



Effect of end-group modification of poly(lactide)s by cinnamoyl chloride on their thermal stability



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ABSTRACT

In order to improve thermal stability of poly(L-lactide) (PLLA), the terminal hydroxy groups of PLLAs were converted to cinnamate esters by the treatment with cinnamoyl chloride. The resulting end-group modified PLLAs exhibited much higher thermal degradation temperature at 10% weight loss (T_{d10}) at around 320 °C than those of the starting hydroxy-terminated PLLAs (ca. 240 °C). The amounts of the residual Sn in the PLLAs were estimated by ICP measurements before and after modification, which indicated the modified PLLAs were still contaminated with ca. 600 ppm of Sn. This suggested that the end-group modification is effective for improving thermal stability of PLLA even in the presence of Sn. The end-group modification was also applicable to the stabilization of stereocomplex poly(lactide)s, whose thermal stability is important due to their high processing temperature.

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1. Introduction

Poly(L-lactide) (PLLA) has been recognized as a representative plant-origin polymer bearing favorable properties such as biodegradability and biocompatibility [1–8]. In general, PLLA is synthesized by the ring-opening polymerization of L-lactide (LLA) in the presence of an appropriate catalyst such as tin(II) 2-ethylhexanoate ($\text{Sn}(\text{Oct})_2$), and the monomer LLA is prepared from the pyrolysis of low molecular weight PLLAs produced by the direct polycondensation of L-lactic acid [9,10]. This also suggests rather low thermal stability of PLLA, and thus improvement of thermal stability of PLLA has been required. Nishida and coworkers reported the drastic effect of Sn catalyst residue in the polymer on its thermal stability [11,12]. End-group modification of PLLA was demonstrated to be effective for the improvement of the thermal stability of PLLA by several research groups. Kim et al. reported that 4-armed PLLAs with $-\text{COOH}$, $-\text{NH}_2$, and $-\text{Cl}$ end-groups exhibited better

thermal stability than that with $-\text{OH}$ end-group [13]. Nishida and coworkers reported terminal acetylation of PLLA to raise degradation temperature [12]. Recently, Akashi and coworkers reported effective stabilization of PLLA by introducing bio-based aromatic end-groups, such as 3,4-diacetoxycinnamic acid (DACA) [14–16]. The PLLAs bearing DACA end-groups demonstrated high thermal degradation temperature at 10% weight loss (T_{d10}) at 290–320 °C in comparison with the parent PLLA (T_{d10} of 220–260 °C). The improvement of thermal stability is especially critical for stereocomplex poly(lactide) (PLA) because of its high melting temperature (T_m) around 230 °C [15–17]. Namely, this means difficulty in processing such as injection molding of stereocomplex PLAs because of their close values of T_m and T_{d10} . However, DACA is not easily available and the effects of residual Sn in the DACA-modified polymers were not mentioned. In order to develop more convenient end-group modification strategy of PLLAs, here we introduced easily available unsubstituted cinnamoyl end-group into PLLA, and evaluated their thermal stability. The effects of residual Sn on the thermal stability of the end-group modified PLLAs were also investigated.

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2. Experimental

2.1. General

^1H NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (400 MHz for ^1H). Chemical shifts of the ^1H NMR spectra were calibrated using residual chloroform ($\delta = 7.26$ ppm) in chloroform-*d*. Molecular weights and polydispersities of the polymers were determined by gel permeation chromatography (GPC) measurements on a Tosoh GPC system (SC-8010) equipped with RI detector. THF was used as an eluent at a flow rate of 1.0 ml/min at 40 °C. The column system consisted of four columns: TSK gel G2000HR, G3000HR, G4000HR, and G5000HR. The data from RI detector were calibrated with standard polystyrenes. The melting temperature (T_m), heat of fusion (ΔH_m) and glass transition temperature (T_g) of the polymers were measured on a differential scanning calorimetry (DSC) using a Seiko SSC DSC 6220 apparatus. The heating rate was 10 °C/min in a nitrogen stream. The thermal degradation behaviors of the polymers were measured by thermogravimetric analysis on a Seiko TG/DTA 6300 apparatus. MALDI-TOF MS spectra were recorded in positive-ion mode using Shimadzu AXIMA-CFR plus mass spectrometer at the Natural Science Center for Basic Research and Development (N-BARD), Hiroshima University. The spectrometer was equipped with a N_2 laser ($\lambda = 337$ nm) and with pulsed ion extraction. Polymer samples were dissolved in chloroform (1 mg/ml). 2,5-Dihydroxybenzoic acid was dissolved in a 1:1 mixture of aqueous 0.1% TFA solution and ethanol as a matrix solution. The polymer solution was deposited on a sample slide with the matrix solution, and the solvents were evaporated before measurements. The residual Sn-contents were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a iCAP 6000 SERIES (Thermo Fisher scientific). Chloroform was used as an eluent.

2.2. Materials

Toluene (Kanto Chemical) was purified by distillation from sodium-benzophenone. Dichloromethane (Kanto Chemical) was distilled and preserved on activated molecular sieves 4 Å. LLA was purchased from Tokyo Chemical Industry and *D*-Lactide (DLA) was donated from Musashino Chemical Laboratory. These lactides were sublimated under nitrogen before use. Diethylene glycol (DEG) (Kanto Chemical) was distilled under vacuum and preserved on activated molecular sieves 4 Å. $\text{Sn}(\text{Oct})_2$ (95%, Sigma-Aldrich) was diluted by dry-toluene to prepare a stock solution (77.2 $\mu\text{mol}/\text{ml}$). Cinnamoyl chloride, acetyl chloride, and dehydrated pyridine were purchased from Sigma-Aldrich, Tokyo Chemical Industry, and Wako Pure Chemical, respectively.

2.3. Polymerization of lactide by using $\text{Sn}(\text{Oct})_2/\text{MeOH}$ or DEG ($[\text{LA}]_0/[\text{I}] = 50$)

A typical procedure (run 3 for example): A dry-toluene solution of the catalyst $\text{Sn}(\text{Oct})_2$ (77.2 $\mu\text{mol}/\text{ml}$, 68.5 μl , 5.29 μmol) was added to a solution of LLA (0.758 g, 5.26 mmol) and DEG (10.0 μl , 105.2 μmol) in toluene (5.0 ml) at 100 °C. After stirring for 24 h, the resulting mixture was poured into methanol. The precipitated polymer (HO-PLLA-OH) was collected by centrifugation and dried in vacuo.

2.4. End-group modification of PLLA by cinnamoyl chloride (CinCl)

A typical procedure (run 4 for example): CinCl (0.052 g, 310 μmol) was added to a solution of HO-PLLA-OH (0.2 g) in CH_2Cl_2 (2.0 ml) and pyridine (0.05 ml). After stirring for 1.5 h at 0 °C and for

another 24 h at r.t., the resulting mixture was poured into methanol. The precipitated polymer was collected by centrifugation and dried in vacuo.

2.5. End-group modification of PLLA by acetyl chloride

Acetyl chloride (22 μl , 310 μmol) was added to a solution of HO-PLLA-OH (0.2 g) in CH_2Cl_2 (2.0 ml) and pyridine (0.05 ml). After stirring for 1.5 h at 0 °C and for another 24 h at r.t., the resulting mixture was poured into methanol. The precipitated polymer was collected by centrifugation and dried in vacuo.

2.6. Hydrolytic degradation

The polymer (film) samples sealed in a polyethylene mesh sheet were placed in a 50 ml-vial tube containing phosphate buffer solution (pH = 8.0). The vial tubes were shaken at 70 °C in a water bath shaker (reciprocating rate 100 times/min). After a definite time the polymer samples were washed with water and dried to constant weight. The degradability was evaluated mainly from the change in weight of the polymers before and after degradation. All chemicals were analytical grade.

3. Results and discussions

3.1. Synthesis of PLLAs with modified end-groups

In the presence of $\text{Sn}(\text{Oct})_2$ as a catalyst, PLLAs with single hydroxy end-group (PLLA-OH) and that with hydroxy groups at the both ends (HO-PLLA-OH) were prepared in good yields from the ring-opening polymerization of LLA using methanol and diethylene glycol as an initiator, respectively (Scheme 1). The results are summarized in Table 1 (runs 1 and 3). The number after “PLLA” in sample name indicates the feed monomer to initiator ratio ($[\text{LLA}]_0/[\text{I}]$), which closely corresponds to the degree of polymerization. The feed $[\text{LLA}]_0/[\text{Sn}]$ ratio was fixed at 1000/1 in this study. The PLLA-OH and HO-PLLA-OH were treated with cinnamoyl chloride (CinCl) in the presence of pyridine to convert the hydroxy groups to cinnamate (PLLA-OCin and CinO-PLLA-OCin) (Scheme 1, runs 2 and 4 in Table 1). The treatments of PLLAs with CinCl did not significantly change their molecular weights and distributions (run 1 vs. 2 and run 3 vs. 4). The glass transition temperature (T_g) values of the modified PLLAs were higher by approximately 10 °C than those of the corresponding unmodified PLLAs, while their melting temperature (T_m) values were scarcely changed by the modification. The higher T_g values of the modified PLLAs should reflect their decreased mobility in comparison with those of the unmodified PLLAs, possibly due to stacking interaction of the cinnamoyl end-groups [14].

Fig. 1 shows the ^1H NMR spectra of HO-PLLA50-OH and CinO-PLLA50-OCin. The ^1H NMR spectrum of HO-PLLA50-OH showed the signals corresponding to α -protons adjacent to terminal hydroxy groups at 4.36 ppm (peak a') and protons for initiating diethylene glycol at 4.28 (peak c) and 3.66 (peak d) ppm as well as those for the main chain (peaks a and b). After the treatment of the HO-PLLA50-OH with cinnamoyl chloride (CinO-PLLA50-OCin), the signal a' in HO-PLLA50-OH completely disappeared and new peaks for the cinnamoyl group (peaks e–i) appeared at 7.76, 7.54, 7.40, and 6.51 ppm, indicating complete conversion of the terminal hydroxy groups in HO-PLLA-OH to cinnamate ester groups in CinO-PLLA-OCin.

In order to further elucidate the end-group modification, the MALDI-TOF MS spectra were recorded for the low molecular weight samples (HO-PLLA10-OH (Fig. 2(a))) and CinO-PLLA10-OCin (Fig. 2(b)) prepared at $[\text{LLA}]_0/[\text{I}] = 10$. Both the mass spectra

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