Shear-induced conformational fluctuations of polystyrene probed by 2D infrared microspectroscopy

Many studies on flow-induced polymer crystallization have been performed since the 1960s. However, the nature of flow-induced crystallization is still a poorly understood fundamental problem owing to its nonequilibrium property. Furthermore, because of the wide use of semi-crystalline polymers, external fields are inevitably applied during polymer processing such as extrusion or injection. Thus, considerable interest has been aroused in polymer engineering as the final morphology and properties of polymer products strongly depend on the processing history.

We discovered the existence of some string-like objects of macroscopic size in isotactic polystyrene (*iPS*) melts at temperatures above the nominal melting temperature (T_m) after applying a shear flow [1]. These aligned objects were assigned as 'row-nucleated' or 'shish-kebab-like' precursors since the epitaxial growth of crystals from them was observed during isothermal crystallization. No specific X-ray scattering intensity was observed on the precursors because there was little or no electronic density fluctuation. After cooling below T_m, we were able to observe the fiber structure, the so-called shish-kebabs structure, in these precursors by X-ray scattering and optical microscopy measurements as shown in Fig. 1.

In this study, the shear-induced conformational fluctuations of 'row-nucleated' or 'shish-kebab-like' precursors in *iPS* melts at temperatures above T_m were studied [2]. A macro-imaging map was demonstrated to investigate intra-molecular ordering of the precursors with the help of the powerful 2D infrared microspectroscopy station at beamline **BL43IR**. A Bruker IFS 120HR/X interferometer with a wide spectral range (100 – 20,000 cm^{-1}) was employed [3]. Because of the long distance (100 mm) between the Schwarzschild mirrors, a Linkam CSS-450 high-temperature shear cell was installed to perform *in situ* rheo-FTIR measurements. The temperature protocol for the shear experiments was as follows: (a) samples were heated to T_{melt} (290°C) from room temperature at a rate of 30°C/min; (b) they were held at T_{melt} for 5 min to erase the thermal history; (c) they were cooled to the shear temperature (T_{shear} = 250°C) at a rate of 30°C/min; (d) they were held at T_{shear} for 2 min to reach the temperature equilibrium and then subjected to a pulse shear flow; (e) after cessation of the shear flow, samples were held at the same temperature for 90 min; (f) finally, *iPS* samples were heated to T_{melt} again. The shear rate was 30 s^{-1}.

It is well known that *iPS* exhibits diverse 3/1 helical bands [4]. The critical sequence length, defined as the minimum length of a helical conformation, is represented by the number of monomeric units *m*. For example, 898 cm^{-1}, $m \geq 16$; 920 and 1053 cm^{-1}, $m \geq 10$; 1194 cm^{-1}, $m \geq 6$; 1084cm^{-1}, $m \geq 5$. On the other hand, the amorphous bands had wavelengths of 1194 and 1084 cm^{-1} as well as weak band at 1053 cm^{-1}.

Figure 2(a) shows the morphology and conformational fluctuations of *iPS* after applying a pulse shear flow (shear rate = 30 s^{-1}) using polarized optical microscope (POM) and 2D FTIR measurements. A 'row-nucleated' or 'shish-kebab-like' precursor in the flow direction was found in the POM measurements. 2D FTIR mapping was performed in a region of 200 × 100 μm^2 (red rectangle in Fig. 2(a)), as shown in Fig. 2(b), with a resolution of 10 × 10 μm^2. The integral wavenumber ranges were 895 – 900 cm^{-1} ($m \geq 16$) and 1050 – 1055 cm^{-1} ($m \geq 10$) and were assigned to the long 3/1 helical segments. The red domains with a high integral intensity in Fig. 2(b) were

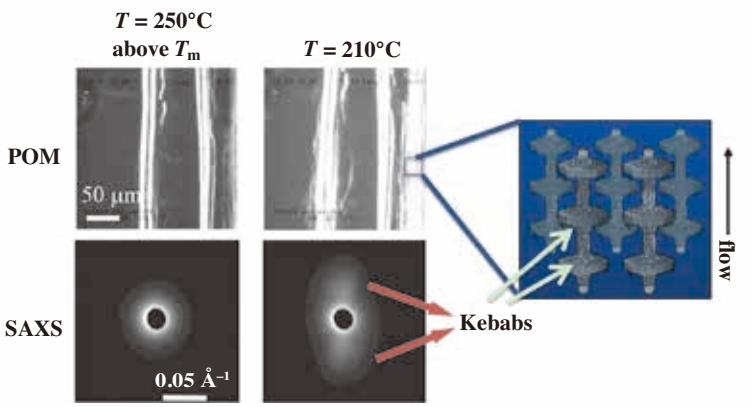

Fig. 1. Polarized optical microscope (POM) figures and in situ small-angle X-ray scattering profiles immediately after applying shear flow (250°C) and after crystallization at 210°C. Schematic drawing on the right is the so-called shish-kebab structure.

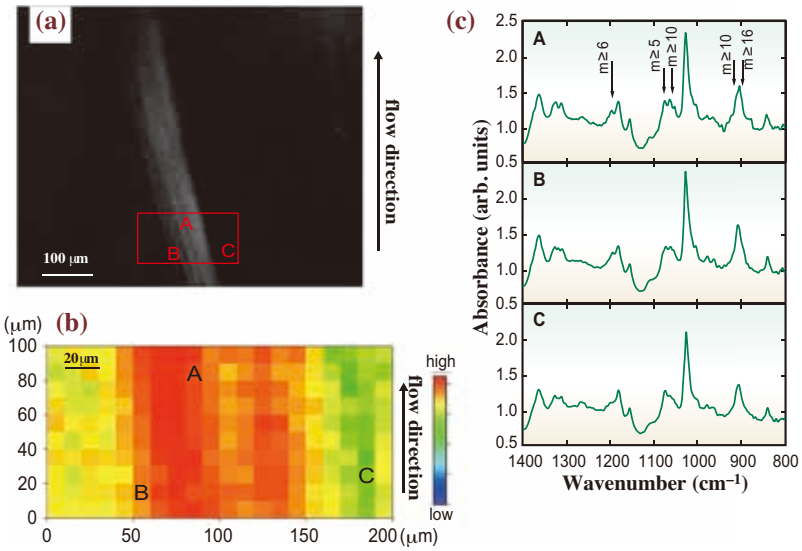

Fig. 2. **(a)** POM observation after cessation of flow. **(b)** Imaging map of *iPS* sample after applying a pulse shear flow obtained by 2D FTIR measurements. The mapping size was 200×100 μm^2 (red rectangle in (a)). **(c)** Infrared spectrum of *iPS* sample at different points in (a) and (b). A) in the center of the shish-kebab-like precursor; B) at the edge of the shish-kebab-like precursor; C) in the amorphous domain.

correlated to the precursor domain in the red rectangle of Fig. 2(a), which suggested the high concentration of long helical bands in the microscale precursor. Three different points were chosen for investigation in more detail; A) in the center of the precursor; B) at the edge of the precursor; C) in the amorphous domain as identified in Figs. 2(a) and 2(b). In the center of the precursor, both long helical bands ($m \geq 16$, $m \geq 10$) and short helical bands ($m \geq 6$, $m \geq 5$) were observed (Fig. 2(c), A). At the edge of the precursor, the intensity of the long helical bands was weaker (Fig. 2(c), B) and in the amorphous domain, almost no long helical bands and only short helical bands were observed (Fig. 2(c), C). It was evident that long helical bands ($m \geq 16$, $m \geq 10$) were detected in the center of the precursor (Fig. 2(c), A) while no long helical bands were detected in the amorphous domain (Fig. 2(c), C).

These precursors were found to disappear during the heating process. Figure 3(a) show micrographs of the shear-induced precursor and imaging maps of long helical bands during the heating process from 250 to 280°C. The region of long helical bands was decreased at 260°C, corresponding to the partial melting of the precursor, while in the center of the precursor, there still was a high concentration of long helical bands. When the temperature reached 270°C, the entire precursor began to melt, and thus the disappearance of the long helical bands was consistent with the results in our previous paper [1]. Finally, almost no long helical bands were observed after the melting of the precursor at 280°C. The disappearance of the long helical bands during the heating process was consistent with the melting of micron-scale precursors. From an intramolecular view, the long helical bands in the precursors may be related to a shear-induced coil-helix transition.

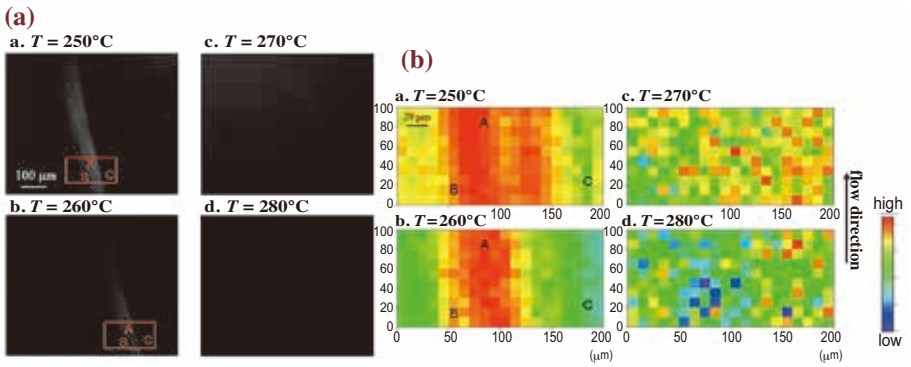

Fig. 3. **(a)** POM observation during the heating process. **(b)** Imaging map of long helical bands during the heating process.

Yunfeng Zhao and Go Matsuba*

Graduate School of Science and Engineering,
Yamagata University

*Email: gmatsuba@yz.yamagata-u.ac.jp

References

[1] Y. Zhao *et al.*: J. Polym. Sci. Part B: Polym. Phys. **49** (2011) 214.
[2] *Y. Zhao, G. Matsuba, T. Moriwaki, Y. Ikemoto, H. Ito: Polymer **53** (2012) 4855.*
[3] Y. Ikemoto *et al.*: Infrared Phys. Tech. **45** (2004) 369.
[4] M. Kobayashi *et al.*: Macromolecules **23** (990) 78.