

## Recent advances in carbon dioxide based copolymers



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### ARTICLE INFO

#### Article history:

Received 8 July 2014

Received in revised form 9 October 2014

Accepted 13 October 2014

Available online 7 November 2014

#### Keywords:

Carbon dioxide

Polycarbonate

Poly(carbonate ether)

Metal catalyst

### ABSTRACT

Carbon dioxide is becoming increasingly important synthetic feedstock for chemicals and materials, since it is abundant, low-cost, non-toxic. One growing area in CO<sub>2</sub> chemistry utilization is the development of catalysts for the polymerization of CO<sub>2</sub> and epoxides to prepare CO<sub>2</sub> based copolymers, including high molecular weight aliphatic polycarbonates and low molecular weight poly(carbonate-ether) polyols. Among all the aliphatic polycarbonates, poly(propylene carbonate) (PPC) has the best opportunity for scale-up commercialization. PPC is not only cheap since it contains over 40 wt% CO<sub>2</sub>, but it also exhibits good biodegradability, which has wide application in throw-away packaging materials, or even gas barrier films. Poly(carbonate-ether) polyols are low-molecular weight polyether carbonates with terminating hydroxyl groups, which are potential large scale raw materials in polyurethane industry. Herein, the recent progress of the CO<sub>2</sub> based polymers will be highlighted, and the future in this area will be discussed.

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Carbon dioxide is the “waste gas” from combustion of fossil resources, chemical processes or grain fermentation, it is therefore abundant and low-cost. As far as chemical utilization of CO<sub>2</sub> is concerned, its thermodynamic stability significantly limits its use as an active reagent in synthetic chemistry. To overcome this limitation, reactions employing CO<sub>2</sub> with highly reactive reagents have been explored using metal catalysts. The catalytic coupling of CO<sub>2</sub> with heterocyclic compounds has received considerable attention, especially the copolymerization of CO<sub>2</sub> with epoxides to polycarbonates [1–5]. In the past four decades, epoxides including propylene oxide (PO), cyclohexene oxide (CHO) and epichlorohydrin (ECH) have been used to copolymerization with CO<sub>2</sub>. Among these, poly(propylene carbonate) (PPC), the alternating copolymer of PO and CO<sub>2</sub>, has received the most attention both in industry and academic research as one of the emerging low-cost and eco-friendly polymer materials [3,4]. In particular, the commercialization of PPC is currently being initiated in several countries, especially in China. In general, the products of the copolymerization of PO and CO<sub>2</sub> fall into two categories according to the utilization, one is PPC with high molecular weight and high carbonate contents exhibiting good biodegradability, which has wide application in packaging materials, or even gas barrier films. The other is polycarbonate polyols with low molecular weight as raw material for polyurethane industry. In the past decade, historical development in this area has been comprehensively

reviewed in the literature [1,4,6–9]. Herein, we will summarize the latest progress in synthesis, modification and applications of high molecular weight CO<sub>2</sub> based polycarbonates, and the progress in low molecular weight polymer polyols will also be discussed.

### 1. Environmental friendly catalysts

Since the pioneer work of Inoue [10,11], various types of catalysts including heterogeneous and homogeneous metal complexes have been developed. Typical heterogeneous catalysts include ZnEt<sub>2</sub>-active hydrogen containing compound systems [11–13], zinc dicarboxylates [14–18], double metal cyanide complexes [19–26], and rare-earth metal coordination ternary catalysts [27–31], though the chemical structures or crystal structures of heterogeneous catalysts are not clear, they are convenient in synthesis and handling, showing more potentiality for industrial purpose.

Homogeneous catalyst is interesting for academic research, Inoue developed the first single-site homogeneous catalyst, metal tetraphenylporphyrin complex, for epoxide–CO<sub>2</sub> copolymerization [32]. Later homogeneous catalysts including metal-porphyrin [33–37], zinc phenolate [38–40], discrete β-diiminate zinc [41–45], and binary or single bifunctional catalyst systems based on metal–Salen or –Salan complexes have been developed [46–58]. Recently, highly active bifunctional SalenCo catalytic systems (TON > 20,000; TOF > 20,000 h<sup>-1</sup>) are introduced for CO<sub>2</sub>/PO copolymerization [59,60], producing high molecular weight copolymers ( $M_n > 300,000 \text{ g mol}^{-1}$ ) in high selectivity.

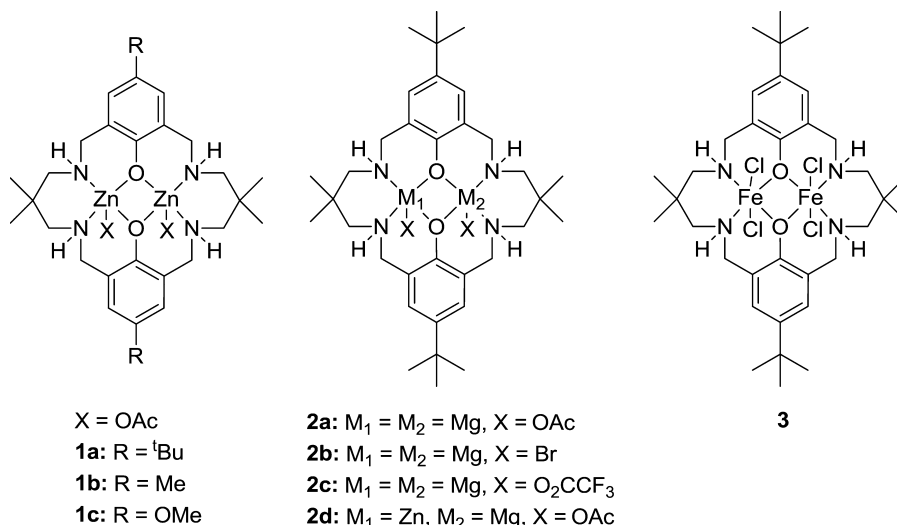
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Homogeneous catalyst system may have well-defined structure, and high catalytic activity can be achieved for epoxide/CO<sub>2</sub> copolymerization even at extremely dilute condition. However, most active catalyst systems comprise a toxic metal center like cobalt, chromium or nickel, and the metal residue in the copolymer product is unacceptable for soil compostable standard, which disfavors their industrial application. Therefore, developing environmental friendly catalysts with non-toxic metal center is necessary. Herein, we will summarize the recent progress on the catalysts with non-toxic metal center, such as Zn, Mg, Fe, Ti, Al, etc.

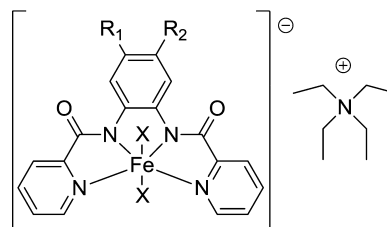
Williams and coworkers reported a series of non-toxic bimetallic catalyst coordinated by a reduced Robson-type ligand for the copolymerization of CHO and CO<sub>2</sub>, and they reported the first zinc Robson-type catalyst in 2009 [61,62], as shown in Scheme 1, one of the complexes, complex **1a** converted CHO to PCHC with a TON in the range of 430–530 and a TOF in the range of 18–25 h<sup>-1</sup> at 80–100 °C and 1 atm under 0.1 mol% catalyst loading. The complex is stable in air, and copolymerization reactions can even be carried out in air using unpurified CHO, resulting comparable TONs and TOFs with those in anaerobic condition.

However, these dinuclear zinc complexes show relatively low catalytic activities in comparison with the dicobalt complexes whose metal center is rather toxic with relatively low abundance [63]. Given the analogous chemistry of magnesium and zinc, including a common tendency to +II oxidation state and closely related ionic radii, Williams and coworkers designed three dimagnesium complexes **2a**, **2b**, **2c** (Scheme 1) for the copolymerization of CHO and CO<sub>2</sub> [64]. Complexes **2a** and **2b** were more active than complexes **2c** for the copolymerization of CHO and CO<sub>2</sub> under 1 atm, a TOF of 750 h<sup>-1</sup> was obtained using **2a** as catalyst at 100 °C and 12 atm, and the selectivity of polymer over cyclic carbonate was above 99%. No cyclic carbonate production was observed, even at elevated temperatures, using **2a–c**, while catalyst **1a** produced 4–6% cyclic carbonate at 100 °C. The significant difference in selectivity of the two metals indicates that the backbiting reaction responsible for cyclic carbonate production can be suppressed by replacing Zn with Mg.

Williams and coworkers designed a heterodinuclear (Zn–Mg) complex **2d** catalyst [65] for the copolymerization of carbon dioxide and epoxides, which showed considerably better performance than the homodinuclear catalysts alone or in combination, and high selectivity for polycarbonate polyols was realized in the presence of excess water (16 equiv.).



Scheme 1. Structure of bimetallic Robson-type catalyst.



- 4a**: R<sub>1</sub> = R<sub>2</sub> = H, X = OAc  
**4b**: R<sub>1</sub> = R<sub>2</sub> = H, X = Cl  
**4c**: R<sub>1</sub> = R<sub>2</sub> = Cl, X = Cl  
**4d**: R<sub>1</sub> = H, R<sub>2</sub> = NO<sub>2</sub>, X = Cl  
**4e**: R<sub>1</sub> = R<sub>2</sub> = Me, X = Cl

Scheme 2. Structure of iron(III) complex with N<sub>4</sub>-chelating ligand.

Williams and coworkers reported a di-iron(III) catalyst **3** (Scheme 1), a TOF of 107 h<sup>-1</sup> at 80 °C for CHO and CO<sub>2</sub> copolymerization was realized [66], and only *cis*-cyclohexene carbonate was formed when bis(triphenylphosphino)iminium chloride (PPNCl) was added. However, catalyst **3** failed to catalyze copolymerization of propylene oxide (PO) and CO<sub>2</sub>. Zevaco and coworkers designed catalyst **4** (Scheme 2) with N<sub>4</sub>-chelating ligand for the coupling reaction of epoxides and carbon dioxide [67], but higher molecular weight copolymer was still difficult to obtain. Though various iron complexes can be designed by variation of the aryl ring substituent [68], these iron complexes failed to catalyze copolymerization of propylene oxide (PO) and CO<sub>2</sub>. In addition to dinuclear complex catalyst, Rieger reported a mononuclear iron catalyst which can produce cyclic propylene carbonate in relatively high yields [69]. Recently, our lab also prepared a novel iron complex **6** which showed excellent activity for the coupling reaction of epoxides and CO<sub>2</sub> to generate corresponding cyclic carbonates [70]. Preliminary experiments also indicate the copolymer formation with CHO/CO<sub>2</sub> and a strong dependence on the cocatalyst system. The above studies indicate that CO<sub>2</sub>/epoxides copolymer can be formed via iron-complexes, in the near future, new catalyst of economic viewpoint for CO<sub>2</sub>/epoxides copolymer may be designed to replace toxic cobalt and chromium complexes (Scheme 3).

Recently, Nozaki [71] designed iron corrole complexes (complex **7** in Scheme 4) for the polymerization of CO<sub>2</sub> and PO in the presence of PPNCl as cocatalyst, copolymer was obtained at 60 °C

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