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Accelerated hydrolytic degradation of Poly(L-lactide)/Poly(D-lactide) stereocomplex up to late stage

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ABSTRACT

Poly(L-lactide) (PLLA)/poly(D-lactide) (PDLA) blend specimens containing only stereocomplex as crystalline species, together with those of pure PLLA and PDLA specimens, were prepared by solution crystallization using acetonitrile as the solvent. Their accelerated hydrolytic degradation was carried out in phosphate-buffered solution at elevated temperatures of 70–97 °C up to the late stage. During hydrolytic degradation, the stereocomplex crystalline residues were first traced by gel permeation chromatography. Similar to the hydrolytic degradation of pure PLLA and PDLA specimens, the hydrolytic degradation of stereocomplexed PLLA/PDLA blend specimens slowed down at the late stage when most of the amorphous chains were removed and crystalline resides were formed and degraded. The estimated activation energy for hydrolytic degradation of stereocomplex crystalline residues (97.3 kJ mol^{-1}) is significantly higher than 75.2 kJ mol^{-1} reported for α-form of PLLA crystalline residues. This indicates that the stereocomplex crystalline residues showed the higher hydrolysis resistance compared to that of α-form of PLLA crystalline residues.

1. Introduction

Poly(L-lactide) [i.e., poly(L-lactic acid) (PLLA)] is a biodegradable polymer produced from plant-derived renewable resources and is used for biomedical, pharmaceutical, environmental, industrial, and commodity applications [1–12]. In some industrial and commodity applications, enhancement of mechanical performance, thermal stability, and hydrolytic degradation resistance is required. For enhancing these properties, stereocomplexation between PLLA and poly(D-lactide) [i.e., poly(D-lactic acid) (PDLA)] is frequently utilized [13–15]. In previous study, the hydrolytic degradation behavior of PLLA/PDLA blends, together with that of pure PLLA and PDLA, was carried out at 37 °C to obtain the basic information of *in vitro* hydrolytic degradation for biomedical and pharmaceutical applications [16–25]. It was found that the hydrolytic degradation rate of PLLA/PDLA blends monitored by number-average molecular weight (M_n) and weight loss is lower that of pure PLLA and PDLA [16,17,19,20,22–24]. This result is confirmed by the theoretical enthalpy calculation [26]. Also, due to the high mechanical performance, the PLLA/PDLA stereocomplexed biomedical materials were prepared and their tissue reaction was studied [27]. The tissue reaction was lower for the stereocomplexed materials than for the pure PLLA materials because of the lower hydrolytic degradation rate of the former. However, in the reported study, PLLA/PDLA blend contained a significant amount of homo-crystallites in addition to stereocomplex crystallites [16,20], the reference pure PLLA and PDLA are amorphous [17,28], or the specimens were monolayer-type or very thin [21,22,24]. Therefore, the effect of coexisting homo-crystallites, crystallinity (not crystalline species), or thickness was not ruled out. Moreover, the hydrolytic degradation period was not long enough to observe the formation and degradation of the stereocomplex crystalline residues in the late stage [16], although those of pure PLLA and PDLA have been reported [10,29].

In the present study, to investigate the pure effect of stereocomplexation on hydrolytic degradation of PLLA/PDLA blends, PLLA/PDLA blend specimens having solely stereocomplex crystallites as a crystalline species were prepared and their accelerated hydrolytic degradation was performed in phosphate-buffered solution at elevated temperatures of 70, 85, and 97 °C. The PLLA/PDLA blend specimens with only stereocomplex crystallites as a crystalline species, together with those of crystallized pure PLLA and PDLA specimens, were prepared by the solution-crystallization method using acetonitrile as the solvent [30]. The hydrolyzed specimens were investigated using wide-angle X-ray scattering (WAXS), gravimetry, gel permeation chromatography (GPC), and differential scanning calorimetry (DSC).

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2. Materials and methods

2.1. Materials

The synthesis and purification of PLLA and PDLA used in the present study were performed according to the procedures reported previously [31,32]. The specimens used for hydrolytic degradation experiments were prepared from the purified polymers by the method stated in previous papers [30]. Each solution of PLLA and PDLA in acetonitrile was separately prepared at 80 °C to have a polymer concentration of 5 g dL^{-1}. For the preparation of PLLA/PDLA blend specimens, the PLLA and PDLA solutions were mixed with each other equimolarly under vigorous stirring and then solution was placed without stirring at 80 °C until the completion of formation and sedimentation of stereocomplexed precipitates. For the preparation of pure PLLA and PDLA specimens, the each solution of PLLA and PDLA prepared at 80 °C was immersed in iced water at 0 °C without mixing and stirring until the completion of formation and sedimentation of PLLA and PDLA precipitates. The thus obtained stereocomplex and pure polymer specimens were rinsed twice with fresh acetonitrile at 80 and 0 °C, respectively. The crystallization temperatures of 80 and 0 °C were selected for the complete recovery of the dissolved polymers to avoid the molecular weight distribution change. At room temperature, the acetonitrile in the precipitates were replaced with fresh methanol three times, dried under reduced pressure for 7 days, and stored in a desiccator before hydrolytic degradation. The dried precipitates were white powders.

2.2. Hydrolytic degradation

Before hydrolytic degradation, to remove the air trapped between the precipitate particles, the specimens were immersed in fresh methanol and inner pressure of the vials was reduced. After removal of the air, the methanol in specimens was replaced with fresh phosphate-buffered solution three times. The hydrolytic degradation of each of the specimens (100 mg of dry weight) was performed in 10 mL of phosphate-buffered solution (pH = 7.4 ± 0.1) containing 0.02 wt% sodium azide at 70, 85, and 97 °C for predetermined periods of time. The phosphate-buffered solution was replaced with fresh one every two days, one day, and 8 h at 70, 85, and 97 °C, respectively. After the hydrolytic degradation, the specimens were rinsed three times with fresh distilled water at room temperature, followed by drying under reduced pressure for at least 2 weeks. The distilled water used for preparation of the phosphate-buffered solution and rinsing of the hydrolyzed specimens was of HPLC grade (Nacalai Tesque Inc., Kyoto, Japan).

2.3. Measurements and observation

The weight-average molecular weight (M_w) and M_n of the specimens were evaluated in chloroform at 40 °C with a Tosoh GPC system (refractive index monitor: RI-8020) with two TSK Gel columns (GMH_{xL}) using polystyrene standards. For the preparation of GPC sample solutions of PLLA/PDLA blend specimens, chloroform containing 10 vol% of 1,1,1,3,3,3-hexafluoro-2-propanol was used as the solvent to dissolve stereocomplex crystallittes, whereas in the cases of pure PLLA and PDLA specimens, only chloroform was used.

The glass transition, crystallization, and melting temperatures (T_g, T_{cc}, and T_m, respectively) and enthalpies of melting of homocrystallites and stereocomplex crystallites [$\Delta H_m(H)$ and $\Delta H_m(S)$, respectively], the specimens were determined by a Shimadzu (Kyoto, Japan) DSC-50 differential scanning calorimeter. The specimens were heated at a rate of 10 °C min^{-1} under a nitrogen gas flow of 50 mL min^{-1} for DSC measurements. The T_g, T_{cc}, T_m, $\Delta H_m(H)$, and $\Delta H_m(S)$ of the specimens were calibrated using tin, indium, and benzophenone as standards. The crystallinities ascribed to homo- and stereocomplex crystallites in the films [$X_c(H)$ and $X_c(S)$, respectively] was evaluated according to the following equations:

$$X_c(H)(\%) = 100\Delta H_m(H)/135 \quad (1)$$

$$X_c(S)(\%) = 100\Delta H_m(S)/146 \quad (2)$$

where 135 and 146 (J g^{-1}) are ΔH_m of the PLLA (or PDLA) and the stereocomplex crystals having infinite crystal thickness reported by Miyata and Masuko [33] and Tsuji et al. [14,34]. WAXS was performed at 25 °C using a Rigaku (Tokyo, Japan) RINT-2500 equipped with a Cu-Kα source (λ = 0.1542 nm).

3. Results and discussion

3.1. Comparison with pure PLLA and PDLA

3.1.1. Crystalline species

To compare the hydrolytic degradation behavior of PLLA/PDLA blend specimens with that of pure PLLA and PDLA specimens, we carried out the degradation of these specimens at a fixed temperature of 97 °C. To specify the crystalline species during hydrolytic

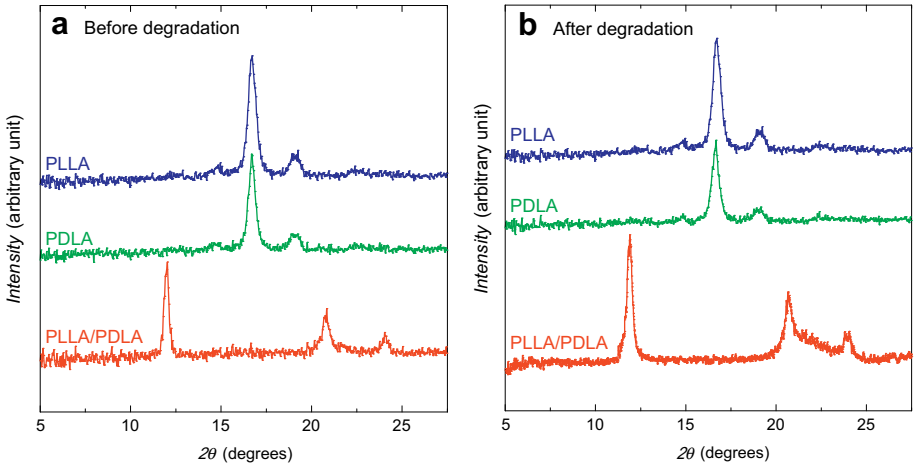

Fig. 1. WAXS profiles of pure PLLA, PDLA, and their blend specimens before (a) and after (b) hydrolytic degradation at 97 °C for 40 h (PLLA and PDLA) and 72 h (PLLA/PDLA blend).