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Study on Phase Transformation Behavior of Strain-induced PLLA Mesophase by Polarized Infrared Spectroscopy

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Abstract The structural transformation of mesophase to crystalline phase of strain-induced poly(L-lactic acid) has been investigated by differential scanning calorimetry (DSC) and *in situ* temperature dependent polarized Fourier transform infrared (FTIR) spectroscopy. It is found that, as the drawing temperature increases, melting of strain-induced mesophase in the heating process can remarkably interfere the crystallization behavior subsequently. Coupling with *in situ* polarized FTIR, from 60 °C to 76 °C, the mesophase melts partially rather than completely melting, and changes immediately to three-dimensional ordered structure. Of particular note, through monitoring the subtle spectral change in the critical phase transformation temperature from 60 °C to 64 °C, it is clearly demonstrated that relaxation of oriented amorphous chains initially takes place prior to the melting of mesophase.

Keywords Structural transformation; Mesophase; Strain-induced; Polarized IR spectroscopy

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INTRODUCTION

Mesophase of polymers, which has an intermediate order between amorphous and crystalline phases, has drawn great attention in recent years.^[1–15] There are different descriptions on the structure of mesophase in the literature: smectic,^[16–18] paracrystal,^[19,20] microcrystal,^[21] condic crystal,^[22] and nano crystal.^[23] In recent years, scientists are prone to describe the structure as mesophase or mesomorphic phase.^[1,23,24] In view of the formation approach, they can be divided generally into two categories, *i.e.* quench-induced mesophase and deformation-induced mesophase. Melt-quenching polymer with high cooling rate is a common path to generate mesophase in extensive work concerning the formation conditions of *i*PP mesophase, morphological structure, and thermal stability.^[5–8] By means of a deformation-induced approach, mesophase in isotactic poly(propylene),^[23,24] poly(diethysiloxane),^[25] poly(ethylene terephthalate),^[26,27] and poly(ethylene naphthalate)^[28] has been found and studied in detail.

As one of the most promising semicrystalline bio-plastics, poly(L-lactic acid) (PLLA) exhibited better mechanical properties compared to traditional plastics to some extent^[29,30] and its chains can be organized into different spatial arrangements, giving rise to such basic crystalline crystals as α , α' , β , and γ .^[31–37] But recently, Stoclet *et al.*^[38,39] found for the first time that cold-drawing induced PLLA can generate

mesophase around T_g (45–70 °C) in amorphous and ascribed a characteristic IR band at 918 cm^{-1} to PLLA mesophase. Similar to what has been observed in the melt-quenched *i*PP, Zhang *et al.*^[40] identified PLLA mesophase from quenched PLLA-PEG-PLLA block copolymer. They found that PLLA mesophase is less thermally stable than the ordered α phase and even the disordered α phase (α') of PLLA. Tashiro *et al.*^[41,42] investigated the melt-crystallization process of PLLA and proposed the crystallization to α' or α phase *via* the mesophase from the melt. By using polarized FTIR, Lv *et al.*^[43] concluded that only part of mesophase endures melting especially in the highly stretched sample during heating process, as a result of the early advent of strain-induced crystallization. As such, it is *a priori* assumed that mesophase acts as the precursor for strain-induced crystallization. Nonetheless, the exact mechanism of the strain-induced PLLA mesophase-crystalline phase transition on heating is not well-explored yet. From the standpoint of its academic interest and industrial application, an investigation on mesophase of polymers as a kind of aggregation state is intensely significative.

In our previous work, we made initial observation of the transient structure in PLLA mesophase with various drawing ratios (λ) from 1 to 6 in melt-quenched PLLA films above T_g and established the correlation between the band positions for this characteristic backbone vibration mode (located around 918–922 cm^{-1}) and the distance of interchain packing of PLLA chain by WAXD and FTIR.^[44] To our knowledge, polarized Fourier transform infrared spectroscopy, which is sensitive to the local molecular environment

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and the orientation of molecular chains, is adopted to monitor the structural change with respect to condensed phase structure of polymer. Accordingly, in the present work, depending on DSC and *in situ* polarized IR measurement, we monitor the phase transition and structural rearrangement of PLLA mesophase on line with the drawing ratio of $\lambda = 3$, which contains only amorphous phase and mesophase rather than crystalline phase, as a function of temperature. The central issue we address in the present paper is to clarify the transition mechanism of strain-induced PLLA mesophase to the ordered crystal phase.

EXPERIMENTAL

Material and Sample Preparation Procedure

PLLA sample used in this study ($M_w = 1.1 \times 10^5 \text{ g}\cdot\text{mol}^{-1}$, $M_n = 4.5 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$) was obtained from Mitsubishi Plastic Co. Ltd. (Japan). Amorphous PLLA films were prepared by compression molding at 190 °C for 5 min at molten state and quenched into ice water subsequently. The samples with 2 cm in length and 5 mm in width were cut out from such melt-quenched films. Then the PLLA films were drawn separately at $T_d = 60, 65$, and 70 °C above glass transition temperature (around 58 °C) in a DMA machine, which was equipped with the crosshead speed about 50 mm·min⁻¹ in a temperature-regulated oven. Parallel ink marks were printed along the sample in order to determine the draw ratio, $\lambda = L/L_0$, where L and L_0 are the intervals of the marks after and prior to the drawn direction, respectively. The uniaxially-oriented samples with $\lambda = 3$ and drawn temperature $T_d = 60, 65$, and 70 °C were prepared. The thickness of the as-prepared films was about 40 μm .

Differential Scanning Calorimetry (DSC)

DSC measurement was performed on a TA Q20 calorimeter under flowing nitrogen at a heating rate of 10 °C·min⁻¹. About 3 mg of sample was sealed in an aluminum pan and equilibrated at 20 °C prior to measurement.

Fourier Transform Infrared Spectroscopy (FTIR)

Polarized FTIR spectra were recorded on a Bruker tensor 27 spectrometer equipped with a DTGs detector and a wire-grid polarizer. The normal transmission mode was employed for IR measurement. To study the thermal behavior of as-drawn PLLA *via in situ* FTIR, the as-prepared film on KBr substrate was set on a Harrick variable temperature cell, which was placed into sample compartment of the spectrometer. Subsequently, the sample was heated at a rate of 2 °C·min⁻¹ from room temperature to 180 °C in a nitrogen atmosphere. During the heating process, FTIR spectra of the specimen were recorded at a 1 min interval from 30 °C to 180 °C. The spectra were obtained by co-adding 32 scans at a resolution of 2 cm⁻¹.

RESULTS AND DISCUSSION

Thermal Behavior of PLLA Mesophase Prepared under Different Drawing Temperatures

Fig. 1 shows the DSC heating traces of different oriented samples with various drawing temperatures (T_d) at the

drawing ratio of $\lambda = 3$. A sharp endothermic peak of mesophase above PLLA T_g (≈ 58 °C) was observed in each sample, which is metastable, and with heating from 65 °C to 110 °C, it undergoes a transformation into the thermodynamically stable crystalline α' or α form. It should be noted that, as the drawing temperatures elevate, this endothermic peak shifts gradually to a bit higher temperature from 68 °C to 71 °C, indicating that the higher drawing temperature may cause more stable mesophase. Subsequently, it is found that not only the exothermic peak corresponding to initial cold crystallization is in advance, but also the peak width narrows as the drawing temperature increases. Therefore, we speculated that the strain-induced mesophase serving as nucleating agent can promote the crystallization kinetic of PLLA. It is interesting to find that, only under the condition of $T_d = 60$ °C, a small exothermic peak about 150 °C is prior to the melt peak of crystallization, which proves that the mesophase changes into α' form instead of directly transforming to α form at the higher drawing temperature.

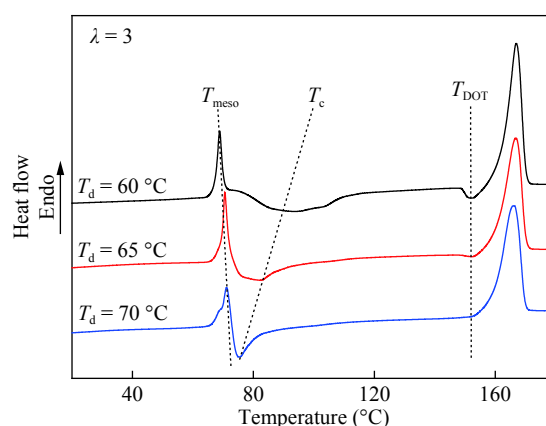


Fig. 1 DSC curves of draw temperature $T_d = 60, 65$, and 70 °C at drawing ratio $\lambda = 3$ of PLLA samples, respectively

Comparison of Polarized Spectra of PLLA in Different Condensed States

PLLA presents a very complex polymorphic behavior that can give rise to various polymorphs, so Fig. 2 shows the polarized IR spectra of α , α' , and mesophase in the C—C backbone vibration region for comparison. In the spectral region of the polarized IR spectra, the α and α' forms are highly similar to each other. However, the spectrum of mesophase is slightly different from those of α and α' crystals. The perpendicular bands of 918 and 708 cm⁻¹ have been identified in the PLLA mesophase, which are different from the characteristic bands at 921 and 689 cm⁻¹ for the α and α' forms. To our knowledge, the band at 921 cm⁻¹ is assigned to the coupling of C—C backbone stretching with the CH₃ rocking mode, in correlation with the 10/3 helix chain conformation of PLLA. Therefore, in comparison with the α or α' form, chain conformation packing of strain-induced mesophase is less ordering.

Phase Transition in the Heating Process of Mesophase Investigated by Polarized Temperature-dependent IR Spectroscopy

Given that the characteristic band at 918 cm⁻¹ is ascribed to

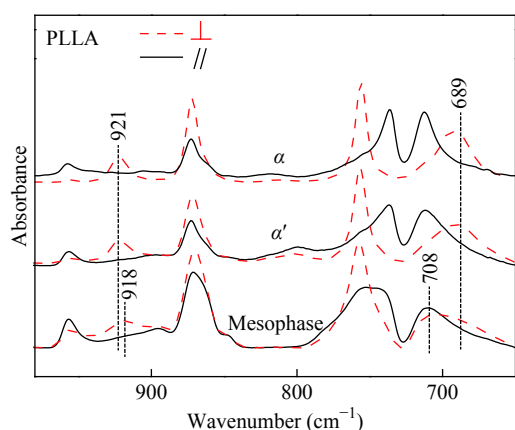


Fig. 2 Polarized IR spectra of three kinds of PLLA samples (α , α' and mesophase)

perpendicular band of the C—C backbone stretching vibration in the 980–820 cm^{-1} region, perpendicular temperature-dependent IR spectra of the strain-induced PLLA mesophase during the heating process from 30 $^{\circ}\text{C}$ to 180 $^{\circ}\text{C}$ are displayed in Fig. 3. With the drawing temperature $T_d = 65$ $^{\circ}\text{C}$ and drawing ratio $\lambda = 3$, an obvious spectral change that the characteristic mesophase band of PLLA at 918 cm^{-1} shifts to the characteristic α/α' band at 921 cm^{-1} within the region can be observed.

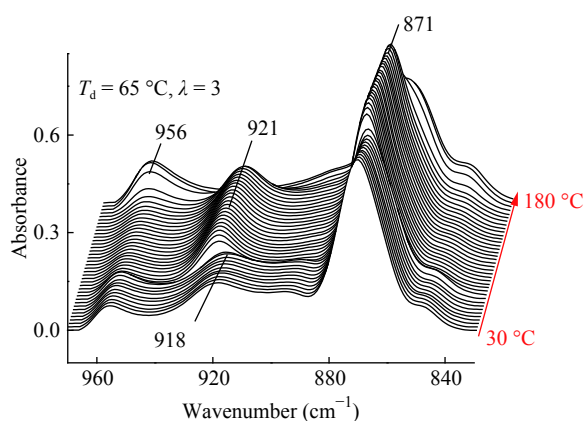


Fig. 3 Perpendicular IR spectral evolution of strain-induced PLLA ($T_d = 65$ $^{\circ}\text{C}$, $\lambda = 3$, heating rate = 2 $^{\circ}\text{C}\cdot\text{min}^{-1}$) during the heating process from 30 $^{\circ}\text{C}$ to 180 $^{\circ}\text{C}$ in the region of the C—C backbone vibration. The spectra are arranged with a 2 $^{\circ}\text{C}$ interval.

To quantitatively analyze the spectral changes, the other two crystallization-sensitive bands at 955 and 871 cm^{-1} as well as 921 cm^{-1} in this region are plotted as a function of temperature in Fig. 4. As shown in Fig. 4(b), by monitoring the intensity changes of the mesophase characteristic band at 921 cm^{-1} and the amorphous band at 956 cm^{-1} , there are remarkably spectral changes involving two melting and one crystallization processes in the whole temperature range from 30 $^{\circ}\text{C}$ to 180 $^{\circ}\text{C}$, that is, a relatively slight melting process around 64 $^{\circ}\text{C}$ and a major melting process around 170 $^{\circ}\text{C}$. The characteristic band intensity at 918 cm^{-1} of mesophase decreases abruptly at the temperature of 64 $^{\circ}\text{C}$, indicative of the melt of mesophase. In the meantime, the in-

tensity of amorphous band at 956 cm^{-1} firstly increases, and then decreases as a result of cold-crystallization. It should be noted that, compared to the intensity of 918 cm^{-1} band, the change of the intensity of 956 cm^{-1} band is more intense, which mainly gives rise to the relaxation of oriented amorphous chains. Moreover, Fig. 4(a) shows that in contrast to the decreasing intensity of the mesophase characteristic band at 918 cm^{-1} , the intensity of crystalline band at 871 cm^{-1} increases rather than decreases, indicating the occurrence of three-dimensional ordered structure in the process of mesophase melting. Furthermore, in order to monitor the changing process of the mesophase and amorphous structure in the melt of mesophase, the backbone stretching region of 980–900 cm^{-1} has been picked out for two phase transition temperature ranges: (a) 60–64 $^{\circ}\text{C}$, (b) 66–76 $^{\circ}\text{C}$, respectively, as shown in Fig. 5. Of particular note in Fig. 5(a), the intensity of amorphous band 956 cm^{-1} increases firstly at the temperature of 62 $^{\circ}\text{C}$, while there is almost no change in the mesophase characteristic band at 918 cm^{-1} . It demonstrates clearly that the relaxation of oriented amorphous chains initially starts to take place before the change of mesophase. Subsequently, within the heating temperature range from 66 $^{\circ}\text{C}$ to 76 $^{\circ}\text{C}$ (Fig. 5b), the position of characteristic mesomorphic band at 918 cm^{-1} shifts regularly to 921 cm^{-1} due to α or α' formation, whereas the amorphous band at 956 cm^{-1} decreases. Combined with Fig. 5(a), we can conclude that the mesophase melts partially rather than completely and changes immediately to ordered three-dimensional crystallization phase from 66 $^{\circ}\text{C}$ to 76 $^{\circ}\text{C}$, which can be considered as a kind of partially solid-to-solid phase transition behavior.

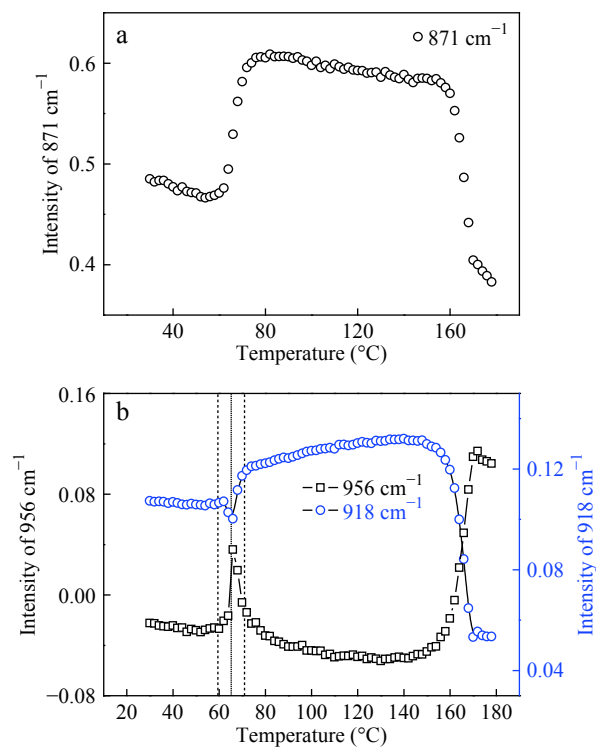


Fig. 4 Intensities of the perpendicular characteristic band at (a) 871 cm^{-1} , (b) 918 and 956 cm^{-1} of PLLA as a function of temperature ($T_d = 65$ $^{\circ}\text{C}$, $\lambda = 3$, heating rate = 2 $^{\circ}\text{C}\cdot\text{min}^{-1}$)

Fig. 6 shows a schematic illustration of the mesophase-to-crystallization phase transition in the heating process of the strain-induced PLLA. At the starting point, the local ordered chains, or the so-called mesophase, are arranged along the drawing direction. At the melting temperature of mesophase, the amorphous chains and partial mesophase start to become a little loose packing and disoriented, which can serve as the nucleus of crystallization.

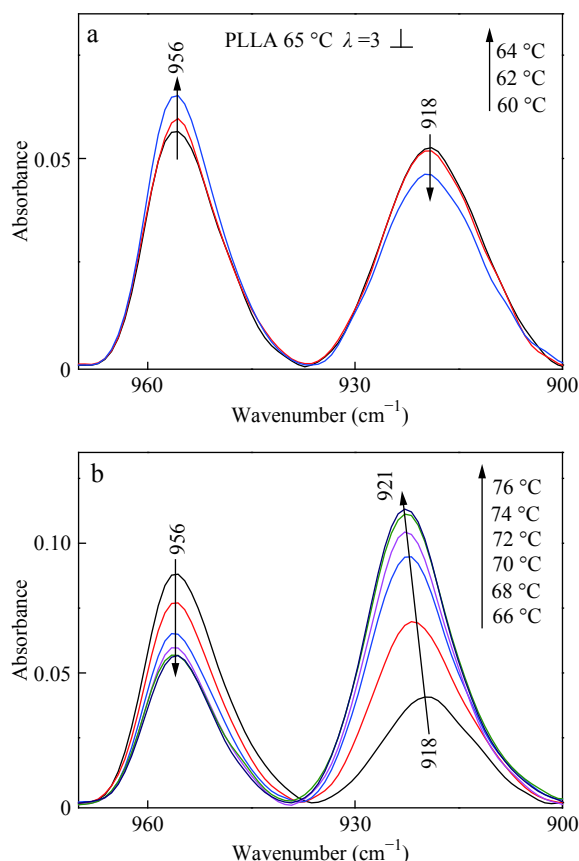


Fig. 5 Time-dependent perpendicular IR spectra in the range of 1000–900 cm^{-1} collected in temperature regions from (a) 60 °C to 64 °C and (b) 66 °C to 76 °C of PLLA sample ($T_d = 65$ °C, $\lambda = 3$, heating rate = 2 °C·min $^{-1}$)

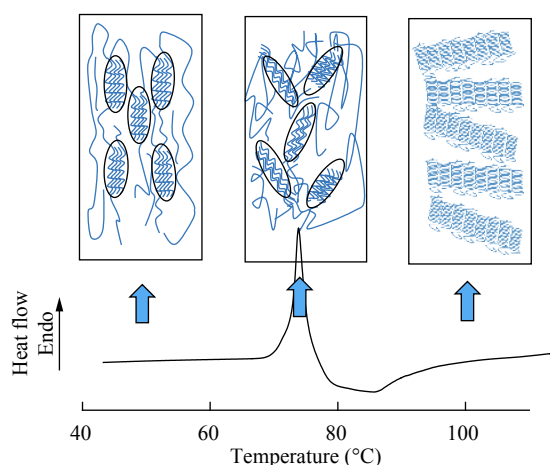


Fig. 6 Schematic illustration of the phase transitions of the mesophase into crystal in the heating process of strain-induced PLLA

CONCLUSIONS

In the present work, the phase transition of strain-induced PLLA mesophase in heating process was investigated in details by combining *in situ* temperature-dependence polarized Fourier transform infrared spectroscopy (FTIR) and DSC. It is found that, as the drawing temperature increases, the subsequent crystallization behavior can be impacted by the melting of mesophase. It should be noted that, as shown by the *in situ* polarized infrared spectroscopy, the amorphous chains start to disorient just prior to the melting of mesophase in the heating process. Furthermore, the thus-obtained mesophase melts partially instead of complete melting, concomitant by the triggering of the subsequent crystallization process. The oriented mesophase including parallel chain stems can reduce the free energy barrier of nucleation. In particular, high quality of mesophase can be formed in the case of high drawing temperature.

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