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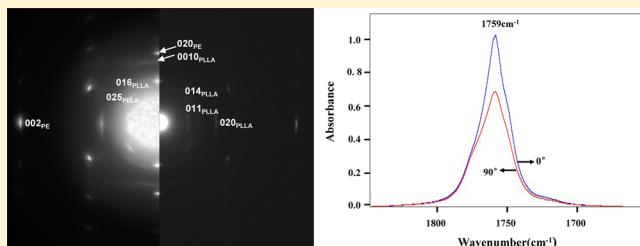
Origin of Epitaxial Cold Crystallization of Poly(L-lactic acid) on Highly Oriented Polyethylene Substrate

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ABSTRACT: Cold crystallization of poly(L-lactic acid) (PLLA) from amorphous state on highly oriented polyethylene (PE) substrate has been studied by electron diffraction and infrared spectroscopy. Both electron diffraction and infrared spectroscopy analyses show that the PLLA in the as-prepared PLLA/PE double layers is in the amorphous state. Annealing of the as-prepared PLLA/PE samples at 130 °C leads to the cold crystallization of PLLA. It is confirmed that the PLLA grown on the oriented PE surface exhibits high orientation with molecular chains aligned perpendicular to the chain direction of PE, indicating the occurrence of heteroepitaxy of PLLA on the PE substrate. This provides a first example of perpendicular chain orientation of polymer epitaxy. Moreover, it demonstrates the capability of polymer epitaxy from amorphous state through annealing. Infrared spectroscopy analysis on the as-prepared PLLA/PE double layers shows that the orientation of PLLA molecules in contact with the PE substrate exists already in the amorphous state. It is these oriented PLLA chains in amorphous phase that transform into crystal nuclei during cold crystallization and initiate the oriented overgrowth of PLLA on the PE substrate.



1. INTRODUCTION

Poly(L-lactic acid) (PLLA), an important environment friendly polymer, can be produced from renewable sources, such as corn, and readily degraded by hydrolysis under mild conditions to lactic acid, a common organic acid naturally presents in human body.^{1–3} It has attracted much attention because of many advantages in its intrinsic properties, such as its high mechanical performances comparable to those of commercial polymers, its melt-spin, and good film-forming abilities. But the use of PLLA as commodity polymer is limited due to several drawbacks, such as its brittleness.⁴ It is well documented that the mechanical properties and chemical stability of a crystalline polymer strongly depend on both the crystal structure and morphology.⁵ Therefore, the crystallization behavior of PLLA has been extensively studied.^{6–11} The PLLA can crystallize in different forms designated as α (with a disordered form referred to as α'), β , and γ with varying morphologies depending on the preparation conditions. The different phases exhibit diverse properties. In this case, the morphology and crystal structure control offers a possibility for regulating the properties of PLLA. It is, however, not sufficient in most cases. As a consequence, copolymerization of it with different comonomer units or blending it with different polymers are frequently adopted for a further improvement of its properties.^{12–16}

For polymer blends, the dependence of properties on the multiscale structures is even protruding. This rests on the existence of complicated phase structure which shows pronounced influence on the property of the materials and influences also the intrinsic multiscale structures of each

component.^{17–19} As an example, the blend systems with peculiar crystallographic interaction will result in the occurrence of heteroepitaxy between the polymer pairs, leading to the strictly fixed mutual orientation between the polymers. This provides us a useful way to control the crystal structure and orientation of a wide variety of semicrystalline polymeric materials.²⁰ The special orientation can cause synergistic effect on property modification.^{21–25} Therefore, there are a vast body of literatures that describe the epitaxial crystallization of polymers on different substrates. Great progress in understanding the mechanism of polymer epitaxy at a molecular level has already been achieved.^{26,27} It should be pointed out that most of the studies on polymer epitaxy focus mainly on the resultant mutual orientation relationship and its origin via atomic force microscopy, X-ray diffraction, and transmission electron microscopy combined with electron diffraction.^{28,29} When the polymer chains start to orient on the ordered substrate was, however, not concerned so much up to date. In our previous work, we found that the chain orientation of polycaprolactone (PCL) on the surface of highly oriented PE film starts already in the melt or supercooled melt, which initiates the oriented overgrowth of PCL on PE substrate during cooling and results in a parallel chain alignment of both polymers.³⁰ A recent study has demonstrated the epitaxy of PLLA cold crystallized from amorphous state on highly

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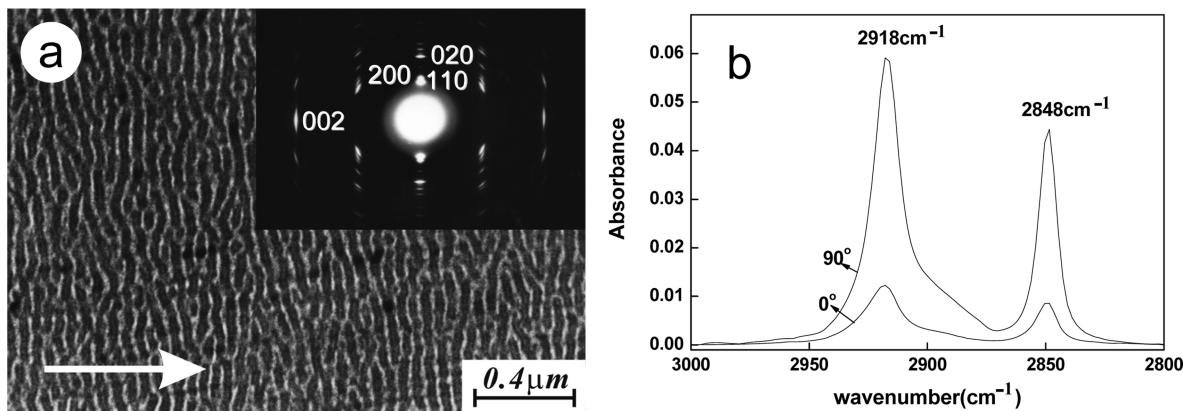


Figure 1. (a) BF electron micrograph and the corresponding electron diffraction pattern (inset of the BF image) of a melt-drawn PE thin film. The arrow indicates the drawing direction during film preparation. (b) Polarized FTIR spectra of a melt-drawn PE thin film in CH₂ stretching region with the electron vector perpendicular (90°) and parallel (0°) to the drawing direction, respectively.

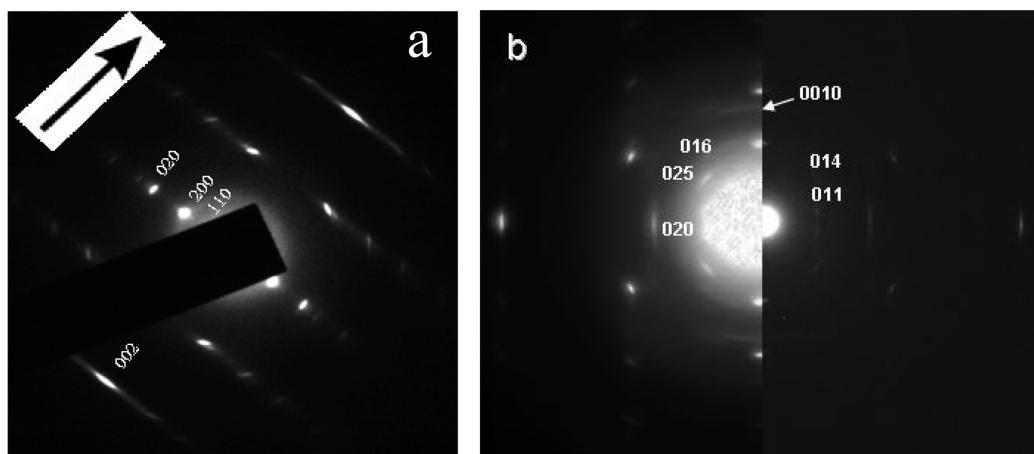


Figure 2. Electron diffraction patterns of a PLLA/PE double-layered thin film before (a) and after (b) the thermal treatment.

oriented PE film with molecular chains oriented perpendicular to the PE chain direction.³¹ This leads to the formation of an unusual structure with the PLLA crystalline lamellae connecting the crystalline and amorphous phase of the PE, and vice versa. In this kind of configuration, excellent mechanical properties are expected for the blend under the consideration that the amorphous mechanical weak regions of one component are bridged by the crystalline lamellae of the other component.^{21,22} Now the problem arises about when the PLLA chains start to align on the oriented PE film. In other words, we want to know whether there are already oriented PLLA chains in the amorphous solid before cold crystallization or not. To this end, the chain orientation status of amorphous PLLA on oriented PE substrate in the as-prepared double layers and after cold crystallization was studied in detail via Fourier transform infrared spectroscopy (FTIR), which is sensitive to both chain conformation and local molecular environment of a polymer.^{32–35} It is especially powerful for revealing the orientation of the molecular chains in the amorphous state, which cannot be done by diffraction technique due to the lack of periodic order.

2. EXPERIMENTAL SECTION

2.1. Materials. Commercial grade polylactide (PLLA), Revo-de213H, with weight-average molecular weight $M_w = 6.5 \times 10^5$ and polydispersity of 2.1 was obtained from Zhejiang Hisuan Bimaterials Co., Ltd. The glass transition temperature of it was estimated by DSC

as 59 °C. High-density polyethylene (PE 5000S) was obtained from Lanzhou Petrochemical, China. The melting point of the used PE is measured by DSC to be 135 °C.

2.2. Preparation. Highly oriented thin PE films were prepared according to a melt-draw technique introduced by Petermann and Gohil.³⁶ According to this technique, a small amount of a 0.5 wt % PE solution in xylene was dispersed uniformly on a preheated glass plate at 130 °C, where the xylene solvent was allowed to evaporate. After evaporation of the solvent, the thin molten PE layer of ca. 1 μm in thickness was then picked up by a motor-driven cylinder with a drawing speed of about 20 cm/s. In this way, highly oriented ultrathin PE films of ca. 50 nm in thickness have been obtained and used as the substrate for epitaxial crystallization of PLLA from its amorphous state.

PLLA/PE double-layered samples were prepared by spin-coating the PLLA on the highly oriented PE film at 2000 rpm for 30 s in air at room temperature. To regulate the thickness of the PLLA layer, 1 and 0.25 wt % chloroform solutions of PLLA were used to get thicker and thinner PLLA films, respectively. The thicknesses of the thus-prepared PLLA layers were estimated to be about 100 nm with a 1 wt % chloroform solution and less than 30 nm with 0.25 wt % chloroform solution. The obtained samples were dried in vacuum oven at 30 °C for 24 h. The double-layered samples were mounted onto 400 mesh copper grids for transmission electron microscopy (TEM) observation while onto KBr plates for infrared spectroscopy study. To promote the epitaxial crystallization of PLLA on the oriented PE film, the as-prepared PLLA/PE films were isothermally cold crystallized on a heating plate at 130 °C for 24 h.

2.3. Characterization. For FTIR analysis, a Spectrum 100 FT-IR spectrometer (PerkinElmer) was used. Polarized light was used

to identify the chain directions of PLLA and PE. FTIR spectra in the wavenumber range from 450 to 4000 cm⁻¹ were obtained by averaging 16 scans at a 2 cm⁻¹ resolution. For TEM observation, a JEOL JEM-2100 TEM operated at 200 kV was used in this study. In order to minimize radiation damage by the electron beam, focusing was carried out on an area, then the specimen film was translated to its adjacent undamaged area for recording the images immediately. Phase contrast bright-field (BF) electron micrographs were obtained by defocus of the objective lens.^{37–39}

3. RESULTS AND DISCUSSION

The orientated structure of the used melt-drawn PE thin films was first characterized by TEM and FTIR. Representative BF

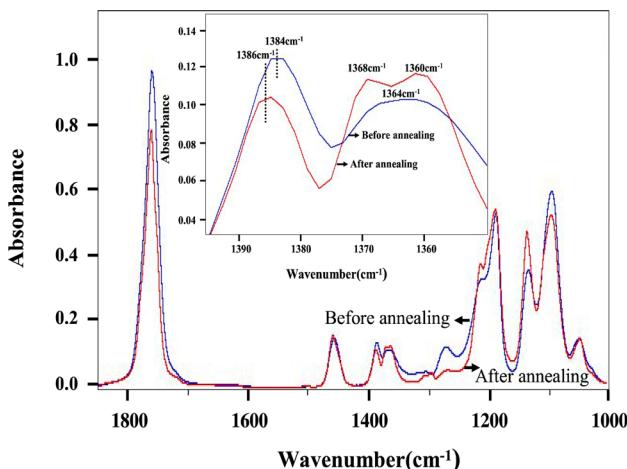


Figure 3. FTIR spectra of PLLA/PE double-layered thin films in the region of 1860–1000 cm⁻¹ before and after the heat treatment as indicated. The enlarged spectral region of 1400–1350 cm⁻¹ is plotted in the inset.

Table 1. Band Assignments of Amorphous and Semicrystalline PLLA

wavenumbers (cm ⁻¹)			
amorphous	semicrystalline	polarization	assignments ^a
2995	2997	⊥	$\nu_{as}(CH_3)$
2945	2946	unclear	$\nu_s(CH_3)$
1757	1759	⊥	$\nu(C=O)$
1454	1458		$\delta_{as}(CH_3)$
1384	1386	⊥	$\delta_s(CH_3)$
1364	1368		$\delta(CH)$, CH wagging (blending)
	1360	⊥	
1268	1268	none	$\nu(CH) + \nu(COC)$
1212	1215	⊥	$\nu_{as}(COC) + \gamma_{as}(CH_3)$
1183	1187		$\gamma_s(CH_3) + \nu_s(COC)$
1133	1133	none	$\gamma_s(CH_3)$
1090	1090		$\nu_s(COC)$
1044	1044	none	$\nu(C-CH_3)$

^a δ = deformation vibration; γ = in-plane rocking vibration; ν = stretching vibration; s = symmetric; as = asymmetric.

electron micrograph and corresponding electron diffraction pattern (inset of the BF image) shown in Figure 1a illustrate the high orientation of the melt-drawn PE thin films. From the BF electron micrograph, we can clearly see edge-on lamellae aligned perpendicular to the drawing direction, indicating an uniaxial orientation with the molecular chains aligned in the drawing direction. The appearance of sharp and well-defined

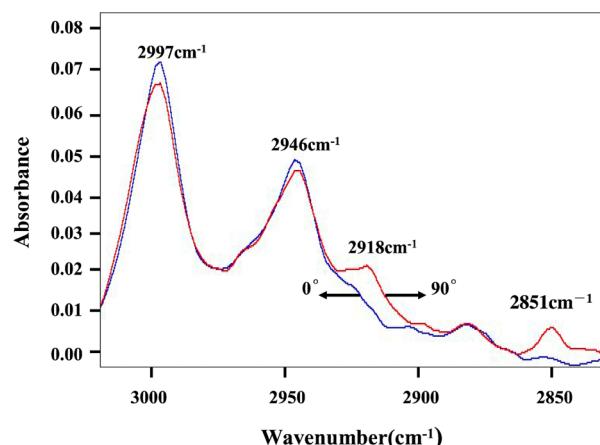


Figure 4. Polarized FTIR spectra of the PLLA/PE double-layered sample in the 3050–2800 cm⁻¹ region with the electron vector perpendicular (denoted as 90°) and parallel (denoted as 0°) to the PE drawing direction, respectively. The PLLA/PE double-layered sample has been annealed at 130 °C for 24 h.

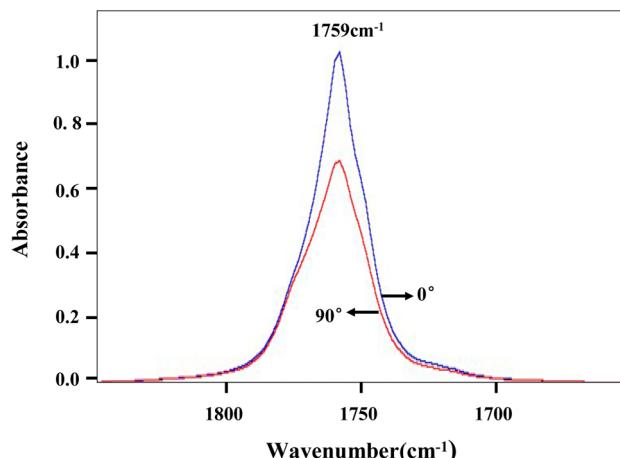


Figure 5. Polarized FTIR spectra of the PLLA/PE double-layered sample in the 1850–1650 cm⁻¹ region with the electron vector perpendicular (denoted as 90°) and parallel (denoted as 0°) to the PE drawing direction, respectively.

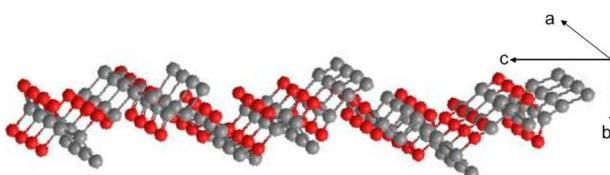


Figure 6. Sketch illustrating the topology of 10₃ PLLA helical chains in the (100) lattice plane.

reflection spots in the electron diffraction pattern confirms the existence of high orientation. The alignment of the (002) diffraction spots along the drawing direction of the sample reflects an orientation with the molecular chain axis in the film plane and along the drawing direction. The coexistence of the (200), (020), and many other (*hk*0) reflection spots in the meridian direction of the diffraction pattern further indicates a high degree of fiber orientation with the crystallographic *a*- and *b*-axes rotated randomly around the *c*-axis.³³ Similar orientation feature of the highly oriented PE thin films is also demonstrated by polarized FTIR spectra, which show different absorption

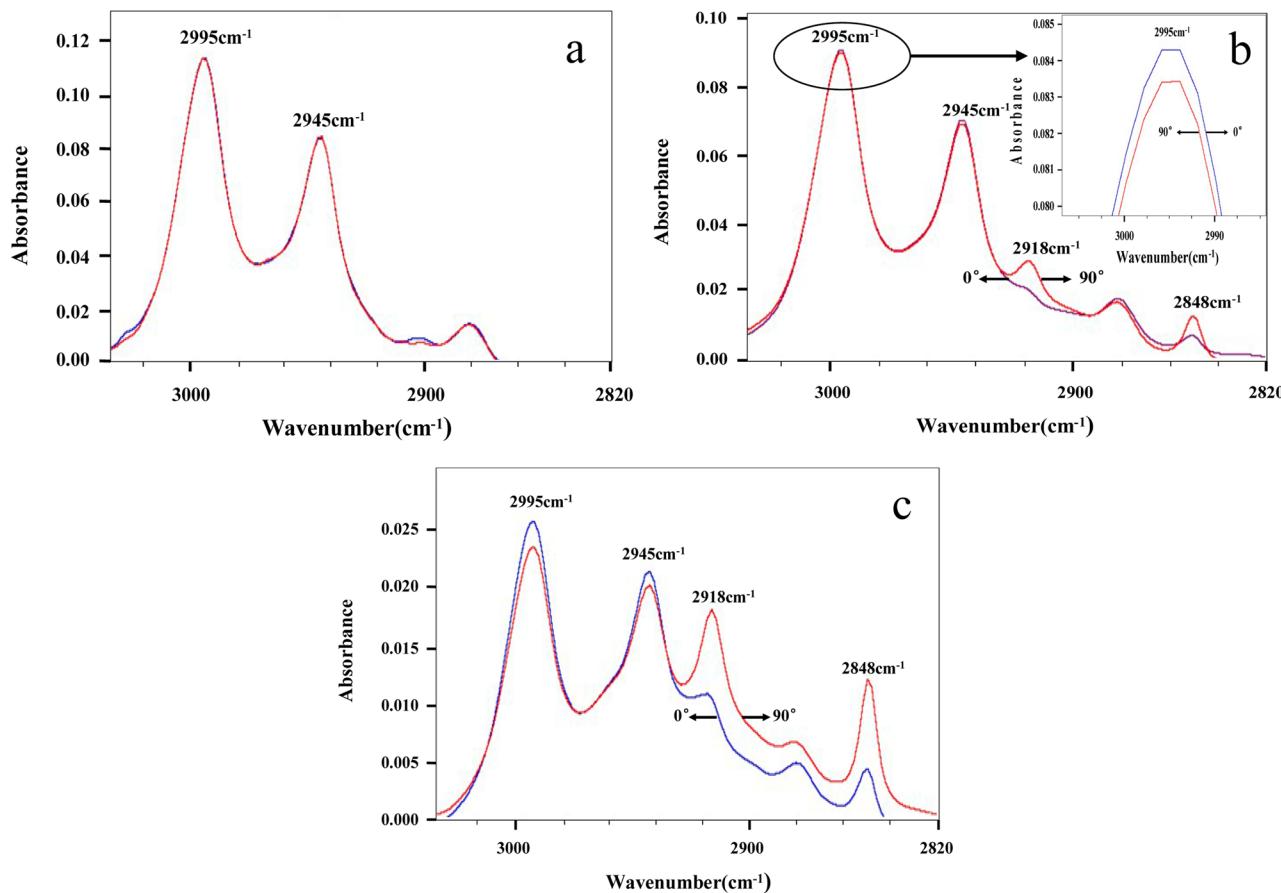


Figure 7. Polarized FTIR spectra of the as-prepared (a) PLLA and (b and c) PLLA/PE double-layered samples in the $3050\text{--}2820\text{ cm}^{-1}$ region with the electron vector perpendicular (denoted as 90°) and parallel (denoted as 0°) to the PE chain direction (b and c), respectively. The concentrations of the solution used for spin-coating the PLLA thin films were 1 wt % for (a and b) and 0.25 wt % for (c). An enlarged part of the 2995 cm^{-1} band is inserted in (b).

intensities of the bands with the electron vector perpendicular and parallel to the main chain direction. As an example, the polarized FTIR spectra of the melt-drawn PE thin films with the electron vector perpendicular “indicated as 90° ” and parallel “described as 0° ” to the drawing direction in the wavenumber range from 2800 to 3000 cm^{-1} are presented in Figure 1b. Clearly, the absorption intensities of the bands at 2918 and 2848 cm^{-1} with perpendicular polarization are much higher than that with parallel polarization. Considering that the bands at 2918 and 2848 cm^{-1} represent the total asymmetric and symmetric CH_2 stretching vibrations of the molecular chains and exhibit perpendicular transition moments with respect to the main chain of PE, the different absorptions of these bands imply unambiguously a parallel alignment of the PE chains along the drawing direction.^{34–36}

From the above discussion, we can see that both the electron microscopy and polarized FTIR spectroscopy results demonstrate that the melt-drawn PE thin films are highly oriented with molecular chains aligned in drawing direction. It should be pointed out that there is an advantage by using polarized FTIR to characterize the molecular chain orientation of polymers. While the electron diffraction provides us only the information about the chain orientation of PE in its crystalline phase, polarized FTIR results tell us the orientation status of the PE chains both in amorphous and crystalline phases. This is of great importance for disclosing the chain orientation of polymers in amorphous state, e.g., before crystallization,

which is impossible by the diffraction technique. Therefore, a comparison between the electron microscopy and polarized FTIR spectroscopy studies about the epitaxial cold crystallization of PLLA on highly oriented PE substrate from the amorphous state is performed.

Figure 2 shows the electron diffraction patterns of a PLLA/PE double-layered film before and after thermal treatment. From Figure 2a, it is clear that there is only electron diffraction spots of oriented PE substrate before thermal treatment. The absence of PLLA diffraction indicates that the PLLA in the as-prepared PLLA/PE double layers is amorphous. In other words, the crystallization of PLLA during spin-coating process does not take place. The electron diffraction pattern shown in Figure 2b indicates the occurrence of PLLA crystallization during the annealing process at $130\text{ }^\circ\text{C}$. The appearance of sharp and well-defined reflection spots of PLLA superimposed on the electron diffraction pattern of the PE substrate reveals an oriented crystallization of PLLA on the PE substrate; i.e., the PLLA grows from amorphous state epitaxially on the PE substrate. As mentioned in the Introduction, the PLLA can crystallize in three different modifications (α , β , and γ forms) depending on the preparation conditions.^{6–42} The reflection spots of the PLLA appeared in the electron diffraction pattern have all been accounted for by an orthorhombic unit cell with axes $a = 1.06\text{ nm}$, $b = 0.61\text{ nm}$, and $c = 2.88\text{ nm}$ as proposed by De Santis and Kovacs in 1968.⁶ This means that the PLLA crystallized on the PE substrate in its α -form. Moreover, the

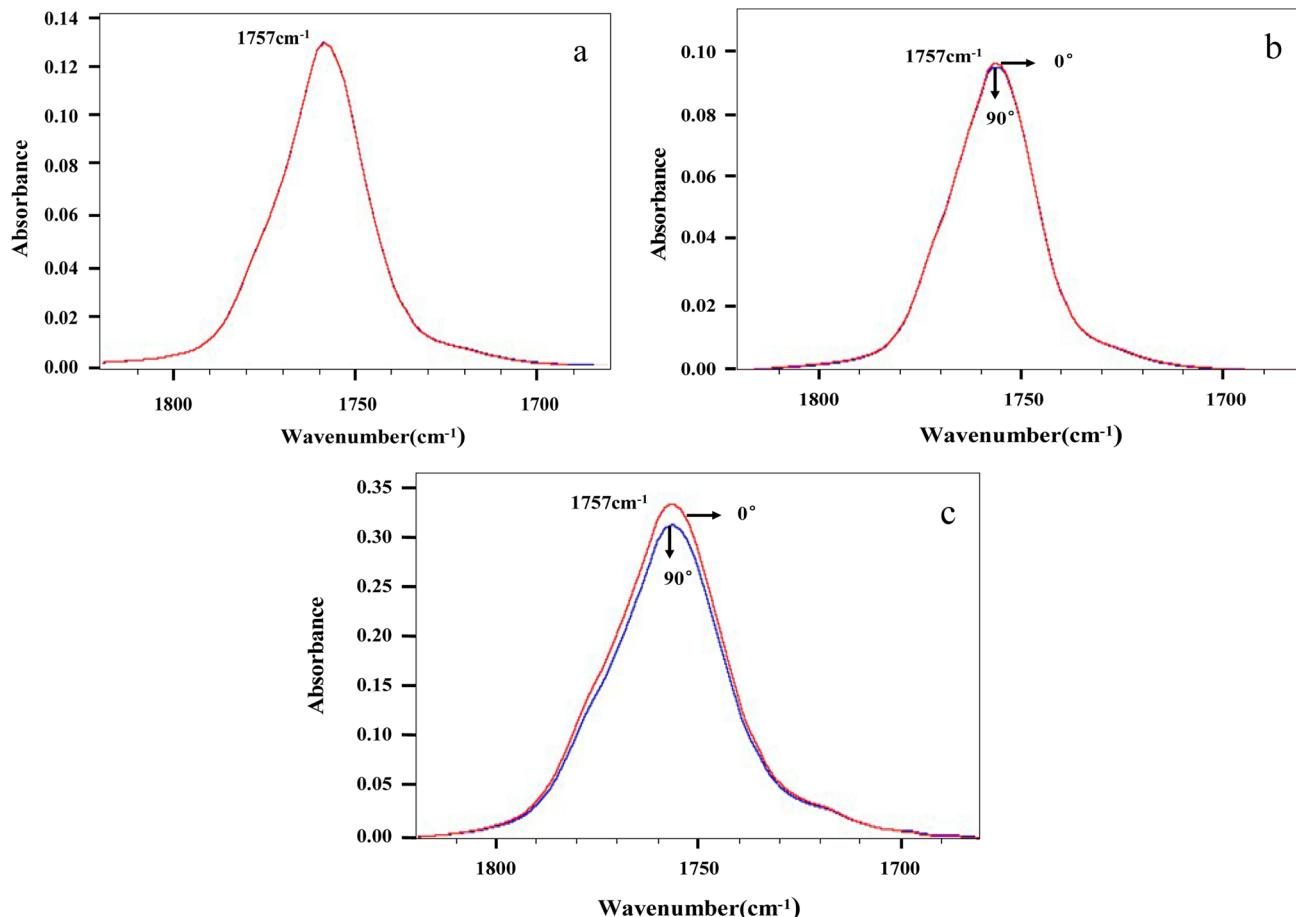


Figure 8. Polarized FTIR spectra of the as-prepared (a) PLLA and (b and c) PLLA/PE double-layered samples in the $1820\text{--}1680\text{ cm}^{-1}$ region with the electron vector perpendicular (denoted as 90°) and parallel (denoted as 0°) to the PE chain direction (b and c), respectively. The concentrations of the solution used for spin-coating PLLA thin films are 1 wt % for (a and b) and 0.25 wt % for (c).

alignments of the PLLA (020) diffraction spots along the (002) reflection of the PE and the (0010) PLLA diffraction spots in the meridian direction of the PE diffraction pattern indicate an epitaxial crystallization of PLLA on PE substrate with molecular chains arranged perpendicular to each other. The (100) lattice plane of the PLLA is in contact with the PE substrate surface.

The epitaxial crystallization of PLLA on the PE substrate is also confirmed by the FTIR analysis. It was reported that two regions of the FTIR spectra are very sensitive to the structural changes during crystallization of PLLA. One is the C=O stretching vibration region of $1860\text{--}1660\text{ cm}^{-1}$, while the other is the region of $1500\text{--}1000\text{ cm}^{-1}$ which involves the CH₃, C-H bending, and C-O-C stretching vibrations. The spectral change of the C-H stretching vibration in the high wavenumber region of $3000\text{--}2800\text{ cm}^{-1}$ is reported to be relatively small after crystallization. However, the bands at 2918 and 2848 cm^{-1} of PE corresponding to the total asymmetric and symmetric CH₂ stretching vibrations with perpendicular transition moments were selected to characterize the chain orientation of PE. For a direct comparison of the chain orientation of the PLLA with respect of the oriented PE substrate, the FTIR spectra in the region of $3000\text{--}2800\text{ cm}^{-1}$ is also used in this study.

Figure 3 shows the FTIR spectra of PLLA/PE double-layered thin films before and after the heat treatment in the region of $1860\text{--}1000\text{ cm}^{-1}$. It can be seen that the FTIR spectra of PLLA/PE double-layered thin films are different before and

after annealing at $130\text{ }^\circ\text{C}$. The published band assignments are summarized in Table 1.^{43–46} From Figure 3, we can see some changes of the bands before and after heat treatment. The band around 1454 cm^{-1} , which is assigned to the CH₃ asymmetric deformation mode,⁴⁶ appears in the spectrum of the as-prepared sample. It is noted that this band shows a small high-wavenumber shift from 1454 to 1458 cm^{-1} and intensity increase after thermal treatment. The high-wavenumber shift of this band is associated with the development of the crystalline phase.⁴⁴ From the enlarged inset of Figure 3, it can be seen that the band around 1384 cm^{-1} corresponding to the CH₃ symmetric deformation has been shifted to 1386 cm^{-1} by heat treatment. This again indicates the occurrence of PLLA crystallization. Moreover, the band around 1364 cm^{-1} in the amorphous state is split into two bands at 1368 and 1360 cm^{-1} , which associated with the combination of $\delta_s(\text{CH}_3)$ and $\delta(\text{CH})$. The bands in the $1300\text{--}1000\text{ cm}^{-1}$ region are assigned to the C-O-C stretching region. Although bands in this region are heavily overlapped (see Figure 3), pronounced spectral bands changes after thermal treatment could be observed. According to the literatures,^{21,27} the bands at 1183 and 1212 cm^{-1} of the amorphous PLLA are assigned to the combination of $\nu_{as}(\text{C}-\text{O}-\text{C})$ and $\gamma_{as}(\text{CH}_3)$. From Figure 3, it can be seen that the band at 1212 cm^{-1} shifts to 1215 cm^{-1} after thermal treatment, whereas the band at 1183 cm^{-1} shifts to 1187 cm^{-1} . The bands around 1133 and 1089 cm^{-1} , corresponding to the $\gamma_s(\text{CH}_3)$ and $\nu_s(\text{COC})$, respectively, appear in both the amorphous and

crystalline states. These bands located at the same place but with different intensities. All of the above-mentioned spectral changes indicate that the PLLA in the as-prepared sample is initially in the amorphous state but transforms into crystalline state by annealing at 130 °C for 24 h through cold crystallization. This is well in agreement with the electron diffraction results.

To check the orientation status of PLLA crystallized on highly oriented PE substrate, polarized FTIR spectra were recorded for the PLLA/PE sample annealed at 130 °C. For a direct comparison of the chain orientation of PLLA and PE, the polarized FTIR spectra with the electron vector perpendicular and parallel to the drawing direction of the melt-drawn PE thin films in the wavenumber range from 2800 to 3000 cm⁻¹ are presented in Figure 4. It can be seen that the absorption intensities of the FTIR band at 2918 cm⁻¹ characteristic for PE with perpendicular polarization is higher than that with parallel polarization. This is in accordance with the result of Figure 1b and indicates a parallel alignment of the PE chains along the drawing direction during sample preparation. Instead, the absorption intensities of the FTIR band at 2997 cm⁻¹ corresponding to the PLLA with perpendicular polarization is lower than that with parallel polarization. Considering that the FTIR band at 2997 cm⁻¹ represents the asymmetric CH₃ stretching vibration with a perpendicular transition moment related to the main chain of PLLA, the different absorption intensity change of the 2997 cm⁻¹ band implies a perpendicular alignment of the PLLA chains with respect to PE chain direction. Moreover, the transition moment of the FTIR band at 2946 cm⁻¹ corresponding to the symmetric CH₃ stretching vibration has not been reported in the literature. From Figure 4, the similar intensity change of this band together with the 2997 cm⁻¹ band leads to the conclusion that the 2946 cm⁻¹ band exhibits also a perpendicular transition moment.

The polarized FTIR spectra of PLLA/PE sample annealed at 130 °C for the stretching vibration of C=O groups show the same result. As presented in Figure 5, the absorption intensity of the band at 1759 cm⁻¹ with parallel polarization is much higher than that with perpendicular polarization. Since this band exhibits also a perpendicular transition moment with respect to the PLLA main chain, the different absorptions of this band further confirm a perpendicular orientation of the PLLA and PE chains.

On the basis of above electron diffraction and FTIR analyses, it is concluded that crystallization of PLLA on the oriented PE substrate from the amorphous glassy state leads to the occurrence of epitaxy. The epitaxial crystallization produces an oriented structure of PLLA on the PE substrate with the molecular chains of both polymers aligned perpendicular. It should be pointed out that the mutual chain orientation relationship of PLLA/PE system is different from that of the PCL/PE system, where parallel chain alignment of both polymers is observed. The different chain orientation is related to the specific crystallographic interaction between the polymer pairs. For the PCL/PE system, both polymers are similar in chemical structure and the planar zigzag chains packed in the almost identical orthorhombic unit cells with slightly varied unit cell parameters ($a = 0.736$, $b = 0.492$, and $c = 0.253$ nm for PE⁴⁷ and $a = 0.747$, $b = 0.498$, and $c = 1.705$ nm for PCL⁴⁸). In this case, perfect matching can be found between every corresponding (h k l) lattice planes of the PCL and PE. This leads to a parallel chain alignment of both polymer chains. On the other hand, the PLLA chains packed in the orthorhombic

unit cell exhibit a 10₃ helical chain conformation. Therefore, interchain distance matching can hardly be found between the PLLA and PE. However, as sketched in Figure 6, the helical conformation of PLLA chains compose grooves in its (100) lattice plane and perpendicular to the chain axis. The inlay of PE chains in the grooves may provide a favorable interaction between the PLLA and PE. Moreover, the interchain distances of PE along *a*-axis (0.74 nm) and *b*-axes (0.494 nm) match the interplanar distances of (004)_{PLLA} (0.72 nm) and (006)_{PLLA} (0.48 nm) very well. The mismatches are only 2.7% and 2.8%, respectively. As a result, a perpendicular chain orientation is obtained.

There is another unsolved problem about when start the alignment of PLLA chains in the perpendicular direction of the PE chain. In other words, whether there are already oriented chains of PLLA in the amorphous phase or not. This will provide different crystallization scenarios about the epitaxial cold crystallization of PLLA on the PE substrate. If some PLLA chains oriented perpendicular to the chain direction of PE in the as-prepared sample due to intermolecular interaction, these oriented PLLA chains will act as "prenuclei". The prenuclei can transform into stable crystal nuclei which initiate fold chain lamellae growth with high orientation in the subsequent cold crystallization process. Otherwise, the alignment of the PLLA chains in the random coil amorphous state should start in the nucleation process during cold crystallization. To find out the origin of epitaxial cold crystallization of PLLA on oriented PE substrate, the orientation status of PLLA in the as-prepared sample, i.e., in amorphous phase, has been followed by polarized FTIR.

Figure 7 presents the polarized FTIR spectra of spin-coated PLLA thin films with and without PE substrate in the 3050–2820 cm⁻¹ region. The appearance of 2995 and 2945 cm⁻¹ bands instead of the 2997 and 2946 cm⁻¹ bands indicates that the PLLA thin films with and without PE substrate are all in the amorphous state. From Figure 7a, the identical band position and height of these bands with parallel and perpendicular polarizations demonstrate the lack of chain orientation in the pure PLLA spin-coated thin film. Figure 7b presents the polarized FTIR spectra of PLLA spin-coated on oriented PE film from a 1 wt % PLLA/chloroform solution. It can be seen that the PE substrate film exhibits a high orientation as judged from the different intensities of the 2918 cm⁻¹ band under parallel and perpendicular polarizations. With close inspection, different intensities of the 2995 and 2945 cm⁻¹ bands with parallel and perpendicular polarizations can also be identified. The difference can be more clearly observed in the enlarged inset of Figure 7b. This indicates that a small amount of PLLA chains in the amorphous state are already oriented in the direction perpendicular to the PE chain. Considering that the chain orientation of PLLA in the amorphous state on the PE substrate reflects the intermolecular interaction between them, these oriented PLLA chains should exist only in a very thin layer directly in contact with the PE substrate. Therefore, the difference in band intensity of the spin-coated film from a 1 wt % PLLA/chloroform solution should be limited since a thick unoriented PLLA layer covered on the thin oriented layer shows stronger absorption. To magnify the band intensity difference of the oriented PLLA chains, thinner PLLA film was spin-coated from a 0.25 wt % PLLA/chloroform solution on the surface of oriented PE substrate. As shown in Figure 7c, now the total absorption is really reduced to ca. 1/4 of the sample prepared with 1 wt % PLLA/chloroform solution. In

this case, the intensity differences of the 2995 and 2945 cm^{-1} bands with parallel and perpendicular polarizations can be clearly observed. This leads to the conclusion that there is a very thin oriented PLLA layer in contact with the PE substrate. It is these oriented PLLA chains in amorphous state that trigger the oriented cold crystallization of PLLA on the PE substrate, i.e., the cold epitaxial crystallization.

The analysis of the polarized FTIR spectra of PLLA/PE as-prepared samples in the stretching vibration region of C=O groups provides a similar result. As shown in Figure 8, the absorption band appeared at 1757 cm^{-1} instead of 1759 cm^{-1} demonstrates that the PLLA in the as-prepared samples are in amorphous state regardless whether they are on the KBr plate or on the PE oriented thin films. The totally overlapping of the FTIR bands with parallel and perpendicular polarizations in Figure 8a indicates the random orientation of the as-prepared pure PLLA sample. The existence of a very thin oriented PLLA layer spin-coated on the PE substrate is reflected by a tiny intensity difference of the bands with parallel and perpendicular polarizations (see Figure 8b). This difference has been well illustrated by a reduction of the spin-coated PLLA layer as shown in Figure 8c.

4. SUMMARY

In summary, cold crystallization of PLLA from the amorphous state on a highly oriented PE film has been studied by electron diffraction and infrared spectroscopy. The electron diffraction pattern of the as-prepared PLLA/PE double layers shows only the electron diffraction spots of oriented PE substrate, indicating the PLLA in the as-prepared PLLA/PE double layers is in amorphous state. After annealing at 130 °C, the crystallization of PLLA takes place. The appearance of well-defined PLLA diffraction spots indicates the occurrence of epitaxy of PLLA on the PE substrate. Analysis of the superimposed diffraction pattern indicates that the epitaxial crystallization of PLLA on highly oriented PE substrate results in the formation of α -PLLA crystals with molecular chains aligned perpendicular to the chain direction of PE substrate crystals. Infrared spectroscopy analysis confirms that the PLLA in the as-prepared PLLA/PE double layers is in the amorphous state. After thermal treatment, the PLLA crystals grown on the oriented PE surface exhibit a high degree of orientation with molecular chains aligned perpendicular to the chain direction of PE substrate. This provides a first example of perpendicular chain orientation of polymer epitaxy and demonstrates the capability of polymer epitaxy from amorphous state. Further infrared spectroscopy analysis on the as-prepared PLLA/PE double layers shows that the orientation of PLLA molecules in contact with the PE substrate starts already in the amorphous state during sample preparation. It is these oriented PLLA chains in amorphous phase that transform into crystal nuclei during cold crystallization and initiate the oriented overgrowth of PLLA on the PE substrate with both polymer chains perpendicular.

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Notes

The authors declare no competing financial interest.

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