

Structure and Properties of Syndiotactic Polystyrene Fibers Prepared in High-speed Melt Spinning Process

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(Received September 17, 2004; Revised January 5, 2005; Accepted January 17, 2005)

Abstract: High-speed melt spinning of syndiotactic polystyrene was carried out using high and low molecular weight polymers, HM *s*-PS and LM *s*-PS, at the throughput rates of 3 and 6 g/min. The effect of take-up velocity on the structure and properties of as-spun fibers was investigated. Wide angle X-ray diffraction (WAXD) patterns of the as-spun fibers revealed that the orientation-induced crystallization started to occur at the take-up velocities of 2-3 km/min. The crystal modification was α -form. Birefringence of as-spun fibers showed negative value, and the absolute value of birefringence increased with an increase in the take-up velocity. The cold crystallization temperature analyzed through the differential scanning calorimetry (DSC) decreased with an increase in the take-up velocity in the low speed region, whereas as the melting temperature increased after the on-set of orientation-induced crystallization. It was found that the fiber structure development proceeded from lower take-up velocities when the spinning conditions of higher molecular weight and lower throughput rate were adopted. The highest tensile modulus of 6.5 GPa was obtained for the fibers prepared at the spinning conditions of LM *s*-PS, 6 g/min and 5 km/min, whereas the highest tensile strength of 160 MPa was obtained for the HM *s*-PS fibers at the take-up velocity of 2 km/min. Elongation at break of as-spun fibers showed an abrupt increase, which was regarded as the brittle-ductile transition, in the low speed region, and subsequently decreased with an increase in the take-up velocity. There was a universal relation between the thermal and mechanical properties of as-spun fibers and the birefringence of as-spun fibers when the fibers were still amorphous. The orientation-induced crystallization was found to start when the birefringence reached -0.02 . After the starting of the orientation-induced crystallization, thermal and mechanical properties of as-spun fibers with similar level of birefringence varied significantly depending on the processing conditions.

Keywords: Syndiotactic polystyrene, High-speed melt spinning, Orientation-induced crystallization, Negative birefringence

Introduction

The successful synthesis of syndiotactic polystyrene (*s*-PS) with a high degree of stereo-regularity was first reported in 1986 [1]. The *s*-PS is a crystalline polymer and exhibits attractive properties for commercial use such as high glass transition and melting temperatures, high crystallization rate, high resistance to chemicals, low moisture regain, and low density.

There have been many fundamental researches on the crystalline structure of *s*-PS. It was reported that *s*-PS have four different crystalline modifications, i.e., α , β , γ , and δ forms. The α -form crystal is hexagonal [2,3]. The unit cell parameters are; $a = b = 2.625$ nm, and $c = 0.5045$ nm [2]. The unit cell of the β -form crystal is orthorhombic with the unit cell parameters; $a = 0.881$ nm, $b = 2.882$ nm, and $c = 0.506$ nm [4]. It was also reported that significant crystallization proceeds if amorphous *s*-PS films were on exposure to vapor of various organic solvents such as toluene [5]. In this case, δ -form crystal can be obtained. The crystalline unit cell of δ -form is monoclinic with the unit cell parameters; $a = 1.758$ nm, $b = 1.326$ nm, $c = 0.771$ nm, and $\gamma = 121.1^\circ$. The packing of the polymer chains in the δ -form enable each toluene molecule

to occupy an isolated hole between the benzene rings of adjacent polymer chains. When δ -form crystal is heated between 120 and 150 °C, toluene molecules are removed, and yields γ -form crystal. The polymer chains in γ -form crystal retain the helical structure.

In comparison with the intensive researches on crystalline structure of *s*-PS, the number of reports on the structure and properties of polymer products such as fibers, films, and moldings prepared through the melt processing of *s*-PS is limited. Uni-axial drawing of *s*-PS film was conducted by Yan *et al.* The highest tensile modulus and strength were reported to be 3.25 GPa and 110 MPa, respectively [6]. It should be noted that the glass transition temperature (T_g) and melting temperature of *s*-PS are similar to those of high- T_g engineering plastics such as poly(ethylene terephthalate), poly(phenylene sulfide), etc. In these polymers, high-order structure of products varies widely from completely amorphous to highly crystalline depending on the processing conditions. On the other hand, it is well known that the high-speed melt spinning of these polymers leads to the development of highly oriented and highly crystallized fiber structure [7,8]. Considering the facts stated above, high-speed melt spinning of *s*-PS was carried out in this study with the expectation of obtaining well-developed fiber structure.

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Experimental

Materials

Syndiotactic polystyrene (*s*-PS) pellets of two different molecular weights supplied by Idemitsu Petrochemical Co. Ltd. were used for preparation of fibers in this study. It was informed from the polymer producer that the weight-average molecular weight of high molecular weight *s*-PS (HM *s*-PS) and low molecular weight *s*-PS (LM *s*-PS) were 190,000 and 140,000, respectively. Prior to the melt spinning, the *s*-PS pellets were dried at 120 °C for 5 hours under vacuum.

Melt Spinning

An extrusion system consisting of an extruder and a gear pump was used for precise control of the throughput rate. The *s*-PS polymers were extruded at 290 °C from a spinneret with single circular hole of 1 mm diameter. The throughput rate was controlled to 3.0 or 6.0 g/min. The polymer extruded from the spinneret was taken up using a high-speed winder placed at 3.3 m below the spinning head. The attained highest take-up velocities in the case of the throughput rate of 3.0 g/min for HM *s*-PS and LM *s*-PS were 3 and 4 km/min, respectively. When the throughput rate was raised to 6.0 g/min, the highest take-up velocities for HM *s*-PS and LM *s*-PS increased to 4 and 5 km/min, respectively.

Birefringence

Measurement of refractive indices parallel and perpendicular to the fiber axis, $n_{//}$ and n_{\perp} , was carried out for the as-spun fibers using an interference microscope (Carl-Zeiss Jena) equipped with a polarizing filter. Birefringence Δn was calculated from the two refractive indices using the following equation.

$$\Delta n = n_{//} - n_{\perp} \quad (1)$$

Wide Angle X-ray Diffraction

Wide angle X-ray diffraction (WAXD) patterns of the as-spun fibers were obtained using an X-ray generator and a CCD camera (Rigaku Denki). The generator was operated at 50 kV and 40 mA, and Ni-filtered CuK_{α} radiation was used. The WAXD patterns of fiber bundles were taken with a camera length of about 4 cm.

Differential Scanning Calorimetry

Thermal properties of the as-spun fibers were investigated using a differential scanning calorimeter (Shimadzu, DSC-50). About 5 mg of the fiber sample, which was cut to small pieces, was measured at a heating rate of 10 K/min and in the temperature range of up to 300 °C. From the obtained differential scanning calorimetry (DSC) thermograms, the cold crystallization peak temperature (T_c) and the melting peak temperature (T_m) were analyzed. Crystallinity was also analyzed from the heat of fusion which was estimated by subtracting the heat of cold crystallization from the heat of melting. The heat of fusion

for an infinitely large crystal of α -form *s*-PS was assumed to be 53.2 J/g [9].

Tensile Test

The load-elongation curves of the as-spun single fibers were obtained using a tensile testing machine (Toyosokki, UTM-4L). The gage length was 20 mm and the tensile speed was 20 mm/min. The tensile modulus, tensile strength, and elongation at break were obtained averaging at least six trials of the tensile test for each sample.

Results and Discussion

WAXD Patterns

WAXD patterns of the as-spun HM *s*-PS and LM *s*-PS fibers obtained at various take-up velocities are shown in Figure 1. An isotropic amorphous halo was observed at the take-up velocity of 1 km/min for all samples. In the case of HM *s*-PS fibers, crystalline reflections started to appear at 2 and 3 km/min for the throughput rates of 3.0 and 6.0 g/min, respectively. In the LM *s*-PS fibers, crystalline reflections started to appear at 3 km/min for both throughput rates, however, the reflections were still vague in case of 6.0 g/min. Crystalline reflections became fairly distinct at higher take-up velocities for all samples. The observed WAXD patterns correspond to the highly oriented α -form crystals of *s*-PS. Appearance of highly-oriented crystalline reflections at high take-up velocities corresponds to the occurrence of orientation-induced crystallization in the spinning process. Similar crystallization behavior was reported to occur in high-speed melt spinning of various polymers such as poly(ethylene terephthalate) (PET) [7], poly(*p*-phenylene sulfide) (PPS) [8], poly(ethylene 2-6-naphthalene dicarboxylate) (PEN) [10], polylactides [11], etc. These are the crystalline polymers with their glass transition temperatures higher than room temperature.

Birefringence and Density

Refractive indices parallel and perpendicular to the fiber axis, $n_{//}$ and n_{\perp} , measured using an interference microscope were plotted against the take-up velocity in Figure 2. As-spun fibers obtained at 0.25 km/min were essentially isotropic regardless of the difference in molecular weight and throughput rate. Refractive indices of these fibers were about 1.59. With an increase in the take-up velocity, $n_{//}$ decreased whereas n_{\perp} increased. Therefore birefringence was negative and decreased with an increase in the take-up velocity as shown in Figure 3. Polystyrenes are known to have negative intrinsic birefringence because of the existence of a large side-chain, i.e. benzene ring. Therefore, decrease in the birefringence or increase in the absolute value of birefringence implies the development of molecular orientation.

If the results for the same throughput rate were compared, molecular orientation of the HM *s*-PS fibers was higher than that of the LM *s*-PS fibers. On the other hand, if the results

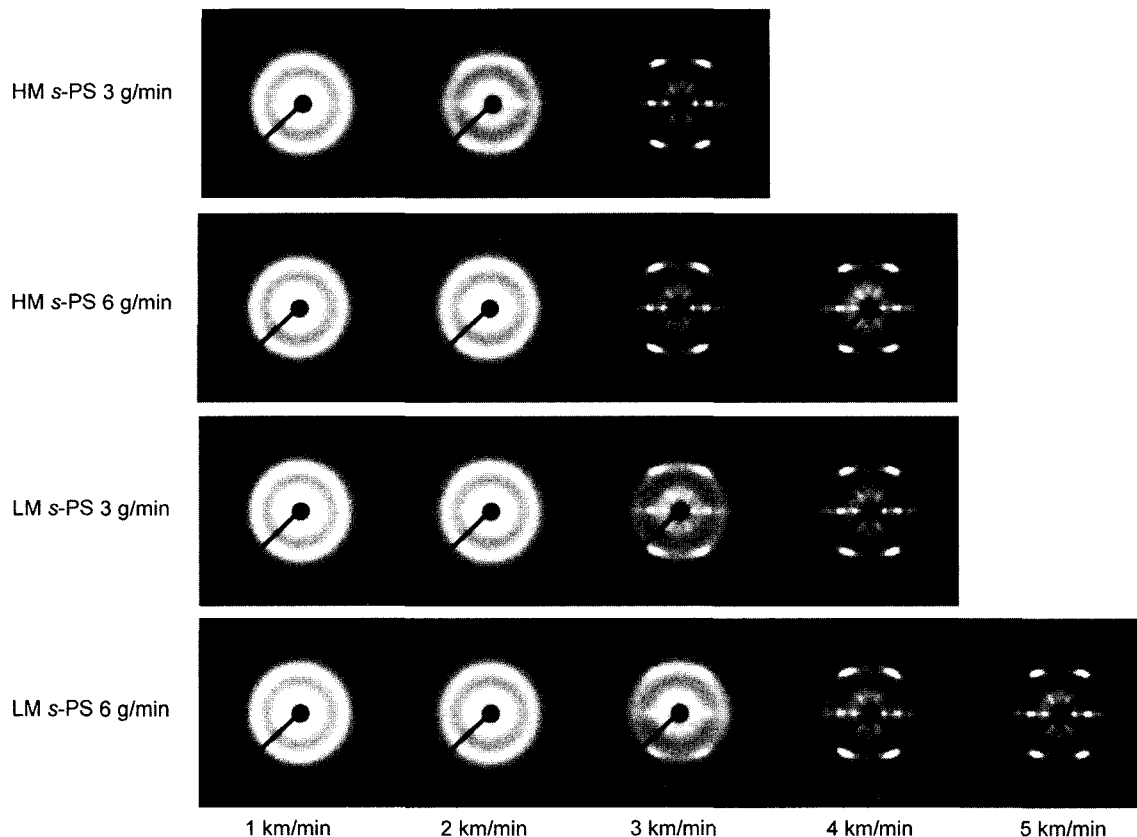


Figure 1. Wide angle X-ray diffraction patterns of as-spun *s*-PS fibers.

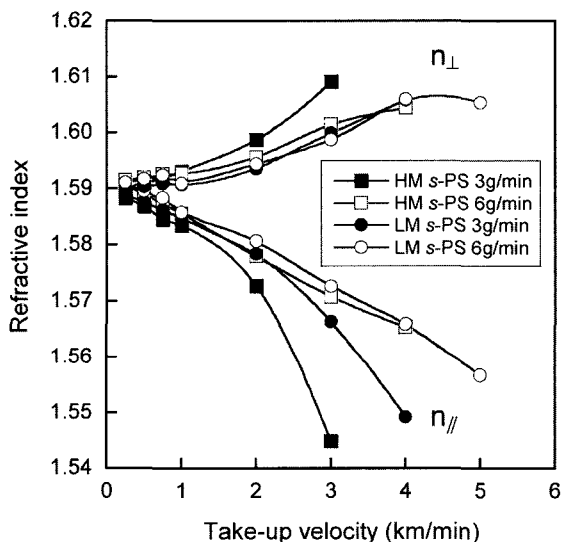


Figure 2. Changes in refractive indices parallel and perpendicular to the fiber axis, n_{\parallel} and n_{\perp} , with take-up velocity for *s*-PS fibers.

for the same molecular weight were compared, molecular orientation of the fibers obtained at the throughput rate of 3.0 g/min was higher than that of the fibers obtained at 6.0 g/min. Accordingly, the highest birefringence of -0.064 was obtained

for the as-spun fibers of HM *s*-PS at the throughput rate of 3.0 g/min even though the attained maximum take-up velocity was only 3 km/min. On the other hand, the results for the throughput rate of 6.0 g/min showed a tendency of saturation at high take-up velocities in cases of both HM *s*-PS and LM *s*-PS.

It is known that the development of birefringence in the melt spinning process depends on the tensile stress applied to the spinning line as far as the effect of spontaneous orientation development caused by the orientation-induced crystallization is negligible [12,13]. On the other hand, the tensile stress at the solidification of the spinning line is predictable based on the governing equations for the melt spinning dynamics [14]. In general, the tensile stress applied to the spinning line increases with an increase in the take-up velocity. The higher molecular weight and lower throughput rate also lead to the increase in the tensile stress. Therefore, it can be said that the experimental results on the birefringence development agreed well with the theoretical prediction.

Concerning the effects of molecular weight and throughput rate on fiber structure development, results of the birefringence and WAXD measurements showed similar tendency, and the comparison of the results shown in Figures 2 and 3 suggested that the orientation-induced crystallization started to occur when the absolute value of birefringence exceeded about 0.02.

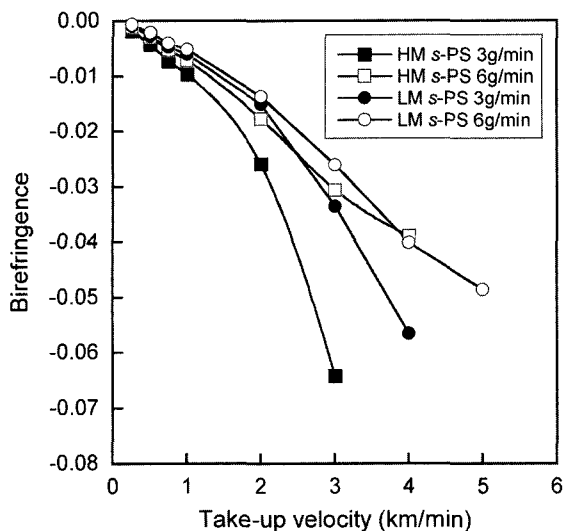


Figure 3. Change of birefringence with take-up velocity for *s*-PS fibers.

The Lorentz-Lorenz equation expresses the relation between the refractive index n and the density ρ of filaments as follows.

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi N \rho P}{3M} \quad (2)$$

where N , M , and P denote Avogadro number, the molecular weight, and the molar polarizability, respectively. Since the value $(n^2 - 1)/(n^2 + 2)$ has linear relation with density, this value is often referred to as "Lorentz density". For materials with uni-axial anisotropy such as filaments, the mean refractive index n may be expressed using the refractive indices parallel and perpendicular to the fiber axis, $n_{//}$ and n_{\perp} , as follows.

$$n^2 = \frac{2n_{\perp}^2 + n_{//}^2}{3} \quad (3)$$

According to equations (2) and (3), Lorentz density was calculated using the data shown in Figure 2, and plotted against the take-up velocity in Figure 4. The Lorentz density did not exhibit a notable change, the variation being within a range of 0.3-0.5 %, even though there should be a significant change in crystallinity as indicated in the WAXD measurement. On the other hand, it has been reported that the densities of amorphous phase and α -form crystal of *s*-PS are 1.04 and 1.033 g/cm³, respectively [2]. Therefore, it can be said that almost negligible change of density observed in the refractive index measurement of various *s*-PS fibers confirmed the small difference between crystalline and amorphous densities.

Differential Scanning Calorimetry

DSC thermograms of as-spun HM *s*-PS and LM *s*-PS fibers measured at the heating rate of 10 K/min are shown in Figure 5. In the fibers obtained at low take-up velocities, the glass transition was clearly observed at about 94 °C. The glass

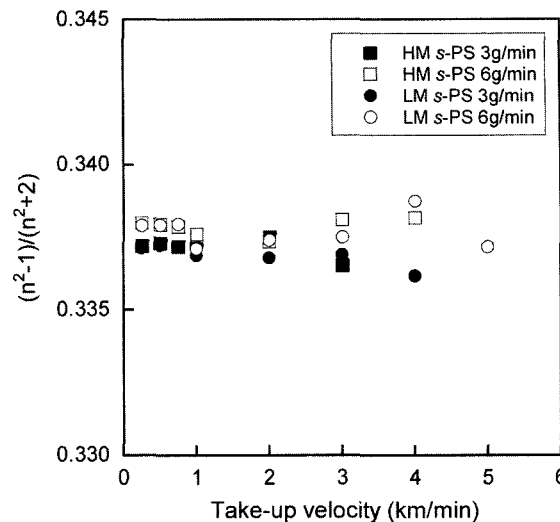


Figure 4. Change of Lorentz density, $(n^2 - 1)/(n^2 + 2)$, with take-up velocity for *s*-PS fibers.

transition became obscure at high take-up velocities because as-spun fibers started to have highly crystallized structure. In general, the DSC thermograms of *s*-PS fibers showed cold crystallization and melting peaks. An exothermic peak of cold crystallization was observed at around 120-140 °C. The peak shifted to lower temperatures and became smaller with an increase in the take-up velocity. Similar cold crystallization behavior was observed in the DSC thermograms of high-speed spun PET [7], PPS [8], and PEN [10]. On the other hand, an endothermic peak of melting appeared at around 274 °C and gradually became narrower with an increase in the take-up velocity in low speed region. With a further increase in the take-up velocity, the melting peak started to have a shoulder and finally showed two peaks when orientation-induced crystallization started to occur.

Peak temperatures of cold crystallization were plotted against take-up velocity in Figure 6. The cold crystallization temperature decreased steeply when the take-up velocity was increased from 1 to 2 km/min for all samples. It is known that the crystallization rate of amorphous fibers increases with the development of molecular orientation. Accordingly, at a constant heating rate in the DSC measurement, the cold crystallization of the fibers with higher molecular orientation took place at lower temperatures. After taking a minimum, the peak temperature of cold crystallization started to increase with an increase in the take-up velocity. The minimum point for each combination of the molecular weight and throughput rate roughly coincides with the take-up velocity where the orientation-induced crystallization started, suggesting that the molecular orientation of amorphous phase decreased at high take-up velocities. It was speculated that the molecules oriented in the spinning line were selectively incorporated into the crystalline phase in the course of orientation-induced crystallization, and consequently, only the molecules with low orientation were

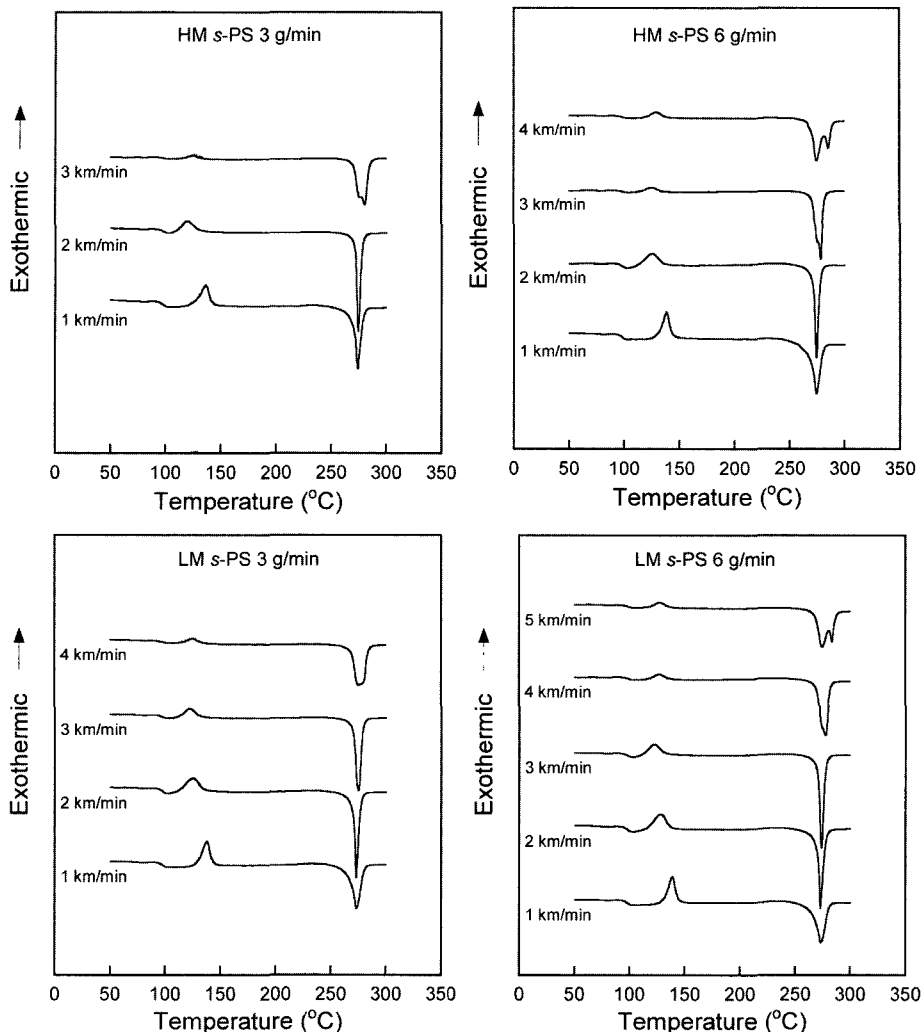


Figure 5. Differential scanning calorimetry thermograms of as-spun *s*-PS fibers.

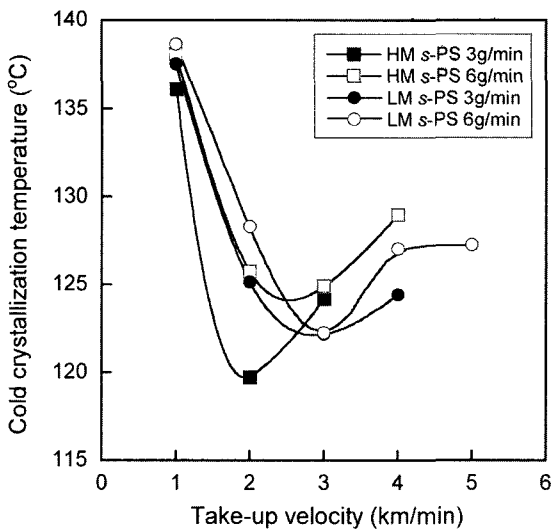


Figure 6. Peak temperatures of cold crystallization plotted against take-up velocity for *s*-PS fibers.

remained in the amorphous region.

Temperatures of melting peak and shoulder for the HM *s*-PS and LM *s*-PS fibers were plotted against take-up velocity in Figure 7. In the case of HM *s*-PS fiber obtained at the throughput rate of 6.0 g/min, the melting temperature on the higher temperature side reached to 285 °C at the attainable highest take-up velocity of 4 km/min.

In the DSC analysis of high-speed spun fibers, the peak on the lower temperature side of melting is considered to be the melting of crystals formed by cold crystallization in the heating process of the DSC measurement, whereas the peak on the higher temperature side is considered to be the melting of highly ordered large-size crystals developed in the spinning line. Increase in the melting peak temperature on the higher temperature side of melting peak with an increase in the take-up velocity usually corresponds to the increase in the crystallization temperature in the spinning line.

Crystallinity of as-spun fibers was analyzed from the DSC thermograms and plotted against the take-up velocity as

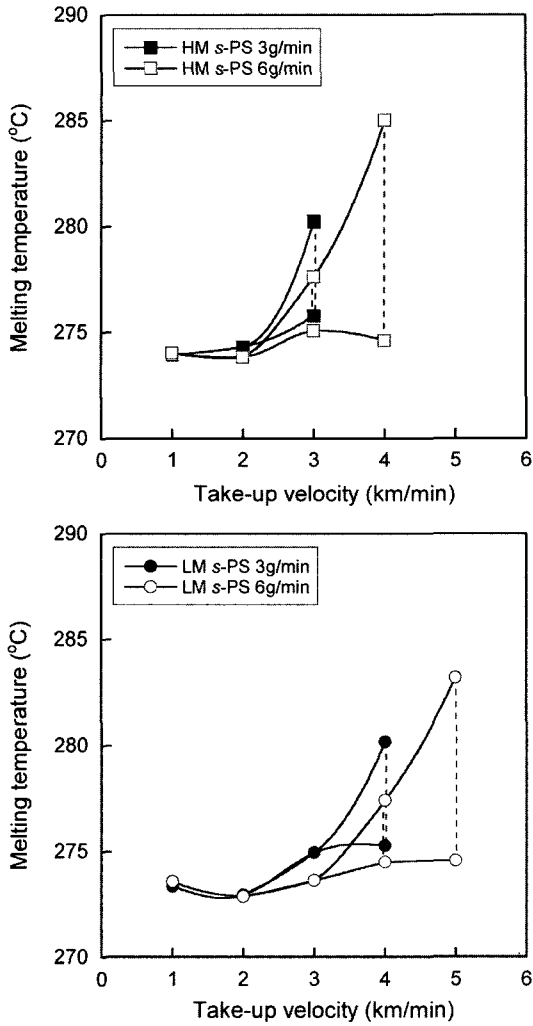


Figure 7. Peak and shoulder temperatures of melting plotted against take-up velocity for *s*-PS fibers.

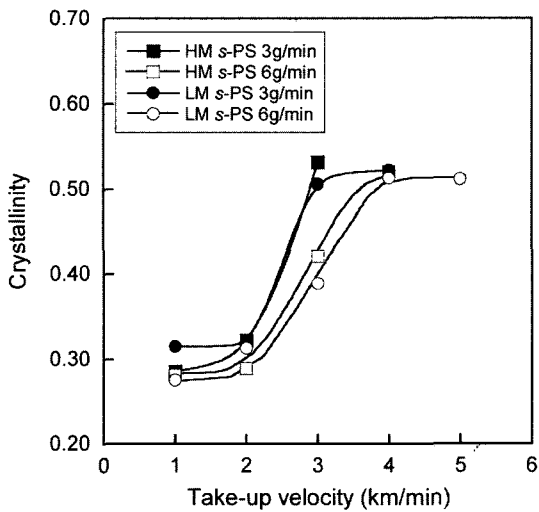


Figure 8. Crystallinity analyzed from differential scanning calorimetry thermogram plotted against take-up velocity for *s*-PS fibers.

shown in Figure 8. The crystallinity started to increase steeply when the take-up velocity exceeded 3 km/min. The on-set point of crystallization estimated from DSC measurement was in agreement with that from the WAXD measurement. The

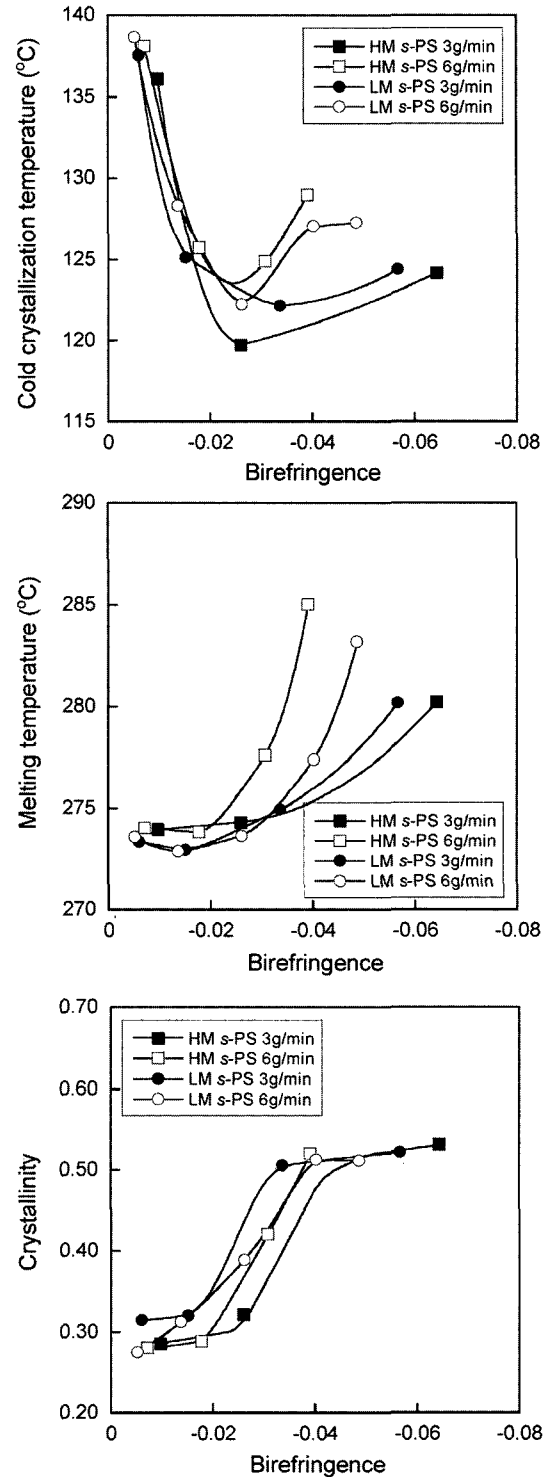


Figure 9. Cold crystallization temperature, melting peak temperature, and crystallinity plotted against birefringence for *s*-PS fibers.

highest crystallinity of *s*-PS fibers was about 52 %.

The cold crystallization temperature, melting temperature, and crystallinity analyzed from the DSC thermograms were plotted against the birefringence in Figure 9. It is obvious that the cold crystallization temperature of as-spun fibers obtained at lower take-up velocities, where orientation-induced crystallization did not occur, was controlled by birefringence. The crystallinity also depended strongly on the birefringence irrespective of the changes of molecular weight and throughput rate. On the other hand, if comparison is made for the fibers with the same level of molecular orientation, melting temperature of the as-spun fibers prepared with higher throughput rate was obviously higher than that of the fibers prepared with lower throughput rate. This result may suggest that the orientation-induced crystallization tends to occur at higher temperatures in the spinning line if the throughput rate is increased.

Mechanical Properties

Tensile modulus, tensile strength, and elongation at break of as-spun fibers were plotted against take-up velocity in Figures 10, 11, and 12, respectively. In general, tensile modulus increased with an increase in the take-up velocity. Steep increase of tensile modulus was observed with the starting of orientation-induced crystallization for each combination of molecular weight and throughput rate. The highest value of 6.5 GPa was obtained for the LM *s*-PS fibers obtained at the take-up velocity of 5 km/min and the throughput rate of 6 g/min. On the other hand, tensile strength showed a maximum at around 2 km/min for all the samples. Maximum value of about 160 MPa was obtained for the HM *s*-PS fibers with the throughput rate of both 3 and 6 g/min. In comparison with the mechanical properties of uniaxially drawn *s*-PS films reported by Yan *et al.* [6], the fibers obtained at high take-up velocities

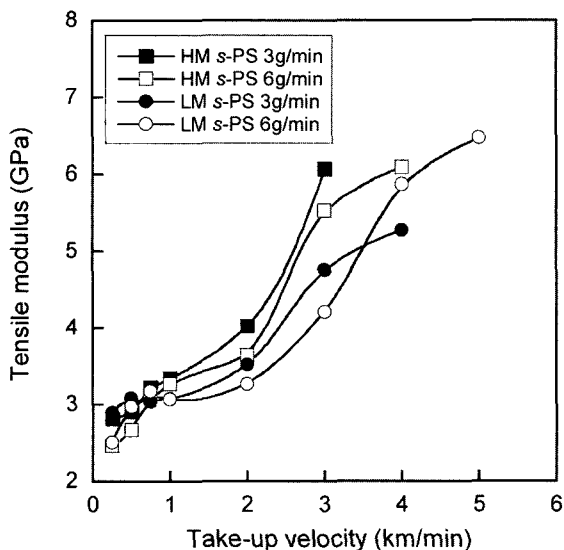


Figure 10. Change of tensile modulus with take-up velocity for *s*-PS fibers.

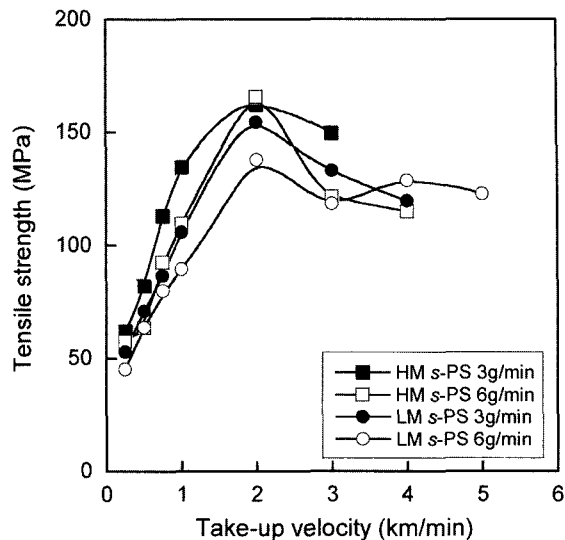


Figure 11. Change of tensile strength with take-up velocity for *s*-PS fibers.

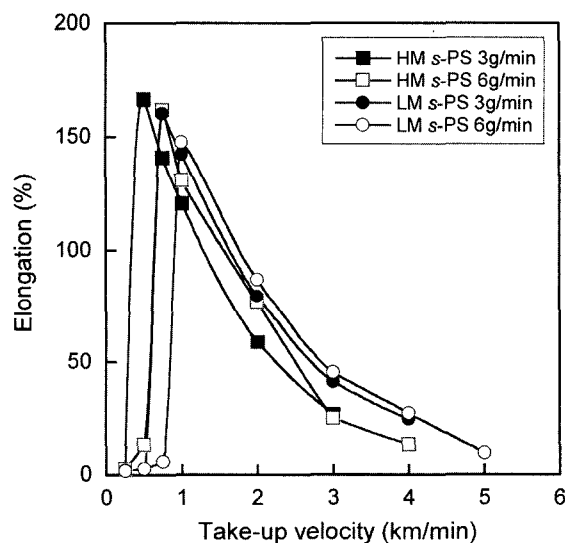


Figure 12. Change of elongation at break with take-up velocity for *s*-PS fibers.

in this study showed higher tensile modulus and strength.

Elongation at break of as-spun fibers obtained at low take-up velocities were low. However, it increased suddenly at a certain take-up velocity for each combination of molecular weight and throughput rate. Such a drastic change of elongation can be regarded as the brittle-ductile transition originated from the development of molecular orientation. Elongation at break of the fibers obtained at take-up velocities higher than the critical velocity of brittle-ductile transition decreased with an increase in the take-up velocity. The spinning conditions of higher molecular weight and lower throughput rate lead to the occurrence of brittle-ductile transition at lower take-up velocities. These conditions also lead to lower elongation at

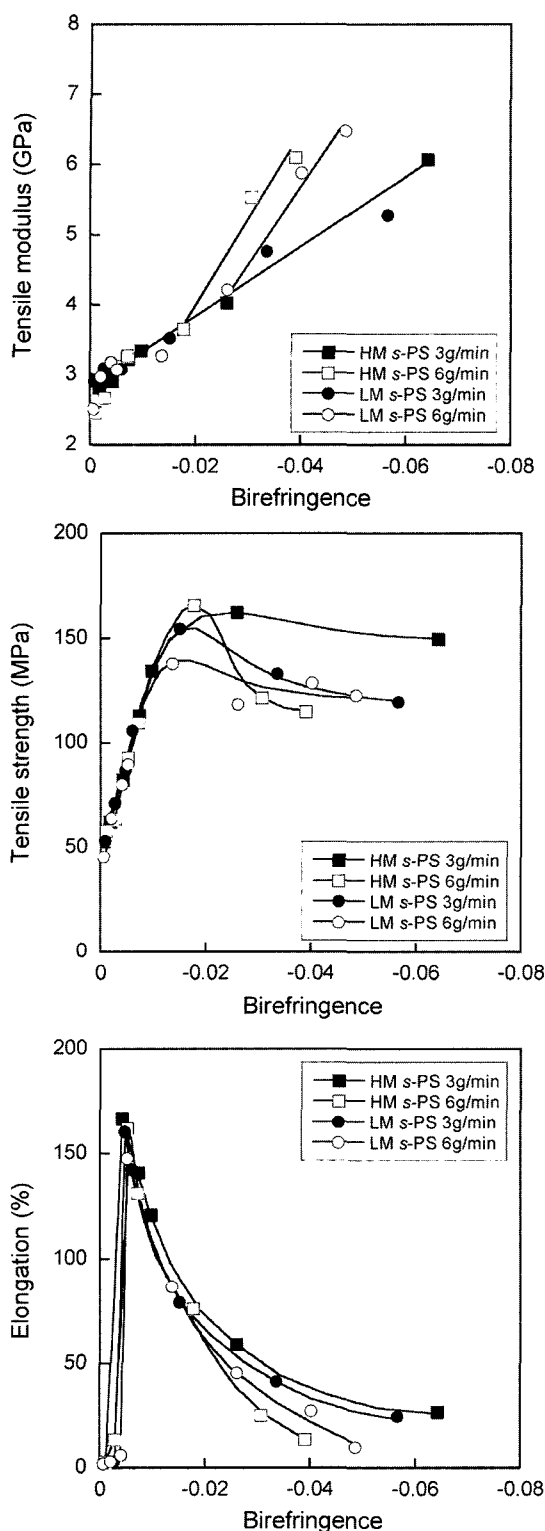


Figure 13. Tensile modulus, tensile strength, and elongation at break plotted against birefringence for *s*-PS fibers.

break after the brittle-ductile transition if comparison is made at the same take-up velocity.

Mechanical properties of as-spun fibers were plotted against birefringence in Figures 13. There was a universal linear relationship between tensile modulus and birefringence when molecular orientation was low. In case of the throughput rate of 6 g/min, tensile modulus showed break points at birefringences of about -0.02 and -0.03 for the HM *s*-PS and LM *s*-PS, respectively. These break points correspond to the onset of orientation-induced crystallization. On the other hand, no break points were found in case of the throughput rate of 3 g/min. The tensile strength vs. birefringence plot also showed a master curve up to the point of the onset of orientation-induced crystallization. In case of the fibers crystallized in the spinning process, however, the mechanical properties could not be described solely by the molecular orientation represented by birefringence. The elongation at break increased steeply at the birefringence of -0.005 indicating that the brittle-ductile transition occurred at the same level of birefringence regardless of other spinning conditions. The elongation at break vs. birefringence plot including the brittle-ductile transition also showed a general tendency up to the starting of orientation-induced crystallization.

Conclusions

High-speed melt spinning of syndiotactic polystyrene of two different molecular weights was performed at two different throughput rates. The attainable highest take-up velocity increased with the decrease in the molecular weight and increase in the throughput rate. WAXD patterns revealed that the orientation-induced crystallization of *s*-PS fibers started to occur at the take-up velocities of 2-3 km/min where the birefringence, of as-spun fibers reached about -0.02 . The crystal modification was α -form. Measurements of WAXD, birefringence, and DSC suggested that the fiber structure development proceeded from lower take-up velocities if the spinning conditions of higher molecular weight and lower throughput rate were adopted. Tensile modulus of as-spun fibers increased with an increase in the take-up velocity, whereas tensile strength showed a maximum at around 2 km/min. The as-spun fibers showed brittle-ductile transition when birefringence reached about -0.005 . Elongation at break decreased with an increase in the take-up velocity after this transition. Plots of thermal properties and mechanical properties of as-spun fibers against birefringence revealed that there were universal relations between birefringence and the properties of as-spun fibers when the fibers were amorphous. On the other hand, when orientation-induced crystallization occurred in the spinning process, the properties of as-spun fibers with similar level of birefringence varied significantly depending on the processing conditions.

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