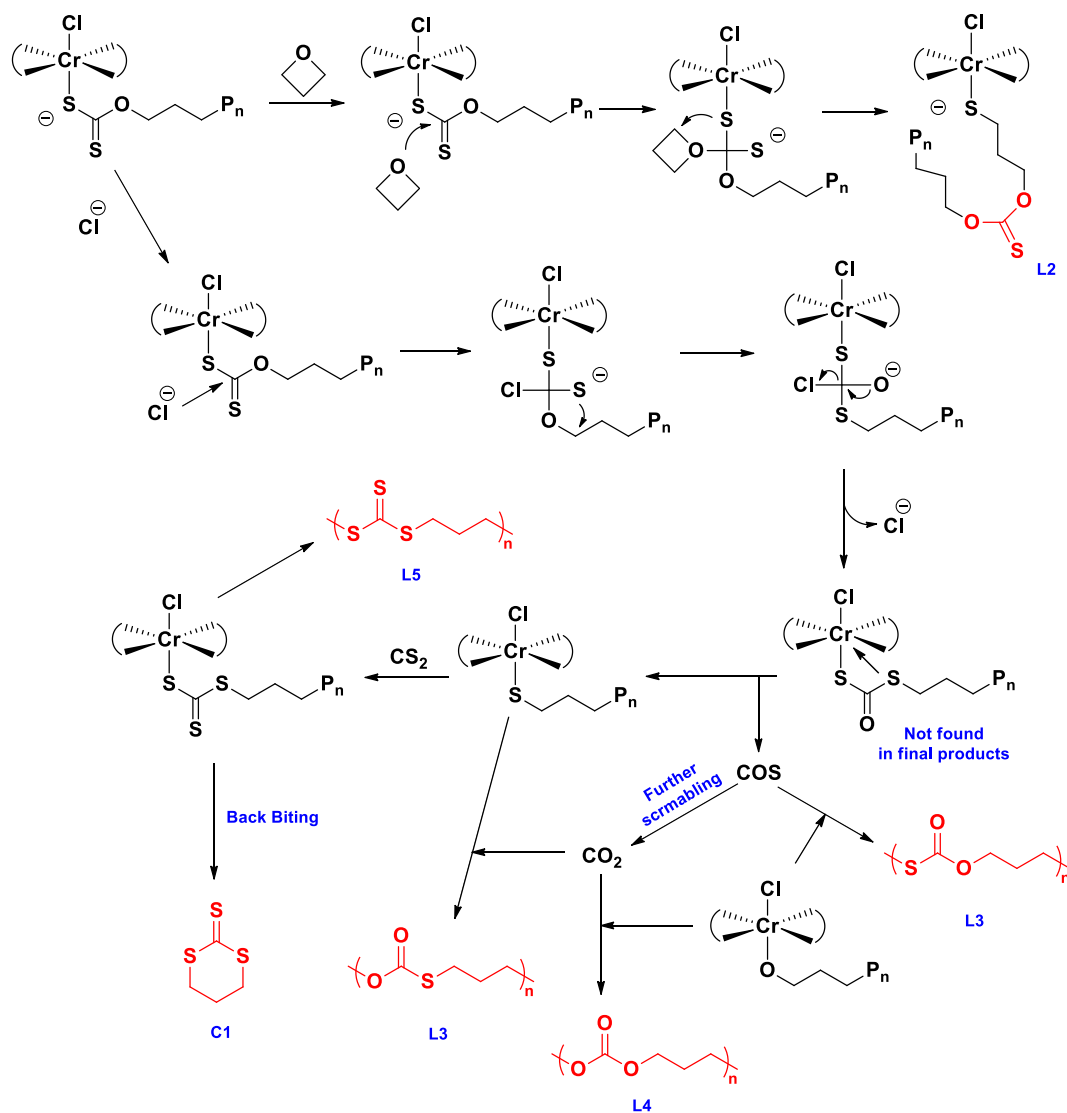


Fig. 39. The plausible mechanism of the oxygen/sulfur exchange reaction and the formation of different linkages in the copolymerization of oxetane and CS_2 . Reproduced with permission from Ref. [205]. Copyright (2015) American Chemical Society.

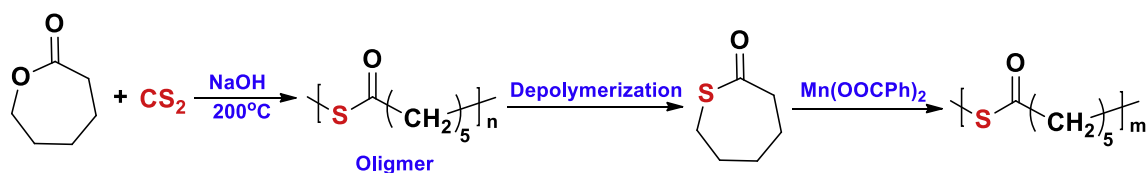


Fig. 40. The synthesis of the poly(thioether) from ϵ -CL and CS_2 .

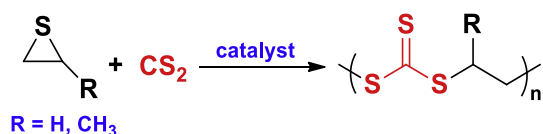


Fig. 41. The polymerization of episulfides with CS_2 .

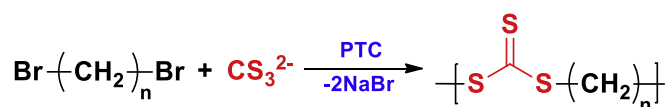


Fig. 42. The synthesis of poly(trithiocarbonate) from α,ω -dibromoalkanes and CS_2 .

thiocarbonates with the use of cationic initiators (Fig. 46). However, the reaction of epoxides and CS_2 often tends to result in mixed products of different thiocarbonates. An exception is that selective

preparation of 5-substituted 1,3-oxathiolan-2-thione was obtained by the use of lithium bromide in tetrahydrofuran [219]. The poor selectivity of the first step and difficult purification of these cyclic thiocarbonates badly limited the abundance of the starting material

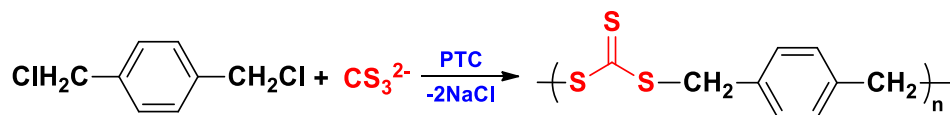


Fig. 43. The synthesis of poly(trithiocarbonate) from bischloromethyl benzenes and CS₂.

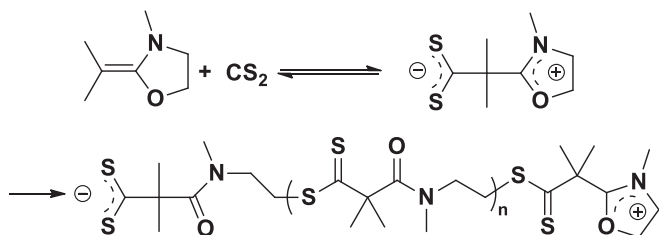


Fig. 44. The copolymerization of ketene cyclic N, O-acetals with CS₂.

for the second step. Moreover, isomerization and depolymerization easily occurred in the second step, reducing the selectivity for the formation of poly(thiocarbonate)s. Massive and comprehensive works have been reported by Endo and his coworkers [220–223]. The synthesis and properties of poly(thiocarbonate)s prepared by this method have been well reviewed in 2005 [170] and in 2007 [224].

6. Polymerization of epoxides with carbonyl sulfide

The first example using COS as a starting material to synthesize polymer was reported in 1965. Osborn reported in his patent that poly(ethylene thiocarbonate) can be prepared by the polyaddition of COS and ethylene oxide promoted with sodiummethoxide [225], however, cyclic monothiocarbonate was produced in most examples.

As mentioned above, in our early research, COS was captured to be a key intermediate caused by the O/S exchange reaction and it enriched during CS₂/PO copolymerization [36]. The discovery of COS intrigued us to use it as a C1 monomer for copolymerizing with epoxides because COS is an asymmetric C1 monomer and its

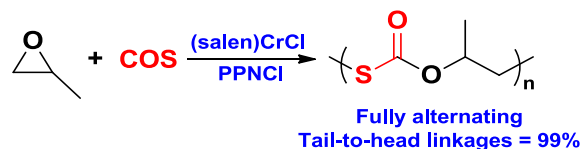


Fig. 47. The copolymerization of propylene oxide with COS.

enrichment in CS₂/PO copolymerization meant that COS is uneasy to trigger O/S exchange reaction. In 2013, we reported the first example of a regioregular and fully alternating poly (propylene monothiocarbonate) from a well-controlled copolymerization of COS and racemic PO, using (salen)CrCl in conjunction with PPNCI (Fig. 47) [39]. COS/PO copolymerization presented a complicated stereochemistry control manner involving the two asymmetric monomers, as shown in Fig. 48. In the propagating stage, when a COS molecular inserts into the propagating center, there are two possible routes **A** and **B**. It was demonstrated that route **A** is the only pathway for COS insertion because of the stronger nucleophilicity of sulfur atom than the oxygen atom of COS to the metal center. The attacking manner of propagating species of –OC(=O)S– via route **A** to the carbon of CH₂ or CH of PO will produce four kinds of consecutive monothiocarbonate diads: head-to-tail (H–T), tail-to-head (T–H), tail-to-tail (T–T), and head-to-head (H–H). Herein, tail-to-head diad is different from head-to-tail diad due to asymmetric monothiocarbonate structure. We observed that the monothiocarbonate linkage and tail-to-head content of the resulting copolymer were determined to 100% and 99.0%, respectively. The copolymer had a *M_n* of 25.3 kg/mol and a refractive index of 1.63 from Abbe's refractometer (cast film, 20 °C). The high regioselectivity was resulted from the preference of sulfur anion to attack the less hindered methene carbon of PO,

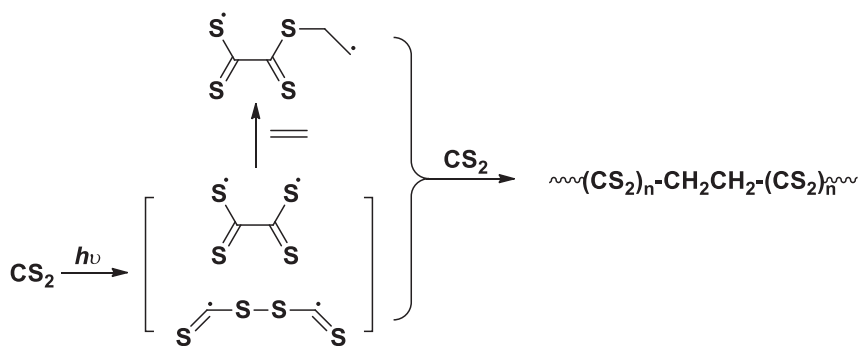


Fig. 45. The copolymerization of olefin with CS₂.

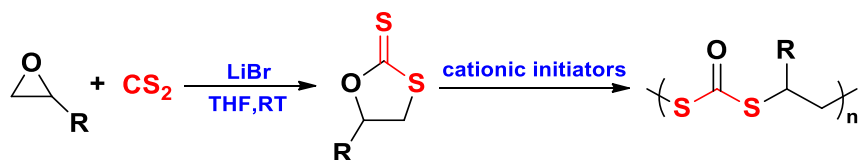


Fig. 46. The synthetic route of poly(thiocarbonate)s from cyclic thiocarbonates derived from coupling reaction of epoxides with CS₂.

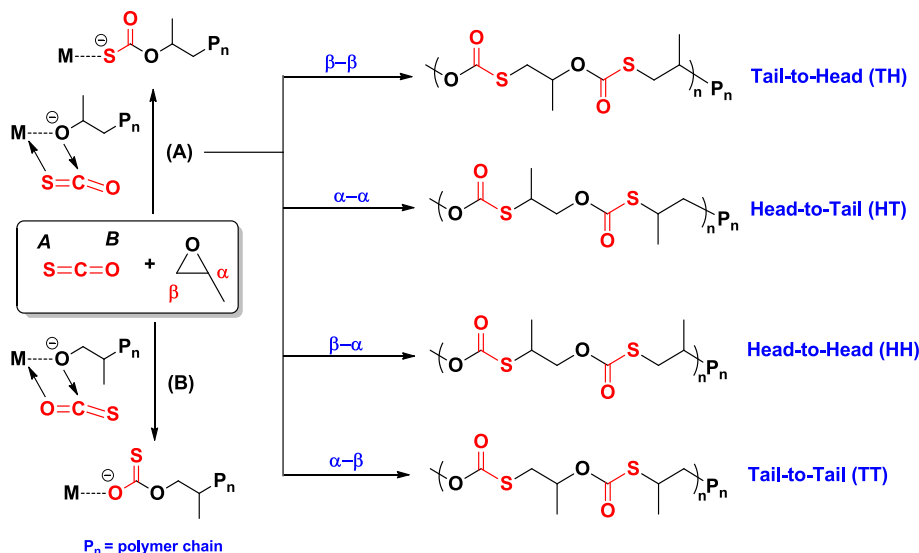


Fig. 48. Different routes for the propagating process in PO/COS copolymerization.

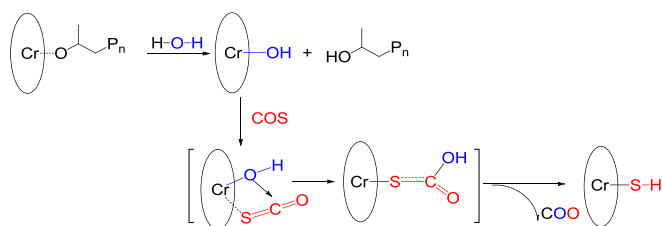


Fig. 49. The plausible mechanism for the O/S exchange reaction in the PO/COS copolymerization. Reproduced with permission from Ref. [39]. Copyright (2013) American Chemical Society.

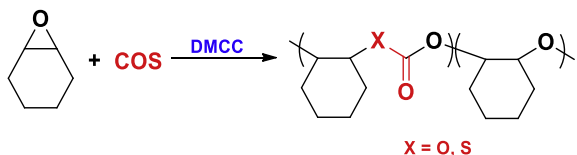


Fig. 50. The copolymerization of CHO with COS catalyzed by Zn–Co(III) DMCC catalyst.

thus the β - β route was the only manner responsible to the propagation. As a result, only tail-to-head linkages were formed. In this case, the O/S exchange reaction occurred at higher reaction temperature, which was consistent with the CS₂/oxetane systems [37].

The plausible mechanism of O/S exchange reaction was proposed as Fig. 49, small amount of H₂O was considered to be a key agent to trigger the O/S exchange reaction. At high reaction temperature, H₂O could react with the metal center to generate a Cr–OH group via chain transfer reaction, and then it could coordinate with a COS molecule to generate a Cr–SH group and simultaneously a CO₂ molecules was released. Afterwards, CO₂ could copolymerize with PO, while Cr–SH could also initiate COS/PO copolymerization. Therefore, the carbonate linkages were formed when severe O/S exchange reaction occurred, which was confirmed by ¹³C NMR spectroscopy. And the proposal on the formation of Cr–SH group was confirmed by Raman spectroscopy and ESI-MS result of the resulting copolymers that meant the production of copolymers with end –SH group.

In 2014, we described the first example of alternating copolymerization of COS with CHO via heterogeneous catalysis of the aforementioned Zn–Co(III) DMCC catalyst (Fig. 50), converting COS

to poly(cyclohexene monothiocarbonate) with an alternating degree up to 93% [226]. The molecular weight of this copolymer was 6.5–25.0 kg/mol with PDI of 1.6–2.1. The productivity of the catalyst was up to 970 g polymer/g catalyst in 5 h and conversion of CHO was up to 95%. O/S exchange reaction could be largely suppressed in tetrahydrofuran at high reaction temperature resulting 90% monothiocarbonate linkages and 2% carbonate linkages in the polymer chain. The monothiocarbonate linkages account for 98% in the total alternating linkages, while the content of the ether linkages was 7%. The obtained poly(cyclohexene monothiocarbonate) is highly transparent and exhibited good solubility in various solvents, high *T_g* of 112 °C, initial decomposition temperature of 214 °C, and high refractive index of 1.705 (measured by Abbe's refractometer, cast film, 20 °C), which might be potentially used as optical materials.

More recently, we reported the well-controlled synthesis of a poly(monothiocarbonate) with high refractive index (*n_d*) and high Abbe's number (*V_d*) values by using COS as a sulfur source. Refractive index and Abbe's number are two decisive parameters for a polymer to be an optical material [227]. Fully alternating COS/CHO copolymers and COS/CHO/PO terpolymers were synthesized by using the binary (salen)CrCl/PPNCl catalyst (Fig. 51) [41]. The alternating COS/CHO/PO terpolymerization was performed at 40 °C, yielding terpolymer with 100% selectivity versus cyclic products. TOF of the terpolymerization was 323 h^{–1} at 40 °C. The resulted terpolymer possesses *M_n* up to 22.3 kg/mol with a narrow PDI of 1.16. Notably, these terpolymers exhibited better *n* and *V_d* values than sole COS/PO and COS/CHO copolymers (Fig. 52). Of importance, by varying the feeding ratio of PO and CHO, *V_d* of the resulting terpolymer was adjustable from 32.1 to 43.1. We proposed that the molecular polarizability of the C–S bond in the terpolymer could be changed by incorporating the other epoxide, leading to the change of the optical properties. *T_g* was almost proportional to the cyclohexene monothiocarbonate linkage's ratio (Fig. 53). This terpolymer is potential to be used as optical plastics with tailored optical and thermal properties.

7. Properties of polymers from C1 building blocks

7.1. Thermal property

T_g is the basic thermal property of a polymer. *T_g*s of CO₂/epoxide

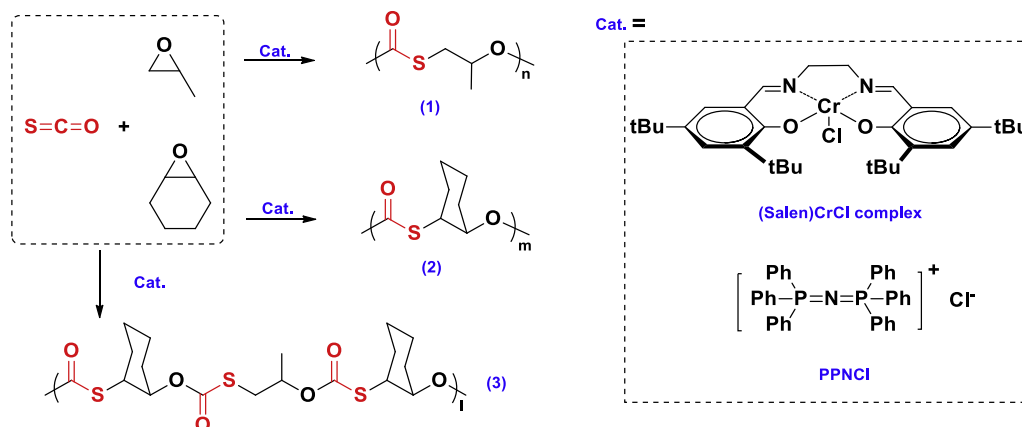


Fig. 51. The copolymerization of CHO with COS and terpolymerization of CHO/PO/COS. Reproduced from Ref. [227] with permission from the Royal Society of Chemistry.

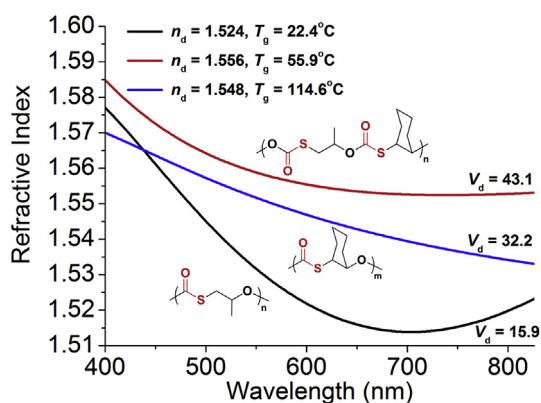


Fig. 52. The variation of the refractive indices (n) via the wavelength from 400 to 800 nm (n_d is refractive index at wavelength 587.6 nm) (Measured by Spectroscopic Ellipsometer). Reproduced from Ref. [227] with permission from the Royal Society of Chemistry.

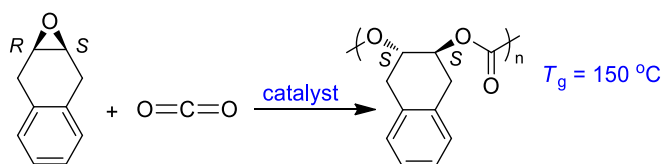


Fig. 54. Copolymerization of 1,4-dihydronaphthalene oxide (CDO) with CO_2 .

which is close to the bisphenol-A polycarbonate. The T_g of -44°C is resulted from the CO_2 /epoxy methyl 10-undecenoate (Fig. 13) copolymerization reported by our group [47].

The synthesis of crystalline CO_2 -based polycarbonates is mainly studied by Lu group. In 2012, he reported the synthesis of highly isotactic poly(cyclohexene carbonate)s from *meso*-CHO using dissymmetrical enantiopure (salen)Co(III) complexes in conjunction with PPNCI as catalyst [228,229], and this copolymer is a typical semicrystalline polymer, possessing a melting point (T_m) of 216°C and a decomposition temperature (T_d) of 310°C . In 2013, the same group cooperated with the Darensbourg group used an enantiopure (salen)Co(III) complex bearing an adamantane group and an appended bulky dicyclohexyl ionic ammonium salt to catalyze the epichlorohydrin/ CO_2 copolymerization [230]. The resulting isotactic poly(chloropropylene carbonate) is also a typical semicrystalline polymer with a T_g of 42°C and a T_m of 108°C . Then they reported the asymmetric copolymerization of CO_2 with CHO mediated by enantiopure dinuclear (salen)Co(III) complexes [87], and a highly isotactic polymer with a T_m of 272°C was produced. Recently, they described the enantioselective copolymerization of 3,4-epoxytetrahydrofuran with CO_2 mediated by biphenol-linked dinuclear cobalt complex [231], affording the corresponding polycarbonate with >99% carbonate linkages and excellent enantioselectivity (up to 99% enantiomeric excess). Notably, the resultant isotactic polycarbonate is a typical semicrystalline polymer, possessing a melting point of 271°C . In 2014, Coates's group employed an enantioselective zinc β -diiminato catalyst to synthesize semicrystalline poly(cyclohexene carbonate) with high isotacticity under mild conditions [232]. And the melting temperatures are ranged from 234°C up to 260°C for polymer samples with isotacticities ranging from 78% ee up to 92% ee. More recently, several stereocomplexed polycarbonates were reported by Coates's group [233] and Lu's group [88,89]. Cocrystallization of amorphous opposite enantiomeric polycarbonates endowed the stereocomplexed polymer more higher T_m s than the individual enantiomers.

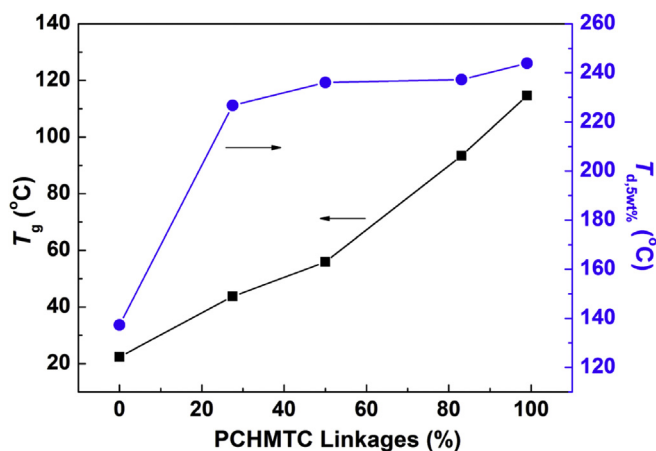


Fig. 53. Plots of the T_g (left) and $T_{d,5wt\%}$ (right) versus PCHMTC linkages percentages in the COS/CHO/PO terpolymers. Reproduced from Ref. [227] with permission from the Royal Society of Chemistry.

copolymer were in the range of -44°C [47] to 150°C [88], highly depending on the carbonate unit structure of the polycarbonate. The highest T_g of 150°C was reported by Lu group [88] resulting from isotactic poly(1,4-dihydronaphthalene carbonate) (Fig. 54),

7.2. Mechanical property

Investigations on the mechanical properties of PPC have been widely reported [102]. The Young's modulus of PPC at room temperature is very sensitive to the actual glass temperature of the material. The numbers reported are somewhere in the range of 700–1400 MPa for a material with a T_g of about 40 °C [234–240]. For PPC with a T_g of 30 °C, the modulus of 200–1000 MPa were measured [241,242]. The tensile strength of this material is found in a likewise broad range of 7–30 MPa. And the elongation at break of PPC extends to 1200% with a median around 600%. The mechanical properties appear to be dependent of the catalyst and reaction conditions used, and vary even within publications of the same group. However, the mechanical properties of other kinds of CO₂-based copolymers are rarely reported.

7.3. Biodegradability

As a representative of polycarbonates from CO₂, PPC has been investigated on its biodegradation on different conditions, such as in buffer [242–244] or in compost [102,245–247]. The results showed that PPC can be degraded, but needs rather critical conditions, i.e. this polymer resists attack of many enzymes in many cases. The rare studies on the biodegradability makes us worry about whether CO₂-based copolymers could survive when competing with current commercial polymers. Our recent work on the synthesis of a multiblock copolymer with alternating poly(cyclohexene carbonate) and poly(caprolactone) blocks is meaningful to make CO₂-based copolymers more competitive and useful. We expect that such multiblock copolymer could have superior biodegradability. However, valuable work is still needed to realize this target. Nevertheless, synthesizing multiblock CO₂-based copolymers containing well-designed biodegradable block is a promising strategy to produce polymers with balanced biodegradability and mechanical property.

7.4. Optical property

Nearly most of the CO₂-based poly(carbonate) are highly transparent. When COS or CS₂ are incorporated into the polymer chain, the resulting poly(thiocarbonate)s possess enhanced infractive indices (n_d) than their analogue poly(carbonate)s. Besides, Abbe number (V_d) is also a key parameter for an optical material. As mentioned above, the terpolymerization of COS, CHO and PO [41] led to a terpolymer with tuable Abbe numbers. By studying COS- and CS₂-involved copolymerization, new optical material with tailored optical and thermal properties could be developed via simple and atom economic pathway.

8. Other C1 copolymerization

Similar to CO₂ and its sulfur analogues (COS and CS₂), other C1 compounds have also been used as building blocks for making polymers. Carbon monoxide (CO) can copolymerize with olefins to synthesize polyketones under the catalysis of efficient palladium catalysts [248–250]. Formaldehyde (HCHO) is a naturally-occurring and the simplest aldehyde that is used as monomer for synthesizing phenol formaldehyde (PF) resins through a step-growth polymerization with phenol via acid or base catalysis [251,252]. Endo [253] reported that chloroform (CHCl₃) could react with dienes providing vinylcyclopropanes, and then these vinylcyclopropanes underwent a clean radical ring-opening process to afford the corresponding polymers. Dichloromethane (CH₂Cl₂) was reported to copolymerize with dibenzofuran smoothly at ambient temperature to yield an insoluble, infusible copolymer [254]. The

above C1 copolymerization needs co-monomers, which is different to the C1 polymerization that has been conceptualized to be that the carbon backbone is built one carbon at a time by Kenneth J. Shea [255]. This concept is demonstrated by the example of the trialkylborane initiated living polymerization of dimethylsulfoxonium methylide for synthesizing poly(methylene) with high molecular weight and narrow PDI [256].

9. Conclusions and outlook

It is still a big challenge to synthesize polymers from CO₂ and its sulfur analogues (COS and CS₂). Our ultimate goal is to develop highly active and simple catalyst that can meet the requirement of the large-scale production of CO₂-based polymeric materials, and understand the catalysis for converting C1 monomers to polymers. It should be restated that a key point for developing an industrial-favorable catalyst for CO₂ copolymerization is that the catalyst can perform well at relative high reaction temperatures, e.g. ca. 100 °C, because operation in large-scale production at ca.100 °C is in general more energy-saving.

On the other hand, the material from C1 monomers should have competitive properties. The CO₂-based polymeric materials should have superior or comparable properties as those of traditional plastics. However, the balance of biodegradability and thermal/mechanical properties is really a big challenge for CO₂-based copolymers. For the copolymerization of CS₂ (and COS) with epoxides, additional challenging issue is how to suppress or even conversely make use of the O/S exchanging reaction. Since sulfur-containing polymers could be synthesized by simple addition polymerization, it is deserved to develop efficient methods for converting COS and CS₂ into polymers.

Finally, referring to the developing history of polyolefin and the corresponding catalyst system, heterogeneous catalyst is still very hopeful for large-scale production of C1-based copolymers. Zn–Co(III) DMCC catalyst might be a practical choice because it presents the best catalytic performance among all the reported heterogeneous catalysts for C1 copolymerization. In fact, Zn–Co(III) DMCC catalyst has been applied in large-scale production of poly(ether-co-carbonate)s. However, 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.

Acknowledgments

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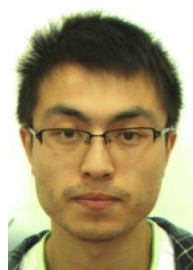
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