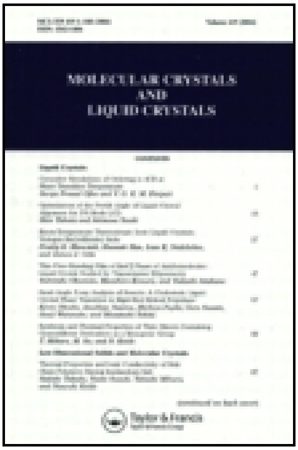

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Stereocomplexation Effects Induced by Mixtures of Enantiomeric Polylactides on Hydrolytic Behaviors and Surface Structure

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*The effects of stereocomplexation of enantiomeric polylactide (PLA) mixture films, (**l**-PLA/**d**-PLA), on hydrolytic behaviors and surface structure were investigated by Langmuir technique and X-ray photoelectron spectroscopy, respectively. The alkaline hydrolysis rate of stereocomplexed monolayers from equimolar **l**-PLA and **d**-PLA was much slower than those of their homopolymers. The (**l**-PLA-**b**-PDMS-**b**-**l**-PLA/**l**-PLA, 50/50 by wt.%) mixture film showed the surface segregation of PDMS at the surface layer while the surface composition of PDMS in (**l**-PLA-**b**-PDMS-**b**-**l**-PLA/**d**-PLA, 50/50 by wt.%) was similar to its bulk composition. These are likely due to strong interaction between **d**- and **l**-lactide unit sequences, which prevents the penetration of water into the bulk and surface segregation of PDMS.*

Keywords: hydrolysis; langmuir; polylactide; segregation; stereocomplexation

INTRODUCTION

In recent years, among biodegradable polymers, poly(lactide)s (PLAs) synthesized by renewable raw material, lactic acid, have been widely investigated for commercial biotechnological applications, controlled-release devices, and disposable degradable plastic articles because of their nontoxicity of products caused by hydrolytic chain scission in metabolism or environment. Since Ikeda *et al.* [1] found the stereocomplexation between equimolar *l*-PLA and *d*-PLA, numerous studies have been

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performed on the physical properties and crystalline structure [2–4]. Generally, the stereocomplex crystallites can occur when the interaction between two polymers having different configurations is stronger than between those having the same configuration. Therefore, stereocomplexed crystals show different thermal stability and mechanical properties [1,2].

In many of these applications, the successful design of polymeric materials is facilitated by modification of surface properties because a desired polymer surface often cannot be obtained from material itself. It is well known that the surface properties of multicomponent polymeric systems with only a small amount of a component having low surface energy, such as silicon or fluorine-containing polymers, are quite different to their bulk in order to minimize the air/material interfacial free energy [5–7]. In this study, we attempt to obtain further insight into the stereocomplexation effects of enantiomeric PLA mixture films on hydrolytic behaviors and surface structure. The hydrolytic behavior of (*l*-PLA/*d*-PLA) mixture monolayers was measured by Langmuir film balance. The material design for study of surface structure is based on principles of surface segregation of poly(dimethylsiloxane) (PDMS) in *l*-PLA-*b*-PDMS-*b*-*l*-PLA copolymer. The result was compared with that of (*l*-PLA-*b*-PDMS-*b*-*l*-PLA/*d*-PLA) mixture.

EXPERIMENTAL

Materials

l- and *d*-lactide were obtained from Aldrich and Purac, respectively and recrystallized from anhydrous ethyl acetate. Stannous octoate (Sigma) and octamethylcyclotetrasiloxane (D4), and 1,3-bis(hydroxy butyl) tetramethyldisiloxane (HO-DMS-OH, Gelest Inc.) were used as received. All other chemicals were of reagent grade and were used without further purification. PDMS containing terminal hydroxyl groups (HO-PDMS-OH) was synthesized by reacting D4 and 1,3-bis(hydroxy butyl) tetramethyldisiloxane with sulfonic acid as a catalyst by a similar method described by Kojima *et al.* [8]. *l*-PLA-*b*-PDMS-*b*-*l*-PLA copolymer was synthesized by ring-openning polymerization of *l*-LA by stannous octoate as a catalyst in the presence of HO-PDMS-OH. The characteristics of polymers used in the study are shown in Table 1.

Measurements

Each solution of *d*-PLA and *l*-PLA in chloroform was separately prepared to have concentration of 2 μmol/ml and 2 mmol/ml for

TABLE 1 Characteristics of the Poly(lactide)s Used in this Study

Code	Mw[a]	Mw/Mn[a]	Tg (°C)[b]	Tm (°C)[b]	Sources
l-PLA-*b*-PDMS-*b*-*l*-PLA[c]	56,000	2.1	n.d.	164	synthesized
l-PLA	66,000	2.0	n.d.	168	Polysciences[c]
d-PLA	40,000	1.4	n.d.	165	synthesized[c]

[a] Calculated from direct PS calibration of SEC.
[b] For as-cast samples.
[c] 2.8 mol% of PDMS.

monolayer and film preparations, respectively. The mixture (50/50 by wt%) solutions of *d*-PLA and *l*-PLA were prepared from each homopolymer solution. Monolayer properties were studied by using a computer-controlled KSV 2200 film balance held at 20°C. The purified water (pH 7.3) was used as a subphase liquid. NaOH was used to adjust a pH of subphase. The surface chemical compositions of (*l*-PLA-*b*-PDMS-*b*-*l*-PLA/enantiomeric PLA) mixture films were obtained using ESCALAB 250 x-ray photoelectron spectrometer (XPS, VG Scientifics). All C1s spectra were referenced to the neutral carbon of PLA at 285 eV.

RESULTS AND DISCUSSION

Figure 1 shows the DSC curves for *l*-PLA, *d*-PLA and their mixture films. It is clearly seen that both homopolymers give a single endothermic peak around 170°C, in good agreement with other reports

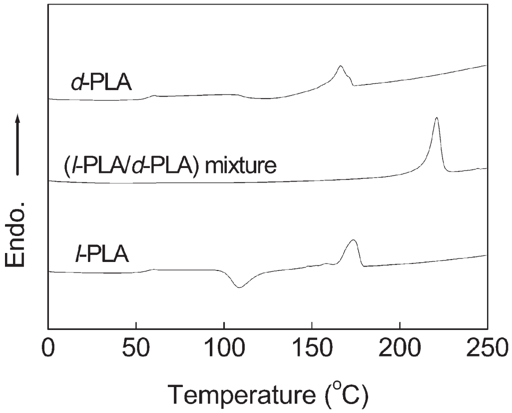

FIGURE 1 DSC thermograms of *l*-PLA, *d*-PLA, and (*l*-PLA/*d*-PLA) mixture.

[1,2], whereas a new peak appears near 220℃ for the mixture films. When the mixture ratio is 50/50 by wt., the peak at 170 ℃ disappears while the peak at 220℃ becomes sharper. This is well supported by the formation of stereocomplexes in which equimolar *l*- and *d*-lactide unit sequences are packed side by side. This new crystalline structure was supported by x-ray diffraction pattern: 16° and 18.5° at 2θ for *l*-PLA and *d*-PLA, whereas 21° and 24° for mixture films (not shown here).

Hydrolysis of Enantiomeric PLA Mixtures

In our previous study [9], we showed that the Langmuir technique is a useful tool to measure the conformational change and the hydrolytic kinetics of hydrolyzable monolayers on a molecular scale. Since the low molecular weight oligomers generated by the hydrolysis of polyester monolayers dissolve into water, the changes of areas occupied by monolayers at a constant surface pressure reflect dissolved monolayers into subphase. Figure 2 shows the change of areas (A/A_0) occupied by each enantiomeric PLA monolayer, *d*-PLA and *l*-PLA, with time at a constant surface pressure of 4 mN/m on alkaline subphases of pHs 7.3 and 10.5, where A_0 and A represent the areas occupied by the monolayers at time 0 and t, respectively. The initial time, t = 0, was considered when the surface pressure reaches a desired surface pressure. Under the condition of this measurement, no significant difference in the area with time upon 140 min was observed when *l*-PLA was exposed to neutral subphase, pH 7.3. A similar behavior was observed in *d*-PLA monolayers. The decrease in the

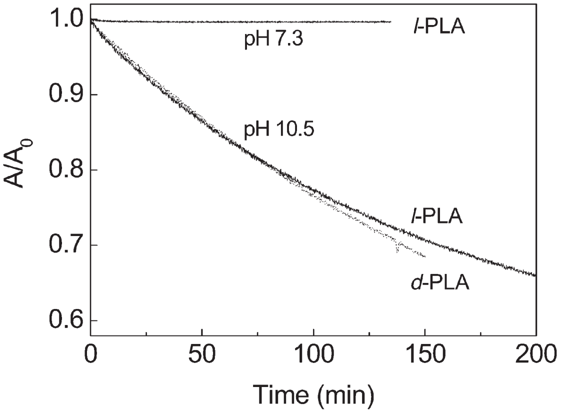

FIGURE 2 Area ratio vs. time for enantiomeric PLA monolayers maintained at 4 mN/m on different subphase pHs.

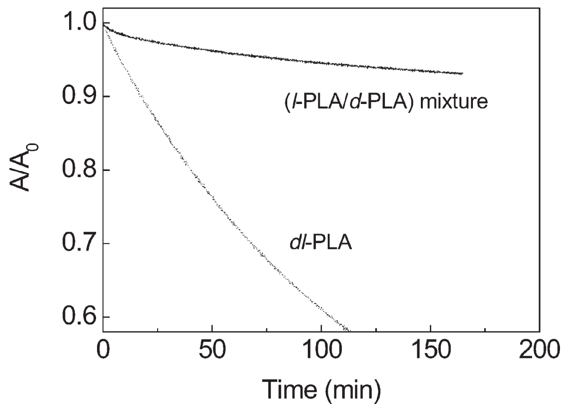

FIGURE 3 Area ratio vs. time for of (*l*-PLA/*d*-PLA 50/50 by wt.%) mixture and *dl*-PLA monolayers maintained at 4 mN/m on subphase of pH 10.5.

A/A_0 of *l*-PLA and *d*-PLA monolayers was observed at alkaline subphase of pH 0.5. This phenomenon is attributed to the hydrolysis of *l*-PLA monolayers which produced water-soluble oligimers. Also, very similar behaviors were observed in *d*-PLA monolayers.

To investigate the hydrolytic behavior of stereocomplexes between enantiomeric PLA mixtures, the kinetic curves of equimolar mixture monolayers of *d*-PLA and *l*-PLA at a constant surface pressure of 4 mN/m on subphase of pH 10.5 were recorded, as shown in Figure 3. The hydrolytic rate of *dl*-PLA monolayers of the same stereochemical composition with the mixture was much accelerated. Therefore, it is clear that the extent of hydrolytic degradation of mixture monolayers is much slower than those of each homopolymer in Figure 2 and *dl*-PLA. This result can be explained by the hydrolytic resistance of stereocomplexed monolayers.

Surface Structure of Enantiomeric PLA Mixtures

It is known that, in general, a component lower surface energy in multi-component polymeric systems is enriched in the surface in comparison to its partner component of higher surface energy. To study the effect of a specific intermolecular interaction (stereocomplexation) on surface structure, *l*-PLA-*b*-PDMS-*b*-*l*-PLA of which middle blocks were composed with short PDMS was used as a model material in order to measure the surface segregation of enantomeric PLA mixtures when they form a stereocomplex.

Figure 4A-a and 4A-b show the theoretically calculated and measured XPS spectra of C1s regions of *l*-PLA-*b*-PDMS-*b*-*l*-PLA film,

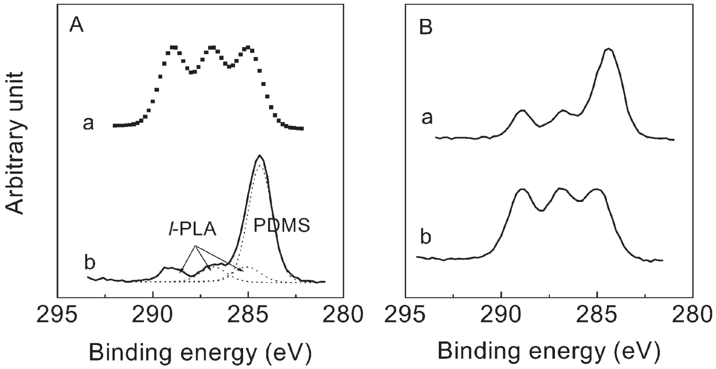

FIGURE 4 A: Measured (a) and theoretical (b) C1s spectra of measured and of *l*-PLA-*b*-PDMS-*b*-*l*-PLA film. B: C1s spectra of (*l*-PLA-*b*-PDMS-*b*-*l*-PLA/*l*-PLA) (a) and (*l*-PLA-*b*-PDMS-*b*-*l*-PLA/*d*-PLA) (b) mixture films.

respectively. The measured C1s region of *l*-PLA-*b*-PDMS-*b*-*l*-PLA film showed four contributions from ***C***-O functional groups at 287.1 eV, O=***C***–O at 289.1 eV from the PLA, and ***C***-C and ***C***–Si at 285.0 and 284.5 eV from PLA and PDMS, respectively. As expected, the concentration of PDMS at the surface region (almost 80 mol%) of *l*-PLA-*b*-PDMS-*b*-*l*-PLA film is much higher than that of bulk (2.8 mol%).

Since the mixture of equimolar *l*-PLA and *d*-PLA forms a new crystal structure, stereocomplex packed side by side, surface compositions of (*l*-PLA-*b*-PDMS-*b*-*l*-PLA/*l*-PLA) and (*l*-PLA-*b*-PDMS-*b*-*l*-PLA/*d*-PLA) mixture films with 50/50 by wt. are investigated by XPS. Figure 4B shows the high-resolution XPS spectra of C1s regions of both mixture films at the 30° takeoff angle. From the intensity ratio of O=***C***–O and (***C***-Si + ***C***-C) regions, the (*l*-PLA-*b*-PDMS-*b*-*l*-PLA/*l*-PLA) mixture film showed the surface segregation of PDMS while the shape of C1s spectrum of (*l*-PLA-*b*-PDMS-*b*-*l*-PLA/*d*-PLA) mixture film is very similar to its theoretical one. Thus, we conclude that the interchain interaction to form stereocomplxes between *l*- and *d*-PLA is strong enough to overcome the driving force of PDMS to the surface.

CONCLUSION

This study demonstrated the effects of stereocomplexation of mixtures of enantiomeric PLAs on hydrolytic behaviors and surface structure. It was found that the hydrolysis rate of stereocomplexed monolayers from *l*-PLA and *d*-PLA was much lower than those of their homopolymers. The surface segregation of PDMS in the (*l*-PLA-*b*-PDMS-*b*-*l*-PLA/*d*-PLA) mixture film was not observed. These results are likely due to strong interaction between *d*- and *l*-lactide unit sequences, which prevents the penetration of water into the bulk and the surface segregation of PDMS.

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