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Polylactide stereocomplexation facilitated by the self-assembly of complementary ion pairs at the terminal group

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ABSTRACT

Herein, we demonstrate that self-assembly promoted by complementary ion pair interactions can facilitate the stereocomplexation of polylactides. Poly-L-lactide (PLLA)-COOH and poly-D-lactide (PDLA)-COOH, and PDLA-Py and PDLA-NH_2 functioned as PLAs with acidic and basic terminal groups, respectively. While two melting temperatures corresponding to the homocomplex and stereocomplex crystalline phases were observed in sc-PLA composed of PLLA-COOH and PDLA-COOH, only one melting temperature corresponding to the stereocomplex crystalline phase was observed in the case of the stereo-ion-complex composed of PLLA-COOH and PLLA-Py or PDLA-NH_2. The self-assembly of PLAs through ion pair interactions was observed in diffusion-ordered NMR spectroscopy (DOSY) analysis. In summary, interactions of complementary ion pairs in PLAs containing an acidic and a basic terminal group facilitated the formation of a stereocomplex composed of PLLA and PDLA, dominated by the stereocomplex crystalline phase.

1. Introduction

Complementary intramolecular interactions such as hydrogen bonding, dipole–dipole interactions, CH-π interactions, and hydrophobic interactions can drive the self-assembly of polymers [1]. Complementary self-assembly strategies with well-defined polymer chains are often used in the synthesis of biopolymers, the most well-known example of which is the DNA base pairs. In the DNA base pairs, complementary hydrogen bonding selectively occurs between the adenine (A)–thymine (T) and guanine (G)–cytosine (C) pairs and facilitates the formation of the double helix structure that helps to stabilize the high order structure. Recently, the strategy has been extended to synthetic polymers for the formation of supramolecular polymers via complementary intramolecular interactions [1–7]. Supramolecular polymers have a specific well-defined structure that can possess unique characteristics.

Stereocomplex polylactides (sc-PLAs) are self-assembled polymers composed of a mixture of enantiomeric polymers, i.e., poly-L-lactide (PLLA) and poly-D-lactide (PDLA), selectively assembled in a 1:1 ratio [8–12]. The melting temperature of sc-PLA can be as high as *ca.* 230 °C, whereas the melting temperatures of both PLLA and PDLA are *ca.* 180 °C. Therefore, the formation of sc-PLA is a critical technique for improving the heat resistance of PLA and many manufacturing companies and researchers have put a great deal of effort into the development of sc-PLA. However, this self-assembly technique has a fatal problem in that the formation of homocomplex PLA (hc-PLA) takes priority over the formation of sc-PLA, even in a 1:1 mixture of PLLA and PDLA [10,13–15]. It may be noted that the high melting temperature of sc-PLA is caused by the sc-crystalline phase. However, all the PLLA and PDLA chains do not form the sc-crystalline phase and some of them end up having the hc-crystalline phase composed of only PLLA or PDLA chains, as described in Fig. 1 [10,15]. The melting temperatures of both the hc-PLLA and the hc-PDLA crystalline phases are *ca.* 170 °C, which is the same as that of pure PLA. Consequently, the presence of the hc-crystalline phase in the mixture of PLLA and PDLA nullifies the thermal property gains arising from the sc-PLA.

A multi-block copolymer of PLLA-*b*-PDLA, formed by the solid-state polymerization of oligo-L-lactide and oligo-D-lactide resulting in the preferential formation of a multi-block stereocomplex PLA was reported [11,16,17]. The Diels–Alder reaction between PLLA and PDLA yielded a diblock copolymer with the selective formation of sc-PLA [18]. Further, the forcible formation of a cyclic stereoblock PLA containing sc-PLA was reported [19]. In these block sc-PLAs, the sc-crystalline phase was preferentially formed, with a covalent bond connecting the PLLA and the PDLA. Complementary interactions

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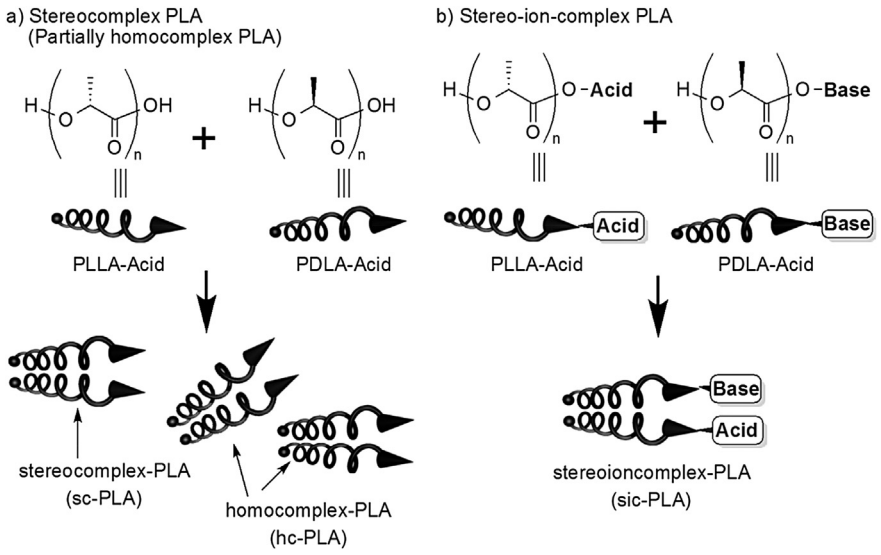

Fig. 1. A schematic illustration of the concept of stereo-ion-complex-PLA formation.

between a single PLLA chain and a single PDLA chain will be sufficient for the PLLA chain and the PDLA chain to sit side by side. The self-assembled polymer, composed of PLLA and PDLA formed as a result of the complementary interactions, can behave as a pseudo-stereoblock copolymer of PLA with the sc-PLA crystalline phase selectively formed. As several self-assembled PLAs have already been prepared using the intramolecular interactions between the terminal functional groups of the PLA chains [20–22], the preparation of the self-assembled sc-PLA should be relatively straightforward.

Herein, we demonstrate that the self-assembly of PLAs through hydrogen bonding between an acid-base terminal group ion pair could promote the formation of sc-PLA. The acid-base terminal group ion pair could be composed of a carboxylic acid and an amino group, acting as the acidic and basic terminal groups, respectively. In fact, a mixture of PLAs having multiple primary amino groups and multiple carboxylic acid groups could lead to the formation of microspheres, resulting in a biodegradable matrix [23].

2. Experimental procedure

2.1. Materials

The L-lactide and D-lactide were purchased from Purac Biochem BV (Gorinchem, Netherlands) and used after recrystallization from ethyl acetate. Tin(II) 2-ethylhexanoate and 2-aminoethanethiol hydrochloride were purchased from Wako Pure Chemical Industries (Osaka, Japan). *n*-Butanol, succinic anhydride, and dichloromethane were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). Tributyl phosphine and 2,2′-dithiodipyridine were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Ethyl acetate and triethylamine were purchased from Kishida Chemical Co., Ltd (Osaka, Japan). *n*-Butanol was used after distillation under reduced pressure with potassium carbonate. Other chemicals were reagent grade and used without further purification. 2-(Pyridin-2-yl-disulfanyl) ethanol was synthesized using methods reported in the literature [24].

2.2. Apparatus

^{1}H NMR and DOSY spectra were recorded using a 600 MHz NMR spectrometer (JEOL, Tokyo, Japan, ECA600) with tetramethylsilane as the internal standard. The concentration of the PLAs for the DOSY experiments was 7.69 mg mL^{-1}. The molecular weight of the PLAs was determined by gel permeation chromatography (GPC) using a refractive index detector and a combination of two columns (Tosoh Co., Tokyo, Japan, TSK GMHXL). The columns were eluted with chloroform (flow rate of 0.5 mL min^{-1} at 40 °C) and the molecular weights were calibrated with polystyrene standards. FT–IR spectra were obtained using an FT–IR spectrophotometer (Thermo Fisher Scientific K.K., Yokohama, Japan, Nicolet iS50 FT-IR) equipped with a single reflection ATR system (Spectra-Tech Foundation Performer). The thermal stability of the PLAs was determined by thermal gravimetric analysis (TGA-50; Shimadzu Co., Kyoto, Japan) using temperatures up to 500 °C ramped at a rate of 10 °C min^{-1}. The melting temperature was determined by a differential scanning calorimetry system (DSC, Seiko Instruments Inc., Chiba, Japan; SSC/5520) where the temperature was increased at a rate of 10 °C min^{-1} from room temperature to 150 °C. Subsequently, the sample was heated to 220 °C and cooled to 30 °C at the rate of 10 °C min^{-1}. Further, it was heated from 30 °C–220 °C at the rate of 10 °C min^{-1} during the second heating scan.

2.3. Polymerization of PLA-COOH

A solution of tin(II) 2-ethylhexanoate (1.0 μL, 3.09 μmol) in dichloromethane (9.0 μL) was added to a Schlenk tube (100 mL) and pumped to remove the dichloromethane. L-lactide or D-lactide (2.00 g, 13.9 mmol) was added to the Schlenk tube at room temperature under a N_2 atmosphere. The mixture was stirred at a temperature of 140 °C for 4 h and the resulting solid was dissolved into chloroform (10 mL). The resulting solution was then poured into methanol (200 mL) for reprecipitation. The product of reprecipitation was collected by filtration and dried at over 80 °C *in vacuo* to obtain 1.58 g of PLLA-COOH (Mn = 73 kg mol^{-1}, Mw/Mn = 1.65) or 1.58 g of PDLA-COOH (Mn = 77 kg mol^{-1}, Mw/Mn = 1.32) as white solid. The PLLA-COOH obtained was hydrolyzed using an autoclave at 120 °C for 45 min, to yield the molecular weight controlled PLLA-COOH. The PDLA-COOH obtained was hydrolyzed using an autoclave at 120 °C for 10 min to yield the molecular weight controlled PDLA-COOH.

2.4. Polymerization of PLLA-n-Bu

Tin(II) 2-ethylhexanoate (8 μL, 24.8 μmol) and L-lactide (2.00 g, 13.9 mmol) were added to a Schlenk tube (100 mL) at room