



Synthesis and post-functionalization of a degradable aliphatic polyester containing allyl pendent groups



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ARTICLE INFO

Article history:

Received 14 January 2017
Received in revised form
9 June 2017
Accepted 14 June 2017
Available online 16 June 2017

Keywords:

Aliphatic polyester
Ring opening polymerization
Allyl pendent group

ABSTRACT

Aliphatic polyesters have been widely used in environmental and biomedical engineering, but a lack of functional groups limits their applications. Here, we reported a facile approach to synthesize vinyl functional polyester via the ring opening copolymerization of ϵ -caprolactone (CL) and allyl glycidyl ether (AGE). NMR analysis confirmed the copolymeric structures and suggested that the copolymerization depended on the epoxide ring of AGE rather than vinyl group. The amount of AGE incorporated into the copolymers (F_{AGE}) increased with the amount of epoxide monomer feed with a maximum incorporation of 16.7%. Increasing temperature helped AGE to incorporate into the copolymer, however, accompanying with lots amount of AGE homopolymers. The resulting copolymer was successfully post-functionalized by thiol-end click, epoxidation, and bromination reactions depending on the reactivity of pendent allyl groups. This facile and efficient approach can be used to functionalize biodegradable polymers and synthesize some new polymers under mild conditions.

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1. Introduction

Aliphatic polyesters have received significant attention due to their good biocompatibility and fast biodegradation profiles, which giving these polymers wide applications in drug delivery vehicles, medical devices, ecological materials, etc. [1–10] Generally, aliphatic polyesters can be synthesized either by the step growth polymerization of diol and diacid or by the ring opening polymerization (ROP) of lactones [5–8,11–13]. In comparing these two mechanisms, the latter is clearly favored because the ROP can be conducted under mild conditions with high monomer conversions and a short polymerization time.

Currently, many cyclic monomers such as ϵ -caprolactone (CL), lactic acid (LA), and glycolide have been used for ROP to prepare aliphatic polyesters [13–18]. However, the corresponding homopolymer lacks functional groups to further modification. It cannot meet the demands of emerging biomedical technology. Many efforts have focused on the preparation of aliphatic polyesters with pendent functional groups. In general, two approaches have been

used to date. The first uses lactone derivatives possessing functional groups [19–27]. This method is highly efficient, while the synthesis of functionalized lactones is time-consuming and is not commercially available [28–30]. Another approach uses copolymerization of cyclic esters with other types of monomer such as epoxides [30–37]. There are a few reports in the literature on the copolymerization of lactones and epoxides. Shastri et al. employed a special epoxide monomer, propargyl 3-methylpentenoate oxide (PMPO), to copolymerize with CL or LA [34]. They found the resulting aliphatic polyester had a high density of alkyne functionality, which could be further tailored by the click chemistry. Taha et al. used a much more commercial monomer, glycidyl methacrylate (GMA), to copolymerize with CL [35]. However, the copolymerization can be conducted from both the methacrylate double bond and the epoxy groups in GMA—this can lead to gelation.

In this study, allyl glycidyl ether (AGE) was copolymerized with CL to afford functional polyesters with pendent vinyl groups. Like GMA, AGE is commercially available, but its double bond has a relatively low reactivity [38–40]. Hence, gelation was largely avoided. The resulting copolymers were post-modified by thiol-end click, epoxidation, and bromination reactions. This method benefits from the commercial availability of monomers, mild

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reaction conditions, and offers wide potential applications in bio-related area.

2. Experimental section

2.1. Materials

Allyl glycidyl ether (AGE) (>99.8%, from Shanghai Chemical Co.) was purified through an alumina column, distilled from CaH₂, and stored under a nitrogen atmosphere. The ϵ -caprolactone (CL) (>99.0%, from Aldrich) was dried over calcium hydride (CaH₂) and distilled under reduced pressure prior to use. Benzyl alcohol (BzOH) (from Sinopharm) distilled from CaH₂, and stored under a nitrogen atmosphere. Tetrahydrofuran (THF) (>99.0%, from Sinopharm) was freshly distilled from sodium/benzophenone and stored under argon. The 18-crown-6 (>99.0%, from Aldrich) was recrystallized from acetonitrile. Potassium hydride (KH) (30 wt% dispersion in mineral oil, from Aladdin), 3-chloroperoxybenzoic acid (75%, from Aladdin), 3-mercaptopropionic acid (>98.0%, from Aladdin), Br₂ (>99.5%, from Lingfeng), and 2-mercaptoethanol (>98.0%, from TCI) were used as received.

2.2. Measurements

The molecular weight and polydispersity were obtained via size-exclusion chromatography (SEC) equipped with a Waters 2414 differential refractive index (dRI) detector, a multi angle laser light scattering (LS) detector, and a Wyatt Visco Star viscometer detector (VD). The eluent was HPLC-grade THF with a flow rate of 1.0 mL/min. A series of narrowly dispersed polystyrene standards were used for calibrating the number-average molecular weight ($M_{n,SEC}$) and the distribution (M_w/M_n). Polymer structures were analyzed using a Bruker ARX-500 type NMR spectrometer at 25 °C with deuterated chloroform (CDCl₃) as the solvent and tetramethylsilane (TMS) as the internal standard. Conversions of monomer were determined using a HP-689 gas chromatography (GC) instrument equipped with a HP-5 column (30 m × 0.54 mm × 0.5 μm); toluene was used as the internal standard. The carrier gas was hydrogen at 1 mL/min, and the column temperature increased from a starting value of 60 °C at sample injection to 300 °C at 10 °C/min. Differential scanning calorimetry (DSC) was performed using a DSC Q2000 analyzer with a nitrogen flow rate of 50 mL/min. Samples were quickly heated to 150 °C and kept for 10 min to remove thermal history, and then cooled to –50 °C at a rate of 10 °C/min. They were finally reheated to 150 °C at the same rate.

2.3. Polymerization

A typical polymerization procedure is as follows: A suspension of KH in mineral oil (30% in weight) was introduced in a dry pre-weighed 50 mL Schlenk flask under argon. The mineral oil was removed by three extractions with THF added to the flask by syringe. The remaining THF was removed by vacuum. When KH was dried, the flask was weighed to determine the amount of KH (0.09 g, 2.27 mmol). Then, 13 mL THF solution with 5 wt% 18-crown-6 and 0.24 g BzOH (2.28 mmol) were added to the flask by syringe. The dispersion was stirred for 30 min at 0 °C. Hydrogen gas evolved after addition of CL (10.38 g, 91.05 mmol) and AGE (2.59 g, 22.72 mmol) by syringe. The solution was stirred for 24 h at 60 °C and terminated with degassed methanol. The product was dissolved in THF. The polymer was precipitated twice from THF solution into *n*-hexane or methanol, respectively. The polymers were dried under vacuum.

2.4. Post-modification of the allyl pendent groups

2.4.1. Thiol–ene click reaction

A typical procedure was performed as follows. The copolymer (1 g, 0.55 mmol of allyl groups) was dissolved in 2 mL dry methanol, followed by the addition of 2-mercaptoethanol (0.43 g, 5.5 mmol) and AIBN (0.027 g, 0.17 mmol of allyl groups), and the solution was stirred for 24 h at 80 °C. After completion of the reaction, the crude product was dissolved in THF, re-precipitated several times, and dried under vacuum.

2.4.2. Epoxidation of the allyl pendent groups

The copolymer (1.0 g, 0.55 mmol of allyl groups) was dissolved in 2 mL of CH₂Cl₂, and 3-chloroperoxybenzoic acid (0.14 g, 0.83 mmol) was added and stirred for 72 h at room temperature. The product was purified by precipitation in cold *n*-hexane and dried under vacuum.

2.4.3. Bromination of the allyl pendent groups

The copolymer (1.0 g, 0.55 mmol of allyl groups) was dissolved in 2 mL of CH₂Cl₂. Then, bromine (0.065 g, 0.83 mmol) in 1 mL of CH₂Cl₂ was added dropwise (showing decoloration of the bromine solution) and stirred for 3 h. The product was purified and isolated by precipitation in cold *n*-hexane and dried under vacuum.

3. Results and discussion

3.1. Synthesis of degradable aliphatic polyester-ethers containing allyl pendent groups by the ring opening copolymerization of CL and AGE

Both CL and AGE are commercially available monomers and can perform ring opening polymerization [11,38–42]. All of these polymerizations refer to oxygen anionic living species following the anionic polymerization mechanism. Based on these studies, the copolymerization of CL and AGE appears to be reasonable, and this would yield a functional polyester with pendent vinyl groups. This functional polyester can be easily changed into other functional groups via reactions on the pendent double bonds.

Here, the copolymerization of CL and AGE with a [CL]/[AGE] molar ratio of 80:20 was first studied at 60 °C. KH and Benzyl alcohol (BzOH) were employed as catalyst and initiator, respectively. THF with 5 wt% 18-crown-6 was used as the solvent. After polymerization for 24 h, soluble poly(CL-AGE)-1 in THF with a number-average molecular weight ($M_{n,SEC}$) of 9.6×10^3 g/mol was obtained.

Fig. 1 shows the ¹H NMR spectrum of poly(CL-AGE)-1. The proton signals at chemical shifts of 4.18–3.89, 2.43–2.22, 1.76–1.51, and 1.46–1.27 ppm were assigned to –OCH₂CH₂CH₂CH₂CH₂C(O)–, –OCH₂CH₂CH₂CH₂CH₂CH₂C(O)–, –OCH₂CH₂CH₂CH₂CH₂C(O)–, and –OCH₂CH₂CH₂CH₂CH₂C(O)– of CL segment. The proton signal at chemical shifts of 3.74–3.33 ppm was ascribed to the methylene and methyne protons close to oxygen in AGE segment. The proton signals at 6.03–5.71 and 5.40–4.98 ppm were attributed to the allylic protons for CH₂=CH– and CH₂=CH– in the AGE segment. This indicates that the copolymerization was performed based on the epoxide ring rather than the allylic group in AGE. In addition, if the copolymerization occurred, then there would be two new signals for *l* and *m* in the ¹H NMR spectrum due to the reaction of CL→AGE or AGE→CL, respectively. Unfortunately, the signal attributed to *l* was overlapped by protons *f*, *g*, and *h* at 3.74–3.33 ppm and hence cannot be quantified. However, the signal assigned to *m* was clearly observed at 4.56–4.50 ppm. This is direct evidence for the synthesis of a copolymeric structure rather than a mixture.

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