Compression-Induced Stereocomplexation of Polylactides at the Air/Water Interface

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ABSTRACT: The conformational and morphological changes occurring at the air/water interface during the compression of pure poly(D-lactide) (PDLA), pure poly(L-lactide) (PLLA), and their equimolar blend have been thoroughly investigated using polarization−modulation infrared reflection−absorption spectroscopy and Brewster angle microscopy. The results obtained show that the plateau region observed in the isotherm of the pure polylactides corresponds to an equilibrium between free 10_3 helices in a fluid phase and 10_3 helices in unstable solidlike domains. For the blend, this plateau corresponds to an equilibrium between free 10_3 helices in the fluid phase, 10_3 helices in unstable solidlike domains of pure polyenantiomers, and 3_1 helices in very stable solidlike domains of the PDLA/PLLA stereocomplex. The results obtained also suggest that the proportion of stereocomplex and pure polyenantiomers domains formed during the compression of the monolayer of the blend can be modulated by different experimental parameters such as the molecular weight of the polymers, the subphase temperature, the compression rate, and the "incubation" time.

Introduction

Poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA) are bioresorbable, biocompatible, and optically active semicrystalline polymers that are produced from renewable resources such as corn, wheat, and sugar beat. They can be extruded, thermoformed, and blow-molded and are used in several applications such as shirts, bottles, sutures and implants.[1] Pure polylactide polyenantiomers possess a glass transition temperature of 55 °C and a melting point of 180 °C.[2,3] When crystallized from the melt or from solution, pure PLLA and PDLA adopt left- and right-handed 10_3 helix conformations, respectively, and produce the α crystal form by arranging by pair in a crystalline unit cell. Some authors have suggested that this unit cell is pseudo-orthorhombic[4] (a = 10.7 Å, b = 6.45 Å, c = 27.9 Å; α = β = γ = 90°), while others have reported that it is hexagonal[2] ($a = b$ = 5.9 Å, c = 27.9 Å; α = β = 90°, γ = 120°). The β crystal form, which is only found in solution-spun fibers drawn at high temperatures, features six 3_1 helices in an orthorhombic unit cell and can rearrange to the more stable α crystal form.[3,5]

When crystallized from the melt or from solution, blends of PLLA and PDLA can form a racemic stereocomplex[6] arising for the stereoselective association (or stereocomplexation) between the optically active polymers. In the polylactide stereocomplex, 3_1 helices are arranged by pair in a triclinic unit cell (a = 9.16 Å, b = 9.16 Å, c = 8.70 Å, α = 109.2°, β = 109.2°, γ = 109.8°).[7] The melting point of this complex (230 °C) is 50 °C higher than that of the α crystal form of the pure polyenantiomers.[6] During crystallization, the formation of the stereocomplex competes with that of the pure polyenantiomers. It has been shown that high molecular weights, low optical purity, nonequimolar PDLA/PLLA ratio, or imperfect mixing of the solution disfavor the formation of the stereocomplex.[8−11] Moreover, the insignificant effect of the solvent nature on the racemic crystallization suggests that the stereocomplexation does not occur in solution but rather during the precipitation process.[9,12]

In addition to polylactides (PLA),[7−16] stereocomplexation has also been reported for different polymer couples, the most studied of them being poly(α-methyl-α-ethyl-β-propiolactones),[17−19] poly(γ-benzyl glutamates),[20−26] and poly(methyl methacrylates)[27−34] (PMMA). Stereocomplexation of polymers at the air/water interface has only been studied only for polylactides[35,36] and for PMMA.[37−42] Indeed, Brinkhuis and Schouten have shown that a stereocomplex could be formed at the air/water interface by compressing a Langmuir film of a 2:1 isotactic:syndiotactic PMMA blend.[39−41] This stereocomplex consists of double-helical structures with a syndiotactic strand winding around an isotactic strand, the stoichiometry being 2:1 at the monomeric level.

The study of Langmuir monolayers of pure polylactides polyenantiomers and their equimolar blend using polarization−modulation infrared reflection−absorption spectroscopy (PM-IRRAS) has recently been reported.[35,36] These studies have shown that the stereocomplex is present in Langmuir monolayers of the equimolar blend, but unfortunately, they did not give precise information about the actual moment when the stereocomplexation takes place. Indeed, Bourque et al. mentioned that the stereocomplexation could occur in the solution before spreading at the air/water interface or during the compression of the film.[35] To gain more information about the different processes occurring during the compression of monolayers of pure poly(L- and D-lactide) and their equimolar blend and to determine more precisely when the stereocomplexation occurs, we have used both PM-IRRAS spectroscopy and Brewster angle microscopy (BAM). These complementary techniques provide extremely valuable information on the conformational and morphological changes occurring during the compression of the polylactides monolayers. To favor the stereocomplexation, polylactides with a low molecular weight were used since it

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has been shown by Tsuji et al.[12] that lower molecular weight favors the stereocomplexation of the polyenantiomers. The results obtained have been used to elaborate a model for the stereocomplexation and the solidification of the polylactides molecules at the air/water interface.

Materials and Methods

Poly(L-lactide) and poly(D-lactide) were synthesized by ring-opening polymerization in toluene.[11] The mean molecular weight (M_w) was 1.32×10^4 g/mol for the poly(L-lactide) and 1.45×10^4 g/mol for the poly(D-lactide) with a polydispersity index of 1.35 for both products.[11]

A previous study[43] has shown that chloroform is one of the best organic solvents for polylactides, so PDLA and PLLA were dissolved in HPLC grade chloroform (Sigma-Aldrich, St. Louis, MO) to a concentration of 0.1 mg/mL, and equal amounts of each solution were mixed to obtain a solution of the equimolar blend. The surface pressure−area isotherms were recorded using a KSV 3000 apparel (KSV Instruments, Finland) equipped a 80 × 500 mm trough. Unless otherwise specified in the text, Langmuir films were formed on a deionized water subphase (NANOpure, Barnstead International, Boston, MA) at 35 ± 1 °C by spreading 160 μL of the polylactides solution. After an equilibrating period of 15 min allowing solvent evaporation, the monolayers were compressed at a rate of 0.36 Å^2/repeat unit per minute.

Images of the Langmuir films were recorded with a Nanofilm surface analysis Brewster angle microscope (Göttingen, Germany) equipped with a 10× objective and with a 100 × 650 mm NIMA trough (Coventry, England). Langmuir films were formed following the same experimental conditions than those used for isotherms recording, except that that 250 μL of the solutions was spread at the air/water interface in order to obtain the right area per repeat unit at the beginning of the compression.

The PM-IRRAS setup has been described in detail elsewhere.[35] The monolayers were formed by spreading 70 μL of polylactides solution on a 360 × 50 mm home-built Langmuir trough. The p-polarized IR beam was focused on the water surface with an incidence angle of 70° and was then reflected on a photovoltaic MCT detector (Kolmar Technologies, Newburyport, MA). The polarization state of the IR beam was modulated by a photoelastic modulator (Hinds Instruments, type II) set for optimum efficiency at 1450 cm^{-1} prior to reflection on the water subphase. All spectra were recorded with a spectral resolution of 8 cm^{-1} by coadding 1000 scans. PM-IRRAS spectra are presented as normalized difference spectra $(S(d) - S(0))/S(0)$, where $S(d)$ and $S(0)$ are the monolayer covered and uncovered water surface spectra, respectively.

Results and Discussion

The air/water interface behavior of poly(L-lactide) being identical to that of poly(D-lactide), the expression "pure polyenantiomers" used in this article refers indifferently to any of the polyenantiomers. The π/A isotherms of the pure polyenantiomers and of their equimolar blend are shown in Figure 1. The isotherm of the pure polyenantiomers shows a sharp knee around 16−17 Å^2/repeat unit and a plateau at a surface pressure near 7 mN/m. In contrast, the isotherm of the blend shows a wider knee and a plateau region at much lower surface pressure (≈4 mN/m). Knees are often observed in isotherms of polymers and can be associated with a kinetic effect related to an autoaccelerating process (often an activated nucleation mechanism followed by a growth of the nuclei formed) for which the conversion rate eventually exceeds the compression rate.[36,37] Plateau regions in isotherms are usually associated with the formation of a new phase. In Figure 1, the presence of a knee followed by a plateau region could thus mean

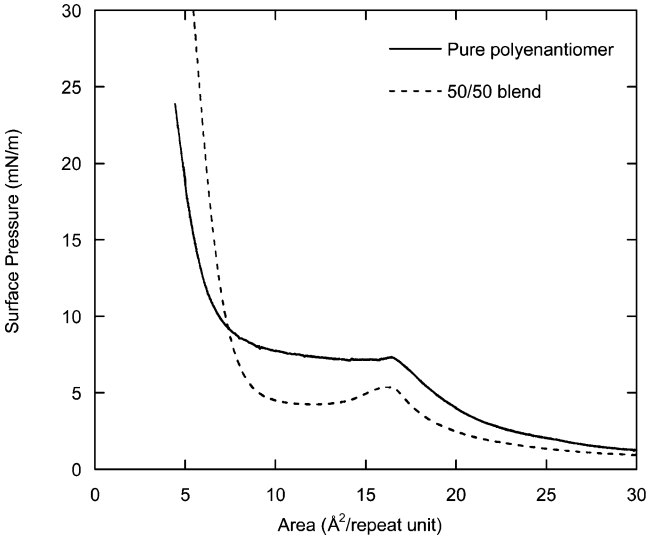

Figure 1. Isotherms of the pure polylactide polyenantiomers and of the equimolar blend at 35 °C.

that the plateau correspond to the formation of a new phase for which the rate of conversion is higher than the rate of compression.

Although the isotherm of the pure polyenantiomers shown in Figure 1 is quite similar to that already published in the literature,[36] important differences can be noted for the blend. Indeed, the isotherm of the blend shown in the present paper displays a much larger knee and a plateau occurring at a much lower surface pressure (4 mN/m) than that previously published (7 mN/m). Moreover, as opposed to what is observed in Figure 1, the previously published isotherms of the blend and of the pure polyenantiomers were very similar to each other. These discrepancies are most likely due to the molecular weight of the polylactides used in the current study, which is about 10 times lower than that used in previous studies (1.32×10^4 and 1.45×10^4 compared to 1.0×10^5 and 1.2×10^5 g/mol).[35,36] Tsuji et al.[12] have shown that the stereocomplexation occurring during the evaporation of dilute solutions of polylactides blends is strongly affected by the molecular weight of the polymers. Indeed, their differential scanning calorimetry results show that polylactides having a molecular weight less than 4×10^4 g/mol display a single melting peak at 230 °C, characteristic of the crystalline stereocomplex, while polylactides weighting more than 6×10^4 g/mol exhibit two melting peaks: a small one at 230 °C and a larger one at 180 °C, characteristic of pure crystalline polyenantiomers. These results indicate that low molecular weight polylactide blends forms stereocomplex crystallites while higher molecular weight polylactides mainly form pure polyenantiomer crystallites. These results have been related to the smaller overall mobility of high molecular weight chains compared to that of the low molecular weight ones. This reduced mobility prevents the rearrangement of the poly(D- and L-lactides) to form the stereocomplex and thus favors intrachain interactions and the formation of pure polyenantiomer crystallites. If some stereocomplexation occurs during the compression of the polylactides monolayer, as suggested by Bourque et al.[35] and Klass et al.,[36] the molecular weight of the polylactides used should have a great influence on the extent of the stereocomplexation and thereby on the shape of the isotherm recorded during the compression. This could explain why the isotherm of the higher molecular weight

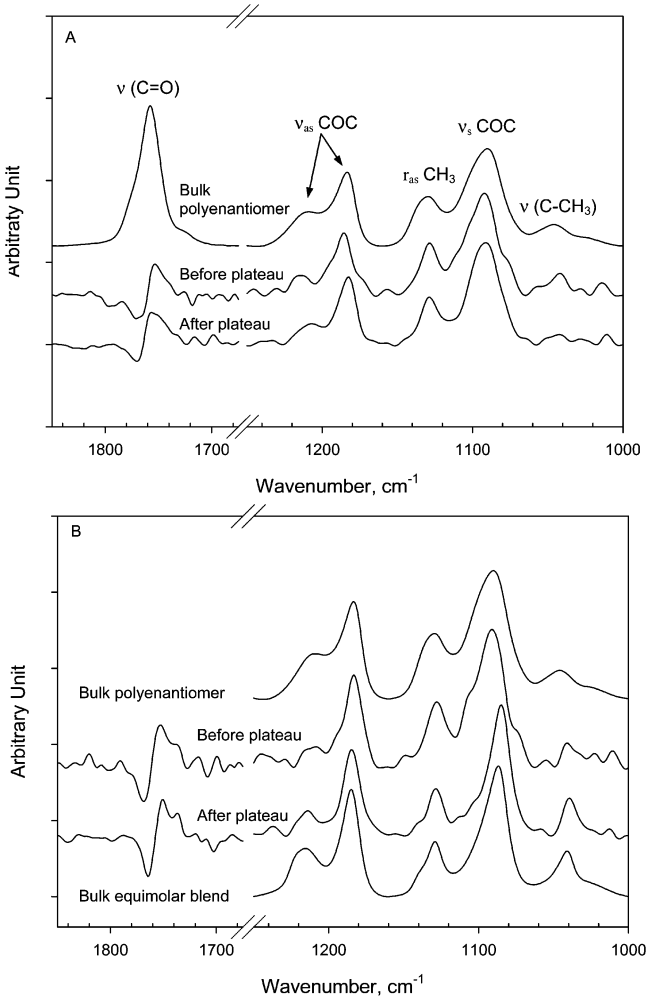

Figure 2. PM-IRRAS and spectra of the bulk of (A) the pure polylactide polyenantiomers and (B) the equimolar blend normalized for the 1085 cm^{-1} band.

polylactides blend previously reported in the literature[36] is so similar to that of the pure polyenantiomers. The polylactides used in the present study have a molecular weight that favors the stereocomplexation, thus leading to an isotherm for the blend that is markedly different from that of the pure polyenantiomers. It is also important to note that the polylactides used in the present work have lower polydispersity indexes (1.35) than those used previously (1.8 and 2.9) that could also favor the formation of the stereocomplex.

Theses results suggest that the shape of the plateau region in the isotherm of the blend is very closely related to the stereocomplexation of the polylactides. To gain a better understanding of the molecular origin of the processes occurring at the plateau region, PM-IRRAS spectra of monolayers of pure polyenantiomers and of the blend were recorded at surface pressures corresponding to the beginning and to the end the plateau region and compared with the spectra of bulk stereocomplex and bulk pure polylactides.

Figure 2 shows the infrared spectra of the bulk pure polyenantiomers and of the blend and the PM-IRRAS spectra recorded before and after the plateau region for both types of samples. All the PM-IRRAS spectra in this figure display band around 1760 cm^{-1} with a derivative shape due to the superposition of two components of opposite signs. These components have been assigned to the parallel (A) and perpendicular (E) modes of the coupled carbonyl vibrations of an helix and indicate that polylactides (pure and in blend) form helices lying on the water subphase as soon as they are deposited on the water subphase.[35,36,44] Figure 2A shows that, for the pure polyenantiomers, the PM-IRRAS spectra recorded before and after the plateau are very similar (except for their absolute intensity). This suggests that no conformational change occurs during the compression of the film. Since both PM-IRRAS spectra are also very similar (except, of course, for the split carbonyl stretching band) to the spectrum of the bulk polyenantiomer (which is constituted of 10_3 helices),[2,4] we can conclude that, when spread at the air/water interface, the pure polyenantiomers form 10_3 helices that remain the same during the compression of the monolayer.

Figure 2B shows significant differences in the 1250−1000 cm^{-1} spectral region between the spectra of the bulk pure polyenantiomers and that of the blend. The most important of these differences concern the bands due to the symmetric and asymmetric stretching of the COC (ν_s COC and ν_{as} COC) that shift from 1090 and 1209 cm^{-1} in the spectrum of the bulk pure polyenantiomers to 1087 and 1215 cm^{-1}, respectively, in the spectrum of the blend. In addition to this shift, the ν_s COC band also becomes much narrower in the spectrum of the blend, the full width at half-height decreasing from 28 to 20 cm^{-1}. Finally, the band due to the asymmetric rocking mode of the methyl group (r_{as} CH_3) at 1129 cm^{-1} becomes narrower in the spectrum of the blend, the full width at half-height decreasing from 23 to 16 cm^{-1}. All these differences can be attributed to the different helix conformations and unit cells present in the bulk pure polyenantiomers and blend. Indeed, the blend crystallizes as a stereocomplex with 3_1 helices in a triclinic unit cell,[7] and the pure polyenantiomers crystallize as 10_3 helices in a pseudo-orthorhombic or hexagonal unit cell.

As seen in Figure 2B, the differences between the PM-IRRAS spectra of the monolayer of the blend recorded before and after the plateau region are very similar to the differences observed between the infrared spectra of the pure polyenantiomers and of the stereocomplex in the bulk state. Indeed, the PM-IRRAS spectrum recorded before the plateau is very similar to that of the bulk pure polyenantiomers while the spectrum recorded after the plateau is much more similar to that of the bulk stereocomplex. This strongly suggests that, when compressed at the air/water interface, the poly(D- and L-lactides) molecules undergo a conformational change from 10_3 helices toward 3_1 helices during the plateau region observed in the isotherm. This conformational change clearly shows for the first time that the stereocomplexation occurs during the plateau region of the isotherm and not before (e.g., in solution before spreading) as previously suggested.[35] This conclusion is further reinforced by the fact that the spectral differences observed in Figure 2B for the blend are not observed for the pure polyenantiomers (Figure 2A) that, indeed, do not form 3_1 helices. These results are in agreement with the work of Tsuji et al. that concluded that the stereocomplexation does not occur in solution but rather during the precipitation process.[9,12]

To gain information about the change of morphology occurring at the plateau region for both the pure polyenantiomers and blend monolayers, Brewster angle microscopy (BAM) images were recorded at different stages of compression and decompression of these films.

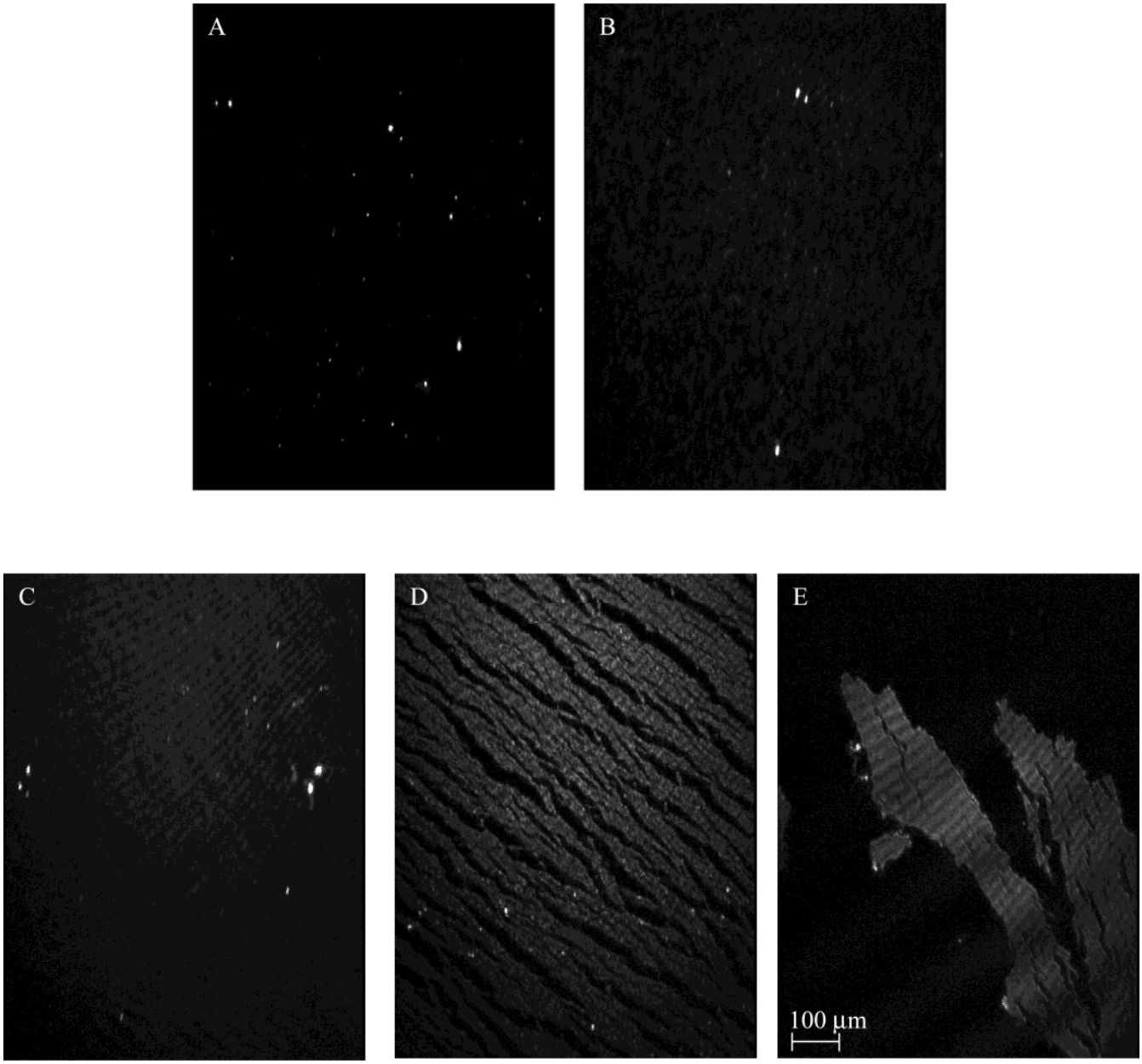

Figure 3. Brewster angle microscope images of the polylactide equimolar blend (A) before, (B) during and (C) after the plateau region, (D) during decompression, and (E) 30 min after decompression.

Figure 3 shows the BAM images recorded for the monolayer of the blend. The first image, recorded just before the plateau region, shows only small bright dots. These dots appeared just after the spreading of the solution and were observed at all time during compression and decompression. They are most likely aggregates caused by the rapid evaporation of chloroform during spreading. During the plateau region (Figure 3B), gray domains appear and grow until they cover the whole surface at the end of the plateau region (Figure 3C). Upon decompression, the gray film fractures into small gray domains (Figure 3D). These domains are very stable since they can still be observed 30 min after the end of the decompression (Figure 3E). The types of fractures observed in Figure 3D strongly suggest that the film is in a solidlike state after the plateau and that this region of the isotherm corresponds to the transformation from a fluidlike film toward a very stiff solidlike film. These results are in very good agreement with the irreversible stereocomplexation of the monolayer during the plateau region. They are also in agreement with the compression−decompression experiments previously published which showed that the blend monolayer displays reversibility before the plateau region, but not after compression beyond the plateau region.[36]

Figure 4 shows the BAM images recorded for a monolayer of pure polyenantiomers. Before the plateau (Figure 4A), only bright small dots are visible at the surface. After the plateau region (Figure 4B), the BAM images show a rigid gray film that fractures upon decompression (Figure 4C). The gray domains formed by the fracture of the film quickly "dissolve" at the air/water interface (bottom left Figure 4D), leaving nothing after 30 min (Figure 4E) except the bright small aggregates. As for the blend monolayer, the fracture pattern suggests that the plateau region corresponds to the solidification of the film, but this time, the process seems to be reversible since the small domains formed during the decompression quickly disappear. These results, which are in good agreement with the compres-

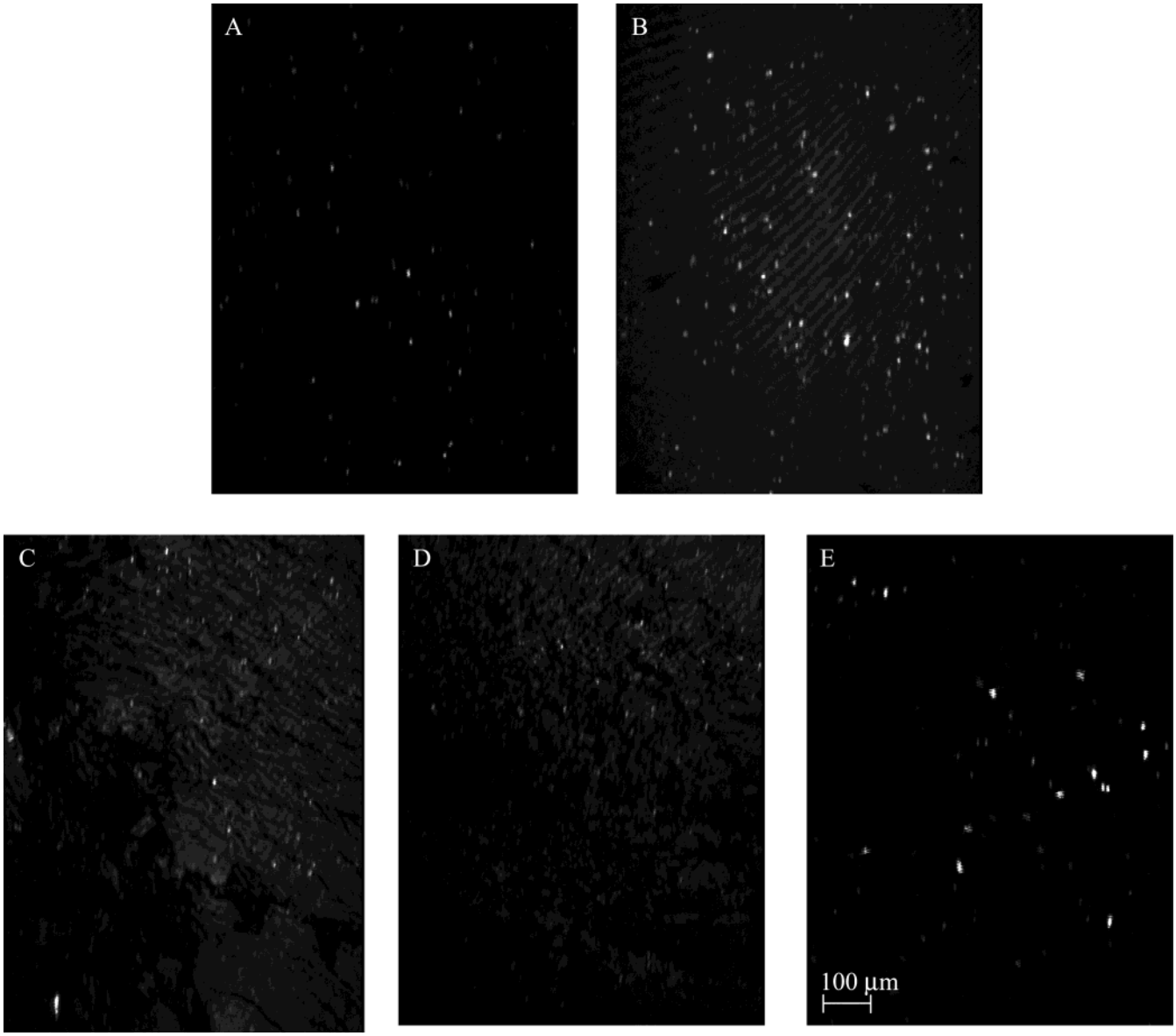

Figure 4. Brewster angle microscope images of the pure polylactide polyenantiomers (A) before and (B) after the plateau region, (C, D) during decompression, and (E) 30 min after decompression.

sion−decompression experiments previously published,[36] provide some very valuable information concerning the molecular processes occurring during the plateau region in the isotherm of the pure polyenantiomers. Indeed, this lead to the conclusion that the plateau corresponds to the reversible solidification of 10_3 helices at the air/water interface.

All results presented above indicate that the plateau region in the isotherms of polylactides corresponds to an equilibrium between free helices and solidlike domains. For the pure polyenantiomers, these domains are constituted of 10_3 helices, while for the blend, these domains are mostly formed of 3_1 helices (stereocomplex). It is very likely that the formation of these stereocomplex domains is in competition with the formation of pure polyenantiomers domains as suggested by the isotherms published of high molecular weight polylactides found in the literature.[36] Considering the facts that the plateau region in the isotherm of the blend is due to an equilibrium between two conformational states and that this equilibrium is affected by the molecular weight of the polylactides used, it is possible that other experimental factors such as the temperature of the subphase and the rate of compression could have an influence on the degree of stereocomplexation. Furthermore, it seems likely that the surface pressure at which the plateau appears in the isotherm of the blend is a good indicator for the quantity of stereocomplex formed.

Figure 5 shows the influence of the subphase temperature and of the rate of compression on the isotherm of the blend. (The isotherms of the pure polyenantiomers are not shown because these parameters have a negligible effect on them.) It is clear from Figure 5 that a decrease of the subphase temperature or an increase of the rate of compression have a similar effect, causing the disappearance of the knee, the deformation of the plateau, and an increase of the surface pressure at which it appears. These higher plateaus are reminiscent of the plateau region observed in the isotherm of the pure polyenantiomers, indicating that less stereocomplex and more pure polyenantiomers domains are formed. Indeed, lowering the subphase temperature decreases the mobility of the molecules and thus hinders

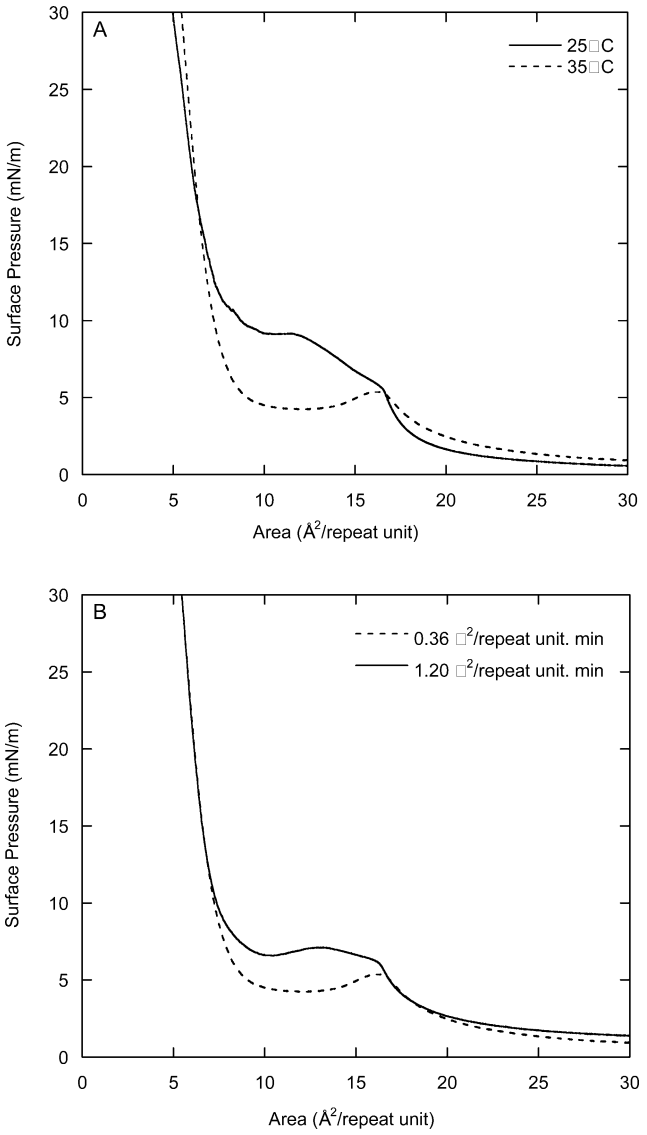

Figure 5. Effect of (A) the subphase temperature and (B) the rate of compression on the isotherm of the polylactide equimolar blend.

the rearrangement of the D and L polyenantiomers to form the stereocomplex. This leads to the formation of more pure polyenantiomers and less stereocomplex domains, thus causing the plateau to occur at a higher surface pressure. Moreover, the disappearance of the knee strongly suggests that decreasing the subphase temperature diminishes the rate of conversion of the process occurring in the plateau region (i.e., the stereocomplexation). Similarly, a faster compression rate for a given subphase temperature gives the molecules less time to form the stereocomplex, leading to the formation of more pure polyenantiomers and less stereocomplex domains and thus causing the plateau in the isotherm to appear at higher surface pressure. The disappearance of the knee in this case indicates that the compression rate is now higher than the conversion rate.

The results shown in Figure 5 are in good agreement with the behavior of the monolayer upon decompression as observed by Brewster angle microscopy (Figures 3 and 4). Indeed, Figure 4D,E shows that the solidlike domains made of pure polyenantiomers are not stable at the air/water interface when the compression is interrupted. This suggests that these domains are probably not very stable during the plateau region when parts of the monolayer are still fluid. In contrast, Figure 3D,E shows that the stereocomplex is formed irreversibly upon compression, suggesting that it should form highly stable solidlike domains during the plateau region. During the compression of the blend, at the beginning of the plateau region, many molecules start to associate with their neighbors (alike or not) to form solidlike domains. If the molecules have enough time and mobility, they will rearrange, leaving the unstable solidlike domains of pure polyenantiomers to irreversibly form solidlike domains of stereocomplex. This implies that a long waiting time, a slower compression of the monolayer, or a greater chain mobility either due to a higher subphase temperature or a smaller molecular weight will favor the formation of the stereocomplex over the formation of pure polyenantiomer domains. This explains why the PM-IRRAS spectra of the high molecular weight blend published by Bourque et al.[35] exhibited the spectral features characteristic of the stereocomplex while its isotherm indicates that the stereocomplexation is not favorable for this system. Indeed, the long time necessary to the acquisition of spectra at several surface pressures, causing the spectrum of the monolayer at high surface pressure to be recorded several hours after the spreading of the polylactides solution, allows the high molecular weight poly(D- and L-lactides) to form the stereocomplex despite their low mobility.

Conclusions

The results shown in this paper demonstrate that poly(D-lactide) and poly(L-lactide) pure or in blend spontaneously form 10_3 helices at the air/water interface. The compression of monolayers of the pure polyenantiomers leads to a plateau region in the isotherm that corresponds to an equilibrium between 10_3 helices in the fluid parts of the monolayer and in solidlike domains. For the blend, the plateau region observed in the isotherm corresponds to an equilibrium between free 10_3 helices in the fluid phase, 10_3 helices in solidlike domains of pure polyenantiomers, and 3_1 helices in solidlike domains of PDLA/PLLA stereocomplex. In this case, the proportion of stereocomplex and pure polyenantiomers solidlike domains formed during the compression of the monolayer can be modulated by varying different experimental parameters such as the molecular weight of the polylactides, the subphase temperature, the compression rate, and the "incubation" time.

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