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Quaternary onium modified SalenCoXY catalysts for alternating copolymerization of CO_2 and propylene oxide: A kinetic study

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ABSTRACT

Quaternary onium modulated SalenCoXY ($X = Cl$, Br, NO_3; Y = phenoxy, benzene-1,4-bisoxy, benzene-1,3,5-trisoxy) catalysts incorporating the *N*,*N*′-bis(salicylidene)ethylene diaminato(Salen) ligand and quaternary onium units were designed, synthesized and applied to the copolymerization of CO_2 and propylene oxide. The impact factors of the axial anion X, the counter anion Y and the property of quaternary onium group evidently affected PPC selectivity and degree of polymerization. Detailed kinetic investigations and mechanisms of the cycloaddition and copolymerization were documented and discussed. A second order of catalyst was restrainedly proposed for polymerization.

1. Introduction

The chemistry of carbon dioxide has received much attention in decades from economical point of view: utilization of the least-expensive C1-feedstock [1]. The syntheses of cyclic carbonates and polycarbonates are technologically viable processes of CO_2 fixation by coupling CO_2 and epoxides (Fig. 1). Both cyclic and polymeric products have important industrial applications. Cyclic carbonates are an important class of compounds that can be used as polar aprotic solvents and degreaser, as electrolytes in lithium ion batteries, and as intermediates for linear dialkyl carbonates synthesis [2–5]. On the other hand, polycarbonates have been proposed as alternatives for commodity applications, including packaging, engineering polymers and elastomers [6–8].

The alternating copolymerization of CO_2 and propylene oxide (PO) was first reported by Inoue using $ZnEt_2$ and water as catalyst in 1969 [9,10]. In next few decades following the initial report, various catalyst systems have been developed for the synthesis of polycarbonates including Salen metal compounds, metalloporphyrins, β-diiminate zinc complexes and others [11–18]. It was noteworthy that SalenCo complexes showed excellent effects, since it was first applied in the copolymerization by Coates in 2003 [19]. Several binary catalyst systems, such as Salen cobalt complexes and organic bases or organic ammonium halogenides, were designed for CO_2/epoxide copolymerization providing high polycarbonate selectivity under mild conditions [20–23]. Meanwhile, different bifunctional catalysts were synthesized and introduced into polyreaction exhibiting extremely high activity and producing a very high molecular weight polymer even at low [catalyst]/[epoxide] ratios [24–30].

The mechanism about the polymerization and cycloaddition of CO_2 and epoxides was rarely investigated [31,32]. Recently, we reported a competition mechanism between the polymerization and cycloaddition using C_{2v} cobaltoporphyrin catalysts [33]. Bimetallic copolymerization is the most efficient way to produce polycarbonates with few papers showing mechanistic and computational support for this. Thus, the design of multinuclear catalyst aiming to favor bimetallic mechanism is attractive.

Herein, a variety of new quaternary onium amended SalenCoXY catalysts (Fig. 2) were fabricated and utilized in the cycloaddition and copolymerization of CO_2 and PO, in which the X and Y anions significantly affected the polymetric degree of polymers. Simultaneously, the possible mechanism of polymerization involving two Lewis acid centers was carefully suggested in virtue of our experimental data.

2. Experimental

2.1. Materials and facilities

Propylene oxide (PO) was distilled from CaH_2 prior to use. Other chemicals and reagents were commercially available and used to the reaction without further purification unless otherwise

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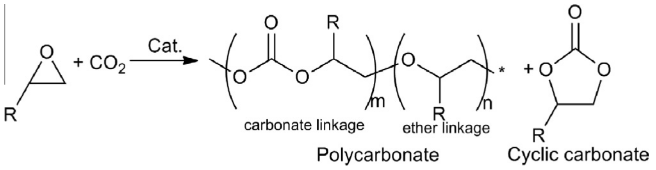

Fig. 1. Copolymerization and cycloaddition of CO_2 and epoxide.

indicated. ^{1}H and ^{13}C NMR spectra were recorded with Varian AM-300 spectrometer using $CDCl_3$ as the solvent and TMS as an internal standard. MS spectra were obtained with a HP_5988 spectrometer and ZAB-HS spectrometer. GPC was performed using a Waters 1515 chromatograph at 35 °C with THF as eluent at a flow rate of 1.0 mL min^{-1} calibrated by polystyrene standards. Elemental analyses were carried out on Carioel elemental analyzer.

2.2. Synthesis of catalysts

The synthetic route and structure of catalysts are shown in Scheme 1.

2.2.1. Synthesis of salicylaldehydes *A–F*

3-*tert*-Butyl-5-chloromethyl-2-hydroxybenz-aldehyde (2.71 g, 10 mmol) in toluene (10 mL) was added dropwise to a solution of trioctylphosphine/amine (10 mmol) in toluene (20 mL) over 20 min at room temperature. The mixture was heated at reflux for 3–24 h. After cooling to room temperature, the product **D** was filtered, washed with toluene (15 mL), and dried under reduced pressure.

Salicylaldehydes **A–C**, **E** and **F** were prepared by the following literature methods [34].

*2.2.1.1. Salicylaldehyde **D**:.* ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.90 (s, 1H), 9.95 (s, 1H), 7.86 (s, 1H), 7.48 (s, 1H), 4.39 (d, J = 14.7 Hz, 2H), 2.39 (s, 6H), 1.96–1.06 (m, 45H), 1.00–0.63 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.24, 160.76, 139.50, 134.99, 133.66, 120.75, 119.03, 34.84, 31.63, 31.50, 30.89, 29.04, 28.93, 28.91, 28.81, 22.48, 22.41, 13.92. ^{31}P NMR (121 MHz, $CDCl_3$) δ 32.01. MS (ESI): m/z = 561.7 [M−Cl]$^+$.

2.2.2. General procedure for the preparation of Salen ligands *1A–1H*

A solution of salicylaldehyde derivative (**A**–**F**, 0.50 mmol) and 1,2-diaminoethane (0.25 mmol) in ethanol (10 mL) was heated at reflux for 5 h under argon. The solvent was evaporated to obtain the residue, which was washed with cool methanol and diethyl ether to yield **1A–1F** as a yellow solid. Silver nitrate (0.30 mmol) was added to a solution of Salen ligand **1C** or **1E** (0.10 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred at room temperature for 12 h in the dark and then filtered. The filtrate was evaporated to give **1G** or **1H**.

*2.2.2.1. Salen ligand **1A**.* ^{1}H NMR ($CDCl_3$, 300 MHz): δ 13.71 (s, 2H), 10.19 (s, 2H), 8.26 (s, 2H), 7.51 (s, 2H), 7.14 (s, 2H), 7.00 (s, 4H), 5.30 (s, 4H), 3.86 (s, 6H), 3.46 (m, 4H) 1.19 (s, 18H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 161.1, 153.7, 137.9, 136.4, 130.3, 128.3, 123.4, 122.9, 122.5, 121.8, 72.2, 65.5, 36.3, 34.6, 29.0. MS (ESI): m/z = 605.38 [M−Cl]$^+$.

*2.2.2.2. Salen ligand **1B**.* ^{1}H NMR ($CDCl_3$, 300 MHz): δ 13.33 (s, 2H), 8.13 (s, 2H), 7.02 (s, 2H), 6.67 (s, 2H), 4.67 (m, 4H), 3.20 (br, 2H), 2.77 (m, 12H), 1.61 (s, 20H), 1.11 (m, 30H), 0.73 (m, 18H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 165.4, 158.9, 136.4, 130.0, 128.7, 122.0, 118.0, 74.6, 57.9, 53.1, 51.7, 34.5, 32.1, 29.3, 24.3, 20.4, 15.1. MS (ESI): m/z = 869.52 [M+Na]$^+$.

*2.2.2.3. Salen ligand **1C**.* ^{1}H NMR (300 MHz, $CDCl_3$) δ 14.13 (s, 2H), 8.49 (s, 2H), 7.46 (s, 2H), 7.17 (s, 2H), 5.32 (s, 2H), 4.13 (m, 2H), 3.94 (s, 2H), 2.36 (s, 8H), 1.43 (m, 28H), 0.93 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 160.4, 138.5, 131.4, 130.3, 118.8, 116.6, 116.5, 109.8, 59.0, 34.7, 29.0, 24.0, 23.8, 23.5, 23.5, 18.7, 18.1, 13.3. ^{31}P NMR (121 MHz, $CDCl_3$) δ 32.01. MS (ESI): m/z = 645.60 [M−Cl]$^+$.

*2.2.2.4. Salen ligand **1D**.* ^{1}H NMR (300 MHz, $CDCl_3$) δ 14.10 (s, 2H), 8.50 (s, 2H), 7.83–6.77 (m, 2H), 4.17 (m, 2H), 3.94 (s, 2H), 2.36 (s, 4H), 1.32 (m, 24H), 0.86 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 160.8, 160.5, 138.6, 131.7, 130.3, 118.9, 116.7, 59.1, 34.8, 31.6, 31.5, 30.9, 30.7, 29.6, 29.2, 28.8, 22.4, 21.8, 21.7, 19.0, 18.4, 13.9. ^{31}P NMR (121 MHz, $CDCl_3$) δ 32.14; MS (ESI): m/z = 1183.0 [M−Cl]$^+$.

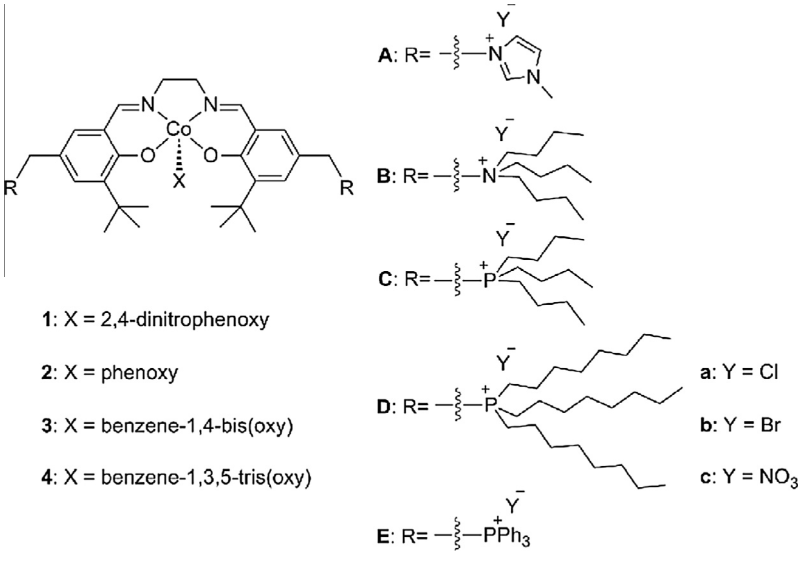

Fig. 2. Configurations of quaternary onium modified catalysts.