Surface Structure and Stereocomplex Formation of Enantiomeric Polylactide Blends Using Poly(dimethyl siloxane) as a Probe Polymer

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Summary: In the stereocomplex between enantiomeric poly(*l*-lactide) (*l*-PLA) and poly(*d*-lactide), crystallites formed as a result of stereocomplexation, equimolar *l*- and *d*-lactide unit sequences are packed side by side. The stereocomplex exhibits a melting temperature higher by about 50 °C than that of each homopolymer. In this study, we attempt to obtain further insight into the stereocomplex-induced surface structure of enantiomeric PLA blend films. The design of the blend systems is based on principles of surface segregation of multicomponent polymeric systems with a low surface energy, triblock copolymer (*l*-PLA-*b*-PDMS-*b*-*l*-PLA) of *l*-PLA and poly(dimethyl siloxane). (*l*-PLA-*b*-PDMS-*b*-*l*-PLA/*l*-PLA) blend films showed the surface segregation of PDMS, regardless of blend composition while the surface composition of PDMS in the (*l*-PLA-*b*-PDMS-*b*-*l*-PLA/*d*-PLA) blend films was strongly depended on blend composition or a degree of complexation. These results are likely due to strong interaction between *d*- and *l*-lactide unit sequences, which prevents the surface segregation of PDMS.

Keywords: poly(*d*-lactide); poly(*l*-lactide); stereocomplex; surface segregation

Introduction

The properties of polymer surfaces play an essential role in many commercial applications of polymers, including wetting, printing, biocompatibility, adhesives, and so on.[1–6] In many of these applications the successful design of polymeric materials is facilitated by modification of surface properties. Several techniques have been developed for modifying polymer surfaces.[2] The common approaches to modify the surface properties of polymeric systems involve either pre- or post-treatments of materials. The latter includes flame treatments,[1,2] chemical surface reactions,[2] and plasma treatments,[2,6] which are useful in producing hydrophilic, hydrophobic, or functionalized surfaces. The former approach may involve synthesis of specific architectures in multicomponent polymeric systems, copolymers and blends. Among synthetic architectures, those having a small amount of a low surface energy component, such as silicon or fluorine-containing polymers have been widely studied.[1,4,6] This is because the low surface energy component in multicomponent polymeric systems is usually preferentially concentrated at the air surface region in order to minimize the air/material interfacial free energy.[3,5,7,11–13] Other variables affecting the surface structure in multicomponent polymeric systems have been revealed, including composition, intermolecular interaction, morphology, molecular weight, and sampling method. Recently, Liu *et al.*[8] investigated the

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surface structure of poly(styrene-*co*-*p*-hexafluorohydroxyisopropyl-α-methylstyrene)/poly(4-vinylpyridine) (PSOH/PVPy) blends which span a wide range of structure, through immiscibility-miscibility-complexation transitions, by varying the hydroxyl content of PSOH. It was revealed that the formation of interpolymer complex in this blend system dramatically decreased the surface excess of PSOH.

Recent trends of biodegradable polymer research are focused on the desired life span. Since the mechanical properties of semicrystalline polyesters are catastrophically lost during an initial degradation,[9] i. e. 66% strength loss for 1.7% weight loss, the development of biodegradable polymer materials with initial stability towards degradation is demanded for applications in disposable items such as packing materials and mulching films in agriculture. As a result of the intensive studies of hydrolyses of polyesters by enzyme and alkali,[10–13] it has become evident that the rate of initiating degradation is dominated by the physical accessibility of the polymer structure to the abiotic attack. Among biodegradable polymers, poly(lactide)s (PLAs) synthesized by renewable raw material, lactic acid, have been widely investigated for commercial biotechnological applications, such as 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.*[14] found the stereocomplexation between equimolar *l*-PLA and *d*-PLA, numerous studies have been performed on the physical properties and crystalline structure.[15,16] 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. In this study, we attempt to control the surface structure of polymer blends by using the formation of stereocomplexes between enantiomeric PLAs. The material design for study of surface structure is based on principles of surface segregation of poly(dimethyl siloxane) (PDMS) in *l*-PLA-*b*-PDMS-*b*-*l*-PLA copolymer. The result was compared with those of (*l*-PLA-*b*-PDMS-*b*-*l*-PLA/*l*-PLA) and (*l*-PLA-*b*-PDMS-*b*-*l*-PLA/*d*-PLA) blends.

Experimental Section

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 buytyl) 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.*[17]*l*-PLA-*b*-PDMS-*b*-*l*-PLA copolymer (hereafter, PDMS-*b*-*l*-PLA) was synthesized by ring-opening polymerization of *l*-LA by stannous octoate as a catalyst in the presence of HO-PDMS-OH. The copolymer composition and the block length of ester copolymers were confirmed by ^{1}H-NMR spectroscopy (INOVA-500, 500 MHz, $CDCl_3$). The characteristics of materials used in the study are shown in Table 1. All other chemicals were of reagent grade and were used without further purification. Each 1 wt% solution of *d*-PLA, *l*-PLA, and PDMS-*b*-*l*-PLA in chloroform was separately prepared. The blend solutions were prepared from each

Table 1.
Characterization of the materials used in this study

Samples	M_n (M_w/M_n)	T_m (°C)
l-PLA	73k (1.8)	178
d-PLA	82k (2.8)	170
PDMS-*b*-*l*-PLA[a)]	56k (2.1)	164

[a)] PDMS-*b*-*l*-PLA: *l*-PLA-*b*-PDMS-*b*-*l*-PLA triblock copolymer with 2.8 mol % PDMS polymer solution and cast into aluminum weighing dishes, and then allowed to air dry slowly at ambient temperature. They were further dried in a vacuum oven (ca. 10 Torr) to a constant weight at room temperature. The film thickness was found to be 5 ± 1 μm.

Measurements

The T_m of homopolymers and blends was measured by DSC (Perkin-Elmer DSC/TGA 7) under nitrogen, calibrated with pure indium as a standard material. In order to minimize the effect of residual stress from the sample packing in the first run, film-type samples were used. The DSC thermograms were obtained at a heating rate of 10 °C/min.

The surface chemical composition of (*l*-PLA-*b*-PDMS-*b*-*l*-PLA/enantiomeric PLA) blend films was obtained using Perkin-Elmer Physical Electronics Model 5300 electron spectrometer for chemical analysis (ESCA). Angle-dependent ESCA measurements were performed with an achromatic MgKα X-ray source (1253.6 eV) at 15 kV and 20 mA. High-resolution scans of the C1s, O1s, and Si2p were acquired at the takeoff angles of 20°, 45°, and 70°, which led to the sampling depths of the C1s region of 3.5, 7, and 9.7 nm, respectively.[7] All C1s spectra were referenced to the neutral carbon of PLA at 285 eV, to correct charging effects. The static contact angle (gravimetric method) of water onto the surface of samples was measured using a contact angle meter (Phoenix 300 with camera, SEO Co.) at room temperature. Ten measurements on different areas were averaged.

Results and Discussion

It has been known that a component lower surface energy in multicomponent polymeric systems is enriched in the surface in comparison to its partner component of higher surface energy. It is generally accepted that the ring-opening polymerization of lactide can be initiated by a hydroxyl group. According to this method, PDMS-*b*-*l*-PLA with 2.8 mol% PDMS was synthesized by ring-opening polymerization of *l*-LA using HO-PDMS-OH as a functional initiator. This triblock copolymer of which middle blocks were composed with PDMS was used as a model material in order to measure the surface structure of enantomeric PLA blends when they form a stereocomplex. To determine the surface composition of PDMS-*b*-*l*-PLA, angle-dependent ESCA was used. The analytical depth of ESCA was varied by changing takeoff angles between the sample surface and the analyzer as 20°, 45°, and 70°. Figure 1A shows the high-resolution ESCA spectra of C1s regions of *l*-PLA and PDMS-*b*-*l*-PLA films at a photoelectron takeoff angle of 20°. According to the architectures, the C1s region of *l*-PLA can be deconvoluted with three peaks at 285, 287.5, and 289.5 eV assigned to that correspond to the neutral carbon, ether carbon, and carbonyl carbon, respectively. Also, the neutral carbon region in the C1s region of PDMS-*b*-*l*-PLA reflects the contributions of both the polyester and PDMS blocks while the other are just due to the ester bond of *l*-PLA blocks. The intensity of natural carbon region of PDMS-*b*-*l*-PLA was much higher than that of O=C–O or C–O. This suggests that the surface concentration of PDMS blocks is high if we consider the bulk composition (2.8 mol%) of PDMS in PDMS-*b*-*l*-PLA. Figure 1B shows the comparison of the theoretically calculated C1s peak of PDMS-*b*-*l*-PLA on the basis of its bulk composition. The shape of theoretical spectrum is very similar to that of *l*-PLA homopolymer due to small amount of PDMS in the copolymer. Thus, the ESCA result of PDMS-*b*-*l*-PLA indicates that the concentration of PDMS is much higher at the topmost surface than at the deeper regions.

Since the blend of equimolar *l*-PLA and *d*-PLA forms new crystal structure, stereocomplex packed side by side, surface compositions of (PDMS-*b*-*l*-PLA/*l*-PLA) and (PDMS-*b*-*l*-PLA/*d*-PLA) blend films with 50/50 by wt% are investigated by ESCA. Figure 2 shows the high-resolution

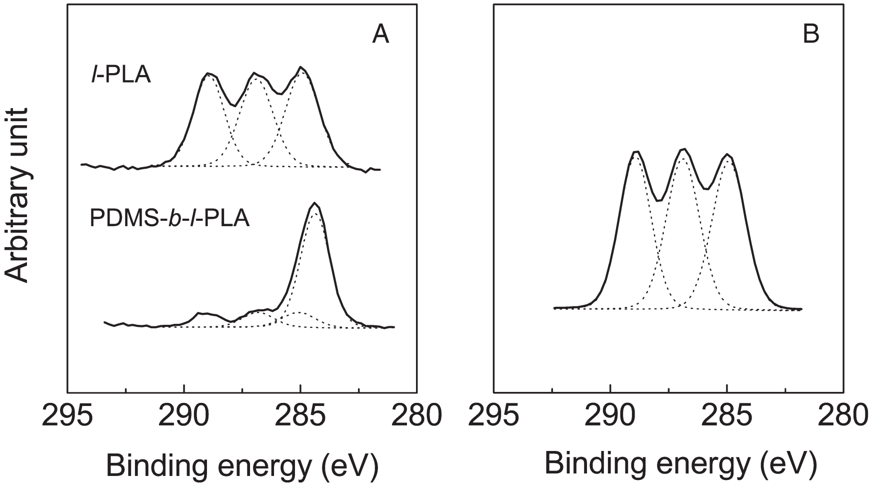

Figure 1.
C1s spectra of *l*-PLA and PDMS-*b*-*l*-PLA at a takeoff angle of 20° (A) and theoretically calculated C1s spectrum of PDMS-*b*-*l*-PLA by using its bulk composition of 2.8 mol% PDMS (B).

ESCA spectra of C1s regions of both blend films at the 20° takeoff angle. From the intensity of natural carbon compared to that from O=C–O or C–O from PLA, the (PDMS-*b*-*l*-PLA/*l*-PLA) blend film shows the surface segregation of PDMS if we consider that its theoretical bulk composition (ca. 2.8 mol%), that is, almost *l*-PLA. However, the (PDMS-*b*-*l*-PLA/*d*-PLA) blend film is within limits of bulk composition. This result suggests that the PDMS chains in the (PDMS-*b*-*l*-PLA/*d*-PLA) blend film homogeneously exist in both surface and bulk, not in surface segregation.

Figure 3 shows water-contact angle images of both blend films. As mentioned above, the (PDMS-*b*-*l*-PLA/*l*-PLA) blend film with the surface segregation of hydrophobic PDMS shows higher water contact angle than that of (PDMS-*b*-*l*-PLA/*d*-PLA) blend film. The contact angle of (PDMS-*b*-*l*-PLA/*l*-PLA) (86°) was toward to that of PDMS-*b*-*l*-PLA (90°) while (PDMS-*b*-*l*-PLA/*d*-PLA) (63°) without the surface segregation of PDMS showed similar contact angle of *l*-PLA (61°). These results are again in accordance with ESCA results of both blend films. Thus, it seems reasonable that the surface structure of enantiomeric PLA blends is strongly related to the formation of stereocomplexes.

Figure 4 shows the surface mole fraction of PDMS of PDMS-*b*-*l*-PLA and its blends with enantiomeric PLAs. These ratios are plotted as a function of photoelectric takeoff angle. The atomic ratios of carbon and silicon were used in the quantitation. According to the structures of the repeating units of PLA and PDMS, the surface DMS mole fraction, X_{DMS} of PDMS-*b*-PLA is expressed in the terms of the Si/C atomic

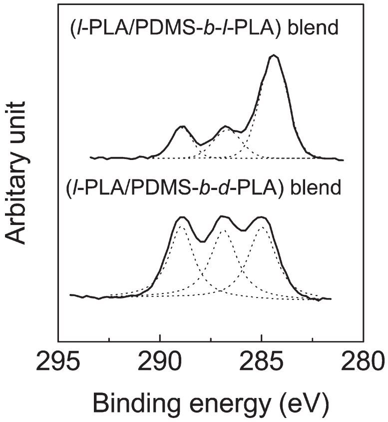

Figure 2.
C1s spectra of (PDMS-*b*-*l*-PLA/*l*-PLA) and (PDMS-*b*-*l*-PLA/*d*-PLA) blend films at a takeoff angle of 20°.

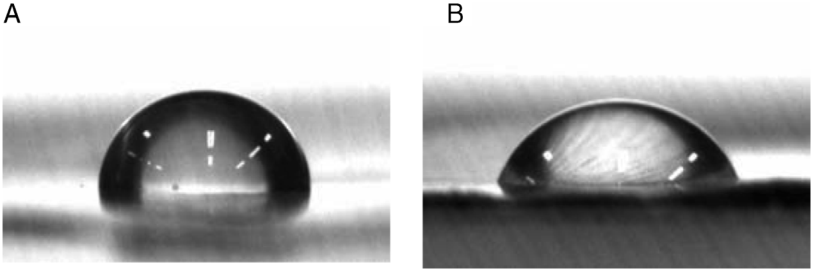

Figure 3.
Water-contact angle images of (PDMS-*b*-*l*-PLA/*l*-PLA) (A) and (PDMS-*b*-*l*-PLA/*d*-PLA) (B) blend films with 50/50 wt% composition.

ratio as

$$\frac{\mathrm{Si}}{\mathrm{C}} = \frac{X_{\mathrm{DMS}}}{3(1 - X_{\mathrm{DMS}}) + 2X_{\mathrm{DMS}}}$$

in which Si and C are the atomic percentages of silicon and carbon from ESCA measurements, respectively. As found in many blend systems, the surface composition in multicomponent systems containing small amount of low surface energy component is dramatically different from the bulk composition due to the surface segregation of lower surface energy component to minimize the surface energy. In the case of (PDMS-*b*-*l*-PLA/*l*-PLA) blend films with two different compositions of 50/50 and 80/20 by wt%, the surface composition of PDMS is proportional to the composition of PDMS-*b*-*l*-PLA in the blend and the surface segregation of PDMS can be expected if we consider that the bulk composition of PDMS of PDMS-*b*-*l*-PLA is 0.028 mol fraction. However, the values of (PDMS-*b*-*l*-PLA/*d*-PLA 50/50 by wt%) blends are within limits of bulk composition, regardless of takeoff angles. Since

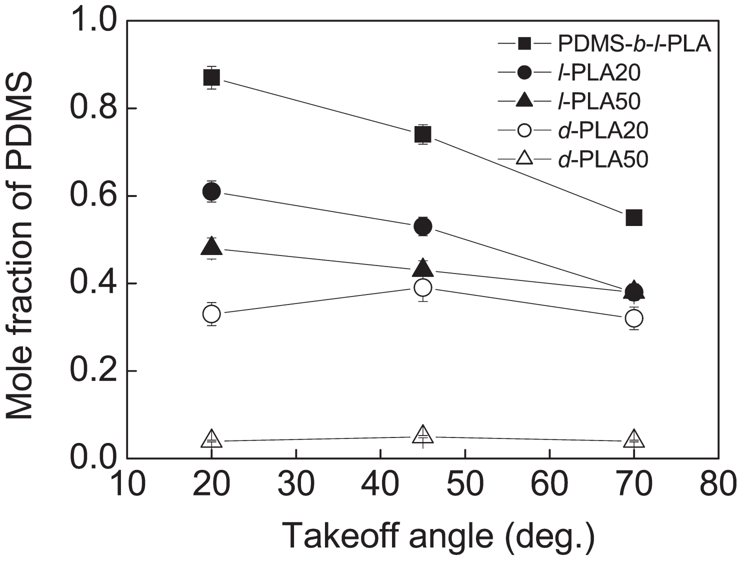

Figure 4.
Surface mole fractions of PDMS-*b*-*l*-PLA and its blend films at different takeoff angles. Digitals give the *d*-PLA or *l*-PLA wt % in the blends with PDMS-*b*-*l*-PLA.

equimolar amounts of *d*- and *l*-PLA form stereocomplexes and leave excess *d*- or *l*-PLA crystals, blends with less than 50 wt% PDMS-*b*-*l*-PLA are composed of uncomplexed *d*-PLA and stereocomplex phases. The T_m of (PDMS-*b*-*l*-PLA/*l*-PLA, 50/50) blend measured by DSC is similar to that of *l*-PLA but the T_m of (PDMS-*b*-*l*-PLA/*d*-PLA, 50/50) blend shifts to higher temperature by 50 °C than that of *l*-PLA (DSC data are not shown here). When a composition of PDMS-*b*-*l*-PLA in the (PDMS-*b*-*l*-PLA/*d*-PLA) blend is less than 50 wt%, *l*-PLA in PDMS-*b*-*l*-PLA is complexed with the same amount of *d*-PLA. Therefore, there is no surface segregation of PDMS. However, the surface PDMS mole fraction of (PDMS-*b*-*l*-PLA/*d*-PLA, 80/20 by wt%) blend film, which is composed with uncomplexed PDMS-*b*-*l*-PLA (theoretically ca. 60 wt%) and stereocomplex phases, is lower than those of (PDMS-*b*-*l*-PLA/*l*-PLA, 50/50 by wt%) blend film. This can be explained that the surface segregation of uncomplexed PDMS-*b*-*l*-PLA is hindered by the complexed chains (*anchoring effect*). Thus, we conclude that the interchain interaction to form stereocomplexes between *l*- and *d*-PLA is strong enough to overcome the driving force of PDMS groups to the surface.

Conclusions

This study demonstrated the effects of stereocomplexation of blends of enantiomeric PLAs on surface structure. *l*-PLA block copolymer (PDMS-*b*-*l*-PLA) with small amounts of PDMS which has low surface energy was used as a model material. PDMS-*b*-*l*-PLA film showed the surface segregation of PDMS in order to minimize surface energy. Thus, two blend systems, (PDMS-*b*-*l*-PLA/*l*-PLA) and (PDMS-*b*-*l*-PLA/*d*-PLA), were used to study the surface structure of uncomplexed and complexed systems, respectively. The uncomplexed (PDMS-*b*-*l*-PLA/*l*-PLA) blend film showed the surface segregation of PDMS, regardless of the blend composition, however, the surface segregation of PDMS in the (PDMS-*b*-*l*-PLA/*d*-PLA 50/50 by wt%) blend film was not observed. These results are likely due to strong interaction between *d*- and *l*-lactide unit sequences, which prevents the surface segregation of PDMS.

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