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A new approach to prepare high molecular weight poly(*p*-dioxanone) by chain-extending from dihydroxyl terminated propolymers

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Abstract

As poly(*p*-dioxanone) (PPDO) with a high molecular weight (viscosity-average molecular weight (M_v) > 100,000 g/mol) is not easy to be obtained in a short time, a new approach has been developed to produce high molecular weight poly(*p*-dioxanone) (HPPDO-T) by chain-extending reaction of hydroxyl-terminated PPDO (HPPDO) prepolymers using toluene-2,4-diisocyanate (TDI) as chain extender. Here HPPDO prepolymers were synthesized via ring-opening polymerization of *p*-dioxanone (PDO) monomer initiated by 1,4-butanediol (BD) with Stannous octoate ($SnOct_2$) as catalyst. The resulting polymers, having a highest M_v of 250,000 g/mol, were characterized by ^{1}H NMR, TG, DSC and WXRD. HPPDO prepolymers can react with TDI more effectively than the PPDO prepolymers initiated by mono-functional initiators, and the molecular weights of resulting chain-extended products increase several decade times in an hour comparing to the prepolymers. The chain extended products HPPDO-T have better thermal stability, and higher glass transition temperatures and lower crystallization rates than PPDO homopolymer.

Keywords: Poly(*p*-dioxanone); Hydroxyl-terminated; Chain extending; Toluene-2,4-diisocyanate

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1. Introduction

Recently, poly(*p*-dioxanone) (PPDO) has attracted many attentions because of its excellent biocompatibility and biodegradability, and it is considered as a candidate not only for medical uses but also for universal uses, such as films, molded products, laminates, foams, non-woven material, adhesives and coatings [1–3]. However, PPDO had not become a focus of aliphatic polyesters for quite a long time due to the high cost and the low activity of the monomer, *p*-dioxanone (PDO) [4]. In general, PPDO can be synthesized by ring-opening polymerization of PDO with effective catalysts, but it is not an easy work to obtain high molecular weight

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PPDO in a short time because the reaction condition is very critical, for example, high purity of monomer and high activity of catalysts, etc. [4] In fact, the molecular weight of aliphatic polyesters is an important factor that determines their properties [5], therefore, many approaches have been employed to enhance the molecular weight of aliphatic polyesters [6,7]. Chain extension has been considered as an effective and convenient method, which has been used frequently in synthesis of polyurethanes [8–11] and biodegradable polymers. Tuominen and co-workers obtained high molecular weight poly(lactic acid) by chain extending with 1,6-hexamethylene diisocyanate and 2,2′-bis(2-oxazoline) [12]. Zhong et al. [13] treated low molecular weight poly(lactic acid) by chain extending with methylenediphenyl diisocyanate. Typical chain extenders for polyesters, which contain –OH and –COOH groups, include diisocyanates, diepoxides, bisoxazolines, dianhydrides and bisketeneacetals [12]. Diisocyanates are the most important chain extenders for polymers containing hydroxyl group [14], although the possible toxicity of its degradation products after hydrolysis or biological decomposition is still an important factor which must be considered [15]. It can connect two chains together through urethane bonds to form a longer chain [16]. Toluene-2,4-diisocyanate (TDI) has been chosen as chain extender for PPDO in our previous work [17,18] as it is easy to get. A PPDO homopolymer chain contains one terminal hydroxyl group and one terminal carboxyl group when it is prepared by ring-opening polymerization of PDO initiated by traces of water and catalyzed by $SnOct_2$. Each isocyanate group can react with one terminal hydroxyl group of PPDO prepolymers, resulting in chain-extension. The decarboxylation may take place between the isocyanate group and terminal carboxyl group when the reaction temperature is higher than 180 °C, at which, however, the thermal degradation may appear, resulting in an obvious decrease in the molecular weight of PPDO. Therefore the molecular weight of chain extended products was limitedly increased for PPDO prepolymer containing only one hydroxyl end group [17]. To prepare high molecular weight PPDO, in the present paper, 1,4-butanediol (BD) as the dihydroxyl compound was employed to produce hydroxyl-terminated PPDO (HPPDO) prepolymers for the first time, and TDI was used as chain extender to synthesize high molecular weight PPDO (HPPDO-T) in a short time.

2. Experimental section

2.1. Materials

p-Dioxanone (PDO), provided by the Pilot Plant of the Center for Degradable and Flame-Retardant Polymeric Materials (Chengdu, China), was dried over CaH_2, and distilled under reduced pressure. Stannous octoate ($SnOct_2$) ($\geqslant 95\%$) from Sigma (USA) was used as received. 1,4-Butanediol (BD) was purchased from Zhiyuan Chemical Company (Tianjin, China) and was used after drying. TDI and other reagents were purchased from Sitong Chemical Company (Chengdu, China) and used without further purification.

2.2. Synthesis of HPPDO prepolymer

Ring-opening polymerization of PDO was performed through bulk polymerization with magnetic stirring in a flame-dried glass reactor. The reactor was evacuated and purged with argon several times prior to addition of PDO and BD with a syringe, and the reactor was immersed into an oil bath at 80 °C with stirring for 10 min. Then $SnOct_2$/toluene solution was injected into the reactor to perform the reaction for a predetermined time. After reaction, the reactor was rapidly cooled to room temperature and the HPPDO product was shattered with crushing machine.

2.3. Chain extending of HPPDO prepolymer

HPPDO prepolymers were added in a dried glass reactor. The reactor was evacuated and purged with argon several times before it was immersed into a temperature-adjusted silicone oil bath. When the prepolymers were melted completely, TDI was injected while stirring for predetermined intervals. The chain extending reaction proceeded for a predetermined time with a continuous argon stream feed under the surface of the melt. After reaction, the reactor was rapidly cooled to room temperature.

2.4. Characterization

The number-average molecular weight (M_n) and molecular weight distribution (MWD, M_w/M_n) of HPPDO were determined by gel permeation chromatography (GPC) (Waters GPC-Wyatt Interferometric Refractometer) at 25 °C. Chloroform was used as solvent and eluent with a flow rate of