Contents lists available at ScienceDirect

Journal of CO$_2$ Utilization

Review Article

Synthesis and thermal degradation kinetics of new terpolymer of carbon dioxide, cyclohexene oxide and alpha-pinene oxide

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ARTICLE INFO

ABSTRACT

Bio-based polycarbonate, which was synthesized by terpolymerization of carbon dioxide (CO$_2$) and epoxides from natural resources, is attractive development direction in polymer fields. Bio-based polycarbonate, however, is difficult to synthesize, and it's also accompanied by inferior thermal properties. In this study, a novel terpolymer was synthesized easily by the terpolymerization of CO$_2$, cyclohexene oxide (CHO) and alpha-pinene oxide using homogeneous SalenCr^{III}Cl as catalyst, and alpha-pinene derived from abundant and natural pinene. Compared to the copolymer (PCHC) formed by copolymerization of CO$_2$ and CHO, the data of GPC shows that the terpolymer has relatively higher average molecular weight with 1.04×10^4 g/mol and narrower polydispersity (PDI) with 1.27. The thermal stability and thermal degradation of the terpolymer were deeply investigated, and the results proved that the terpolymer exhibits excellent thermal properties, and it has different thermal degradation mechanism compared with PCHC.

1. Introduction

CO$_2$ is the primary cause of greenhouse effect although it is a non-toxic, stable and abundant resource [1–3]. Therefore, controlling of CO$_2$ emission and effective utilization of CO$_2$ have become an imperative. The alternating copolymerization of CO$_2$ and epoxides to synthesize biodegradable polycarbonates has been widely studied in the past decades. Most of the researches aim at the binary copolymerization of CO$_2$ and epoxides such as propylene oxide [4–9], CHO [1,10,11], ethylene oxide [12,13] and so on. Despite the impressive advancements in this field by using various types of epoxide monomers, chemical processes leading to polycarbonate still depend on petroleum-based feed-stocks. Meanwhile, using bio-renewable monomers such as limonene oxide have been far less noticed. In addition, the bio-polycarbonate obtained presents low molecular weight, inferior mechanical and thermal properties. For example, Coates et al. discovered an efficient single-site β-diiminate zinc catalyst for copolymerization of CO$_2$ and limonene oxide to produce polycarbonate with low molecular weight [14]. This copolymerization incorporated only *trans*-limonene oxide, and it is uneconomical because there is amount of unreacted high boiling epoxide which is 45% of *cis*-limonene oxide in the commercial mixture. Later, using of Al(III) catalyst had been proven that both isomers were incorporated into the copolymer chain, but molar masses

were still less than 11 kDa [15]. Recently, based on having double bands in poly(limonene carbonate), Hauenstein et al. showed synthetic routes to demonstrate that poly(limonene carbonate) is the perfect green platform polymer, from which many functional materials can be derived [16]. However, it is difficult to modify the double bonds of the poly(limonene carbonate).

In recent years, investigators introduced the third monomer into terpolymerization of CO$_2$ and epoxide in order to improve thermal stability and degradability of production, for example, the terpolymerization of CO$_2$, CHO with different epoxides (propylene oxide, ethylene oxide [17–22]). However, most epoxides of terpolymerization systems focus on petroleum and petroleum derivatives [23–26], and the third monomer based on natural renewable resources has not been reported. On the basis of our previous works on the copolymerization of CO$_2$ and CHO using homogeneous SalenCr^{III}Cl catalyst [27], we devoted ourselves to alpha-pinene oxide, which is a cheap and renewable resource derived from pine plants. In this paper, an original polycarbonate was successfully synthesized and characterized by terpolymerizing from CO$_2$, CHO with alpha-pinene oxide using homogeneous SalenCr^{III}Cl catalyst. Meanwhile, we focused research on the thermal degradation kinetic of the terpolymer, and the terpolymer was compared with PCHC according to Kissinger-Akahira-Sunose (KAS) and Flynn-Wall-Ozawa (FWO) method [28–32], respectively. The thermal

stabilities and kinetics parameters of thermal degradation were also investigated.

2. Materials and methods

2.1. Materials and instruments

CO₂ (Kunming Messer Gas Co.) of a purity higher than 99.999%, cyclohexene oxide (CHO, Shanghai Crystal Pure Reagents Co., A.R. grade) of a purity more than 98% and alpha-pinene oxide (Tokyo Chemical Industry Co., A.R. grade) of a purity more than 95% were used without further treatment. All the other reagents and solvents were of analytical grade and used directly, such as hydrochloric acid, methyl alcohol, dichloromethane, etc.

FT-IR spectra were recorded on a PerkinElmer Spectrum 100 FT-IR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-400HMz type (^{1}H, 400HMz; ^{13}C NMR, 400HMz) spectrometer with chloroform-D (CDCl₃) as the solvent. The thermal degradation analysis of polymers was performed on a NETZSCH STA 449 F3 with different heating rates from ambient temperature to 500 °C under the protection of nitrogen (50 mL/min). The molecular weights (M$_w$ and M$_n$) and polydispersity of polymers were determined by a PL-GPC 220 high temperature chromatography (Polymer Laboratories Ltd) equipped with the HPLC (LC-98) series pump and choose tetrahydrofuran as eluent (elution rate 0.5 mL/min) at 40 °C.

2.2. Synthesis of catalyst SalenCr^{III}Cl

The structure of catalyst SalenCr^{III}Cl is shown in Scheme 1, which was synthesized according to the literature [33].

2.3. Synthesis of polycarbonate by CO₂, CHO and alpha-pinene oxide

The synthesis of the terpolymer was carried out in a 50 mL stainless steel micro-autoclave equipped with a magnetic stirrer under a CO₂ atmosphere. The micro-autoclave was dried for 24 h under vacuum at 60 °C and cooled down to ambient temperature before the terpolymerization. SalenCr^{III}Cl catalyst, cocatalyst PPNCl and the comonomers including CHO and alpha-pinene oxide (the molar ratio is 1:1:1000:100–1:1:1000:400, the volume of CHO is 3.225 mL) were immediately injected into the micro-autoclave. The micro-autoclave was pressurized to the appropriate pressure (3.5–5.5 MPa) with a high purity CO₂ and taken a breath several times before the terpolymerization. Then the mixture was reacted at certain temperature (60–90 °C) for a period of time (16–24 h) under magnetic stirring. At the end of reaction, the pressure in the micro-autoclave was released and cooled down to ambient temperature. The resulting product was dissolved in CH₂Cl₂ and precipitated from 5 wt% hydrochloric acid methanol solution after removed from the micro-autoclave. The crude terpolymer product was getting after dried in a vacuum at a temperature of 60 °C for keeping overnight.
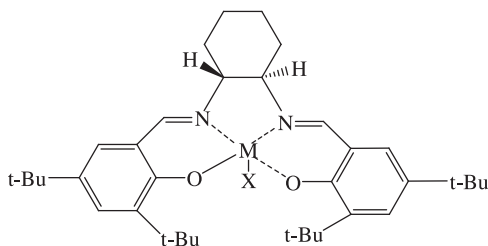
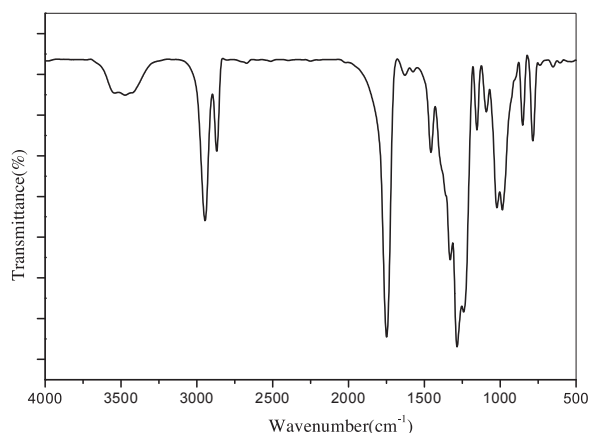**Scheme 1.** The structure of the catalyst SalenCr^{III}Cl (M: Cr^{3+}, X: Cl$^-$).

Fig. 1. FT-IR spectra of the terpolymer.

2.4. Kinetic analysis of the thermal degradation

The thermal degradation kinetic analysis of terpolymers was studied by thermogravimetry (TG). For the dynamic analysis [34–36], the basic representation of thermal degradation can be according to the following equation:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where α is degradation rates (known as the weight loss ratio of the terpolymer), t is the time of degradation reaction, k(T) is the constant of reaction rate, f(α) is the dynamic model function that can be expressed different forms according to the different reaction mechanism model.

When the reaction rate constant is assumed to obey the Arrhenius equation:

$$k(T) = A\exp\left(\frac{-E_a}{RT}\right) \tag{2}$$

where A, E$_a$, R and T are the pre-exponential factor, the apparent activation energy, the universal gas constant and the degradation temperature, respectively. If β is assumed for the heating rate, β = dT/dt, a new Eq. (3) can be got by combining Eqs. (1) and (2):

$$\frac{d\alpha}{dT} = \left(\frac{A}{\beta}\right)e^{-\left(\frac{E_a}{RT}\right)}f(\alpha) \tag{3}$$

2.5. Kissinger-Akahira-Sunose method

The advantages of KAS method is that we don't need to know the specific degradation process and degradation products. We assume the reaction is n orders, the dynamic model function f(α) can be represented as follows:

$$f(\alpha) = (1-\alpha)^n \tag{4}$$

Meanwhile, a new equation can be obtained by combining Eqs. (3) and (4).

$$\frac{d\alpha}{dT} = \left(\frac{A}{\beta}\right)e^{-\left(\frac{E_a}{RT}\right)}(1-\alpha)^n \tag{5}$$

We can obtain Eq. (6) by differentiation of Eq. (5) and define the temperature under the maximum degradation rate is T$_P$.

$$g = \frac{E_a\frac{dT}{dt}}{RT_p^2} = An(1-\alpha_p)^{n-1}e^{-E_a/RT_p} \tag{6}$$

Kissinger-Akahira-Sunose method considered that the formula n(1−α$_p$)$^{n-1}$ is unrelated to β and approximate to 1, then to bring it into the Eq. (6) and take logarithm on both sides,