Analysis on Fiber Formation Behavior during High-Speed In-Line Drawing Process of Poly(ethylene terephthalate)

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Abstract

High-speed in-line drawing process, in which melt spinning and drawing processes are connected, is one of the most widely used processes for production of commodity fibers. In this study, on-line measurements of diameter, velocity and birefringence were conducted in the high-speed in-line drawing process of poly(ethylene terephthalate) (PET). Filament started to deform immediately after passing through the first godet roller. The maximum strain rate under the drawing condition of from 2 to 4 km/min reached a high value of 510 s^{-1}. Birefringence of filament increased steeply in this region. Comparison of orientation development during melt spinning and drawing processes revealed that the birefringence measured in the high-speed spinning line showed lower values than that in the in-line drawing line at the same diameter. Structure evolution of in-line drawn filament prepared under various processing conditions was investigated through off-line measurements of wide-angle X-ray diffraction (WAXD), birefringence, and density. Although drawing temperature was slightly higher than the glass transition temperature (*T*g) of PET, significant development of oriented mesophase was confirmed. At the same time, a sharp meridional (001’) peak, which is reported to be originated from well-ordered smectic-C phase, also was clearly observed. In-situ measurement of WAXD pattern during heating process of highly drawn filament revealed that the intensity of (001’) peak started to increase gradually below *T*g and started to decrease above *T*g. Along with the reduction of the intensity of (001’), crystalline reflections of ordinary triclinic crystal started to appear above *T*g, indicating that the mesophase acts as a transitional precursor for crystallization.

Keywords: In-line drawing, Poly(ethylene terephthalate), On-line measurement, Birefringence, mesophase

1. Introduction

High-speed in-line drawing process, in which melt spinning and drawing processes are connected, is one of the most widely used processes for production of commodity fibers. Development of fiber structure and characteristics of resultant fibers are known to be affected both by the melt spinning and drawing conditions [1-3], however, number of research papers on the mechanism of fiber formation is limited. In this study, on-line measurements of diameter, velocity and birefringence were conducted in the high-speed in-line drawing process of poly(ethylene terephthalate) (PET), and the results were compared with those for the high-speed melt spinning process [4-6].

On the other hand, for the past decade, several research groups [7,8] have investigated the structure evolution of poly(ethylene terephthalate) with off-line drawing and annealing processes paying particular attention to the properties of mesomorphic phase, *i.e.* the non-crystalline phase with high chain extension. It was also reported that cold-drawn non-crystalline PET shows a weak but sharp meridional peak (001') in the wide-angle X-ray diffraction (WAXD) analysis. The mesomorphic phase is reported to act as a precursor for crystallization in oriented amorphous PET. Despite of these intensive fundamental investigations, studies on the structural development of PET under the industrial drawing conditions are rarely found. In this study, structure of in-line drawn PET fiber was also investigated paying particular attention to the evolution of mesomorphic structure.

2. Experimental

2.1 High-speed melt spinning and in-line drawing processes

The polymer material used was PET with Intrinsic viscosity of 1.0 dl/g supplied by Toyobo Co. Ltd. The polymer was melted and extruded using a single screw extruder and a gear pump. The spinneret has a single hole of 1 mm diameter. The throughput rate and spinning temperature were controlled to 6.0 g/min and 300 ^{o}C, respectively.

High-speed melt spinning was executed by varying the take-up velocity from 2 to 5 km/min (S2 ~ S5). On the other hand, high speed in-line drawing (Fig. 1) was conducted under various conditions. For the on-line measurement, speed of the first roller was kept at 2 km/min, and the take-up velocity was increased

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from 3.5 to 4.5 km/min (D2035 ~ D2045). Temperature of the first roller was set at 85 °C. For obtaining the in-line drawn fibers for structural characterization, take-up velocity was kept at 5 km/min, and the speed of the first roller was varied from 2 to 4 km/min. For preparation of drawn fibers (D25 ~ D45), temperatures of the first and second rollers were set at 85 °C, whereas for the preparation of drawn and annealed fibers (DA25 ~ DA45), temperature of the second roller was increased to 135 °C. Some additional fibers were prepared increasing the take-up velocity to 6 km/min.

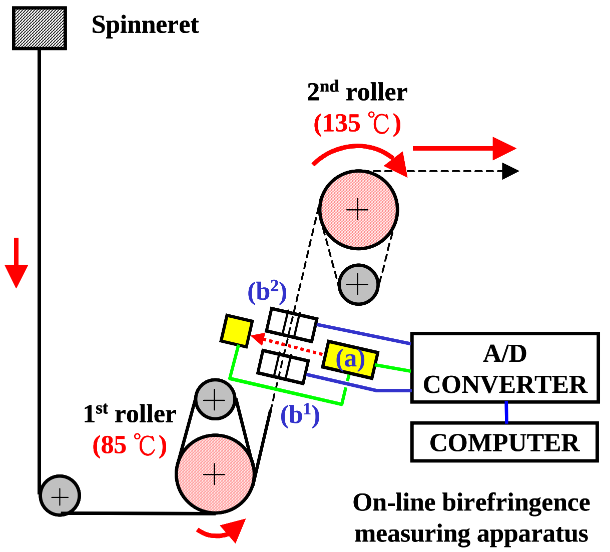

Fig.1 Schematic diagram of the melt spinning and in-line drawing apparatus equipped with on-line birefringence measuring system.

2.2 On-line measurements

On-line measurements of diameter and birefringence were carried out at various positions of the spinning and drawing lines using a pair of optical diameter monitors and an optical retardation measurement system, which is composed of a He-Ne laser light source (543.5 nm), polarizing filters, quarter-wave plates, a rotating polarizing filter, photo detectors *etc.* (Fig. 2). Sampling rate of the light intensity was 10 kHz, and a period of the light intensity oscillation caused by the rotating polarizing filter was 1.0 ms. As the spinning line is thinner than the diameter of laser light, the light intensity detector was offset 23° from the primary laser beam.

The phase shift a_1 caused by the oriented running filament can be obtained from equations (1) and (2): the cross correlation function $C(\tau)$ of the time-course intensity variations of reference light $I_{ref}(t)$ and the light passed through the running filament $I_{meas}(t)$, and its sinusoidal fitting function.

$$C(\tau) = \int_{t_2}^{t_1} I_{meas}(t-\tau) I_{ref}(t) dt \quad (1)$$

$$C(\tau) = a_0 \sin(\tau + a_1) + a_2 \quad (2)$$

where t is time and τ is the lag. Birefringence Δn of the filament can be then obtained from the optical retardation of filament δ using equations (3) and (4).

$$\delta = 2\pi N + a_1 \quad (3)$$

$$\Delta n = \delta\lambda / 2\pi L \quad (4)$$

where λ is the wave length of laser light, L is the geometrical path for light in the filament cross-section, and N is the order of interference. It should be noted that a_1 varies only within a range of 0 ~ 2π, and therefore N needs to be estimated separately in this measurement. More detailed principles for the optical retardation measurement and calculation are described elsewhere [4].

2.3 Structure analysis of prepared fibers

Structure and property of obtained fibers were analyzed by measurements of wide-angle X-ray diffraction (WAXD), birefringence, modulated differential scanning calorimetry (MDSC), and thermo-mechanical analysis (TMA).

Analysis on the structural change during the heating process of fibers was also conducted measuring the series of WAXD patterns at the heating rate of 2 K/min.

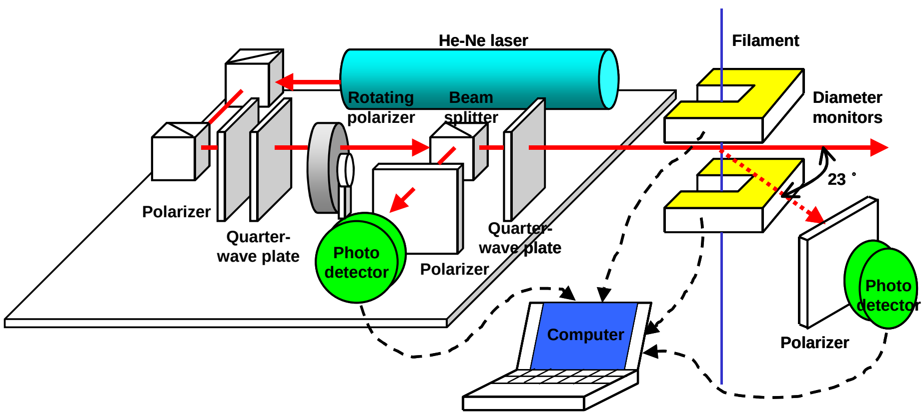

Fig.2 Schematic diagram of the on-line birefringence measuring system composed of diameter monitors and an optical system for measurement of retardation.

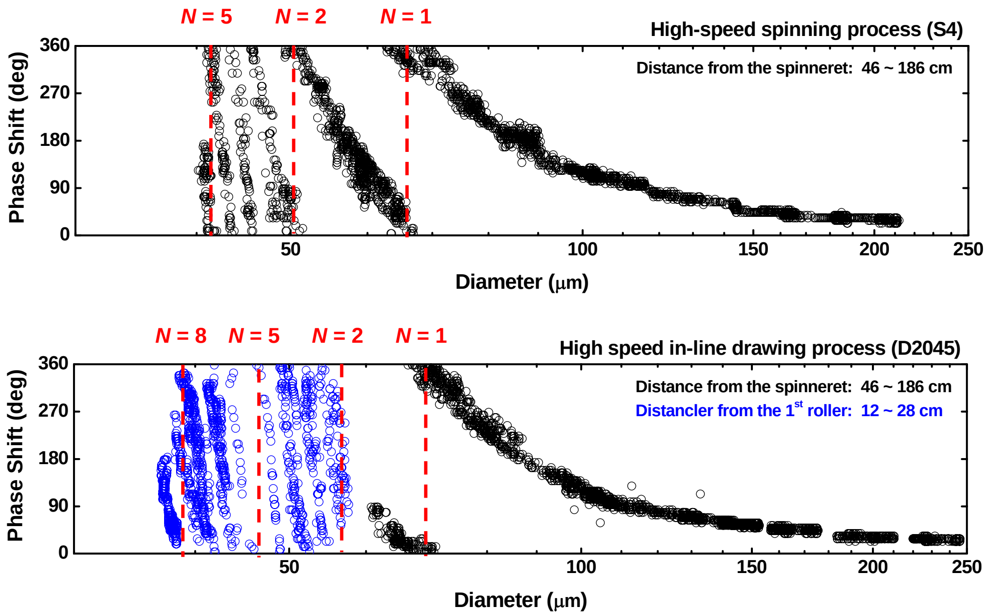

Fig.3 Correlation between diameter and phase shift for high-speed melt spinning process of 4 km/min and high-speed in-line drawing process of 2 to 4.5 km/min. Time-course variations of data acquired at various positions could be assembled to draw master curves.

3. Results and Discussion

3.1 On-line Diameter and birefringence measurements

During the simultaneous on-line measurements of filament diameter and phase shift at a certain position in the high-speed spinning and high-speed in-line drawing processes, both diameter and phase shift fluctuated within certain ranges. It was found that the data collected at each measuring position could be successively assembled and unique variation curves of phase shift as a function of filament diameter were obtained as shown in Fig. 3. In this manner, the order of interference *N* could be estimated.

In the high-speed spinning line of 4 km/min (S4), the first order of interference (N = 1) started to appear at around 66 μm, and N = 2 appeared from around 50 μm. On the other hand, in the high speed in-line drawing line with a drawing condition of 2 to 4.5 km/min (D2045), N = 1 started to appear at the same diameter of around 66 μm in the spinning line, whereas N = 2 started to appear from relatively higher diameter of around 60 μm. This diameter corresponds to the filament in the in-line drawing region. In other words, the PET filament in the in-line drawing process showed higher retardation than that in the high-speed spinning process at the same filament diameter. The difference of the order of interference reached around 2 at 50 μm where the order of interference for S4 and D2045 were 2 and 4, respectively.

Diameter and birefringence were plotted against the distances from spinneret and first roller as shown in Fig.4. The plotted diameter at each position was determined as the mean value of the accumulated diameter data of 3 seconds. On the other hand, plotted birefringence was obtained consulting the relationships between retardation and diameter shown in Fig. 3.

In the high-speed melt spinning process, neck-like deformation started to occur in the spinning line at 4 km/min (S4), whereas the running filament showed a steep deformation immediately after passing through the first roller of 2 km/min (D2035 ~ D 2045). Position of these steep deformations shifted toward upstream with increases in the take-up velocity and the in-line draw ratio.

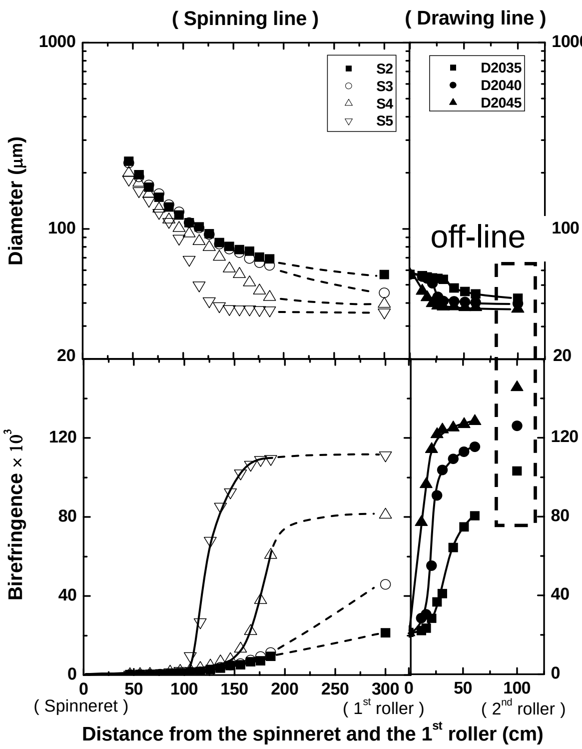

Fig.4 Diameter and birefringence profiles in the melt spinning and drawing lines for various spinning and in-line drawing conditions.

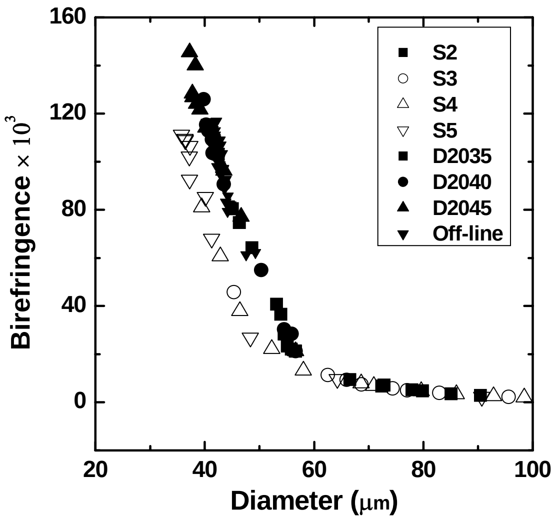

Fig.5 Correlation between diameter and birefringence for high-speed melt spinning and high-speed in-line drawing processes.

Birefringence of filament increased steeply in the vicinity of neck-like deformation in the high-speed melt spinning line and in the region near the first roller where steep diameter reductions was observed in the in-line drawing line. The maximum birefringence for the high-speed spinning at 5 km/min (S5) was even lower than that of in-line drawing at the first and second roller speeds of 2 and 4 km/min (D2040). The origin of this difference can be traced from the relation between diameter and birefringence data. As shown in Fig.5, birefringence of the spinning line started to increase remarkably when the filament diameter decreased to around 50 μm, where orientation-induced crystallization started to occur. On the other hand, birefringence of the drawing line started to increase steeply at a higher diameter of around 60 μm, which corresponds to the diameter of the fibers at the velocity of 2 km/min. In other words, thinning in the drawing process was found to be more effective for the development of molecular orientation in comparison with that in the melt spinning process. This difference mainly originated from the difference in the filament temperature.

3.2 Structure Development in Spinning and Drawing Processes

WAXD patterns for PET filaments prepared at various high speed spinning and in-line drawing conditions are shown in Fig. 6. In the high-speed spinning process, WAXD pattern for the low spinning velocity of 2 km/min (S2) indicated that even though the fiber was still amorphous, it started to show an anisotropic distribution, *i.e.* concentration of intensity on the equator,

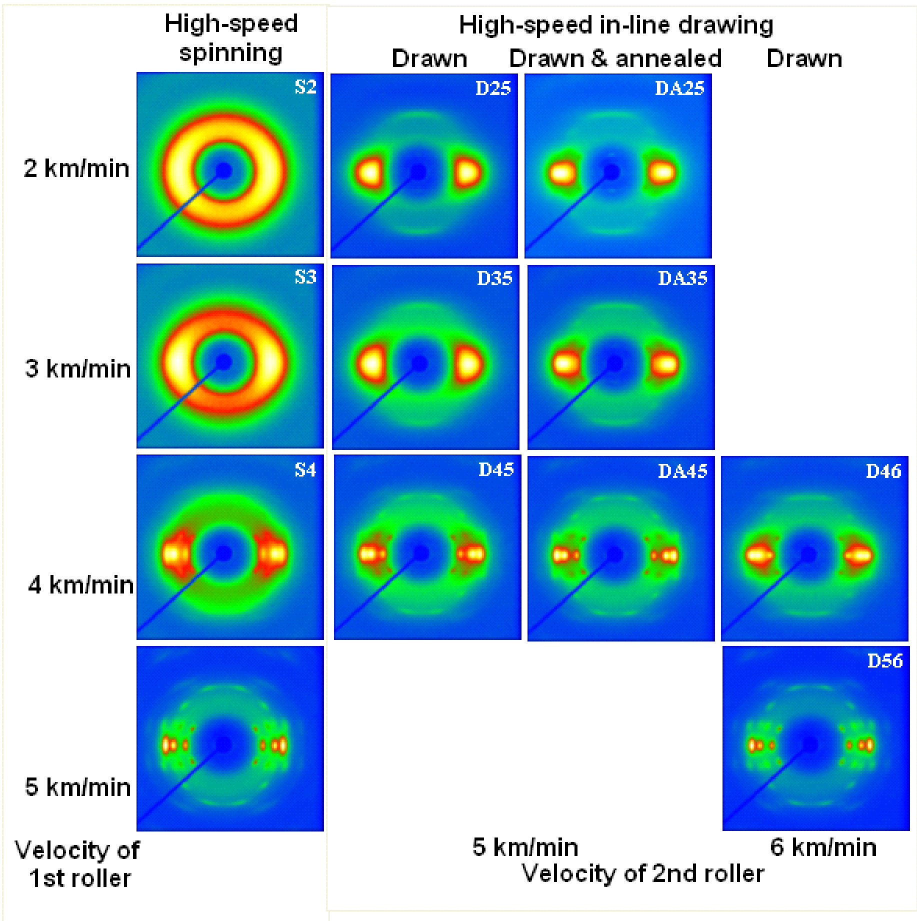

Fig.6 WAXD patterns of fibers prepared in high-speed melt spinning and high-speed in-line drawing processes.

reflecting the development of molecular orientation. The crystalline reflections appeared at the spinning velocity of 4 km/min (S4), where neck-like deformation started to occur. There was a distinct increase of peak intensity and improvement of crystal perfection when the spinning velocity was increased from 4 to 5 km/min (S5). On the other hand, PET filaments of D25 and D35, drawn from non-crystalline state corresponding to S2 or S3, respectively, to 5 km/min showed only a highly oriented non-crystalline structure. Weak crystalline peaks could be observed only after annealing at 135 °C by the second roller (DA25 and DA35).

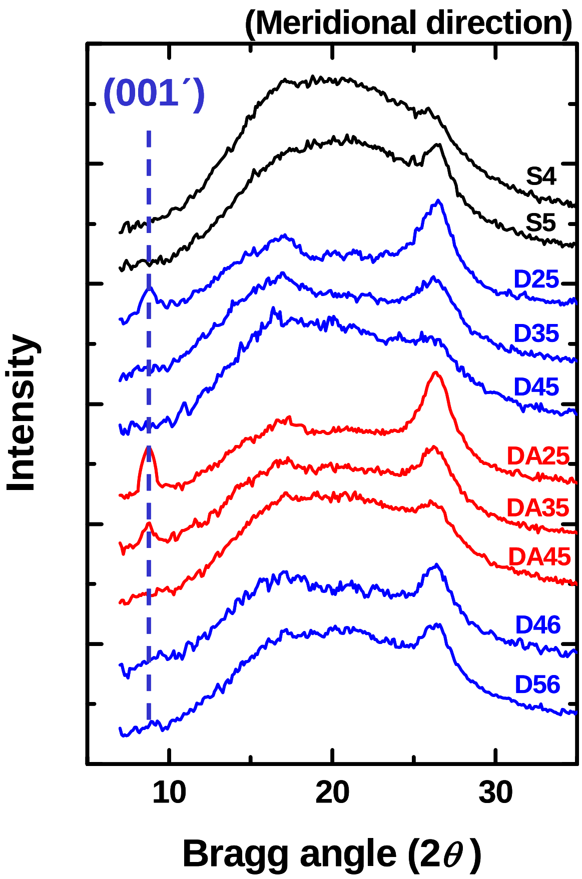

Fig.7 Meridional intensity distributions for the fibers prepared under various high-speed melt spinning and high-speed in-line drawing conditions. Peak position for (001') reflection is indicated.

It has been known that cold-drawn non-crystalline PET shows unique weak but sharp (001') peak on the meridian of WAXD [7, 8]. This peak is considered to be from well-ordered smectic-C mesophase. Recently, Kawakami *et. al.* reported that the meridional (001') peak does not appear during off-line drawing of amorphous PET above *T*g.

Meridional intensity distributions for the fibers prepared under various conditions are summarized in Fig.7. It is interesting to note that the meridional (001') peak was observed for the in-line drawn fibers of relatively high draw ratios. The peak located at the diffraction angle of 2θ ≈ 8.75 deg, which corresponds to the inter planar spacing of 1.01 nm. Variation of peak area for (001') reflection was also analyzed and plotted against the draw ratio as shown in Fig. 8.

In this study, high speed in-line drawing of PET filament was conducted at 85 °C. In other words, there was an appearance of (001') reflections even though drawing temperature was higher than *Tg*. It appears that the intensity of (001') reflections increased with an increase in the draw ratio. Annealing at 135 °C also enhanced the development of this mesomorphic phase. These results indicate that structure evolution of PET by high speed in-line drawing shows different behavior from that by off-line drawing of low strain rate, and the development of smectic mesophasic structure in PET by drawing process considerably depends on deformation rate as well as drawing temperature. It also is interesting to note that there was no indication of the appearance of (001') reflections in the series of high-speed spun fibers prepared at various take-up velocities.

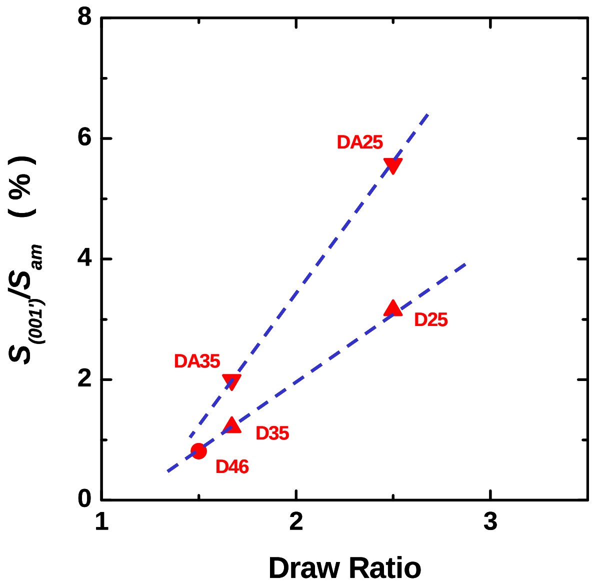

Fig.8 Variation of peak area of (001') reflection with increasing draw ratio for the in-line drawn fibers prepared with and without annealing.

3.3 Structural Change during heating process

Variations of the mass fraction of crystalline phase, oriented mesophase and isotropic amorphous phase as well as the intensity change of (001') reflection are plotted against temperature in Fig. 9. It should be noted here that the structure corresponding to the (001') reflection is not considered to match directly with the oriented mesophase, which is represented by the anisotropic component of the amorphous halo. When temperature reached close to *Tg*, intensity of (001') reflection started to increase. After the further increase of temperature of about 10 degrees, the mass fraction of crystalline phase showed an abrupt increase. At the same time, the mass fractions of oriented mesophase and isotropic amorphous phase as well as the intensity of (001') reflection started to decrease. The change in the mass fraction of oriented mesophase was more prominent in comparison with that of the amorphous phase. Intensity of (001') reflection totally disappeared at around 100 ^{o}C, whereas the amount of oriented mesophase kept decreasing through this temperature. This result confirmed that the structure corresponding to the (001') reflection is not same as the structure corresponding to the anisotropic amorphous halo.

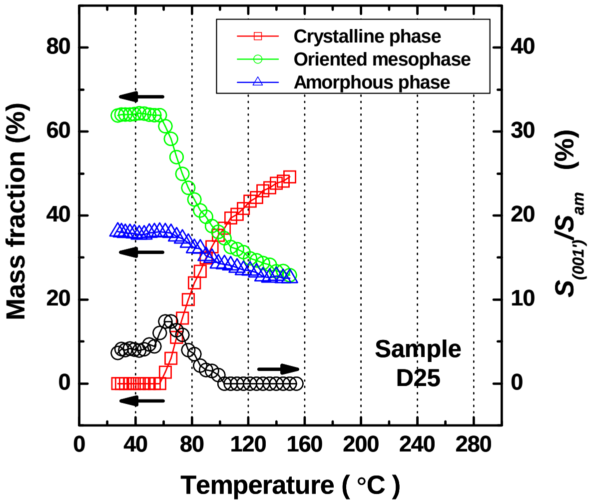

Fig.9 Variations of the mass fraction of crystalline phase, oriented mesophase and amorphous phases with increasing temperature for high-speed in-line drawn fiber. Change of the intensity of (001') is also plotted..

4. Conclusions

Difference in the mechanism of structure development in the high-speed melt spinning and high-speed in-line drawing processes was clarified through the on-line measurement of structure development behavior and structural analysis of prepared fibers. Condition for the development of unique mesomorphic structure represented by (001') reflection was also clarified.

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