2009 年 3 月

Structural analysis of lamellar twisting in polymer spherulite by polarized optical microscopy and microbeam x-ray scattering

偏光顕微鏡およびマイクロビーム X 線散乱法による
高分子球晶におけるラメラのねじれ構造の解析

物質系専攻 076140　橋本佳也
指導教員：雨宮慶幸

Keywords: Lamellar twist, Microbeam x-ray scattering, polymer crystal, chirality

1 Introduction

Some of polymer crystals exhibit banding structure under polarized microscope. For example, in case of PCL/PVB blend system, pure PCL does not show clear banding, whereas the blending PVB gives rise to extremely coherent banding structure. The purpose of our research is to investigate the nano structure which triggers the formation of banding structure.

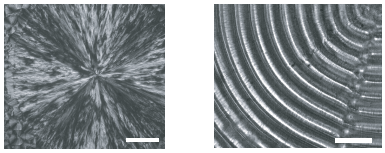

Figure 1: Left: Pure PCL. Right: PCL/PVB = 99/1. Banding structure appears when PVB is added. Scale bar: 100 μm

X-ray scattering measurement is suitable for the investigation of hierarchical structures in polymeric material; crystal packing structure of ∼0.1 nm order, and the crystal and amorphous layer structure (lamella) of ∼10 nm order. Lamellar structure and crystal packing structure can be analyzed by small angle x-ray scattering (SAXS) and wide angle x-ray scattering (WAXS), respectively. The beam size is several 100 μm in standard scattering experiment. Local information inside the banding can be obtained only by reducing the beam size smaller than band period and scanning the microbeam.

Lamellae twist helicoidally in radial direction in banded structure. The mechanism how achiral polymers assume chirality in higher order structure is intriguing. Although unified theory about the origin of lamellar twisting has not been established, there is a common theoretical foundation where chains are folded, inclined with respect to lamellar surface normal [1] as shown in Figure2.

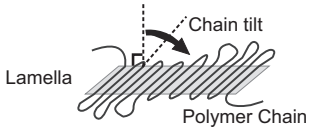

Figure 2: Chain tilt with respect to lamellar normal. Lamella grows in direction perpendicular to the paper.

However, the observation of the chain tilt in intact spherulite remains electron diffraction method, where it is impossible to observe lamellar diffraction. For example, chain tilt by 25 degree has been reported in single crystal of PVDF/PEA blend [2]. In our research, we analyzed the chain tilt by simultaneously observing the diffraction of lamellae and that of crystal packing structure.

On the other hand, nonuniform lamellar twisting has been observed in previous works by microbeam x-ray scattering, where the phase of lamellar twist proceeds slowly when they are perpendicular to substrate (edge-on lamellae) than when they are parallel to substrate (flat-on lamellae) [3]. We suspect that the origin of the stepwise twisting is attributable to the spherulite growth in two dimensionally confined space. The second aim of our research is to clarify the mechanism of the stepwise lamellar twisting.

2 Experimental Section

The sample was prepared by film casting method. First, PCL and PVB or PVDF and PEA were dissolved into mutual solvent. After the solvent was removed, the film sample was cut and placed on the mica substrate to be melted. Finally, the sample was crystallized at various temperatures (PCL/PVB: T_c =35 ℃ - 45 ℃, PVDF/PEA: T_c =167 ℃). We also prepared spherulite grown in three dimensional space. Thin sample which includes spherulite center was cut out by microtome.

Micromeam WAXS scannning experiment was conducted at BL-4A, Photon Factory. Kirkpatrik-Baez mirror was set at the upstream of the sample to focus the incident x-ray beam. The beam position was monitored by microscope. The x-ray beam size was 5 μm × 5 μm (FWHM) and microbeam scanned the band spherulite along the radial direction with a micron step. The x-ray wavelength was 0.83 Å.

Micromeam SAXS/WAXS simultaneous scannning experiment was conducted at BL40XU, SPring-8. The pinhole (ϕ = 5 μm) was set at the upstream of the sample to shape the incident beam from helical undulator. Microbeam scanned the band spherulite along the radial direction with a micron step. The x-ray wavelength was 1.15 Å.The sample was rotated around the spheurulite radii.

3 Result and discussion

3.1 Chain tilt to lamellar normal

- PCL/PVB

The result of microbeam SAXS/WAXS simultaneous measurement is shown in Figure3. The discrepancy between the phase of lamellar twist and that of chain was not detectable, which means the chain tilt, if any, was within 3-4 degrees. It is probable that the chiral factor other than chain tilt exists in PCL/PVB blend system.

- PVDF/PEA

The integrated scattering intensity of SAXS/WAXS is shown in Figure4. The phase shift by about 20 degrees was observed. Moreover, relationship between the sense of lamellar twist and chain tilt coincides with prevailed theory [1].

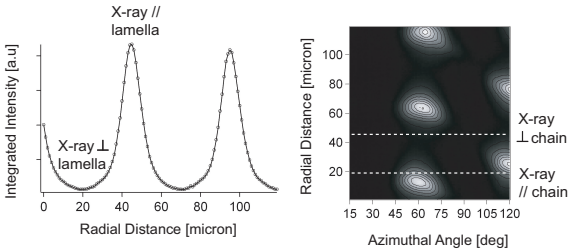

Figure 3: Left: Integrated SAXS intensity profile along radial direction. Right: Azimuthal distibution of WAXS (110) reflection along radial direction. PCL/PVB = 99.5/0.5, Tc = 53 ℃.

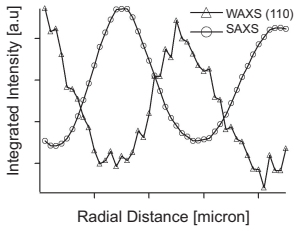

Figure 4: Integrated SAXS intensity and WAXS intensity of (110) reflection observed in PVDF/PEA spherulite.

3.2 The influence of PVB on PCL lamellar structure

It was found that higher crystallization temperature or the increase of PVB concentration lead to the broadening of the azimuthal distribution of (hk0) reflection. FWHM of the azimuthal distribution of (200) reflection under various PVB concentration is plotted against crystallization temperature (Figure5).

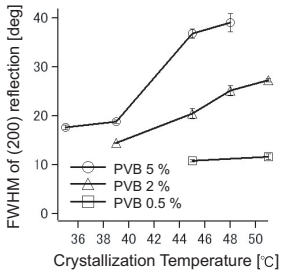

Figure 5: FWHM of the azimuthal distribution of (200) reflection.

On the other hand, crystal size can be evaluated by FHWM of diffraction peaks in scattering angle direction. It was confirmed that ordering of PCL crystal is amplified under higher crystallization temperature (Data not shown). These re-

sults indicate that the broadening of (hk0) reflection can be ascribable to the fluctuation in lamellar scale, and that the PVB concentration varies PCL lamellar growth direction. The distribution of lamellar orientation in lamellar perpendicular direction was also evaluated by the azimuthal distribution of SAXS (Figure6 Left). The fluctuation was observed to be smaller and less dependent on crystallization temperature, compared with WAXS (200) reflections. It can be concluded that the lamellar orientation has selectivity, where the fluctuation in lamellar plane is greater than lamellar perpendicular (Figure6 Right).

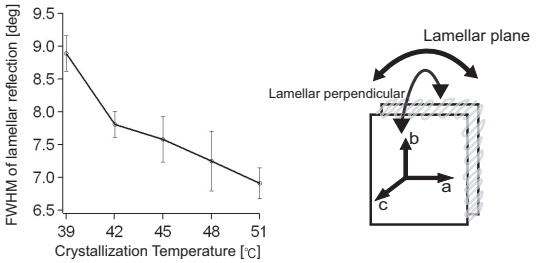

Figure 6: FWHM of the aziuthal distribution of lamellar diffraction, PCL/PVB = 95/5 (Left). The definitions of the lamellar orientations (Right).

3.3 The origin of stepwise twisting

The radial growth rate of PCL spherulite was analyzed by POM. It was found that the growth rate fluctuates and that the growth rate of edge-on lamellae is slower than flat-on lamellae as shown in Figure7.

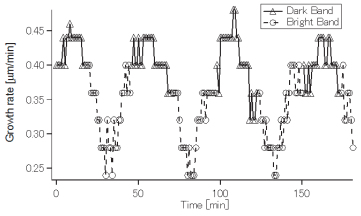

Figure 7: Rhythmic growth in radial direction. PCL/PVB = 95/5, Tc = 48 ℃. Dark band and Bright band correspond to flat-on lamellae and edge-on lamellae, respectively.

Secondly, we compared the twisting manner of spherulites grown in three dimensional space and those from two dimensionally space. The sample was rotated around the radii of spherulite, which is the axis of lamellar twisting. When the profile of the integrated SAXS intensity along the radial direction is not in coincidence after the sample rotation, we can judge that the lamellar does not rotate uniformly. Subtle difference in two dimensional spherulite was observed compared with 3D spherulite (Figure8).

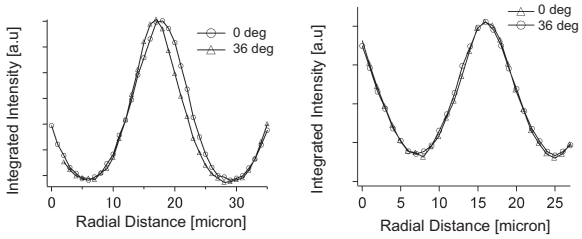

Figure 8: Integrated SAXS intensity along radial direction. The two profiles with and without sample rotations are compared. Left: 2D spherulite. Right: 3D spherulite. PCL/PVB = 95/5, Tc = 48 ℃.

These results indicate that the origin of stepwise lamellar twisting may well derive from the two dimensional space confinement.

4 Summary

In our research, we analyzed the lamellar twisting structure in sherulite by POM and microbeam x-ray scattering. The conclusions are the followings;

- Chain tilt with respect to lamellar normal in spherulite of PCL/PVB and PVDF/PEA blend system was analyzed by simultaneous SAXS/WAXS measurement.
- It is probable that chiral factor other than chain tilt exists in PCL/PVB spherulite.
- PVB increases the variance of lamellar growth direction of PCL in lamellar plane direction.
- The origin of stepwise lamellar twisting may well reside in the two dimensional space confinement.

References

1 B.Loz et al., Polymer. 46 577 (2007)

2 A.Toda et al., Polymer. 42 2223 (2007)

3 Y.Nozue et al., Polymer. 44 6394 (2003)