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ARTICLE

PLLA Mesophase and Its Phase Transition Behavior in the PLLA−PEG−PLLA Copolymer As Revealed by Infrared Spectroscopy

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ABSTRACT: A detailed analysis of the IR spectrum of melt-quenched PLLA−PEG−PLLA sample and its change with temperature is presented. It was found that, in the initial state of the melt-quenched PLLA−PEG−PLLA sample, the PLLA constituent does not exist as a normal amorphous or crystalline phase but as a kind of mesophase, which is confirmed by the WAXD data. The IR data suggest that both chain conformation and chain packing are disordered to some extent in such a mesophase. Therefore, this mesophase is less thermally stable than the ordered α phase and even the disordered α phase (α′) of PLLA. In the heating process, the mesophase of PLLA in the PLLA−PEG−PLLA copolymer starts the partial melt first upon heating in a stepwise way, and subsequently it is reorganized directly into the stable α phase but not through the α′ phase of PLLA. These phase transition behaviors are examined and discussed at the molecular functional group level.

1. Introduction

Poly(L-lactic acid) (PLLA) is one of the most popular *bioplastics* nowadays.[1,2] The "*bio-*" means that it is not only biodegradable at the ambient environment but also can be produced from the renewable biomass such as corn.[3] Moreover, PLLA exhibits the biocompatibility and excellent mechanical performances comparable to those of petroleum-based traditional polymers. Therefore, the biomaterials based on PLLA have gained biomedical attention in recent years due to their acceptance by living organism and have been used to construct three-dimensional scaffold and as suture and drug delivery matrix materials.

Recently, the synthesis, characterization, and medical applications of the triblock copolymer, PLLA−PEG−PLLA, have attracted great interest from a number of researchers.[4−8] It is well-known that poly(ethylene glycol) (PEG), a kind of water-soluble polymer, has excellent biocompatibility. The copolymers of L-lactide with hydrophilic monomer of ethylene glycol show great potential in medical and pharmaceutical applications due to its amphiphilic nature and biodegradability. Both drug permeability and biodegradability depend on the crystalline and phase structure. Thus, it is necessary to understand the phase behavior of the PLLA−PEG−PLLA copolymer.

Self-assembly of a soft matter into ordered structure is an important issue in material and biology sciences. It has been recognized that three physical events compete with each other in forming final morphologies in amorphous−crystalline or crystalline−crystalline block copolymers (BCPs).[9−11] These are the microphase separation of the copolymer, the crystallization of crystallizable blocks, and the vitrification of amorphous/crystalline blocks. Accordingly, three temperature parameters associated with these physical events are the order−disorder transition temperature of block copolymer (T_{ODT}), the crystallization temperature of crystallizable blocks (T_c), and the glass transition of amorphous/crystalline blocks (T_g). Depending on the segregation strength and the relative values of T_g, T_c, and T_{ODT}, many different morphologies can be generated in BCPs. Both PLLA and PEG are crystalline polymers. PEG has a flexible chain with low T_g (−30 to −20 °C) acting as soft segments in BCPs,[11] whereas PLLA has stiff chain with relative higher T_g (50−60 °C) as the hard blocks.[1] Meanwhile, the melting point of PEG with low molecular weight is around room temperature. Therefore, in some cases, the PLLA−PEG−PLLA copolymer can be treated as a crystalline−amorphous copolymer, and the self-assembling of the PLLA constituent plays a main role in deciding the final morphologies and phase structures. To our knowledge, there is no systematic research reporting on the phase behavior of the PLLA−PEG−PLLA copolymer.

The morphologies and phase behavior of BCPs are usually investigated mainly by time-resolved small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) techniques.[9−13] By these scattering methods, some quantitative information, such as the long period, lamellar thickness, and lattice spacing, can be unambiguously deduced with the Bragg equation. However, no information about the molecular configurations and molecular interaction involved in the microphase separation or crystallization process of BCPs can be derived by these scattering methods. Fourier-transform infrared spectroscopy (FTIR) is sensitive to the molecular conformation, interaction, and local chemical/physical environment of polymers.[14−17] Therefore, an introduction of IR method may give us complementary information to the SAXS and WAXS techniques.[18,19]

In our previous work, we have studied the various crystal modifications of PLLA and their crystallization processes in detail by using IR spectroscopy.[20−23] It is found that IR spectroscopy is a very useful tool to characterize the polymorphism of PLLA. For example, based on the IR spectra of PLLA crystallized at various

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temperatures, a kind of disorder α form (α′) of PLLA was first revealed and suggested in our previous work.[22] Compared with the studies by other researchers and ours,[20−26] the spectra−structure relationship of various PLLA crystal modifications has been well established.

The purpose of this study is to explore the complex thermal/phase behavior of PLLA−PEG−PLLA triblock copolymer at the molecular level by using temperature-dependent IR spectroscopy. Unexpectedly, a kind of mesophase of PLLA in the melt-quenched PLLA−PEG−PLLA sample is identified, and it is found that this mesophase can be transferred to the ordered α phase of PLLA via the partial melt−reorganization process.

2. Experimental Section

2.1. Material and Preparation Procedures. The synthesis and purification of PLLA$_x$−PEG2000−PLLA$_y$ ($x+y = 100$, weight-average molecular weight (M_w) = 8800 Da, M_w/number-average molecular weight (M_n) = 1.04) used in this work were performed according to procedures reported previously.[6,7]

2.2. FTIR Spectra. FTIR spectra were measured with a Thermo Nicholet Magna 870 spectrometer equipped with a MCT detector. The normal transmission mode was employed for the IR measurement. The PLLA−PEG−PLLA sample for IR analysis was casted on a KBr plate and then melt-quenched with liquid nitrogen for erasing the thermal history. For studying the thermal behavior of PLLA−PEG−PLLA via *in situ* FTIR, the sample thus prepared was set on a Instec HCS302 variable temperature cell, which was placed in the sample compartment of the spectrometer. The sample was then heated at a 1 °C/min up to 165 °C from room temperature (25 °C). During the heating process, FTIR spectra of the specimens were recorded at a 1 °C interval from 25 to 165 °C with a 1 min interval. The spectra were obtained by coadding 16 scans at a 2 cm^{-1} resolution.

The intensities of IR bands were automatic calculated by a numerical data processor program for vibrational spectroscopy, Spina Version 3, which was developed by Yukiteru Katsumoto in the Ozaki Group of Kwansei Gakuin University.

2.3. Differential Scanning Calorimetry (DSC). DSC measurement of melt-quenched PLLA−PEG−PLLA (sample weight: ca. 5 mg) was performed on a Perkin-Elmer Pyris6 DSC system over a temperature range from 20 to 170 °C at heating and cooling rates of 10 °C/min under a nitrogen gas flow at a rate of 50 mL min^{-1}.

2.4. WAXD and SAXS. The Bruker D8 focus was used for the WAXD measurement, and the X-ray beam used was Cu Kα radiation. SAXS measurement of melt-quenched PLLA−PEG−PLLA was performed at the Shanghai National Synchrotron Radiation Center, China. The wavelength of the incident X-ray beam was 1.24 Å.

3. Results and Discussion

3.1. Thermal Behavior of PLLA−PEG−PLLA Copolymer. Figure 1 shows a DSC heating curve of PLLA−PEG−PLLA sample. For erasing the thermal history, the melt-quenched sample was used. Upon heating from room temperature, a small endothermic peak appears first in a wide temperature range of 69−86 °C. Subsequently, a very sharp exothermic peak is observed around 92 °C. In this work, PEG2000 was used for the synthesis of PLLA−PEG−PLLA sample. As reported, the melting point of PEG2000 homopolymer is around 56 °C,[7] whereas the glass transition temperature and melting point of PLLA homopolymer with the normal molecular weight is 59 and 170 °C,[1] respectively. Therefore, this sharp exothermic peak around 90 °C should be associated with the crystallization of PLLA rather than that of PEG. Another endothermic peak at 145 °C is attributed to the melting of PLLA component with low molecular weight.

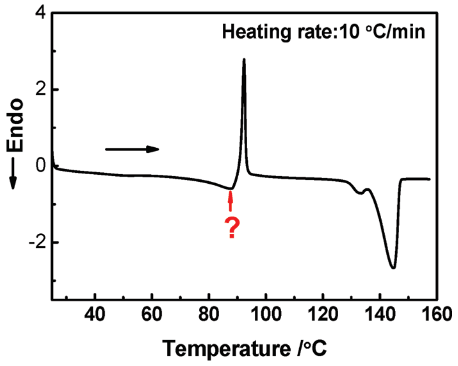

Figure 1. A DSC heating curve of melt-quenched PLLA−PEG−PLLA copolymer.

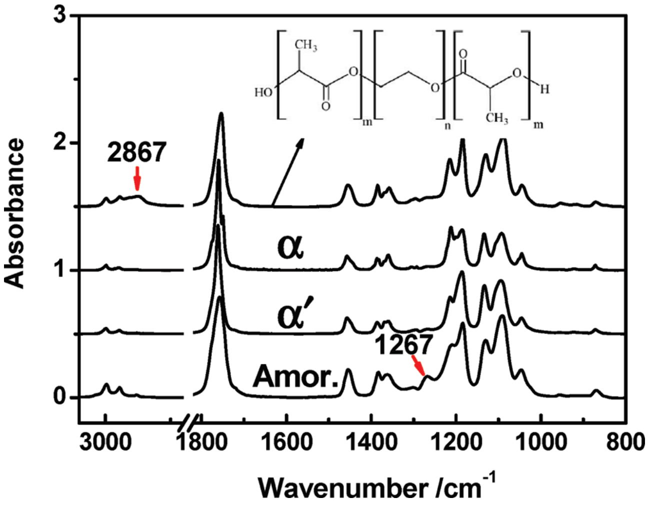

Figure 2. IR spectra of three kinds of PLLA samples (amorphous, α′, and α form) and the melt-quenched PLLA−PEG−PLLA copolymer. The inset graph is the chemical structure of the PLLA−PEG−PLLA triblock copolymer.

However, it is unclear that what the origin for the small endothermic peak around 86 °C is (note the red arrow in Figure1). At this temperature range of 69−86 °C, which is far above the melting point of PEG, the PEG component should be always in the molten state. Therefore, this weak endothermic peak may also be related to the phase transition behavior of PLLA constituent. In effect, the small melting peak just prior to the crystallization peak of PLLA was also observed in the DSC data of PLLA−PEG−PLLA copolymer based on PEG4600 as reported by Kricheldorf et al.[7] But at that time, no explanation was assigned to this phenomenon. Before we clarify this point by temperature-dependent IR spectroscopy, it is necessary to explore the initial state/phase structure of the melt-quenched PLLA−PEG−PLLA sample.

3.2. Initial State of PLLA in the Melt-Quenched PLLA−PEG−PLLA. Under normal crystallization conditions, that is, melt or cold crystallization from bulk, PLLA homopolymer is known to form two kinds of crystal modifications, order α and disorder α (α′) at crystallization temperature above 120 °C and below 100 °C, respectively.[22,23,27,28] An IR spectrum of melt-quenched PLLA−PEG−PLLA copolymer is depicted in Figure 2. For comparison, IR spectra of amorphous and crystalline PLLA (α′ and α form) measured at room temperature are also included in the same figure. The amorphous PLLA sample was prepared by melt quenching method, whereas the PLLA α′ and α form was

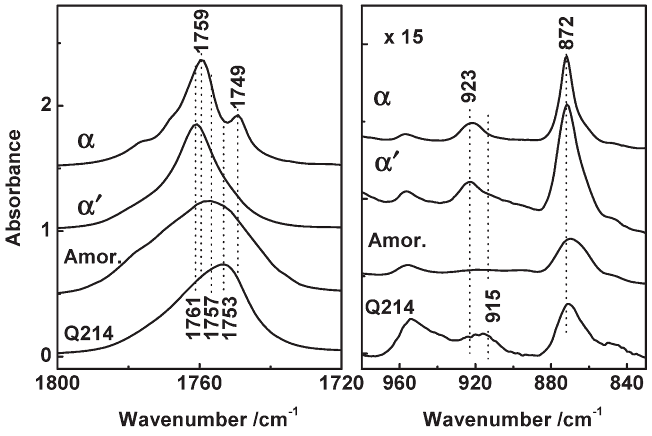

Figure 3. Detailed IR spectral comparison of three kinds of PLLA samples (amorphous, α′, and α form) and the melt-quenched PLLA−PEG−PLLA copolymer in the regions of C═O stretching vibration (a) and C−C backbone vibration (b).

obtained by annealing the melting-quenched PLLA at 80 and 150 °C for 1 h, respectively.

Compared with the spectra of PLLA homopolymer, a characteristic band of PEG is identified at 2867 cm^{-1}, which is assigned to CH_2 stretching vibration of PEG. The PLLA−PEG−PLLA copolymer lacks polar groups in the PEG blocks, and the weight fraction of PEG (ca. 18 wt %) constituent is relatively low in our sample so that the spectrum of PLLA−PEG−PLLA copolymer is dominated by the signals of PLLA in the spectral region of 1800−800 cm^{-1}. At the first glance, the IR spectra of PLLA in the three states are very similar to each other in Figure 2, except a band at 1267 cm^{-1} as indicated by the red arrow, which is associated with the coupling of ν_{as}(C−O−C) and δ(CH) vibration modes.[24] Pan et al.[27] had assigned this band to the less energy-favorable gg conformers of PLLA. However, vibrational modes in this spectral region are highly coupled with skeletal modes, and the chance to assign this band to individual conformers is very unlikely. Our previous IR studies on the crystallization process of PLLA show that the intensity of this band decreases with crystallization time.[20−23] Thus, it is safe to conclude that this band is sensitive to the amorphous phase of PLLA. As shown in Figure 2, it is obvious in the spectrum of amorphous PLLA, whereas it is relative weak in those of the crystalline PLLA (α and α′) and melt-quenched PLLA−PEG−PLLA copolymer.

It is noted that obvious spectral differences can be identified in the C═O stretching vibration region (1800−1720 cm^{-1}) and the chain backbone vibration region (970−730 cm^{-1}) of the PLLA samples as shown in the enlarged spectra of Figure 3. First, in the C═O stretching region, typical IR bands for amorphous, α′, and α form of PLLA homopolymer are located in 1757, 1761, and 1759/1749 cm^{-1}, respectively.[21,22] It is surprising to notice that none of them are consistent with a characteristic band (1753 cm^{-1}) of PLLA in the melt-quenched PLLA−PEG−PLLA sample. The band at 1753 cm^{-1} shows a noticeable shift compared to the location observed for the amorphous phase (1757 cm^{-1}). In the lack of specific interactions, shifting of IR bands is usually associated with conformational sensitivity. In this context, Meaurio et al.[28,29] had proposed that the bands in the C═O stretching region of PLLA are sensitive to chain conformers. They assigned the observed bands at 1776, 1759, and 1749 cm^{-1} corresponding respectively to gg, gt, and tt conformers. Therefore, the band at 1753 cm^{-1} may suggest an increase of the relative population tt conformers in the melt-quenched PLLA−PEG−PLLA sample.

Table 1. Observed Characteristic Bands of Various PLLA Modifications

vibration mode	observed bands	assignment
ν(C═O) (localized vibration mode)	1759/1749	α
	1760	α′
	1753	mesophase
	1757	amorphous
ν(C−C) + r(CH_3) (backbone vibration mode)	923	α
	923	α′
	915	mesophase
		amorphous

It should be mentioned that the band splitting phenomenon (1759/1749 cm^{-1}) of PLLA α form is due to the ordered chain packing in the unit cell, which induces the so-called correlation field splitting effect.[29] On the basis of the this observation, we have proposed that the α′ form has loose 10_3 helical chain packing, and it is less thermally stable than the standard α form of PLLA.[22] Recently, detailed X-ray studies in several groups strongly evidence this viewpoint.[23,30]

In the backbone vibration region (970−730 cm^{-1}, assigned to skeletal C−C stretching coupled with CH_3 rocking mode[24]), the melt-quenched PLLA−PEG−PLLA sample shows a band at 915 cm^{-1}, whereas a band at 923 cm^{-1} is observed for the α′ and α forms of PLLA homopolymer and there is no band around 920 cm^{-1} for the amorphous PLLA. It has been found that the band around 920 cm^{-1} is related to the ordered helical chain conformation of PLLA.[24−27] For example, the bands at 923 and 908 cm^{-1} are the characteristic bands of 10/3 (α′ and α form) and 3/1 (β form) helical chain conformation of PLLA, respectively . The β form of PLLA is acquired by uniaxailly drawing PLLA at high temperature or high pressure.[31,32] According to the temperature-dependent IR spectra, it will be evidenced later that this band does not come from PEG constituent. Therefore, this may be the first report of the observation of a conformational band at 915 cm^{-1} for PLLA.

Meanwhile, it is found that the band at 872 cm^{-1}, which is attributed to the C−C backbone stretching ν(C−COO),[21] is sharper in the melt-quenched PLLA−PEG−PLLA than that in the amorphous PLLA, and there is a low wavenumber shift of 872 cm^{-1} band in the amorphous sample. These spectral observations strongly suggest that the PLLA chains in the melt-quenched PLLA−PEG−PLLA sample are more ordered than in the amorphous state, and their ordering is also totally different with those in the normal crystalline states (α′ and α) of PLLA. The observed characteristic bands of various PLLA modifications are summarized in Table 1. These new observations in the C═O stretching region (1800−1720 cm^{-1}) and the C−C backbone vibration region (970−730 cm^{-1}) stimulate us to speculate that the PLLA component exists as a kind of mesophase with distinct chain packing and chain conformation in the melt-quenched PLLA−PEG−PLLA sample.

As reported,[33−35] for semicrystalline polymers with very fast crystallization rate, a mesophase can often be acquired by the melt-quenched method. For example, isotactic polypropylene (iPP) is a crystalline polymer also having a fast crystallization rate, and it can be solidified into an intermediate state between crystal and amorphous states when a thin specimen of molten state is rapidly quenched.[33] Such an intermediate state of iPP is called “mesomorphic phase” or abbreviated as “mesophase”. However, the crystallization rate of PLLA homopolymer is not so high that amorphous

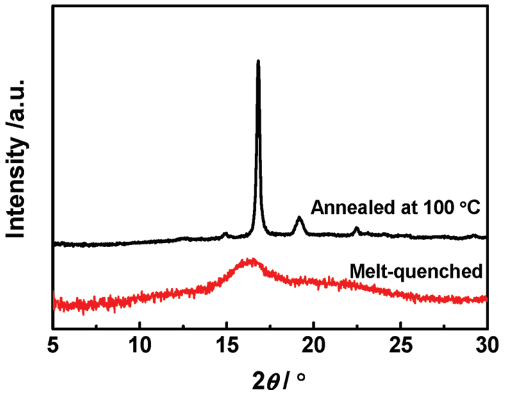

Figure 4. WAXD of melt-quenched PLLA−PEG−PLLA copolymer and that of annealed at 100 °C for 1 h.

rather than mesophase sample can be attained by the melt-quenched method.

In the PLLA−PEG−PLLA copolymer used here, the molecular weight of the PLLA block is very low and the PEG block has very low T_g (< 0 °C), which should enhance the molecular mobility of PLLA blocks. Therefore, the self-assemble mobility or crystallization rate of the PLLA in the copolymer is enhanced so that the mesophase can be formed under the melt-quenched condition.

Of particular note, the term "mesophase" has also been used to indicate "transition layer" or "interface" between the crystalline and amorphous regions of semicrystalline polymers, such as PET.[36] For differing these concepts, rigid amorphous phase (RAP) rather than mesophase may be better for describing the confined interface phase between the crystalline and amorphous regions.[37] Here, the proposed mesophase of PLLA in the melt-quenched PLLA−PEG−PLLA copolymer seems be an intermediate state between crystal and amorphous states, which is more similar to the mesophase of iPP rather than the RAP of PET.

To support our speculation, the WAXD data of melt-quenched PLLA−PEG−PLLA sample are presented in Figure 4. For comparison, the WAXD data for a PLLA−PEG−PLLA sample annealed at 100 °C for 1 h is also included. As shown in the DSC data of Figure 1, a crystallized sample will be obtained at such annealing temperature. It can be clearly seen that only a broad diffraction peak is observed for the melt-quenched sample, while the annealing sample show the characteristic diffraction peak of the PLLA α/α′ phase. The WAXD data strongly support that a mesophase rather than a crystalline phase is formed in the melt-quenched PLLA−PEG−PLLA copolymer. As indicated by the previous IR data, the PLLA chain conformation in the melt-quenched copolymer is disordered to some extend compared to the regular helical chain of PLLA, and there is also disordering in the chain packing mode in such a mesophase. Therefore, no diffraction peak can be observed for the melt-quenched PLLA−PEG−PLLA copolymer. Because the WAXD profiles of PLLA α and α′ phase are highly similar,[23] we will discuss the actual crystal modification after the cold crystallization process of melt-quenched PLLA−PEG−PLLA by the temperature-dependent IR data later.

Usually, some ordering structure in larger scale (nanometers) exists in the mesophase of polymer. As shown in Figure 5a, the 2D-SAXS data reveal that a microphase-separated structure is presented in the melt-quenched PLLA−PEG−PLLA copolymer. The corresponding one-dimensional profile is shown in Figure 5b, in which $q = (4\pi/\lambda) \sin \theta = 2\pi/L$, where 2θ is the scattering angle, λ is the wavelength of the X-rays, and L is the long period, from which it can be calculated that the long period for such ordering structure is around 60 nm. In summary, these data of WAXD/SAXS and IR data suggest that PLLA constituent does exist as a kind of mesophase in the microphase-separated domains of melt quenched PLLA−PEG−PLLA copolymer.

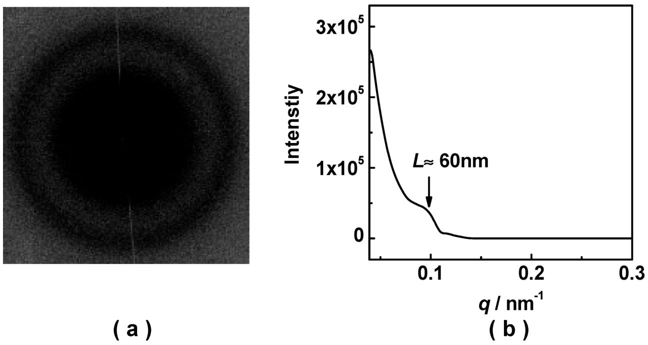

Figure 5. 2D-SAXS of melt-quenched PLLA−PEG−PLLA copolymer (a) and its corresponding one-dimensional profile (b).

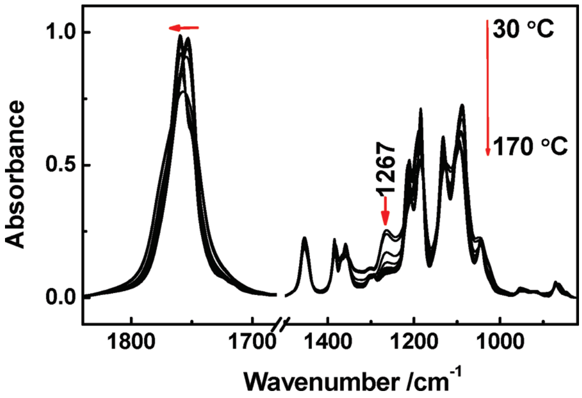

Figure 6. IR spectral evolution of melt-quenched PLLA−PEG−PLLA during the heating process from 25 to 165 °C in the region of C=O stretching vibration.

3.3. Phase Transition in the Heating Process of Melt-Quenched PLLA−PEG−PLLA Triblock Copolymer. Temperature-dependent IR spectra of melt-quenched PLLA−PEG−PLLA copolymer during the heating process from 25 to 165 °C are displayed in Figure 6. An obvious spectral change in the characteristic amorphous band of PLLA at 1267 cm^{-1} can be observed. The intensity changes of this amorphous band as a function of temperature is depicted in Figure 7. The intensity changes of the amorphous band at 1267 cm^{-1} clearly indicate that there are two melting and one crystallization processes in the whole temperature range from 25 to 165 °C. That is, a relatively small melting process around 80 °C and a bigger melting process around 165 °C. By comparing the relative intensities of the amorphous band at 1267 cm^{-1} at the end of these two melting processes (that is, H_1 and H_2 indicated in Figure 7), it can be found that only partial melting (around 20 wt %, calculated by H_1/H_2) of the mesophase takes place in the early stage of the first melting process. Subsequently, the abrupt decrease of the amorphous band indicates that there is a recrystallization or phase transition process. Does the mesophase totally melting or disappear in the recrystallization or phase transition process? This point can be clarified by monitoring the characteristic crystalline bands in the C=O stretching region and C−C backbone vibration region.

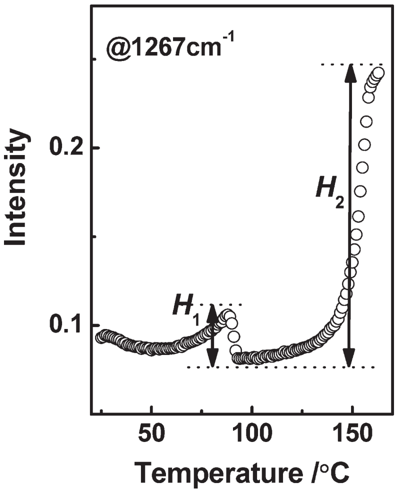

Figure 7. Intensity changes of the amorphous band at 1267 cm^{-1} of PLLA during the heating process of melt-quenched PLLA−PEG−PLLA copolymer from 25 to 165 °C.

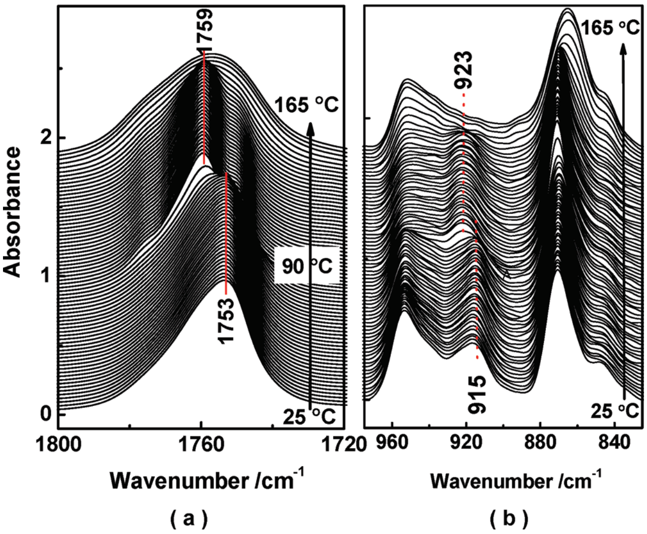

Figure 8. IR spectral evolution of melt-quenched PLLA−PEG−PLLA during the heating process from 25 to 165 °C in the region of C═O stretching vibration (a) and C−C backbone vibration region (b) of PLLA. The spectra are arranged with a 2 °C interval.

Enlarged spectral evolution of the C═O stretching region and the backbone vibration region is depicted in parts a and b of Figure 8, respectively. It can be clearly seen that the band at 1753 cm^{-1} for mesophase turns to the band at 1759 cm^{-1} for α phase and the PLLA mesophase (915 cm^{-1}) transforms to the ordered α phase (923 cm^{-1}) with increasing temperature above 90 °C.

For investigating the phase transition behavior in the smaller melt process around 80 °C in detail, the DSC curve together with the intensity changes in the amorphous region (1267 cm^{-1}), mesophase (1753 cm^{-1}/915 cm^{-1}), and α phase (1759 cm^{-1}/923 cm^{-1}) in the temperature range of 50−110 °C are plotted in Figure 9. Corresponding to the smaller melting peak in the DSC curve of Figure 1, it can be found that a partial melting appears in the temperature range of 68−86 °C because the intensities at 1753 and 915 cm^{-1} decrease slowly. The increases of the band at 1759 and 923 cm^{-1} starting from 86 °C indicate PLLA ordered α phase is formed after the partial melting of mesophase. Of note, the intensity of the band at 915 cm^{-1} reaching zero value at 94 °C suggests that the mesophase is totally disappeared after the formation of α phase. The disappearance of this band at 94 °C also shows that it is the IR band of PLLA rather than that of PEG constituent.

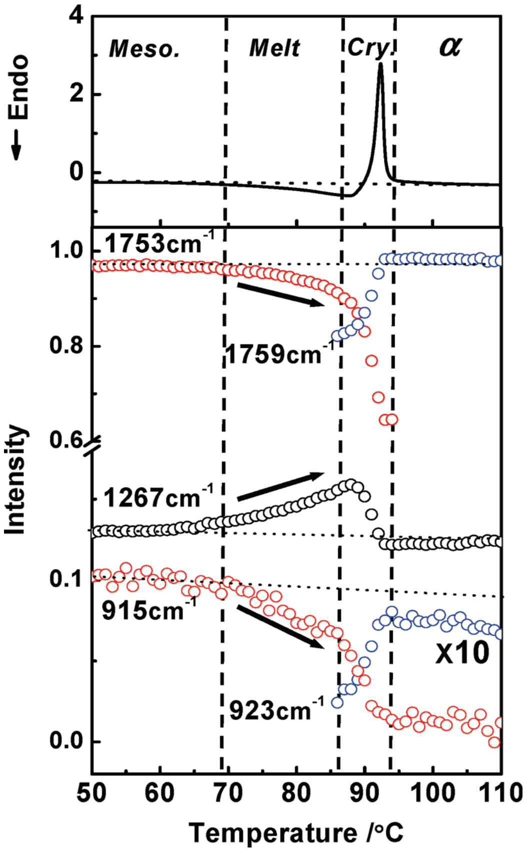

Figure 9. Comparison of the DSC heating cure (top) and the intensity changes of several characteristic IR bands of PLLA during the heating process (bottom) of melt-quenched PLLA−PEG−PLLA copolymer from 50 to 110 °C.

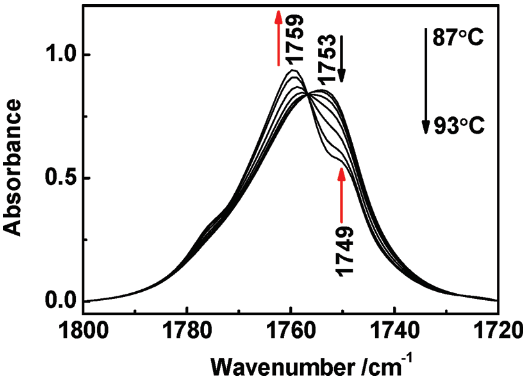

Figure 10. Overlapped IR spectral evolution of the C═O stretching vibration in the temperature region of 87−93 °C.

It is found that, in the temperature range from 87 to 93 °C, the formation of PLLA α phase and the melting of the mesophase take place simultaneously. As shown in Figure 10, the overlapped IR spectral evolution of the C═O stretching vibration in this temperature range demonstrates such a trend clearly. The appearance of the band at 1749 cm^{-1} also evidenced that the α phase rather than α′ is formed. Of particular note is that an isosbestic point is observed, which may indicate that there is a first-order transition between the mesophase and the α phase of PLLA.

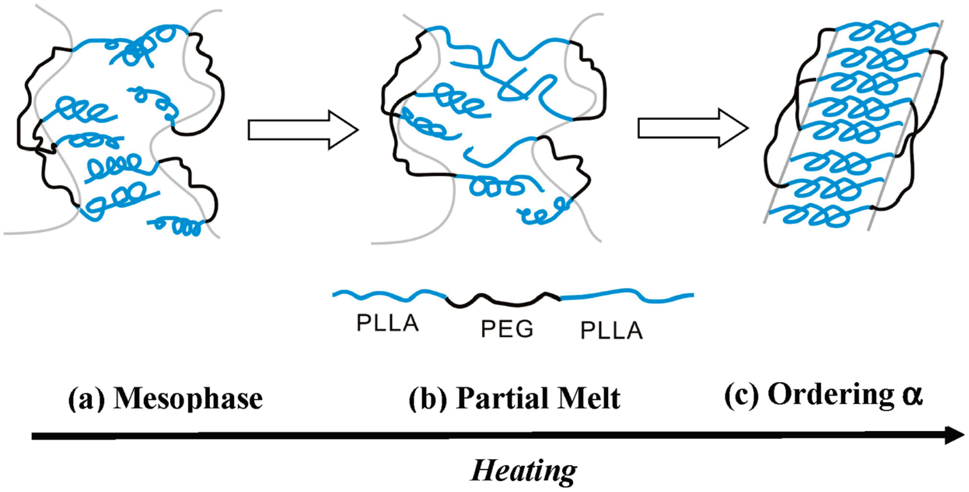

Figure 11. Schematic illustration of the phase transitions of the mesophase to partial melt to ordered α crystal in the heating process of the melt-quenched PLLA−PEG−PLLA.

As mentioned previously, the ordered α and disordered α (α′) are usually formed at crystallization temperature above 120 and below 100 °C. Here, the crystallization of PLLA around 90 °C produces the ordered α phase instead of the α′ phase. This phenomenon may be ascribed to two reasons. One is that the molecular mobility in the PLLA−PEG−PLLA copolymer is higher than that of the PLLA homopolymer. The other is that different crystallization mechanisms exist in these two cases. That is, the crystallization of PLLA homopolymer is from the glassy state or molten state. However, in the case shown here, the crystallization of PLLA is from the mesophase.

Usually, a mesophase is believed to be a precursor for a polymer crystallization, which will accelerate the crystallization process.[33] In the present case, the mesophase-to-crystal phase transition by partial melting is observed. A schematic illustration of the phase transitions of the mesophase-to-partial melt-to ordering crystal in the heating process of the melt-quenched PLLA−PEG−PLLA is depicted in Figure 11. By the above analysis, the origin of the smaller melting peak as shown in Figure 1 is clearly clarified.

In the view of larger scale (> 1 nm), the melt and reorganization process of such PLLA mesophase may be associated with the order-to-disorder (ODT) phase transition of PLLA−PEG−PLLA triblock copolymer. The correlation between the order-to-disorder (ODT) phase transition and the partial melt−recrystallization of the PLLA mesophase in the PLLA−PEG−PLLA copolymers should be further clarified by the morphology methods, such as SAXS and AFM.

4. Conclusion

The present study has revealed that, in the initial melt-quenched PLLA−PEG−PLLA sample, the PLLA constituent does not exist as a normal amorphous or crystalline phase but as a kind of mesophase, which is totally different than the conventional α phase and the recently proposed disordered α phase (α′) of PLLA. The confined self-assembly process in the microphase-separated domains should be the reason for the msophase formation. On the basis of the C−C backbone vibration modes of PLLA constituent in the PLLA−PEG−PLLA triblock copolymer, we have proposed that the PLLA chain conformation in such mesophase is disordered to some extent. The lack of sharp diffraction peaks in the WAXD data of melt quenched PLLA−PEG−PLLA sample suggests that there is also disordering in the chain packing mode of such mesophase. Thus, it is less thermally stable than the standard α phase and even the α′ phase of PLLA. This conclusion has been evidenced by the *in situ* temperature-dependent IR measurements of melt-quenched PLLA−PEG−PLLA sample. During the heating process, partial melting of the PLLA mesophase appears upon heating to the temperature range of 69−86 °C in a stepwise way. Subsequently, the remaining mesophase is quickly transformed to the ordered α phase without through the disorder α phase.

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References and Notes

(1) Lim, L. T.; Auras, R.; Rubino, M. *Prog. Polym. Sci.* **2008**, *33*, 820–852.
(2) Pan, P. J.; Inoue, Y. *Prog. Polym. Sci.* **2009**, *34*, 605–640.
(3) Dorgan, J. R. *Poly(lactic acid) Properties and Prospects of an Environmentally Benign Plastic*; American Chemical Society: Washington, DC, 1999; pp 145−149.
(4) Fujiwara, T.; Kimura, Y. *Macromol. Biosci.* **2002**, *2*, 11–23.
(5) Mukose, T.; Fujiwara, T.; Nakano, J.; Taniguchi, I.; Miyamoto, M.; Kimura, Y.; Teraoka, I.; Lee, C. W. *Macromol. Biosci.* **2004**, *4*, 361–367.
(6) Bishara, A.; Kricheldorf, H. R.; Domb, A. J. *Macromol. Symp.* **2005**, *225*, 17–30.
(7) Kricheldorf, H. R.; Rost, S.; Wutz, C.; Domb, A. J. *Macromolecules* **2005**, *38*, 7018–7025.
(8) Slivniak, R.; Langer, R.; Domb, A. J. *Macromolecules* **2005**, *38*, 5634–5639.
(9) Hamley, I. W.; Parras, P.; Castelletto, V.; Muller, A. J.; Pollet, E.; Martin, C. M. *Macromol. Chem. Phys.* **2006**, *207*, 941–953.
(10) Hamley, I. W.; Castelletto, V.; Castillo, R. V.; Muller, A. J.; Martin, C. M.; Pollet, E.; Dubois, P. *Macromolecules* **2005**, *38*, 463–472.
(11) Sun, l.; Liu, Y. X.; Zhu, L.; Hsiao, B. S.; Avila-Orta, C. A. *Polymer* **2004**, *45*, 8181–8193.
(12) Mothe, C. G.; Drumond, W. S.; Wang, S. H. *Thermochim. Acta* **2006**, *445*, 61–66.
(13) Mortensen, K.; Vigild, M. E. *Macromolecules* **2009**, *42*, 1685–1690.
(14) Chalmers, J. M.; Hannah, R. W.; Mayo, D. W. Spectra-structure correlations: Polymer spectra. In *Handbook of Vibrational Spectroscopy*; Chalmers, J. M., Griffiths, P. R., Eds.; John Wiley & Sons: Chichester, UK, 2002; Vol. *4*, pp 2441−2443.
(15) Tashiro, K.; Sasaki, S.; Kobayashi, M. *Macromolecules* **1996**, *29*, 7460–7469.
(16) Painter, P. C.; Coleman, M. M.; Koenig, J. L. *The Theory of Vibrational Spectroscopy and Its Applications to Polymeric Materials*; John Wiley & Sons: New York, 1982.

(17) Koenig, J. L. *Spectroscopy of Polymer*, 2nd ed.; Elsevier Science: New York, 1999.
(18) Duan, Y. X.; Rettler, E.; Schneider, K.; Schlegel, R.; Thunga, M.; Weidisch, R.; Siesler, H. W.; Stamm, M.; Mays, J. W.; Hadjichristidis, N. *Macromolecules* **2008**, *41*, 4565–4568.
(19) Cao, W. Y.; Tashiro, K.; Hanesaka, M.; Takeda, S.; Masunaga, H.; Sasaki, S.; Takata, M. *J. Phys. Chem. B* **2009**, *113*, 2338–2346.
(20) Zhang, J. M.; Tsuji, H.; Noda, I.; Ozaki, Y. *J. Phys. Chem. B* **2004**, *108*, 11514–11520.
(21) Zhang, J. M.; Tsuji, H.; Noda, I.; Ozaki, Y. *Macromolecules* **2004**, *37*, 6433–6439.
(22) Zhang, J. M.; Duan, Y. X.; Sato, H.; Tsuji, H.; Noda, I.; Yan, S. K.; Ozaki, Y. *Macromolecules* **2005**, *38*, 8012–8021.
(23) Zhang, J. M.; Tashiro, K.; Tsuji, H.; Domb, A. J. *Macromolecules* **2007**, *40*, 1049–105.
(24) Kister, G.; Cassanas, G.; Vert, M. *Polymer* **1998**, *39*, 267–273.
(25) Kang, S.; Hsu, S. L.; Stidham, H. D.; Smith, P. B.; Leugers, M. A.; Yang, X. *Macromolecules* **2001**, *34*, 4542–4548.
(26) Meaurio, E.; Lopez-Rodriguez, N.; Sarasua, J. R. *Macromolecules* **2006**, *39*, 9291–9301.
(27) Pan, P. J.; Zhu, B.; Dong, T.; Koji, Y.; Schimizu, T.; Tansho, M.; Inoue, Y. *J. Chem. Phys.* **2008**, *129*, 184902–10.
(28) Meaurio, E.; Arenaza, M.; Lizundia, E.; Sarasua, J. R. *Macromolecules* **2009**, *42*, 5717–5727.
(29) Meaurio, E.; Zuza, E.; Lopez, R.; Sarasua, J. R. *J. Phys. Chem. B* **2006**, *110*, 5790–5800.
(30) Kawai, T.; Rahman, N.; Matsuba, G.; Nishida, K.; Kanaya, T.; Nakano, M.; Okamoto, H.; Kawada, J.; Usuki, A.; Honma, N.; Nakajima, K.; Matsuda, M. *Macromolecules* **2007**, *40*, 9463–9469.
(31) Lee, J. K.; Lee, K. H.; Jin, B. S. *Eur. Polym. J.* **2001**, *37*, 907–914.
(32) Sawai, D.; Takahashi, K.; Sasashige, A.; Kanamoto, T. *Macromolecules* **2003**, *36*, 3601–3605.
(33) Qiu, J.; Wang, Z. Q.; Yang, L.; Zhao, J. C.; Niu, Y. H.; Hsiao, B. S. *Polymer* **2007**, *48*, 6934–6947.
(34) Konishi, T.; Nishida, K.; Matsuba, G.; Kanaya, T. *Macromolecules* **2008**, *41*, 3157–3161.
(35) Strobl, G. *Prog. Polym. Sci.* **2006**, *31*, 398–442.
(36) Stribeck, N. *Colloid Polym. Sci.* **1993**, *271*, 1007–1023.
(37) Sanz, A.; Nogales, A.; Ezquerra, T. A. *Macromolecules* **2010**, *43*, 671–679.