

Copolymerization of CO₂ and propylene oxide using ZnGA/DMC composite catalyst for high molecular weight poly(propylene carbonate)



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ABSTRACT

The high yield and high molecular weight poly(propylene carbonate) (PPC) was synthesized via copolymerization of propylene oxide (PO) and carbon dioxide (CO₂) catalyzed over zinc glutarate/double metal cyanide (ZnGA/DMC) composite catalyst. A fine crystalline ZnGA component was prepared using the crosslinked restrain effect of nonionic surfactant. Combined with a small amount of DMC, the ZnGA/DMC (molar ratio = 10:1) composite catalyst system showed an excellent synergistic effect on CO₂/PO copolymerization with higher activity, selectivity, and shorter reaction time than those of the traditional ZnGA catalyst. Under the optimized reaction conditions, the molecular weight of PPC was up to 3.8×10^5 g/mol at the highest yield of 508.0 g_{polym}/g_{cat}, and the selectivity was over 97.7% towards polycarbonates rather than polyether linkages. The alternating copolymer PPC exhibited good thermostability, high glass transition temperature (42.0 °C) and high decomposition temperature (5% weight loss at 253.4 °C). A synergistic mechanism of ZnGA/DMC composite catalyst was speculated.

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1. Introduction

Carbon dioxide (CO₂) is an ideal synthetic C1 feedstock since it is abundant, inexpensive, nontoxic and nonflammable [1]. As a main greenhouse gas, the utilization of CO₂ into commercially-viable products becomes increasingly important nowadays [2]. It can be used as a renewable carbon source for the synthesis of various molecules [3]. The monomeric and the polymeric products of CO₂/epoxides coupling have been employed in many important

industrial applications. Polycarbonates possess outstanding properties, including strength, lightness, durability, high transparency and good electrical insulation. Therefore, these materials have wide-scale potential uses in electronics, optical media, glazing and sheeting, the automotive industry, the medical and healthcare industry, and many other consumable goods [3].

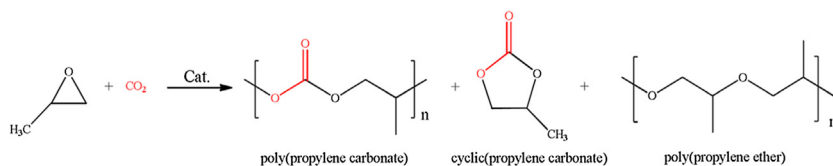
Since the work of Inoue and coworkers using a diethyl zinc/water as catalyst in 1969 [4], many efficient and selective catalysts for CO₂ and epoxides copolymerization have been developed. This initial experiment was followed by innumerable consecutive works, which all struggled with the low catalytic efficiency and undesired side products, such as cyclic carbonates or high contents of ether linkages in the polymer chain (Scheme 1) [5–8]. The challenges involved in the material properties of PPC relate to its low onset decomposition temperature and low glass transition temperature (T_g), which severely limited its usefulness [9].

The synthesis of polycarbonates from the copolymerization of CO₂ and epoxides has been carried out by Lewis acids, transition-metal complexes and organometallic compounds as catalysts at high pressures. The typical heterogeneous catalyst systems are zinc dicarboxylates, double metal cyanide, and rare earth ternary catalysts [10]. The typical homogeneous catalyst systems are single-site aluminum, [(tpp)CrX], salen-metal complex and zinc phenoxides [21]. Compared with the homogeneous catalyst

Abbreviations: CO₂, carbon dioxide; PO, propylene oxide; PPC, poly(propylene carbonate); ZnGA, zinc glutarate; DMC, double metal cyanide; ZnCl₂, zinc chloride; K₃Co(CN)₆, potassium hexacyanocobaltate; NP-40, polyoxy ethylene nonyl phenyl ether; Na₃Co(NO₂)₆, sodium hexanitrocobaltate(III); CaH₂, calcium hydride; N₂, nitrogen; TBA, tert-butyl alcohol; CH₂Cl₂, dichloromethane; CHCl₃, trichloromethane; DSC, differential scanning calorimetry; GPC, gel permeation chromatography; SEM, scanning electron micrographs; MW, molecular weights; MWD, molecular weight distribution; FTIR, fourier transform infrared spectroscopy; WXR, wide-angle X-ray diffraction; W_{ppc}, carbonate linkage content; TOFs, turnover frequency; T_g, glass transition temperature; TGA, thermogravimetric analysis; Lc, mean crystallite dimension; Xc, overall crystallinity.

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Scheme 1. Copolymerization of carbon dioxide and propylene oxide, main product: poly(propylene carbonate); byproduct: cyclic(propylene carbonate) and poly(propylene ether).

systems, heterogeneous catalyst generally showed the advantages of low usage cost and easy separation. Unfortunately, no catalyst with both high reaction efficiency and high selectivity to achieve alternating copolymer has been found yet [11].

Series of zinc dicarboxylates catalysts, such as Zn(OAc)₂, ZnCO₃/glutaric acid, Zn(OH)₂/adipic acid and ZnO/isophthalic acid/propionic acid have been reported over the past decades [12–15]. Among them, zinc glutarate (ZnGA) seems to be a promising catalyst because of the low cost and the high molecular weight of main product poly(propylene carbonates) [11]. In 1995, Darensbourg et al., reported the preparation of heterogeneous ZnGA catalysts by addition of the corresponding dicarboxylic acids to the zinc oxide [16]. A white precipitate was obtained after heating the solution in toluene. However, the exact structure of these catalysts has yet to be clarified, while its catalytic activity was found to be rather low (turnover frequency (TOFs) of 6 h⁻¹) when PO was used as a monomer. In 1999, Ree and co-workers reported a zinc glutarate system using ZnO as the zinc source. By changing reaction temperature and pressure, an optimal TOF of 3.4 h⁻¹ was achieved for PO/CO₂ copolymerization at 60 °C and 2.5 MPa. PPC with *M_w* of 2.7 × 10⁵ g/mol and *T_g* of 38 °C was obtained [17,18]. Recently, Ree et al., synthesized a series of zinc dicarboxylates with various molecular structures by modulating the aliphatic chain structure of the dicarboxylic acids. Alternating copolymer in high yield can be synthesized only by using zinc glutarate catalyst [19]. However, the large particle size and low surface area led to the low catalytic efficiency, limiting the industrial applications [20,21]. Many researchers have focused on the modification of zinc dicarboxylates catalysts to obtain copolymer with high yield, but the effects were not obvious. In 2002, Meng and coworkers successfully synthesized ZnGA using ultrasonic stirring methods [22]. However, the yield of PPC copolymer was low. Later, they synthesized ZnGA from zinc oxides with various purities via different stirring routes [23]. The crystallinity and crystalline perfectness of ZnGA were found to be the crucial factors to affect the catalytic activity. ZnGA catalyst with a small particle size dramatically increased the yield of the copolymer. To further increase the specific surface area of ZnGA catalyst, they also reported a supported ZnGA catalyst with montmorillonite [24]. The yield of obtained PPC was 115.2 g_{polymer}/g_{ZnGA} with the highest *T_g* of 38 °C. In 2006, Ree confirmed that ZnGA-catalyzed copolymerization was initiated by PO rather than CO₂ [25]. Modification of ZnGA resulted in an increased catalyst surface area and crystallinity of 77%, leading to the increased catalytic efficiency of PO/CO₂ copolymerization. The yield of obtained PPC was 64 g_{polymer}/g_{ZnGA}. In 2011, Klaus and Rieger, investigated the different zinc-dicarboxylic catalysts, their copolymerization efficiency, solid state structure and supplemented the results with theoretical calculations [26]. An ideal Zn–Zn distance suggested an optimal separation of Zn atoms in the range of 4.5–5.0 Å. Accordingly, the activity of ZnGA catalyst was restricted due to a restrained surface area and diffusion limitations, which was strongly hindered due to limitations in further downsizing the ZnGA single crystal. The modification on zinc dicarboxylates systems were all aimed to increase the catalytic activity to form alternating copolymer with high

molecular weight, high *T_g* and good thermostability, however there was no evident effect till now.

Another ideal catalyst for CO₂/epoxide copolymerization was the DMC catalyst. Originally reported by Kruper and Smart [27], DMC was effective for the ring-opening polymerization and copolymerization of epoxides [28]. The empirical formula of a Zn–Co(III) DMC catalyst was Zn₃[Co(CN)₆]₂: x ZnCl₂·y tBuOH·z H₂O (x, y, and z vary with the preparation method), in which zinc and cobalt atoms were linked by cyanide bridges [29]. DMC were found to be extremely active for the copolymerization of CO₂ and epoxides. For example, zinc hexacyanoferrate(III) converted epoxides, ethylene oxide, PO, 1-butene oxide and cyclohexene oxide to polycarbonates (20–95% carbonate linkages and dispersity of 2–6) with TOFs of 4 h⁻¹ [30,31]. There have been several studies focused on optimizing reaction conditions, modifying DMC catalyst, and understanding the mechanism for the copolymerization. Dharman et al., showed a mild copolymerization under microwave-assisted irradiation by employing Co–Zn DMC [32]. Varghese et al., investigated the detailed structure-activity relationship of the Co–Zn DMC and showed that the high activity came from Lewis acid Zn sites particularly those in a pseudo-octahedral environment [33]. Although the high activity was attractive for industrialization, the poor selectivity towards polycarbonate linkages has hindered the application of DMC catalyst.

In addition, the combined heterogeneous catalyst systems were used in CO₂/epoxides copolymerization. In 2011, Wang and coworkers achieved the poly(ether carbonate)s with carbonate unite content ranging from 57.8 to 97.1% and *M_n* around 1.0 × 10⁵ g/mol via copolymerization of CO₂ and PO [34]. This copolymerization system was catalyzed by the combinatorial catalyst of rare earth ternary complex and DMC complex. The *T_g* of obtained copolymer was controllable from 6.7 to 36.3 °C. Dai and coworkers found a Zn–Mg–Al composite oxide as high efficiency catalyst for CO₂ and propylene oxide copolymerization. This catalyst showed the best performance at Zn/Mg=4.0 to obtain PPC, pH 10, with polycarbonate selectivity of 99.2% and yield of 88.8% (140 °C, 12 h). The molecular weight of copolymer was *M_w* < 10⁴ g/mol [35].

In this work, considering the high catalytic activity of DMC complexes and the high selectivity of ZnGA catalyst, heterogeneous composite catalyst systems of ZnGA/DMC were tested in the polymerization of CO₂/PO. As the particle size and surface area of ZnGA affected significantly on the catalytic efficiency, nonionic surfactant was introduced during the synthetic process to decrease the particle size of ZnGA catalyst with better crystallinity.

2. Experimental

2.1. Materials

Zinc oxide (>99.99%), glutaric acid (>99%), Zinc chloride (ZnCl₂) (>99%), potassium hexacyanocobaltate (K₃Co(CN)₆) (>98%) and polyoxy ethylene nonyl phenyl ether (NP-40) (>99%) were used as received. Liquid propylene oxide was distilled over calcium hydride (CaH₂) and stored under nitrogen (N₂). Carbon dioxide of 99.99% purity was used without further purification. Propylene oxide (PO),

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