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# The Control of Surface Structure of Fluorocarbon End-Capped Poly(L-lactide)/Stereochemical Polylactide Blend Films

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**Summary:** The propose of this study is to investigate stereocomplexation-induced surface structure of enantiomeric PLA blends on the basis of complex formation between L- (LLA) and D-lacide (DLA) unit sequences. In order to control the complexation, stereochmical PLAs with % D repeat unit contents of 100, 98, 95, 90, and 80 were synthesized from the mixtures of DLA and LLA using stannous octoate as catalyst. Fluorocarbon end-capped PLLA (F-PLLA) instead of PLLA was used as a surface probe material because of the surface segregation of fluorocarbon groups. Large changes in the melting temperature (Tm) behavior and the surface structure for (F-PLLA/stereochmical PLA) blend films were observed by differential scanning calorimetry and electron spectroscopy for chemical analysis, respectively. (F-PLLA/stereochmical PLA) blend films showed the increase in both Tm and heat of fusion from the stereocomplexes with the optical purity of stereochmical PLAs in the blend. Also, the surface composition of fluorocarbon groups in the blends was proportionally increased with decreasing the optical purity in the blend because the stereocomplex formation in (F-PLLA/stereochmical PLA) blends prevents the surface segregation of fluorocarbon groups. These results indicate that surface structure of (F-PLLA/stereochmical PLA) blends could be controlled by changing a degree of complexation.

**Keywords:** blend; fluorocarbon; stereochemical PLA; stereocomplexation; surface segregation

## Introduction

Polylactide (PLA) is a polyester produced either from the ring-opening polymerization of lactide or from the polycondensation of lactic acid and has received much attention over the past few decades due to its biocompatible and biodegradable. Lactic acid, synthesized by the bacterial fermentation of carbohydrates such as sugar from starch, has two enantiomeric forms because of the presence of a pendent methyl group on the alpha carbon. This structure causes chirality at the alpha carbon and thus, L, D, and DL isomers are possible. Depending upon tacticity and optical purity, stereochemical PLAs can range from completely amorphous to semi-crystalline. Thus, modulation of the stereochemical composition leads to PLAs with quite different properties, such as degradability and mechanical properties.[1,2] Since its first report in 1987 thorough research has been conducted on the synthesis,[3] extensive investigations of physical and chemical characteristics of the stereocomplex in enantiomeric (PDLA/PLLA) blends have been reported.[4–7] Generally, the stereocomplex crystallites can occur when the interaction between two polymers having

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different configurations is stronger than between those having the same configuration. Therefore, the stereocomplex formation from the equilmolar mixture results in crystal structure and physical properties that differ markedly form those of the individual homopolymers.

Since there are strongly related to the associated functional properties, the surface layer properties of polymeric systems play an essential role in many commercial applications of polymers, including wetting, degradability, biocompatibility, adhesives, and so on.[8–10] In many of these applications the successful design of polymeric materials is facilitated by modification of surface properties. The common approaches to modify the surface properties of polymeric systems involve syntheses of specific architectures and blends.[8–11] Although blending is an attractive method to change surface properties because of the common use of commercially available polymers, one limitation to blending is the need to have polymer miscibility in many cases. Much emphasis has been placed on controlling the surface structure of copolymers [8,9] because copolymers limit the very large-scale phase separation that occurs in polymer blends which are incompatible. Modification for low energy surfaces, which provides opportunity to control properties, adhesion, wetting, dewetting, and mobility, can be achieved by copolymerizing only a small amount of a block component having low surface energy, such as silicon or fluorine-containing polymers.[7–11] Recent trends of biodegradable polymer research are focused on the desired life span. 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,[11–13] it has become evident that the rate of initiating degradation is dominated by the physical accessibility of the polymer structure to the abiotic attack. The material design for this study is based on principles of the surface segregation of fluorocarbon chain-attached PLLA and the stereocomplexation between PLLA and PDLA. In order to control stereocomplex, stereochemical PLAs with different D- and L-unit contents instead of PDLA in the blend were used.

## Experimental Part

### Materials

L- (LLA) and D-lactide (DLA) were obtained from Aldrich and Purac, respectively and recrystallized from anhydrous ethyl acetate. 2-(Perfluorodecyl) ethanol (F- OH, Daikin) was dried in a vacuum oven at room temperature before use. F-PLLA ($CF_3(CF_2)_9$-$CH_2CH_2O$-PLLA) was synthesized by ring-opening polymerization of LLA by stannous octoate as a catalyst in the presence of F-OH. The details of synthesis and characterization of F-PLLA were discussed elsewhere.[10] The bulk polymerizations of LLA, DLA and their mixtures were carried out in vacuum-sealed ampules with stannous octoate. PLA products were purified by dissolving the products in chloroform, removing undissolved materials by filteration, and precipitating the polymer solutions into 5 volume excess of methanol. 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 F-PLLA and stereochemical PLAs in chloroform was separately prepared. The mixture solutions at 50 wt% were prepared from each polymer solution and cast into aluminum weighing dishes, and then allowed to air dry slowly at room 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 $5 \pm 1$ μm.

### Measurements

The Tm and Tg of homopolymers and as-cast blends were measured by DSC (Perkin-Elmer DSC/TGA 7) under nitrogen,

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***Table 1.***
Characterization of the materials used in this study.

| Sample codes | $M_n$ ($M_w/M_n$) | Tg (°C) | $T_m$ (°C) | $\Delta H_m$(J/g) |
|---|---|---|---|---|
| F-PLLA | 73k (1.8) | 53 | 170 | 18.0 |
| PLLA | 320k (1.5) | 59 | 179 | 20.0 |
| D100 | 740k (1.6) | 58 | 178 | 21.3 |
| D98 [a] | 800k (1.7) | 57 | 158 | 12.3 |
| D95 | 710k (1.7) | 55 | 149 | 8.2 |
| D90 | 440k (1.6) | 55 | n.d. | |
| D80 | 330k (1.6) | 56 | n.d. | |

[a] D98 indicates the polymer with DLA 98% and LLA 2% by mol and has 98% of optical purity.

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 Tg was obtained during reheating process after quenching from melting. The DSC thermograms were obtained at a heating rate of 10 °C/min.

The chemical compositions of (F-PLLA/stereochemical PLA) blend films were obtained using a Perkin-Elmer Physical Electronic Model 5300 ESCA. ESCA measurements were performed with MgK$\alpha$ X-ray source at 15 kV and 20 mA at takeoff angles of 20°, 30°, and 90°, which led to the sampling depths of the C1s region of 2.4, 5, and 10.3 nm, respectively.[14] When exposed to x-ray radiation, fluoropolymers are known to defluorinate. In order to minimize this effect, shorter exposure times (four minutes) was determined from the relationship between exposure time and atomic ratio for poly(vinylidene fluoride) (PVDF) as a standard material. No defluorination of PVDF during this period was detected within the 95% confidence level. All C 1s spectra were referenced to the neutral carbon of PLA at 285 eV, in order to correct charging effects.

## Results and Discussion

It has been known that the stereochemical compositions of PLAs are identical to those of in the monomer feed and the polymers formed a random stereosequence distribution.[2,15] PLA films including blends were prepared by solution casting from chloroform (see Experimental section). DSC analyses on the as-cast film PLA samples with stereochemical compositions ranging from 100 to 80% of DLA were performed and the measured melting points (Tm) and heat of fusion ($\Delta H_f$) values are shown in Table 1. As the % DLA in the stereochemical PLAs is decreased from 100 (D100) to 95% (D95), the Tm and $\Delta H_f$ values decrease from 178 to 149 °C and 21.3 to 8.2 J/g, respectively. Although the stereochemical PLAs with optical purity higher than 70% were crystallized by annealing,[16,17] the as-cast D90 and D80 films did not show any melting peak in the DSC curve under the prepared condition in this study.

Based on the DSC analyses over the compositional range between D100 and D80, the change of stereochemical composition is needed to cause dramatic changes in the crystalline order. This then creates an opportunity to investigate the stereocomplexation of (PLLA/stereochemical PLA) blends as a function of optical purity of stereochemical PLAs.

As found in many blend systems, the surface composition in multicomponent systems containing small amounts of specific materials is dramatically different from the bulk composition due to surface segregation which minimizes the surface energy. To determine the surface composition of fluorocarbon end groups of F-PLLA film, angle-dependent ESCA was used. The analytical depth of ESCA was varied by changing take-off angles between the sample surface and the analyzer of 20°, 30°, and 90°. Figure 1 shows the high-resolution

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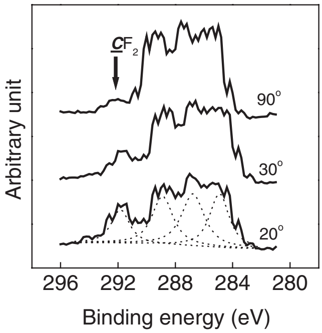

**Figure 1.**
High resolution C 1s spectra of F-PLLA films measured at different takeoff angles.

ESCA spectra of C 1s regions of F-PLLA film at various photoelectron takeoff angles. The C 1s region measured at takeoff angle of 20° showed contributions from C–O functional groups at 286.8 eV and O=C–O at 288.9 eV from the PLA, and C-$F_2$ at 292 eV from the fluorocarbon. The intensity of the C–$F_2$ fraction compared to that from O=C–O or C–O increases gradually with decreasing a photoelectron takeoff angle. This suggests that the concentration of fluorocarbon end groups is much higher at the topmost surface than at the deeper regions due to the surface segregation of lower surface energy fluorocarbons.

To investigate the stereocomplexation-induced surface structures in (PLLA/stereochemical PLA) blends, fluorocarbon end-capped PLLA (F-PLLA) instead of PLLA in the blend was used because the fluorocarbon of F-PLLA shows the surface segregation of fluorocarbon groups. Our previous study,[7] the uncomplexed (PDMS-*b*-PLLA/PLLA) blend film showed the surface segregation of poly(dimethylsiloxane) (PDMS), regardless of the blend composition, however, the surface segregation of PDMS in the (PDMS-*b*-PLLA/PDLA 50/50 by wt%) blend film was not observed. These results were due to strong interaction between LLA and DLA unit sequences, which prevents the surface segregation of PDMS. Since the stereocomplexation bewteen PLLA and PDLA occurs as a result of side-by-side packing of equimolar LLA and DLA unit sequences, a complexation in the enantiomeric PLA blend will be controlled by the change of optical purity in a blend component. Figure 2 shows the DSC curves for as-cast (F-PLLA/stereochemical PLA) blend films with 50/50 by wt%. The blends of F-PLLA with D100, D95, and D90 give two endothermic peaks: one is around 170 °C and the other indicated as the arrows is higher than 170 °C. The lower melting peaks are due to the melting of PLLA homocrystals while higher one, which is increased with the optical purity in the blend component, is from stereocomplexes. Although the stereocomplex was formed more rapidly and more complete when the ratio of PLLA to PDLA approached 1:1, it is not surprising that the (F-PLLA/D100) blend film shows two endothermic peaks if we consider that the factors affecting the stereocomplexation are molecular weight, sequence lengths, and preparation conditions.[18] However, (F-PLLA/D80) blend film showed a single endothermic peak at 170 °C due to PLLA homocrystals. Sarasua *et al*. reported that PLA with 70% optical

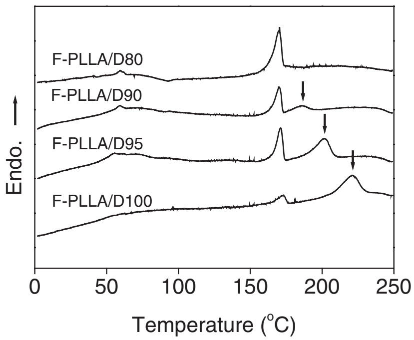

**Figure 2.**
DSC curves of as-cast (F-PLLA/stereochemical PLA) blend films.

**Table 2.**
Tm and ΔH$_f$ of as-cast (F-PLLA/stereochemical PLA) blend films.

| Blends | PLLA homocrystals | | Complexes | |
|---|---|---|---|---|
| | Tm (°C) | ΔH$_f$ (J/g) | Tm (°C) | ΔH$_f$ (J/g) |
| F-PLLA/D100 | 173 | 4.4 | 221 | 18.9 |
| F-PLLA/D95 | 171 | 8.4 | 201 | 10.4 |
| F-PLLA/D90 | 170 | 11.3 | 185 | 4.1 |
| F-PLLA/D80 | 170 | 12.9 | – | – |

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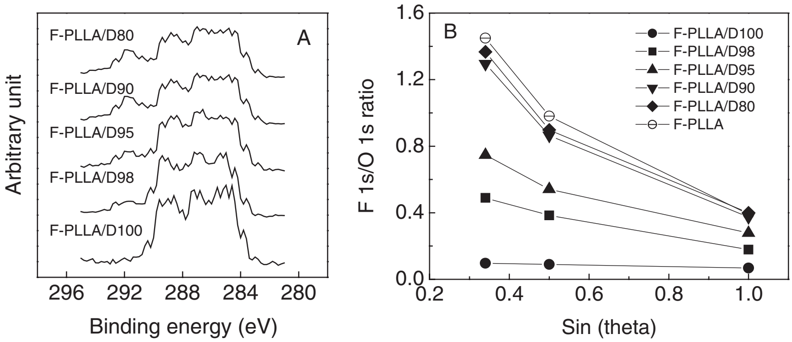

***Figure 3.***
High resolution C 1s spectra at a takeoff angle of 20° (A) and surface atomic ratio profiles (B) of as-cast (F-PLLA/stereochemical PLA) blend films.

purity could not form stereocomplexes.[19] The $\Delta H_f$ and Tm of the blends are reported in Table 2. The $\Delta H_f$ from PLLA homocrystals at 170 °C increases with decreasing the optical purity of stereochemical PLA in the blends while both $\Delta H_f$ and Tm of stereocomplexes increase with the optical purity. This result indicates that a degree of stereocomplexation between LLA and DLA unit sequences increases with the optical purity of blend components.

In order to study the stereocomplexation-induced surface structure between LLA and DLA unit sequences, surface compositions of (F-PLLA/stereochemical PLA) blend films are investigated by ESCA. Figure 3A shows the high-resolution ESCA spectra of C 1s regions of the blend films at the 20° takeoff angle. The intensity of $CF_2$ compared to that from O=C–O or C–O from PLA is increased with decreasing the optical purity of stereochemical PLAs in the blend systems.

Usually, there are two ways to evaluate the surface composition from ESCA data, elemental analysis and curve fitting.[14] The ESCA sampling depth depends on both takeoff angle and the kinetic energy of emitted photoelectrons which are excited by the X-ray source. At a particular takeoff angle, therefore, the signals from emitted photoelectrons reflect different sampling depths for each element. In this case, one could use the atomic concentration ratio of fluorine, which can be related to the fluorocarbon group, and oxygen from the PLA because the small amount of fluorocarbon makes the curve fitting in the C 1s region difficult. To investigate complexation-induced surface structure as a function of optical purity, the atomic ratio (F 1s/O 1s) of (F-PLLA/stereochemical PLA) blend films were investigated by angle-dependent ESCA measurements, as shown in Figure 3B. As decreasing the optical purity of stereochemical PLAs in the blend system, the atomic ratios of F 1s/O 1s increase: the atomic ratio of the (F-PLLA/D80) blend film, which did not show a stereocomplex formation, is similar to that of F-PLLA while the surface structure of the complexed (F-PLLA/D100) blend film is almost bulk one, not surface segregation of fluorocarbons. This means that the lower the degree of stereocomplexation, the higher the atomic ratio. As shown in the melting behavior of (F-PLLA/stereochemical PLA) blend films, the surface segregation of fluorocarbon groups in the blend films is inversely proportional to a degree of stereocomplexation. Thus, we conclude that the surface structure of (F-PLLA/stereochemical PLA) blend films is controlled by changing the stereochemistry of PLAs.

## Conclusions

This study demonstrated the relationship between surface structure and stereocomplexation of blends of F-PLLA and stereo-

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chemical PLAs with different optical purities on the basis of the complex formation between PLLA and PDLA and the surface segregation of fluorocarbon groups. As increasing the optical purity of stereochemical PLAs in the blends, Tm and $\Delta H_f$ due to stereocomplexes were gradually decreased and the (F-PLLA/D80) blend did not show a Tm from stereocomplexes. Also, the surface composition of fluorocarbon in the blend system was increased with decreasing the optical purity of stereochemical PLAs. These results indicate that the surface segregation of fluorocarbon groups in (F-PLLA/stereochemical PLA) blend films was controlled by the change of optical purity in stereochemical PLAs.

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