



Lipase-catalyzed synthesis and characterization of polymers by cyclodextrin as support architecture

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ABSTRACT

Diesters and diols were successfully converted into aliphatic polyesters by enzymatic lipase *Candida* sp.99-125 catalysis, with β -cyclodextrin acting as supporting architecture (in a similar way as chaperone proteins). No organic solvents were used. The polytransesterification was a much greener process, being solvent-free and without metal residues. Lipase *Candida* sp.99-125 showed a high catalytic activity for bulk polymerization of diesters and diols with various numbers of methylene groups in their chains. β -Cyclodextrin encircled the linear polymer chain and maintained the chain in a proper configuration to avoid its coagulation. Lipase initiated the polymerization and β -cyclodextrin threaded onto the polymer chain to control the structure for producing high molecular weight polyesters. From a combination of diesters and diols, polyesters with a high molecular weight of 62,100 Da were obtained at 70 °C. The corresponding polyesters showed an excellent thermal stability till 350 °C and had a strong ability to crystallize with up to 72% crystallinity, contributing to their high storage modulus.

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1. Introduction

Biodegradable polymers have been extensively used in the field of biomedical application such as tissue engineering and control drug delivery because of their good biocompatibility, non-toxicity and environmental acceptability (Gu, Wang, Zhang, & Ren, 2008; Liu, Jiang, Zhang, & Saltzman, 2009; Matsumura, 2002; Wang, Zhou, Sun, & Huang, 2010; Ye, Kennedy, Li, & Xie, 2006;). Aliphatic polyesters with good thermal stability and mechanical strength are a remarkable group of the biodegradable materials family, which can be used as thermoplastics and biocompatible medical materials (Jiang, 2008).

Enzyme-catalyzed synthesis of polyesters provides a good example to achieve green polymer chemistry, which is a new synthetic strategy and an eco-friendly process for the synthesis of useful polymers (Kobayashi, Uyama, & Kimura, 2001). Synthesis of aliphatic polyesters with lipase catalysis is achieved by means of ring-opening polymerization (Cai et al., 2010; Målberg, Finne-Wistrand, & Albertsson, 2010; Srivastava & Albertsson, 2005; Srivastava & Albertsson, 2007; van As et al., 2005; van Buijtenen et al., 2007), condensation polymerization (Jiang, Liu, Xie, & Gross, 2007; Kaar, Jesionowski, Berberich, Moulton, & Russell, 2003;

Olson, Gratton, DeSimone, & Sheares, 2006; Olson & Sheares, 2006) and copolymerization (Fehling, Klein, Vosmann, Bergander, & Weber, 2008; Hagstrom, Nordblad, & Adlercreutz, 2009; Liu, Jiang, Decatur, Xie, & Gross, 2011; Palsule & Poojari, 2010; Tsujimoto, Uyama, & Kobayashi, 2002; Takwa, Simpson, Malmstrom, Hult, & Martinelle, 2006).

Polycondensation is a precise and effective way to obtain homopolymers with tailored properties. Aliphatic dicarboxylic acids and diols are the most convenient substrates for synthesis of linear polyesters. However, phase separation was found in the reaction mixture due to solid dicarboxylic acids with low solubility in diols under mild reaction temperatures during the enzyme-catalyzed process. As a result, the substrates were difficult to diffuse to the catalyst particles. Polyesterification between the two monomers was tedious and it took 7–15 days to yield the desired polyesters. Thus, organic solvents such as diphenyl ether were supplied into the reaction mixture to promote diffusion among the reactants during polyesterification (Uyama & Kobayashi, 2006). Polytransesterification with a mono-phase reaction mixture instead of polyesterification was adopted by replacing dicarboxylic acids with dicarboxylic acid derivatives (such as *bis*(2,2,2-trifluoroethyl) sebacate) as the acyl donor. Polytransesterification could avoid phase separation, yielding the corresponding aliphatic polyesters molecular weight of 46,000 Da with *Mucor miehei* lipase catalyst in the presence of diphenyl ether at 168 h (7 days) (Linko, Wang, & Seppala, 1995a; Linko, Wang, & Seppala, 1995b). Nevertheless, polytransesterification still had disadvantages

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because an undesirable alcohol with halogen atoms would be produced during the process and released to the air, leading to environmental pollution. Then, diethyl succinate was applied for polytransesterification with diols to avoid the poisonous halogen alcohol (Azim, Dekhterman, Jiang, & Gross, 2006). Reducing the amount of the organic solvents has been attempted. The polyesters molecular weight was only 3300 Da in the absence of organic solvents by vacuum process with *Candida antarctica* Lipase B catalysts, compared with 38,000 Da obtained in the presence of diphenyl ether. Accordingly, these previous methods are typically not eco-friendly due to the toxicity of diphenyl ether. Organic solvents should moreover be removed completely from the polyesters before they were applied for biomedical applications.

In our research, we utilized the lipase-catalyzed polytransesterification of aliphatic diesters and diols as reaction substrates in the absence of organic solvents under mild condition, concentrating on yielding aliphatic polyesters of high molecular weights. Also, we employed β -cyclodextrin into the post-polymerization stage. Since the cavities of β -cyclodextrin could encircle the linear polymer chain and play a supplementary role to maintain the chain proper conformation avoiding it coiling, the polymer chain was elongated rapidly (Harada, Osaki, Takashima, & Yamaguchi, 2008). Lipase initiated the polymerization and β -cyclodextrin threaded onto the polymer chain to control the structure for producing high molecular weight polyesters. It was a much greener polymerization process without any environmental pollution. Solvent-free methods were adopted to take place of the use of organic solvents which were toxic. Even the cost of production would be decreased greatly without the high cost organic solvents. It was furthermore an extremely eco-friendly approach that only ethanol was produced during the polytransesterification process. In addition, the reaction mixture of the diesters and diols formed a monophasic liquid so that the problem of phase separation was avoided. Simultaneously, the reaction rate was accelerated efficiently during the polymerization process.

A series of diesters (C1, C4, C6, C10) and diols (C4, C6, C8) were employed to synthesis multiple biodegradable aliphatic polyesters. Polycarbonates synthesized by substrates of C1 had good optical properties, being colorless and transparent, and had been specially used in goggles and bulletproof glass. Polyesters prepared by substrates of C4 and C6 were widely applied in the field of packaging, tableware, bottles of medicines, disposable medical supplies and agricultural film ascribable to their advantage of rapid degradation by microorganisms. As a plasticizer, polyesters produced by substrates of C10 were a kind of largely used industrial polymer additives in the plastics processing to increase the flexibility. They could replace many conventional plasticizers on account of their good thermal stability and mechanical strength.

Various kinds of lipases have been utilized for polymerization until now (Puskas, Sen, & Seo, 2009). The lipase used in our research was from *Candida* sp.99-125 (belonging to *Yarrowia lipolytica*) with high lipase activity (Tan, Zhang, Wang, Ying, & Deng, 2003). The polymerization of aliphatic diesters and diols was performed under mild reaction conditions with lipase *Candida* sp.99-125 as catalyst and β -cyclodextrin as supporting architectures, successfully producing aliphatic polyesters with high molecular weights. The structure, thermal, crystalline, morphology properties and dynamic mechanical analysis of the corresponding polyesters have been investigated comprehensively.

2. The experimental

2.1. Materials

Free lipase from *Candida* sp.99-125 was obtained previously in our laboratory (Tan et al., 2003) and the activity of the crude lipase

powder used in this study was 168,000 U/g, which was measured on the basis of an olive oil emulsion method (Gargouri et al., 1986). Diethyl carbonate, diethyl succinate, diethyl adipate, diethyl sebacate, 1,4-butanediol, 1,6-hexanediol, 1,8-octanediol and β -cyclodextrin were of analytical grade, commercially available and used without further purification.

2.2. Measurements

To measure the weight-average molecular weights (M_w) and polydispersity (PDI), gel-permeation chromatography (GPC) analysis was used with a refractive index detector and a styragel (HT6E-HT5-HT3) column. Tetrahydrofuran was treated as the eluent at a flow rate of 0.1 ml/min. M_w and PDI were measured based on the calibration curves obtained using polystyrene as standard.

Both ^1H and ^{13}C NMR spectra were recorded through a Bruker AVANCE 400 spectrometer, performed at 400 and 100 MHz respectively in chloroform-*d*. The chemical shifts for ^1H and ^{13}C NMR spectra were referenced to internal tetramethylsilane at 0.00 ppm (electron shift) or to the solvent resonance. The results of chemical shifts were listed in Table 1.

Thermogravimetric (TGA) analysis was operated using a NETZSCH TG 209C instrument and scanned at 20 °C/min from room temperature to 600 °C under nitrogen flow.

A NETZSCH DSC 204 F1 instrument recorded the thermal properties of the polymers (Differential scanning calorimetry). The samples were first heated from –100 °C to 100 °C and then cooled to 20 °C. Melting temperatures (T_m) with corresponding transition enthalpies (ΔH_m) were measured from the first heating run at 20 °C/min while crystallization temperatures (T_c) with corresponding transition enthalpies (ΔH_c) were measured from the second cooling run at 10 °C/min. The peak maximum of endotherm and exotherm were taken as T_m and T_c , respectively.

Wide-angle X-ray diffraction (WAXS) was carried out at room temperature by a Rigaku X-RAY Diffractometer (D/max-Ultima III) with a Cu radiation used as X-ray source (40 kV, 40 mA) to measure the degree of crystallinity (χ_c). The diffraction range 2θ was from 3° to 50° and the data collected were evaluated to the degree of crystallinity from the intensity of amorphous and crystalline peaks in the diffractogram, after stripping the background of the diffraction curve. The degree of crystallinity (χ_c) was calculated through the ratio of the crystalline peak intensity to the total diffraction intensity.

A polarizing optical microscope (POM) equipped with Olympus BX51 and a hot stage (Linkam THMS 600) was used to investigate the morphology of the semi-crystalline polyesters. The samples were first heated at 80 °C above the melting temperature for 10 min and then cooled to the selected crystallization temperature of 50 °C at 5 °C/min rate.

The crystal lattice arrangements of the polyesters were detected by transmission electron microscopy (TEM) with a JEOL JEM 2100 apparatus operated at an accelerator voltage of 200 kV. The samples were dissolved in chloroform at a concentration of 1.2 mg/ml and 5 μl of the solution dropped onto a copper grid. The samples were dried in air for 24 h before measurement.

In dynamic mechanical thermal analysis (DMTA), polyester samples were molded into rectangular bars of 40 mm (length) \times 10 mm (width) \times 1.1 mm (thickness). The data were collected by a Rheometric scientific instrument (DMTA V) performed from –150 °C to 70 °C at a heating rate of 5 °C/min and frequency of 1 Hz in tensile mode.

2.3. General procedures for lipase-catalyzed synthesis of aliphatic polyesters

A typical polycondensation of diesters and diols was carried out as follows. Aliphatic diesters (0.05 mol) and diols (0.05 mol)

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