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Confirmation of Disorder α Form of Poly(L-lactic acid) by the X-ray Fiber Pattern and Polarized IR/Raman Spectra Measured for Uniaxially-Oriented Samples

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Summary: In the present research, we report for the first time the X-ray fiber pattern and polarized IR/Raman spectra taken for the uniaxially oriented disorder α form of PLLA, which can confirm the existence of the disorder PLLA α form (α′-form) and provide some new insight on the structural difference between the order and disorder α forms.

Keywords: diorder α form; poly(L-lactic acid); polarized IR/Raman; X-ray fiber diagrams

Introduction

In the past decades, there has been increasing interest in using poly(L-lactic acid) (PLLA) ($-[CH(CH_3)COO]_n-$) as an environment-friendly plastic material. As a semicrystalline polymer, its crystal structure and crystallization behavior have been extensively investigated by many techniques.[1–6] Usually, it is believed that PLLA can form three kinds of crystalline modifications (α, β and γ).[2–5] The most common α form had been thought to grow during cooling from the melt or by the cold crystallization from the glassy state no matter what is the crystallization temperature (T_c).[2] But this conclusion incurs doubt when the peculiar crystallization behavior of the PLLA α form is taken into consideration. That is to say, in the curve of PLLA spherulite growth rate (G) vs T_c, there is a discontinuity in the spherulite growth rate around 100–120 °C, showing a clear deviation from the usual bell-shaped curve of polymer crystal growth.[6] The bulk crystal morphology produced at high T_c is totally different from that at T_c. Macroscopic size of PLLA spherulites grown at high T_c is in the order of several hundreds μm, while only tiny crystal is observed at low T_c.[7] Additionally, the crystal thicknesses and long period have a minimum at 120 °C and increase at both of higher and lower crystallization temperatures.[7] In order to explain these peculiar crystallization behaviors of PLLA α form, several authors proposed recently that there might be a new crystal modification named α′-form or disorder α form when PLLA crystallizes at temperature lower than 120 °C.[7,8] This new crystal modification, different from the order α form, is supported by the experimental data of X-ray powder pattern and IR data.[7,8]

However, the structural difference between the order and disorder α forms has not yet been clarified enough well. Due to the high similarity of the X-ray powder diffraction pattern of these two samples crystallized at low and high T_c, more strong evidences for confirming the new crystallization modification are desired. In the present research, we report for the first time the X-ray fiber pattern and polarized IR/Raman spectra taken successfully for the uniaxially oriented disorder α form of PLLA, which can confirm the existence

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of the disorder PLLA α form (ά-form) and provide some new insight on the structural difference between the order and disorder α.

Experimental

Materials and Preparation Procedures

For preparing the uniaxially oriented film for polarized infrared spectral measurement, a solution-cast PLLA ($M_w = 64{,}920$, $M_n = 27{,}318$) film was stretched by 5 times the original length on a hot stage around 90 °C followed by annealing in oil bath at 85 or 150 °C for 3h. For preparing the uniaxially oriented rods for the polarized Raman and WAXD measurements, the amorphous PLLA ($M_w = 840{,}000$, $M_n = 360{,}000$) sheets prepared by melt-quenched method were stretched by 5 times the original length in oil bath at 85 °C and then annealed for 3h. For the uniaxially oreinted rods with order α form, the melt-quenched sheets were stretched on a hot stage at around 120 °C and then annealed in oil bath at 150 °C for 3h.

Measurements

Polarized IR spectra were measured with FTS-7000 Fourier-transform infrared spectrometer (Varian Co., Ltd). Polarized Raman spectra were measured with a JASCO NRS-2100 laser Raman spectrophotometer in the backscattering geometry with exciting laser of 532.0 nm. Three different polarization geometries: X(ZZ)X, X(YZ)X and X(YY)Z were measured at room temperature on the Cartesian coordinates system XYZ, where the Z was parallel to the draw axis and the X and Y were perpendicular to the Z axis. The resolution for both the IR and Raman measurements was 2 cm^{-1}. The wide angle X-ray diffraction (WAXD) data were collected by using an imaging plate system DIP 1000 (MAC Science, Ltd., Japan). The X-ray generator was a SRA-MXHF ((MAC Science Co., Ltd.) with graphite-monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å).

Results and Discussion

X-ray Fiber Patterns of Order and Disorder *α* Forms

Figure 1a and b display the X-ray fiber pattern of highly oriented PLLA samples crystallized at low (85 °C) and high temperature (150 °C), respectively. The WAXD pattern of PLLA sample crystallized at high temperature is essentially the same as that of the α form reported in literature.[2,5] Many sharp reflections on all the layer lines indicate a three-dimensionally regular crystal structure. When the X-ray fiber diagram shown in Figure 1b is compared with that of Figure 1a, we notice several remarkable differences: many streaks on the layer lines are observed in the WAXD pattern of Figure 1b. PLLA α form shows the strong reflections on both the sixth and seventh layer lines. In the X-ray pattern of α′ form, strong reflections appear only on the sixth layer line. This feature could not be explained simply by the difference in crystallinity between the two samples. The X-ray diagram of Figure 1b is as a whole diffuse and some layer lines are relatively weak and show the streaks.

As for the crystal structure of α form, there are two main proposes on the chain conformation in the unit cell. One is the regular 10/7 helix,[3] and the other is the so-called "distorted" 10/7 helix conformation owing to the interchain interactions between methyl groups.[5] Table 1 shows the diffraction characteristics of the order and disorder α forms and the order of the Bessel function (n) derived for the helical conformation by solving the equation $l = 7n + 10m$ for 10/7 helix, where l is the lth layer line and n and m are integers. It is found that the observed diffraction characteristics of the layer lines of the order α pattern are in good agreement with the regular 10/7 conformation. But when we compare this intensity distribution tendency for the α′ form, some specific layer line reflections, in particular the 7th

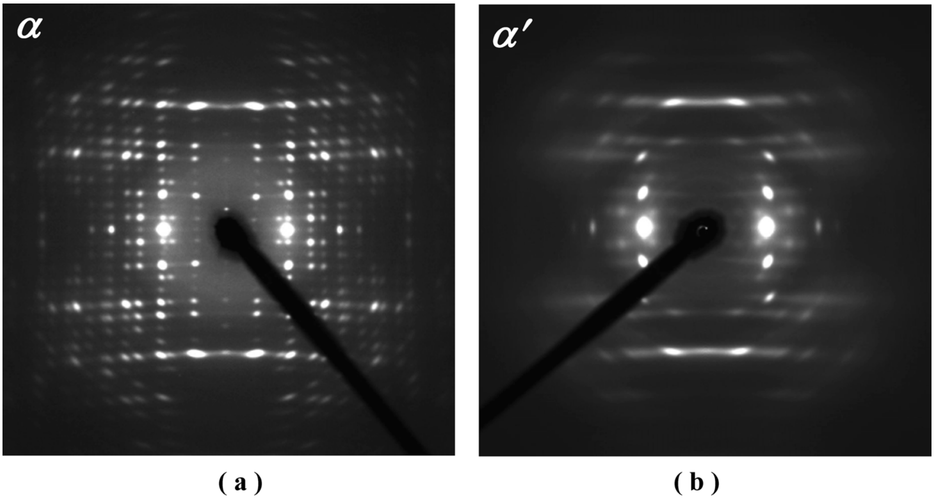

Figure 1.
WAXD patterns and of uniaxially oriented PLLA α (a) and α′ (b) forms.

layer line, do not correspond very well to the above-mentioned equation, suggesting some conformational disorder in the helical chain of the α′ form.

Polarized IR and Raman Spectra of Order and Disorder α Forms

In order to understand the structural difference between the order and disorder α forms, the polarized IR and Raman spectra of highly oriented samples were measured and compared. In the whole spectral region, both the polarized IR and Raman spectra of the α and α′ forms are similar, which indicating the similar chain conformation of these two forms. But we can detect some distinct spectral differences bewteen them as shown in Figures 2 and 3. For example, in the far-IR frequency region of 550–200 cm^{-1}, both the perpendicular and parallel bands of α′ form demonstrate obvious differences from the polarized IR spectra of α form.

Figure 3 show the polarized Raman spectra of uniaxially oriented PLLA α and α′ forms in the C=O stretch region

Table 1.
Diffraction Data of Order and Disorder α Forms of PLLA

l	*n*[a]	Observed characteristic features	
		α	α′
0	0	Sharp points (vs)[b]	Sharp points (vs) and continuous distribution
1	3	Sharp points	Weak points and continuous distribution
2	−4	Sharp points	—
3	−1	Sharp points (vs)	Sharp points (vs) and continuous distribution
4	2	Sharp points	Weak points
5	5	Sharp points	—
6	−2	Sharp points (vs)	Sharp points (vs) and continuous distribution
7	1	Sharp points (vs)	Weak points and continuous distribution
8	4	Sharp points	—
9	−3	Sharp points	—
10	0	Sharp points (vs) and continuous distribution	Sharp points (vs) and continuous distribution

[a] Solutions of the equation $l = 7n + 10m$ for 10/7 helix.
[b] vs = very strong.

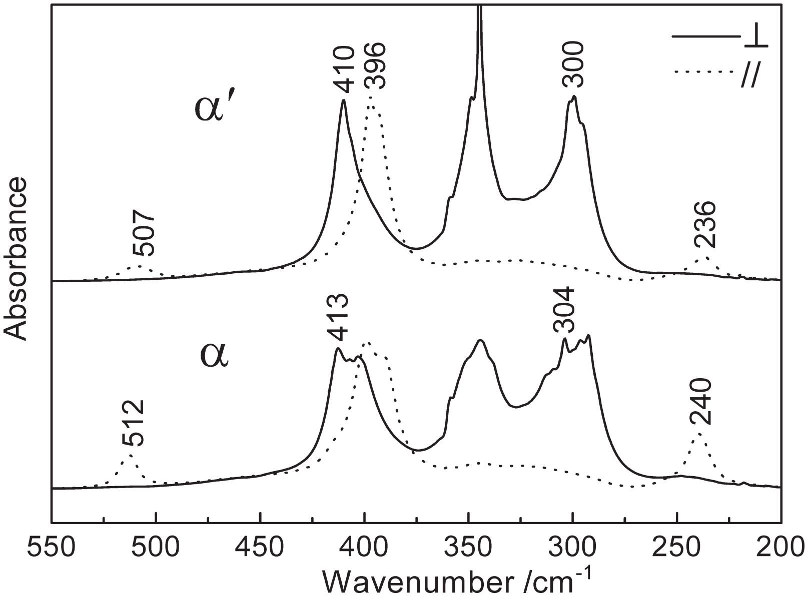

Figure 2.
Polarized far-IR spectra of uniaxially oriented PLLA α and α′ forms in the region of 550–200 cm^{-1}.

(Figure 3a) and low freqency region (Figure 3b). In the polarized Raman spectra of α form, the multiple bands in the C=O stretch region may be attributed to the correlation splitting and the symmetry lowering of molecular in the crystal lattice. In the low frequncy region, we can find that there are slight differences in the peak

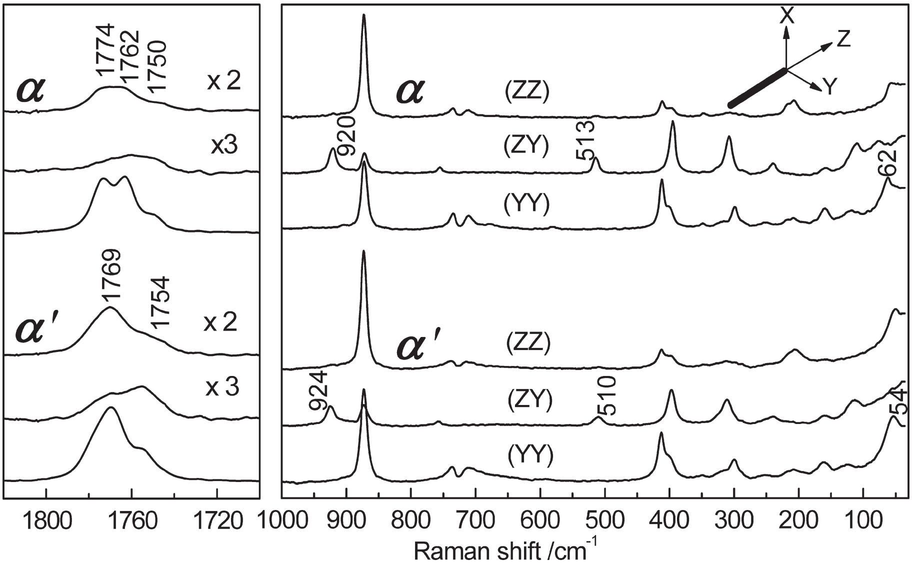

Figure 3.
Polarized Raman spectra of uniaxially oriented PLLA α and α′ forms in the regions of (a) 1820–1700 cm^{-1} and (b) 1000–36 cm^{-1}.

position and shape of several conformation-sensitive bands. For example, the sharp bands at 920 and 513 cm^{-1} in the poloarized Raman spectra of α form appear as the relatively broad bands at 924 and 510 cm^{-1} in the spectra of α' form. The lattice vibrational mode of α and α' forms also appear at 62 and 54 cm^{-1}, respectively. These Raman spectral differences indicate that in the disorder α form, its chain confomation and chain packing mode are slightly different from the order α form.

Conclusion

The disorder α form (α' form) of PLLA acquired under low crystallization temperatue ($<120\,^{\circ}C$) has been confirmed by the X-ray fiber pattern and polarized IR/Raman data. It is suggested that there are slight differences in both the chain conformation and chain packing mode between the order and disorder α forms. But more effort is needed to make clear the so-called ‘‘disorder’’ in more concrete way. We are performing the structure analysis based on these data.

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