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Synthesis and biodegradability of L-lactide/glycidol copolymers

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ABSTRACT

Random copolymers of L-lactide (LA) and glycidol (G) were systematically synthesized via ring-opening polymerization (ROP). It was found that thermal properties of copolymers were strongly dependent on polymer composition which was successively controllable by changing comonomer feed ratio. The effects of polymerization conditions as well as polymer compositions on polymer properties were thoroughly studied. The biodegradation and enzymatic hydrolysis of copolymers were also examined. It was found that the biodegradability by an activated sludge of L/G copolymers was strongly affected by both polymer composition and crystallinity whereas their hydrolyzability by proteinase K was merely influenced by polymer composition.

1. Introduction

Polylactic acids (PLAs) are well-known biodegradable polymers produced by ring-opening polymerization of lactide monomer. PLA has excellent physical and mechanical properties making it a good candidate for substitution of petrochemical thermoplastic polymers. The properties of homopolymer, however, are deficient in some properties, such as biodegradability and flexibility, as well as thermal stability. A number of researchers have devoted their efforts to improve these properties by copolymerization of lactide with lactones such as butyrolactone, valerolactone and caprolactone [1–4]. Several literatures have described copolymers of PLA and PEO or PEG, which broaden the range of their potential applications into medical areas [5–8].

For decades, polyglycidol has received more attention as a hydrophilic and highly hydroxyl-functional polymer. The availability of monomer from dehydration of glycerol, a byproduct from biodiesel production, makes it more attractive for substitution of petroleum-based monomer. Polyglycidol was first reported in 1966 [9]. It can be polymerized either by cationic or anionic ring-opening polymerization to linear or branching, which was previously considered as an undesirable side reaction. Lately, several studies of glycidols have been focusing on the formation of hyperbranched polyether [10,11]. The most recent one has combined linear and branched architectures of polyglycerol, which formed from glycidol and lactide using different polymerization conditions to control the occurrence of epoxide ring opening [12]. Epoxide ring opening was prevented at low polymerization temperature leading to linear architecture. At high polymerization temperature, epoxide ring and lactide ring were simultaneously opened leading to hyperbranched structure. In both cases, glycidol acted as co-initiator to initiate polymerization. The actual random copolymer of glycidol and lactide, as well as their biodegradation, is still absent in literature.

Our interest, therefore, focused on preparation of random copolymers of lactide and glycidol and investigated their properties including thermal properties, biodegradability, as well as hydrolyzability of the copolymers.

2. Experimental

2.1. Materials

L-Lactide monomer was obtained from Purac, Holland and was used as received. Glycidol comonomer was purchased from Wako, Japan and was purified by vacuum distillation prior to use. All catalysts: tin octoate ($Sn(Oct)_2$), tetraphenyl tin ($Sn(Ph)_4$) and magnesium diethoxide ($Mg(OEt)_2$) were also purchased from Wako, Japan and were used without further purification. All solvents such

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as chloroform, ethanol and methanol, were used as received. Glasswares were oven dried prior to use. Activated sludge was provided by the Chemicals Evaluation and Research Institute, Japan.

2.2. Copolymerization

Along with polylactic acid (PLLA) homopolymer and polyglycidol (PG) homopolymer, a series of lactide/glycidol (L/G) copolymer at various compositions including 95/5, 90/10, 80/20, 70/30 and 50/50 L/G feed ratios, were synthesized. All polymers were produced by ring-opening polymerization in bulk process using various catalysts such as tin octoate, magnesium diethoxide and tetraphenyl tin. For a typical polymerization reaction, 90/10 L/G feed ratio copolymer (L: lactic unit/G: glycidol unit), 0.068 mol (9.7 g) of L-lacitde and 0.015 mol (1.1 g) of glycidol were placed in a 100 ml flask which was equipped with condenser and the reaction was performed under inert nitrogen gas. Then 0.25 μmol (28 mg) of tin octoate was injected into the reaction flask and polymerization was carried out at 130 °C. After 10–12 h reaction, the obtained copolymer was purified by dissolving in chloroform and was precipitated with ethanol. Purified polymer was filtered and vacuum dried at 50 °C. All copolymers were purified the same way except PG homopolymer which was purified by dissolving in water and was precipitated with 50/50 methanol/toluene solvent mixture.

2.3. Characterization

Molecular weight and molecular weight distribution of copolymers were determined by TOSOH GPC system (HLC-8020) at 40 °C using mono-disperse polystyrene standards. The columns were a TSKgel G4000HXL and a TSKgel G3000HXL with the limited exclusion molecular weight of 4×10^5. Chloroform was used as elution solvent with the flow rate of 0.6 ml/min. Thermal properties such as melting temperature (T_m) and glass transition temperature (T_g) of copolymers were measured using differential scanning calorimetry, DSC 3100S Bruker AXS K.K., Japan. The DSC scan was carried out in the range of −60 °C–200 °C at heating and cooling rate of 10 °C/min. T_m and T_g were obtained from the first and the second heating cycle, respectively. Polymer composition and chemical structure were determined from ^{1}H NMR and 2D ^{1}H NMR spectra using the JEOL JNM A-500 spectrometer. Deuterated chloroform ($CDCl_3$) was used as solvent of all L/G copolymers except a 50/50 copolymer and PG homopolymer, for which the deuterated methanol (MeOD) and deuterated water (D_2O) were used, respectively. Chemical shift of polymers was calibrated with respect to tetramethylsilane. FTIR was performed on a NICOLET 6700 FTIR system using polymer film (~10 μm thickness) cast on potassium bromide (KBr).

2.4. Biodegradation by an activated sludge

Biodegradation of polymers was evaluated through the determination of the amount of oxygen consumption, which was measured as a decrease of gas volume in the testing bottle, by a standard activated sludge metabolism using a BOD tester. Typically, 100 mg of copolymers was added into 250 ml BOD testing bottle, followed by 180 ml phosphate buffer, which was prepared according to ISO14852, and 20 ml activated sludge (MLSS = 15.3 g/20 ml). Evolved carbon dioxide gas (CO_2) was removed from the BOD closed system by calcium chloride ($CaCl_2$). The biodegradation test was carried out at 27 °C for 60 days. The observed O_2 consumption volume was corrected by subtraction to O_2 consumption volume of the blank. The theoretical O_2 consumption volume was calculated according to the structural formula of copolymers that degraded products were completely mineralized to CO_2. Biodegradation (%) of copolymers was calculated according to the following equation:

$$\%\ \text{Biodegradation} = (\text{observed } O_2 \text{ consumption volume} / \text{theoretical } O_2 \text{ consumption volume}) \times 100$$

2.5. Enzymatic hydrolysis

Along with the BOD testing, the hydrolyzability of copolymers was also evaluated. Typically, 20 mg of polymer samples was added into each of four tubes, followed by 3 ml of phosphate buffer (KH_2PO_4/Na_2HPO_4, pH 7.0). Then 200 U of Proteinase K (Tritirachium alkaline proteinase, Wako, Japan) was added in only two tubes leaving the other two for polymer control and blank control. The hydrolysis was carried out at 37 °C for 24 h. The polymer solution was then filtered and the total organic carbon concentration (TOC) was measured in duplicate using a total organic carbon analyzer (TOC-5000, Shimadzu, Japan). The observed total organic carbon amount of copolymer was corrected by subtraction of total organic carbon of the polymer blank and enzymatic blank control, respectively. The hydrolyzability (%) of copolymers was calculated by dividing the corrected experimental TOC values with the theoretical TOC as followed:

$$\text{Hydrolyzability } (\%) = \text{TOC}_{\text{exp.}} / \text{TOC}_{\text{theor.}} \times 100$$

3. Results and discussion

3.1. Copolymerization

L/G copolymers were systematically synthesized by ring-opening polymerization with the feed ratio of 95/5, 90/10, 80/20, 70/30 and 50/50 L/G. Along with copolymers preparation, PLA and PG homopolymer were also synthesized in order to compare their properties. The synthesis route to L/G copolymer is shown in Scheme 1. The catalysts selected were tin octoate ($Sn(Oct)_2$), tetraphenyl tin ($Sn(Ph)_4$) and magnesium diethoxide ($Mg(OEt)_2$). Tin catalysts are well-known catalysts for ring-opening polymerization of lactide whereas magnesium diethoxide is favored for ring-opening polymerization of glycidol. According to Spassky [13] and Vandenberg [14], high polymerization temperature is required to open the glycidol ring. Although the cationic polymerization of glycidol not only gives structure G1 (–O–CH(CH_2OH)–CH_2–) but also structure G2 (–O–CH_2–CH(OH)–CH_2–) which is given by hydride transfer [15], little information on mechanistic polymerization of glycidol by tin octoate is present. To our knowledge, the polymerization proceeds by ring-opening mechanism, and simply, polyether having oxyethylene unit with –CH_2OH side chain (G1) is produced. But with some frequency, hydrogen migration will be occurred in a glycidol molecule. As a result, oxy trimethylene structure (G2) is produced. Migration with other molecule will be a rare case because of long migration distance. Migration should be occurred harmonic with cleavage of C–O bond. From this reason, it is highly possible that the majority of the obtained copolymer contains linear structure. The evident from FTIR spectra also showed the existing of the O–H stretching band at 3500 cm^{-1} indicating the hydroxyl side chain groups. Qualitatively, the intensity of the O–H stretching band increased as the content of glycidol incorporation increased as shown in Fig. 1. For branched type polymer, the O–H stretching band at 3500 cm^{-1} should be absent. The proposed main products of these copolymers, therefore, incorporated both G1 and G2 repeat units of glycidol in polymer chain as shown in Scheme 1.