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Influence of catalysts used in synthesis of poly(*p*-dioxanone) on its thermal degradation behaviors

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ABSTRACT

Thermal degradation behavior and mechanism of aliphatic poly(ether-ester) poly(*p*-dioxanone) (PPDO) have been intensively explored from the view of chemical structure of polymer. Actually, the trace metal ions derived from synthetic catalyst in the polymer act a non-ignorable role during its thermal degradation. In present work, a series of PPDO were prepared via ring-opening polymerization catalyzed by Novozym 435, $SnOct_2$, $ZnEt_2$ and $AlEt_3$ compounds. Pyrolysis-gas chromatography/mass spectroscopy (Py-GC/MS) was employed to analyze the pyrolysis products of PPDO samples, and thermogravimetry (TG) was used to investigate isothermal and non-isothermal degradation behavior of PPDO under nitrogen as well as air atmosphere. It revealed that the metal residues would accelerate the decomposition of PPDO owing to their catalysis effect, and the activity order was found in Al > Zn > Sn > Novozym 435 in nitrogen atmosphere, otherwise Sn > Al > Zn > Novozym 435 in air atmosphere. Meanwhile, the content of the metal residue was also proved as a key factor to affect the thermal stability of PPDO. Compared a metal-free sample PPDO Sn-0 (Sn content: 0 ppm) with PPDO-Novozym 435, similar decomposition behavior was obtained, which further confirmed that the residual metal from catalyst played a dominant role to deteriorate the thermal stability of PPDO.

1. Introduction

As an aliphatic poly(ether-ester), poly(*p*-dioxanone) (PPDO) exhibits excellent biodegradability and biocompatibility as well as good mechanical performance [1–4], moreover, it is worth mentioning that PPDO can be called as eco-friendly polymer with excellent feedstock recyclability [5]. These unique characters make it good candidate for biomaterials as well as general uses. As we known, PPDO is synthesized via the ring-opening polymerization (ROP) of *p*-dioxanone (PDO) with the presence of catalyst. In recent few decades, a series of high efficient metal compounds have been developed to catalyze the ROP of PDO, such as tin(II) bis(2-ethylhexanoate) $SnOct_2$ [6–9], triethylaluminum ($AlEt_3$) [8,10,11], diethylzinc ($ZnEt_2$) [5], derivatives of La [12], Ti, Zr [13,14], Cd and Hg [15]. Meanwhile, some nontoxic metal-free catalytic systems have been reported [16–18]. Nishida et al. [16] demonstrated that PPDO polymerized by effective enzyme such as immobilized lipase CA derived from Candida Antarctica, PPDO with a higher molecular weight ($M_w = 41{,}000$) was obtained by polymerization at 60 °C for 15 h with 5 wt% lipase CA. Dong et al. investigated the ROP of PDO catalyzed by ionic liquid [BMIM][PF_6] coated Novozym 435, PPDO with a maximum molecular weight (M_w) of 182,100 g mol^{-1} was obtained for 6 h [17].

Incontrovertibly, thermal stability is an important feature for a polymer material, which concerns its processability and application. Yang et al. investigated the kinetics of the thermal degradation and thermal oxidative degradation of PPDO by thermogravimetric analysis, and the results showed that the thermal stability of PPDO in pure nitrogen was higher than in air atmosphere [19]. Nishida et al. investigated the thermal decomposition behavior of PPDO, and they found that the decomposition of PPDO proceeded by both the unzipping depolymerization as the main reaction and the random degradation process with lower E_a and A values. Some random reactions also competitively proceeded in the initial, especially under the rapid heating condition, and the induction process was important in the degradation, because the induction process would considerably influence the following main process [5,20].

Recently, the researchers found that the existence of metal ions would affect the thermal stability of aliphatic polyesters dominantly,

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such as polylactide (PLA), poly(ε-caprolactone) (PCL) and poly(-hydroxybutyrate) (PHB) [21–33]. Wachsen et al. found the catalytic effect of tin on degradation and recombination reaction of PLA, as well as the effect of tin concentration on its existing ring-chain equilibrium [26]. Nishida et al. employed pyrolysis-gas chromatography/mass spectroscopy (Py-GC/MS) and thermogravimetry (TG) to investigate the dynamic pyrolysis of PLLA, the results indicated that the Sn-catalyzed pyrolysis started through a random degradation behavior and then shifted to a zero-order weight loss as the main process, and the degradation shifted to a lower temperature range with the increase of Sn content. The authors put forward the three reactions as the possible mechanisms of the zero-order weight loss including an unzipping reaction accompanying a random transesterification, the Sn-catalyzed pseudo-selective and selective lactide elimination reactions from random positions on a polymer chain [27]. Masaki et al. evaluated the activity of a series of Al, Ti, Zn, Zr, and Sn compounds as intramolecular transesterification catalysts for the thermal depolymerization reaction of poly(L-lactic acid) oligomer, and concluded that the activity of each metal was in the following order: Sn > Zn > Zr > Ti > Al [28]. However, Cam et al. reported a contrary degradative effect on the PLLA thermal stability in an order of Fe > Al > Zn > Sn according to the TG analysis [29]. Abe et al. investigated the influence of residual metal compounds on thermal degradation of PCL, they revealed that the thermal degradation of PCL samples containing high amounts of residual zinc compounds from synthesis process started the selective unzipping depolymerization step at temperatures below 300 °C producing ε-caprolactone exclusively. In contrast, the thermal degradation of zinc-free PCL samples occurred only at temperatures above 300 °C, and the main degradation products were the cyclic monomer and oligomers [30]. Kim et al. found that the presence of either Ca or Mg ions enhanced the depolymerization of P(3HB) molecules, while that Zn ion hardly catalyzed the reaction [32]. The authors also investigated the influence of sodium, tin, and aluminum chlorides on the thermal stability of PHBs, and practically no effect on PHBs thermal stability was observed in the case of aluminum and tin chloride, but sodium chloride affected thermal stability of PHBs significantly [33]. Overall, the residual catalytic metal is a principle parameter which affects thermal degradation of polyesters at high temperature.

As we mentioned above, several metal compounds have been employed to synthesize PPDO. As a poly(ether-ester), however, PPDO owns different structure feature compared with typical aliphatic polyesters such as PLA, PCL and PHB. Therefore, it is important to clarify the influence of the metal residue from mechanism in order to improve its thermal stability. The attempt to enhance the thermal stability of PPDO has been reported by Ding et al. via adding a chelator PMBP, which could deactivated catalytic activity of tin by the formation of stable chelate complexes [34]. Unfortunately, there are no comprehensive and systematical research has been reported concerning the influence of different residual metals on the thermal degradation of PPDO. In present work, a series of PPDO with similar intrinsic viscosity were prepared via ring-opening polymerization catalyzed by metal compounds including $SnOct_2$, $ZnEt_2$ and $AlEt_3$, a metal-free PPDO sample was also prepared from Novozym 435 for comparison. The influence of Sn, Zn and Al on the thermal degradation behavior of PPDO has been addressed, and the mechanism has also been explored.

2. Experimental

2.1. Materials

Monomer PDO that was obtained from the Pilot Plant of the Center for Degradable and Flame-Retardant Polymeric Materials (Chengdu, China), was dried over CaH_2 for 48 h, distilled twice in vacuum immediately before use. Novozym 435, lipase *Candida antarctica* B (CALB) immobilized on methacrylate macroporous resin, was purchased from Novo Nordisk Bioindustrials, Inc. (China). Sn 2-ethylhexanoate ($SnOct_2$) and triethylaluminum ($AlEt_3$) were obtained from Sigma Aldrich (USA). Diethylzinc ($ZnEt_2$) was obtained from Credit Chemical Co. LTD. (Dalian, China). Concentrated nitric acid specifically produced for Inductively Coupled Plasma-atomic Emission Spectroscopy and other reagents such as hydrochloric acid, phenol, 1, 1, 2,2-tetrachloroethane and methanol were all of A.R. grade were purchased from Kelong Chemical Co., LTD. (Chengdu, China).

2.2. Synthesis of PPDO and purification

PPDO was synthesized via ROP of PDO by employing different catalysts. The reaction was performed in the bulk with magnetic stirring in flame-dried glass reactors. Firstly, the reactors were evacuated and purged with nitrogen several times, PDO and metal Compounds catalyst solution (mole ratio: [catalyst]/[PDO] = 1/500) or enzyme (5 wt% Novozym 435 based on PDO) were charged in successively under a nitrogen atmosphere. Then the reactors were immersed into a temperature-adjusted silicone oil bath for predetermined intervals. After polymerization, the reactors were cooled down rapidly to room temperature and the products catalyzed by metal compounds were purified by precipitation from the phenol/1,1,2,2-tetrachloroethane (1:1 v/v) solution with methanol and dried under vacuum to a constant weight. The product catalyzed by Novozym 435 was dissolved in phenol/1,1,2,2-tetrachloroethane (1:1 v/v) solution and the unreacted Novozym 435 was removed by filtration before precipitation. PPDOs, which were catalyzed by $SnOct_2$, $AlEt_3$, $ZnEt_2$ and Novozym 435, were coded as PPDO-Sn, PPDO-Al, PPDO-Zn and PPDO-N435, respectively.

2.3. Preparation of PPDO samples with different Sn contents

In order to obtain the PPDO with different Sn ion contents, dissolved as-polymerized PPDO-Sn in chloroform and treated it by 1M HCl aqueous solution to extract Sn-catalyst residue, then washed with distilled water until the aqueous phase became totally neutral, finally, the polymer was precipitated with methanol and dried under vacuum to a constant weight. PPDO-Sn with varying Sn ion contents were prepared by controlling the treating time.

2.4. Characterization and measurements

2.4.1. Intrinsic viscosity measurements

Intrinsic viscosities of PPDO were measured at 30 °C with concentration of 0.1 g/dL in phenol/1,1, 2,2-tetrachloroethane (1:1 v/v) solution using an Ubbelohde viscometer.

2.4.2. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES)

ICP-AES determination of metallic residues in PPDO was performed with a Plasma Spectrometer, type IRIS-HR-DUO from Thermo-Electron. A measurement average of three samples was performed for each datum. About 0.2 g of PPDO samples were digested with concentrated nitric acid. After cooling, the system was brought to suitable concentration for ICP-AES measurement with dilute nitric acid. Standards were prepared by diluting 1000 ppm stock solutions purchased from Sigma Aldrich to suitable concentrations.

2.4.3. Gel permeation chromatography (GPC)

The molecular weight and distribution of samples were analyzed by GPC using a Waters instrument equipped with a model