



Rigid linked dinuclear salen-co(III) catalyst for carbondioxide/epoxides copolymerization

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ARTICLE INFO

Article history:

Received 20 July 2015

Received in revised form 9 October 2015

Accepted 10 October 2015

Available online 22 October 2015

Keywords:

Carbon dioxide
Propylene oxide
Copolymerization
Dinuclear
Polycarbonate

ABSTRACT

Mononuclear and dinuclear salen-co(III) catalysts were designed for carbon dioxide (CO₂) and propylene oxide (PO) copolymerization. The dinuclear system maintained its activity with a turn over frequency (TOF) of 406 h⁻¹ at [PO]/[Cat] = 20,000. In contrast, the mononuclear catalyst system almost lost its activity with a TOF of 3 h⁻¹. The two cobalt centers in dinuclear structure may work synergistically due to the conjugated structure. This may contribute to the enhancement of the activity. The dinuclear catalyst system offered the highest molecular weight (Mn = 200,000) among reported dinuclear catalysts heretofore. Polymerization mechanism for the dinuclear catalyst system was postulated based on the subtly designed experiments. Synergy effect with the positive help of cocatalyst was explored. To further enhanced the thermal property of poly(propylene carbonate) (PPC), poly(cyclohexene carbonate) (PCHC) was incorporated. The glass transformation temperature of the copolymer of PPC-PCHC could be adjusted by the feed ratio of PO and cyclohexene oxide (CHO).

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1. Introduction

Carbon dioxide (CO₂) is a main origin of the unpopular greenhouse effect. Because it is inexpensive, abundantly available in high purity, and nonhazardous, CO₂ is considered as an ideal synthetic feedstock [1–4]. The innovative concept for beneficial use of CO₂ including the alternative coupling of CO₂ and epoxides to make degradable polycarbonates were popular. The first successful copolymerization of CO₂ and epoxide was reported by Inoue et al. in 1969 [5,6]. Inspired by Inoue's pioneering work, researchers have developed many catalysts [7–22]. Among them, salen-Co catalyst is one of the successful candidates [7,23–30]. To improve the performance of salen-Co catalysts, structures with piperidinium end-capping arms, quaternary ammonium salts or other functional groups were explored [31–35].

Recently, dinuclear catalysts have aroused much attention [36,37]. The two metal centers could work cooperatively in propylene oxide (PO) and CO₂ copolymerization. Nakano et al. prepared a series of flexibly linked dinuclear salen-co catalysts [38]. With a suitable distance, the two metal centers showed an obvious synergy

in high dilution, but the distance between the two metal centers resulted in a low selectivity of carbonate linkages. They proposed a bimetallic mechanism for the dinuclear catalyst in absence of cocatalyst. Klaus et al. designed flexibly linked dinuclear salen-cr complexes, the same trend upon dilution was observed as reported by Nozaki et al. [39]. The optimal dinuclear catalyst with a spacer length of $n = 6$ showed a TOF of 49 h⁻¹ at a [PO]/[Cr] ratio of 2000, and the TOF increased to 82 h⁻¹ at a [PO]/[Cr] ratio of 20,000. In contrast, the TOF of the mononuclear catalyst system in Rieger's research dropped from 67 h⁻¹ to 7 h⁻¹ upon dilution from 2000 to 20,000. Although these catalysts were impressive, they were less active and no high molecular-weight copolymer was obtained [38,39]. Liu et al. reported a series of excellent work about the chiral dinuclear cobalt catalysts. By using the chiral dinuclear catalyst, crystalline polycarbonates were obtained [40–42].

It is well known that cocatalysts played very important role in the binary system [43]. Hence, to explore the dinuclear synergy effect with the addition of cocatalyst is a challenging and meaningful work. Intrigued by those successful dinuclear complexes, we designed rigid linked dinuclear catalysts (Fig. 1, complex 2) and evaluated it for PO and CO₂ copolymerization with bis(triphenylphosphine) iminium chloride (PPNCl) as cocatalyst. Complex 2 was proofed to be highly efficient for PO and CO₂ copolymerization. To the best of our knowledge, it provided the highest

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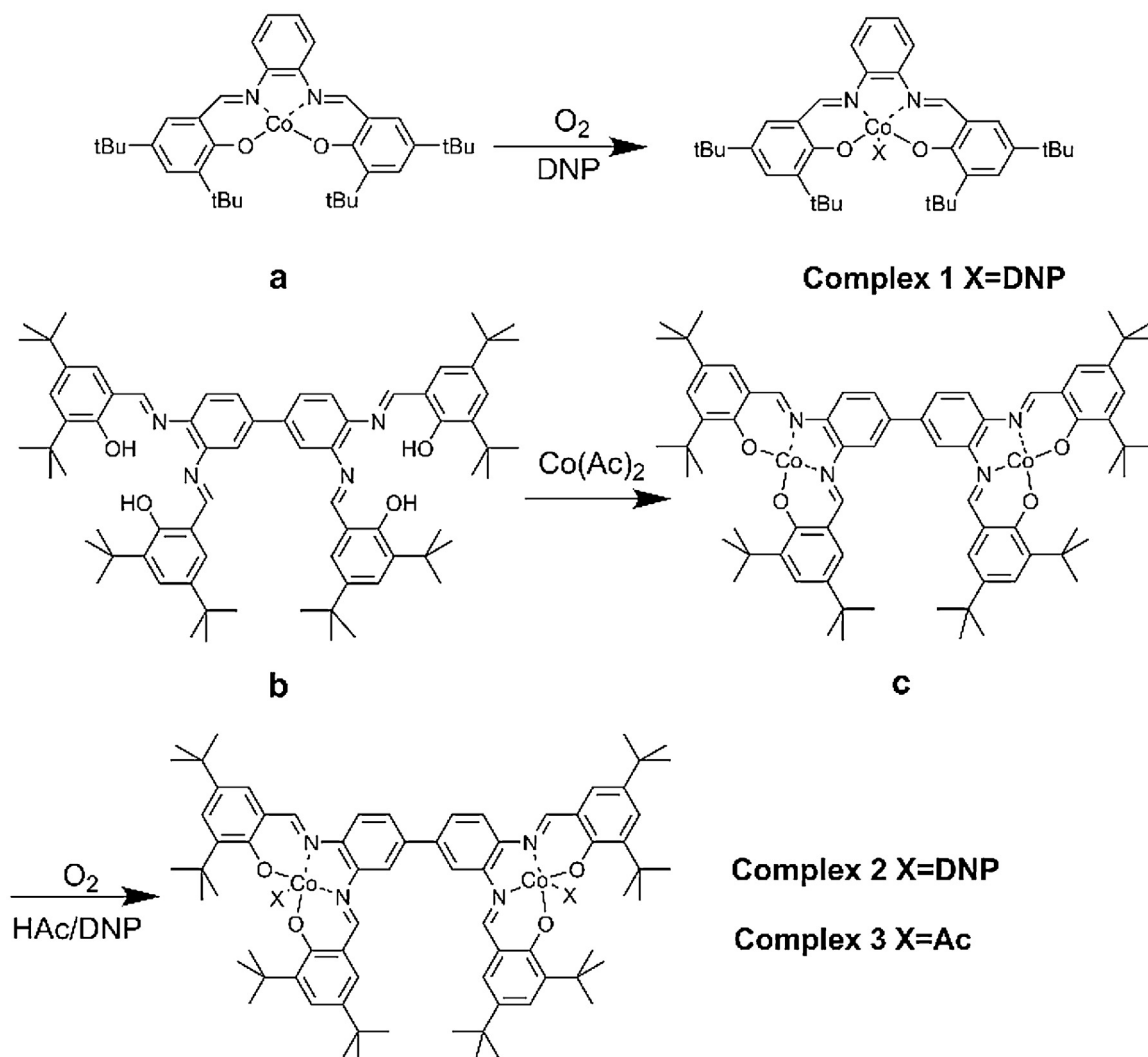


Fig. 1. Synthetic pathway for the preparation of mononuclear and dinuclear catalysts.

molecular weight polycarbonates ($M_n = 200,000$) reported for dinuclear catalysts heretofore. And the two metal center synergy was also observed in presence of cocatalyst. In comparison, we also synthesized a mononuclear salen-Co(III) catalyst (Fig. 1, **complex 1**) which is one half of the dinuclear salen-Co(III) catalyst structurally.

2. Experimental

2.1. Materials and characterization

All manipulations were carried out using standard Schlenk techniques under a dry argon atmosphere or an argon-filled glovebox. Propylene oxide and cyclohexene oxide were distilled from CaH_2 under argon atmosphere. CO_2 (99.95%) was purchased from Siping Jianxin Gas Company and used as received. Solvents were purchased from Aldrich and used as received.

NMR spectra were recorded on Bruker AV 400 M in CDCl_3 at 25°C . Chemical shifts were given in parts per million from tetramethylsilane. Gel permeation chromatography (GPC) measurements were conducted with a Waters 515 GPC with CHCl_3 as eluent. The molecular weights were calibrated against Polystyrene (PS) standards. Differential scanning calorimetry (DSC) was carried out with a TA Q100 thermal analyzer.

2.2. Copolymerization

All copolymerization were performed in 25 mL steel autoclaves. The autoclaves were heated to 110°C for 12 h, then cooled down to room temperature in glovebox prior to use.

Catalysts, cocatalyst and PO/CHO in desired ratio were added into an autoclave. The autoclave was sealed, filled with CO_2 and heated to the desired temperature. When the reaction reached completion, CO_2 was released slowly. Then a sample of crude reaction mixture was taken for ^1H NMR test. The remainder was dissolved with CH_2Cl_2 and slowly dropped into acidified (HCl) methanol. The PPC/PCHC precipitated immediately, and then the process was repeated three times. The copolymer was dried under vacuum at 50°C before analysis by GPC in CHCl_3 .

The diblock copolymer of PPC-PCHC was synthesized by one-pot method. PO, catalyst, cocatalyst and CO_2 were added into the autoclave. After a period of time, when PO reached completion, CHO was added. Intermediate product was taken for ^1H NMR test. When the reaction reached completion, CO_2 was released slowly. The processing procedure of diblock copolymer was the same as for the PPC/PCHC. The sequence could be changed by adding CHO first. The random copolymer of PPC-PCHC was synthesized as the recipe of PPC by adding PO and CHO in desired ratio.

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