

# Structure Development and Characteristics of Fibers Prepared in High Speed Melt Spinning and Drawing Processes of Polypropylenes with Controlled Stereo-regularity Distribution

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## Abstract

Polypropylenes (PPs) with controlled stereo-regularity distribution were prepared by blending the high molecular weight and low molecular weight polymers, which have different degree of stereo regularity. High-speed melt spinning and subsequent drawing processes were applied to these polymers. Both types of blend polymer exhibited high spinnability, even though these polymers have relatively high polydispersity. It is also noteworthy that the behaviors of neck-like deformation and crystalline structure formation of these polymers are significantly different. On the contrary, drawing of low-speed spun fibers prepared from these polymers suggested that the structure development in the drawing process is mainly controlled by the draw ratio, and the effect of polymer characteristics on the structure development is insignificant in comparison with that in the melt spinning process.

## 1 Introduction

There have been many researches on the structure and properties of *isotactic* polypropylene (*i*-PP) products such as fibers, films, bottles, injection moldings *etc.* Properties of the polymer products are closely related to the higher-order structure. Therefore, especially in the field of polyolefins, recent research activities are more concentrated on the control of the structure development in the polymer processing through the designing of the starting materials. Molecular designing including controls of molecular weight and its distribution, tacticity and its distribution, copolymer composition *etc.* is considered to be an effective method for the control of structure development [1-3].

In the polymer processing, structure development proceeds in the flow field, and in many cases so-called shish-kebab structure [4] is formed consequently. In such a case, it is usually recognized that the development of higher-order structure starts from the formation of the shish consisting of relatively high molecular weight molecules, which are extended in the direction of flow, followed by the epitaxial growth of the kebab on the shish. The kebab is consisting of relatively low molecular weight molecules, which form folded lamellae structure [5-8]. Therefore molecular weight distribution is one of the most effective parameters for the control of structure development behavior. On the other hand, stereo regularity is recognized as another important parameter for the control of structure development as the self-ordering of molecules through crystallization is highly affected by the tacticity [9,10].

In this study, a new concept of stereo-regularity distribution is introduced by combining the controls of the molecular weight distribution and the tacticity for the designing of polymers. Accordingly, two types of PP were prepared; one has low tacticity in the high molecular weight region and high tacticity in the low molecular weight region, and the other has high tacticity in the high molecular weight region and low tacticity in the low molecular weight region. High-speed melt spinning and subsequent drawing of these PPs were performed, and structure and properties of resultant fibers were investigated. In these fibers, it is expected that the shish and kebab are composed of molecules with high and low crystallizability, respectively, or vice versa. Our main interest is on the possibility of controlling the processability of PPs through the control of the crystallizability of the shish and kebab components independently.

## 2 Experimental

### 2.1 Materials

Two types of blend PPs, PP-A and PP-B were prepared. PP-A is a blend of high molecular weight/low tacticity PP and low molecular weight/high tacticity PP, whereas PP-B is a blend of high molecular weight/high tacticity PP and low molecular weight/low tacticity PP. A homo-PP with similar melt flow rate and *mmmm* pentad fraction, PP-STD, was used for comparison. In some experiments, two other types of homo-PPs with relatively high and low levels of tacticity, PP-H and PP-L, were also investigated. Melt flow rate, *mmmm* pentad fraction, and polydispersity, Mw/Mn, for the used polymers are summarized in Table 1.

Molecular weight distribution of PP-STD, PP-A and PP-B are compared in Fig.1. In comparison with PP-STD, PP-B has larger tail in the high molecular weight region, whereas both PP-A and PP-B have larger tail in the low molecular weight region. Accordingly, the Mw/Mn values for these three polymers are in the order of PP-STD < PP-A < PP-B.

Table 1: Melt flow rate, isotactic pentad fraction and polydispersity of polypropylenes used.

|        | MFR (g/10min) | mmmm (mol%)      | Mw/Mn |
|--------|---------------|------------------|-------|
| PP-STD | 16.5          | 91.0             | 2.75  |
| PP-H   | 18.7          | 97.0             | 2.86  |
| PP-L   | 17.0          | 74.9             | 2.39  |
| PP-A   | 18.1          | 91.0 [45.0,97.0] | 3.61  |
| PP-B   | 20.1          | 91.0 [97.0,45.0] | 4.17  |

[High Mw, Low Mw]

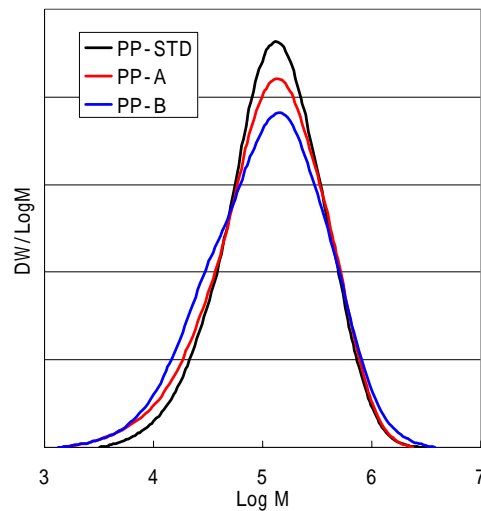


Figure 1: Molecular weight distribution of three polypropylenes.

### 2.2 Melt spinning

Extrusion of the polymers was performed using a 25 mm $\phi$  single screw extruder equipped with a gear pump. The spinneret has ten spinning holes of 0.6 mm diameter. Extrusion temperature and throughput rate were set at 230 °C and 2.0 g/min per hole, respectively. Take-up velocity was increased from 1 km/min to the highest attainable speed with an interval of 1 km/min. Thinning behavior of the spin-line was measured at 1, 2 and 4 km/min using a back-illumination type diameter monitor (Zimmer OHG, Model 460 A/10).

## 2.3 Drawing

Continuous drawing of the as-spun fibers prepared at 0.3 km/min was performed using a drawing machine consisting of a feed roller, a take-up roller and a winder. Drawing temperature was set at 120 °C. The surface velocity of the feed roller was 12 m/min, and the draw ratio was increased by changing the velocity of the take-up roller up to the highest attainable draw ratio, which is defined as the ratio of the surface velocities of feed and take-up rollers.

## 2.4 Characterization

*Wide angle X-ray diffraction:* Wide angle X-ray diffraction (WAXD) patterns of the as-spun and drawn fibers were obtained using an X-ray generator and a CCD camera (Rigaku Denki). The generator was operated at 40 kV and 300 mA, and the WAXD patterns of fiber bundle were taken using  $\text{CuK}\alpha$  radiation. Camera length was about 4 cm.

*Tensile test:* The load-elongation curves of the as-spun and drawn fibers were obtained using a tensile testing machine. The gauge length was 100 mm and the tensile speed was 100 mm/min. The tensile modulus, the tensile strength and the elongation at break were obtained averaging at least ten trials of the tensile test for each sample.

## 3 Results and Discussion

### 3.1 Spinning behavior in high-speed melt spinning process

As described in the experimental section, take-up velocity was increased gradually in the melt spinning process. With an increase in the take-up velocity, occasional spin-line breakage started to occur, and further increase of the take-up velocity lead to more frequent breakage, and eventually spinning became impossible. Thus obtained highest attainable take-up velocities for the five different PPs are summarized in Fig.2. Both PP-A and PP-B showed significantly higher spinnability in comparison with the PP-STD.

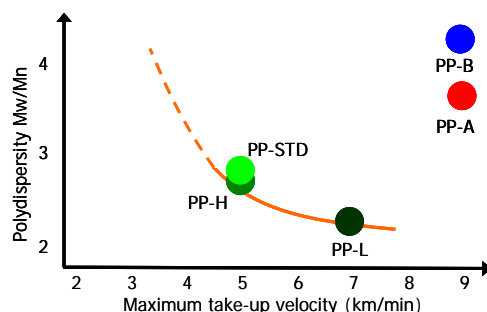


Figure 2: Relation between polydispersity and highest attainable take-up velocity polypropylenes

In general, increase in the polydispersity is known to lead to inferior spinnability. Typical examples are the good spinnability of metallocene catalyzed PPs with low polydispersity [11], and the poor spinnability of high-melt tension PPs prepared by adding a small amount of high molecular weight component [12]. It is interesting to note that the spinnability of PP-A and PP-B are fairly high despite of their relatively large polydispersities.

Photographs of as-spun fibers cut from the take-up bobbin are shown in Fig.3. In case of PP-STD, as-spun fibers started to show the formation of crimp at 5 km/min, whereas the as-spun fibers of PP-A and PP-B were almost straight even at 9 km/min. On the other hand, PP-H and PP-L fibers obtained at the highest attainable take-up velocity, 6 km/min, showed totally different appearance; PP-H is severely crimped, whereas PP-L is almost straight. Results of the latter two polymers suggest that the crimp formation occurs only when highly crystallizable polymer is melt-spun at the condition near the limit of spinnability. If this consideration is acceptable, it can be concluded that both PP-A and PP-B have high spinnability and low crystallizability.

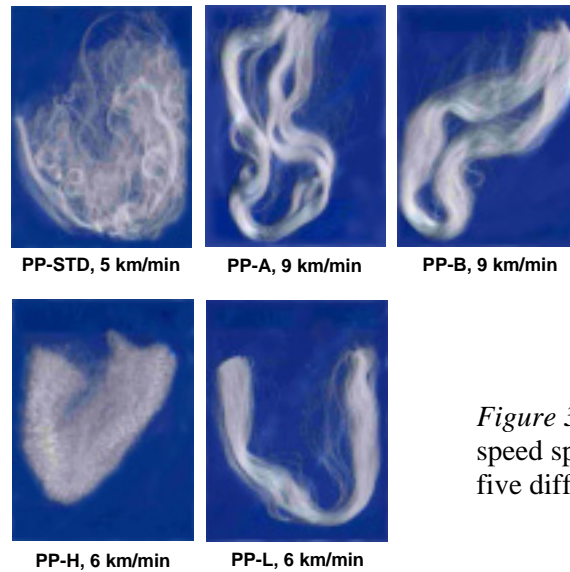


Figure 3: Appearance of high-speed spun fibers prepared from five different polypropylenes.

Diameter profiles of the spin-line for PP-STD, PP-A and PP-B are compared in Fig. 4. In case of PP-STD, thinning was monotonous at 1 km/min, whereas so-called neck-like deformation [13, 14] was clearly observed at 4 km/min. Slight indication of the occurrence of neck-like deformation was also observed at 2 km/min. It is noteworthy that the diameter profiles of PP-A and PP-B are significantly different even though both polymers showed fairly high spinnability. In comparison with the PP-STD, neck-like deformation was suppressed in case of PP-A, whereas that was enhanced in case of PP-B. In the latter, neck-like deformation was observed even at 1 km/min. Difference in the thinning behavior can be clearly recognized from the solidification position of the spin-line at the take-up velocity of 4 km/min. Those were at around 50, 70 and 80 cm down from the spinneret for PP-B, PP-STD and PP-A, respectively.

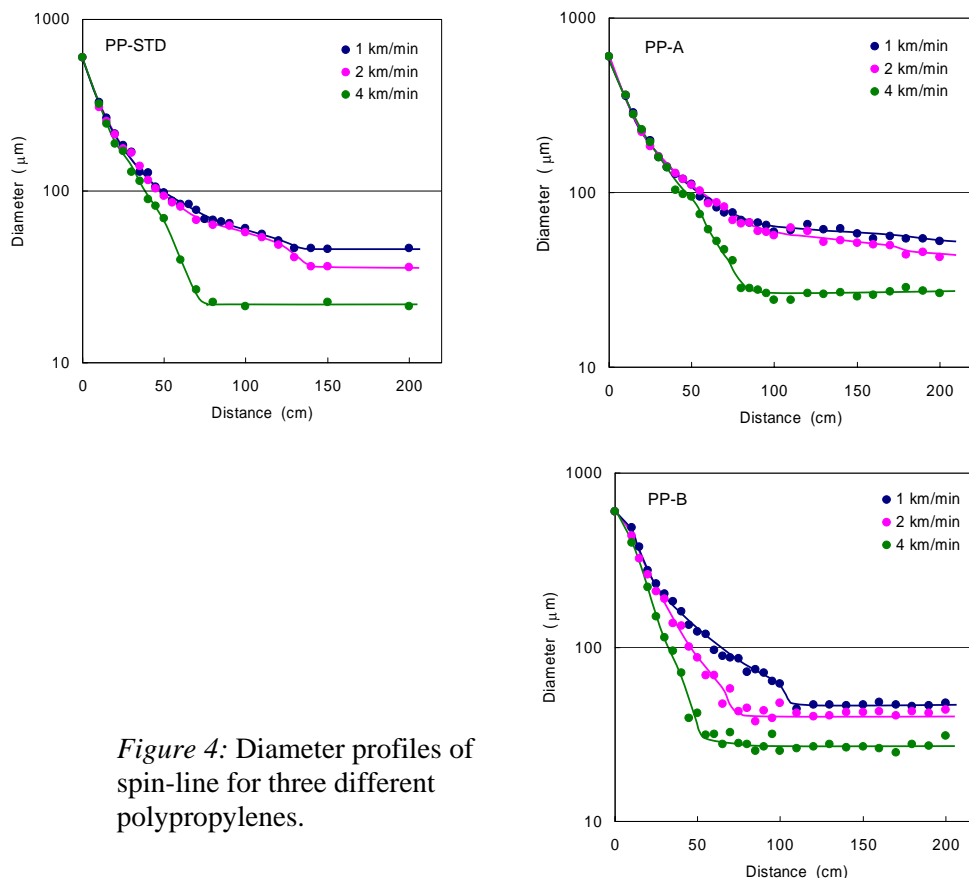


Figure 4: Diameter profiles of spin-line for three different polypropylenes.

Enhancement of the neck-like deformation in PP-B was speculated to be caused by the presence of a large amount of ultra-high molecular weight component ( $>10^6$ ) as was shown in Fig.1. On the other hand, suppression of the neck-like deformation of PP-A in comparison with PP-STD suggested that the neck-like deformation behaviour is affected not only by the presence of high molecular weight component, which forms the shish, but also the crystallizability of high molecular weight component.

There can be several factors affecting the improvement of spinnability in PP-A and PP-B. Low crystallizability, which was suggested by the suppression of the crimp formation, is a possible reason for the improvement of spinnability but with different mechanisms for PP-A and PP-B. In case of PP-A, suppression of the neck-like deformation caused by the low crystallizability of the high molecular weight component prevents the application of high spin-line stress in the high temperature region of the spin-line, and also leads to the low spin-line stress in the down stream because of the reduction of the air-friction force. In case of PP-B, although the formation of neck-like deformation is enhanced because of the presence of high molecular weight component, low crystallizability of the low molecular weight component may slow down the crystallization of spin-line after the neck-like deformation, which possibly maintains the flexibility or deformability of the spin-line. Presence of a large amount of low molecular weight component, which was also confirmed in Fig.1, may also enhance the flexibility of the spin-line through the plasticization effect. As a whole, it was speculated that the control of the tacticity distribution with respect to the molecular weight distribution can be an effective strategy for the improvement of the processability.

### 3.2 Structure and properties of high-speed spun fibers

WAXD patterns of the as-spun fibers are summarized in Fig.5. In case of PP-STD, the fibers obtained at 1 km/min showed slightly oriented pseudo-hexagonal (smectic) structure, and the oriented monoclinic crystals were developed from 2 km/min, whereas the PP-A fibers showed pseudo-hexagonal structure at 1 and 2 km/min, and formation of oriented monoclinic crystals started only from 3 km/min. On the contrary, the PP-B fibers exhibited the structure of oriented monoclinic crystals from 1 km/min. At higher take-up velocities as-spun fibers of the three different PPs showed highly oriented monoclinic crystals. Appearance of 110 reflections near the meridian indicates the co-existence of a significant amount of  $a^*$ -axis oriented crystals along with the ordinary  $c$ -axis oriented crystals [15].

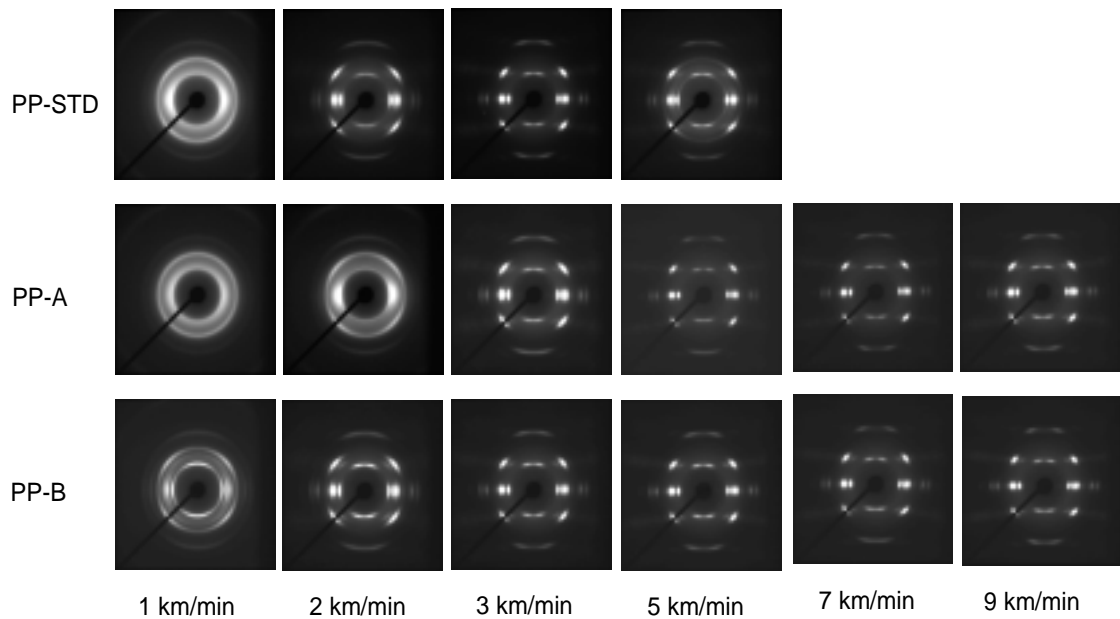


Figure 5: Wide-angle X-ray scattering patterns of high-speed spun fibers prepared from three different polypropylenes.

It has been speculated that the transition of crystalline form from pseudo-hexagonal to monoclinic indicates the increase of crystallization temperature in the spin-line [1]. Pseudo-hexagonal crystals can be formed even after the spinning process, *i.e.* on the spinning bobbin because glass transition temperature of PP is lower than room temperature. It has been speculated also that the major part of crystallization starts at the solidification point of the spin-line, *i.e.* immediately below the neck-like deformation [14]. Shift of the position of neck-like deformation closer to the spinneret indicates the increase of crystallization temperature. Therefore, neck-like deformation behavior has close correlation with crystalline structure of as-spun fibers as can be seen from the comparison of results shown in Figs.4 and 5.

Mechanical properties of as-spun fibers are summarized in Fig.6. In case of PP-STD, tensile modulus and tenacity showed a maximum at 2 km/min and decreased at higher take-up velocities. In comparison with the PP-STD fibers, PP-A and PP-B fibers showed fairly high mechanical properties even at extremely high take-up velocities. The PP-A fibers showed higher tensile modulus, higher tenacity and lower elongation at break than the PP-B fibers in the take-up velocity region higher than 6 km/min. In other words, molecules in the PP-A fibers are highly elongated or oriented in comparison with those in the PP-B fibers. It is noteworthy that the elongation at break of 250% is maintained in the PP-B fibers prepared at the extremely high take-up velocity of 9 km/min. This may be the evidence of the plasticization effect caused by the large amount of low molecular weight molecules with low crystallizability.

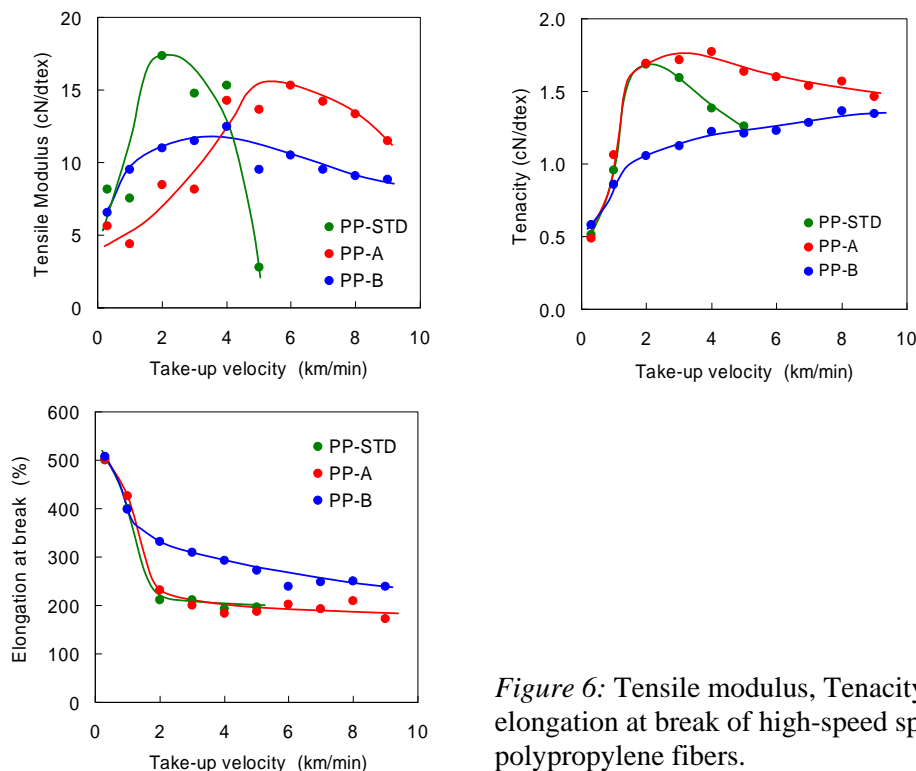


Figure 6: Tensile modulus, Tenacity, and elongation at break of high-speed spun polypropylene fibers.

### 3.3 Off-line drawing

Off-line drawing of low-speed spun fibers prepared from the above mentioned polymers was performed. The maximum attainable draw ratio is summarized in Fig.7. It can be seen that the drawability has positive correlation with the stereo-regularity of the polymers. The results for PP-A and PP-B also follow this correlation.

WAXD patterns of the drawn fibers prepared from the as-spun fibers of PP-STD, PP-A and PP-B obtained at 0.3 km/min are compared in Fig.7. All the starting fibers showed pseudo-

hexagonal structure with almost negligible molecular orientation. Irrespective of the difference in the characteristics of polymers, the drawn fibers at the draw ratio of 2.0 showed slightly oriented monoclinic structure, and at the draw ratios of 4.0 and 6.0 (or 5.5 for PP-B) highly oriented monoclinic structure was observed for all the fibers. There was a slight increase in crystalline orientation when the draw ratio was increased from 4.0 to 5.5 or 6.0. On the contrary to the results for as-spun fibers, the amount of a\*-axis oriented crystals is very small at the draw ratio of 4.0, and almost negligible at the draw ratio of 5.5 or 6.0.

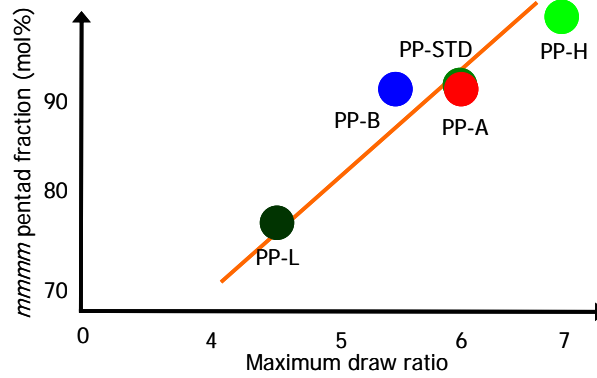


Figure 7: Relation between isotactic pentad fraction and highest attainable draw ratio for five different polypropylenes.

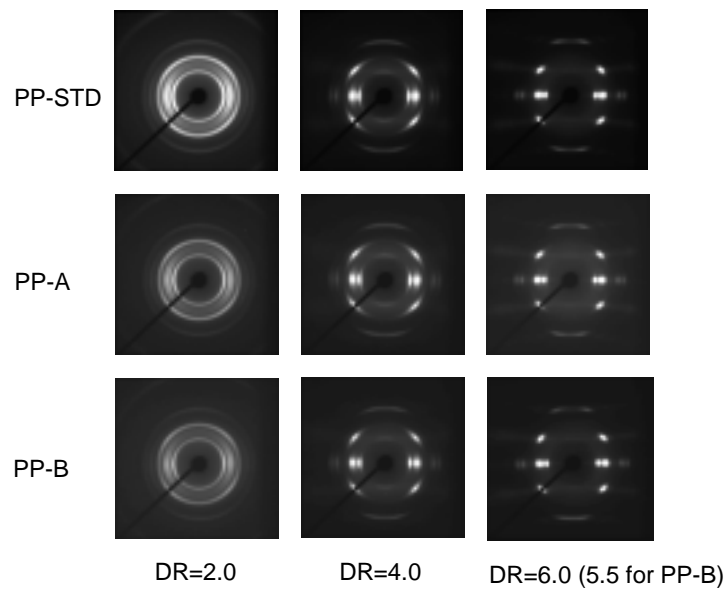


Figure 8: Wide-angle X-ray scattering patterns of drawn fibers prepared from three different polypropylenes.

These results suggest that the structure development in the drawing process is mainly controlled by the drawing temperature and draw ratio, and the effect of the differences in the characteristics of the polymers on the structure development behavior is small, even though the drawability is appeared to be controlled by the stereo regularity.

Mechanical properties of drawn and annealed fibers are summarized in Fig.9. As in the case of structure formation revealed by X-ray, effect of the difference in polymer characteristics on the mechanical properties of drawn and annealed fibers is relatively small.

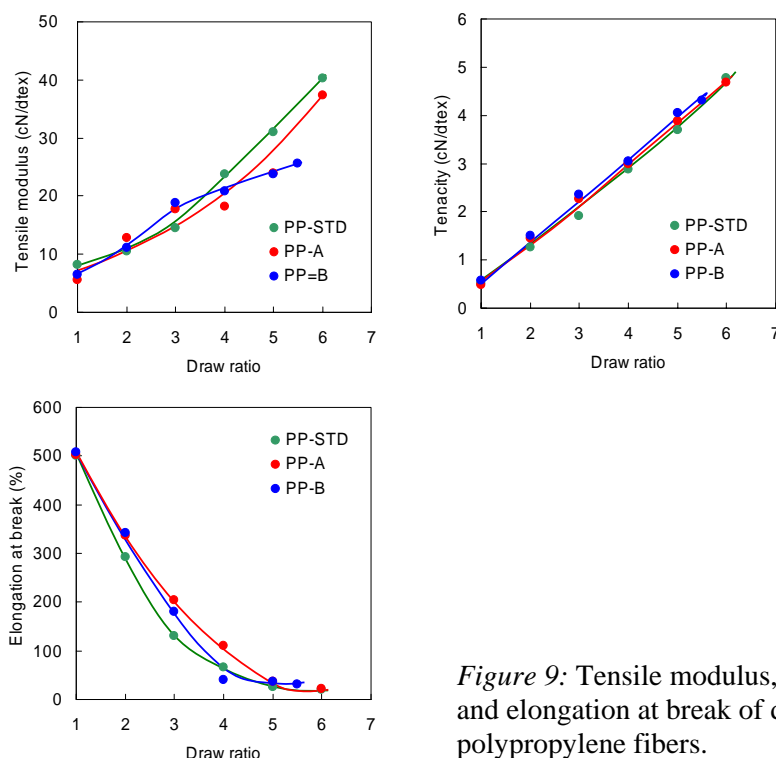


Figure 9: Tensile modulus, tenacity, and elongation at break of drawn polypropylene fibers.

## 4 Conclusions

Two types of blend PPs, a blend of high molecular weight/low tacticity PP and low molecular weight/high tacticity PP, and a blend of high molecular weight/high tacticity PP and low molecular weight/low tacticity PP were prepared. High-speed melt spinning and subsequent drawing processes of thus prepared polypropylenes with tacticity distribution with respect to the molecular weight distribution was performed. Both polymers exhibited high spinnability even though these polymers have relatively high polydispersity. It is also noteworthy that the behaviors of neck-like deformation and crystalline structure formation of these polymers are significantly different suggesting that the mechanism for the improvement of spinnability also is different. The fibers from both polymers showed fairly high mechanical properties even at extremely high take-up velocities. On the contrary, drawing of low-speed spun fibers prepared from these polymers suggested that the structure development in the drawing process is mainly controlled by the draw ratio, and the effect of polymer characteristics on the structure development and resultant properties is insignificant in comparison with those in the melt spinning process.

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