

Nonisothermal Orientation-Induced Crystallization in Melt Spinning of Polypropylene

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Synopsis

Two kinds of polypropylene with different molecular weight ($MI = 15$ and 30) were melt-spun at the spinning temperatures of 210 – 290°C and take-up velocities of 0.15 – 3 km/min. In the cases of the spinning temperatures of 270 and 290°C for $MI15$ and 250 and 290°C for $MI30$, the density showed a minimum with increasing take-up velocity at around 0.5 – 1 km/min. This result suggests that crystallization behavior is influenced by two competitive effects, i.e., cooling rate and crystallization rate both of which are enhanced by the increase in take-up velocity. Crystal structures of slightly oriented monoclinic, slightly oriented pseudohexagonal, highly oriented pseudohexagonal, and highly oriented monoclinic were successively observed with increasing take-up velocity. The change of crystallization temperature may result in the different kinds of crystal modifications. Numerical calculations on nonisothermal orientation-induced crystallization in the melt spinning process and experimental results showed qualitative agreement in the change of crystallinity with take-up velocity, spinning temperature, and molecular weight.

INTRODUCTION

In recent years, the concept of orientation-induced crystallization started drawing more attention with the development of high-speed melt spinning technology.¹ It is widely known that crystallization rate of polymers increases with increasing molecular orientation. However, the mechanism of fiber structure formation in melt spinning process is difficult to understand since crystallization process is affected by many factors such as spinning stress, molecular orientation, cooling rate, and thinning of polymer fluid. If crystallization behavior is considered as a function of take-up velocity, "time" and "stress" are among the most important factors from the view point of crystallography. Thus, mechanism of crystallization can be separated into two regions. In the region of lower spinning velocity, and if the effect of spinning stress is low, crystallinity of as-spun filaments may decrease with increasing take-up velocity since cooling rate dominates the crystallization process. On the other hand, crystallinity of as-spun filament may increase with increasing take-up velocity in higher take-up velocity region if the crystallization rate becomes sufficiently high because of high spinning stress and high molecular orientation.

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Nevertheless, the phenomenon explained above cannot be observed easily. For example, polyethylene filaments spun under the ordinary melt spinning conditions always have high crystallinity.² In melt spinning of poly(ethylene terephthalate), which has a low crystallization rate and a high glass transition temperature, the effect of orientation-induced crystallization can be observed at take-up velocities higher than 4 km/min. However, filaments spun at low take-up velocities always have noncrystalline structure.^{3,4}

Thus, it is important to give an experimental evidence for the concept of the competitive effects of cooling rate and crystallization rate in melt spinning process. In the present paper, isotactic polypropylene (PP) was selected as the material and crystallization behaviors under various spinning conditions were investigated.

EXPERIMENTAL

Polymers

Two kinds of isotactic polypropylene (Ube Industries Ltd., PP-S115M and PP-S130MV) with different molecular weight were used. PP-S115M has a melt index of 15, and a viscosity average molecular weight of 185,000. Molecular weight was measured in dekalin solution at 135°C. PP-S130MV has a melt index of 30 and a molecular weight of 135,000. Hereinafter, PP-S115M and PP-S130MV will be called MI15 and MI30, respectively.

Melt Spinning

The experimental system for the melt spinning was made up of an extruder with screw diameter of 20 mm, a gear pump, and a take-up device. Molten polymer was extruded from a single hole spinneret with a 1-mm diameter at the extrusion temperatures from 210 to 290°C. Mass outflow rate was 1.2 g/min. The take-up device was located 250 cm down from the spinneret. Filaments were spun at take-up velocities from 0.15 to 3 km/min.

Changes of filament diameter and temperature along spinline were measured for a part of spinning conditions. Filament diameter was measured after cutting the polymer fluid from the spinline. Filament temperature was measured with a thermocouple (Tokyo Seiko, TYPE TS-3). The temperature measurement was based on a detectable temperature difference between the heated thermocouple and the running filament. Spinline tension was measured with a tension meter (Kanai Koki, TYPE-CB).

Birefringence

Refractive indices parallel and perpendicular to the filament axis (n_{\parallel} , n_{\perp}) were measured using an interference microscope (Carl Zeiss, Jena) with a polarization filter. Birefringence (Δn) was calculated as $\Delta n = n_{\parallel} - n_{\perp}$.

Density

Density of as-spun filament was measured at 25°C in an iso-propanol/ethylene glycol density gradient column.

X-Ray Analysis

Wide-angle X-ray diffraction photographs of as-spun filaments were obtained using a nickel-filtered $\text{CuK}\alpha$ radiation source (Rigaku Rotaflex, RU-100PL, 40 kV \times 60 mA). The camera length and exposure time were 30 mm and 15 min.

The change of equatorial diffraction intensity of PP filaments with increasing temperature was measured at a heating rate of 5°C/min using a PSPC (position sensitive proportional counter) system (Rigaku Denki Co.). The intensity profile was followed every 15°. The exposure time for the PSPC measurement was 20 s.

RESULTS AND DISCUSSION

Orientation and Crystallinity

The relation between take-up velocity and birefringence of PP filaments spun under the various spinning conditions is shown in Figure 1. Birefringence increased with increasing take-up velocity. At spinning temperatures of 290°C for MI15 and 250 and 290°C for MI30, birefringence showed a sigmoidal increase. When take-up velocity was lower than 1 km/min, filaments spun at higher extrusion temperature or from the lower molecular weight polymer had lower birefringence. The development of molecular orientation in spinline is closely related to spinning stress,⁵ which becomes higher for spinning conditions of lower spinning temperature and higher molecular weight due to higher elongational viscosity. Thus, the change in birefringence of as-spun filaments with spinning conditions can be qualitatively explained by the change in spinning stress.

The relation between density of as-spun filaments and take-up velocity is shown in Figure 2. In the cases of 210 and 250°C for MI15 and 210 and 230°C for MI30, density was higher than 0.9 Mg/m³ and no dependence of density on take-up velocity was observed. At spinning temperatures of 270 and 290°C for MI15 and 250 and 290°C for MI30, notable results were obtained. Density decreased with increasing take-up velocity at take-up velocities lower than 0.5–1 km/min, showed minimum, and then started increasing with increasing take-up velocity. The change of density with take-up velocity may represent the concept of the competitive effects of cooling rate and crystallization rate in the melt spinning process described in the previous section.

Crystal Structure of As-Spun Filaments

Two kinds of crystal modification can be obtained in melt spinning of PP. One is the monoclinic crystal and the other is the pseudo-hexagonal crystal.⁶ Compostella et al.⁷ and Ishizuka⁸ have reported that slow cooling of polymer melt results in the monoclinic modification, whereas rapid cooling results in the pseudo-hexagonal modification. To investigate the crystal modification and crystal orientation of as-spun filaments, wide-angle X-ray diffraction (WAXD) patterns of filaments spun at spinning temperatures of 210, 250 and 290°C and take-up velocities of 0.3–3 km/min were obtained as shown in Figure 3. At 210°C, highly oriented monoclinic crystal was observed at all take-up

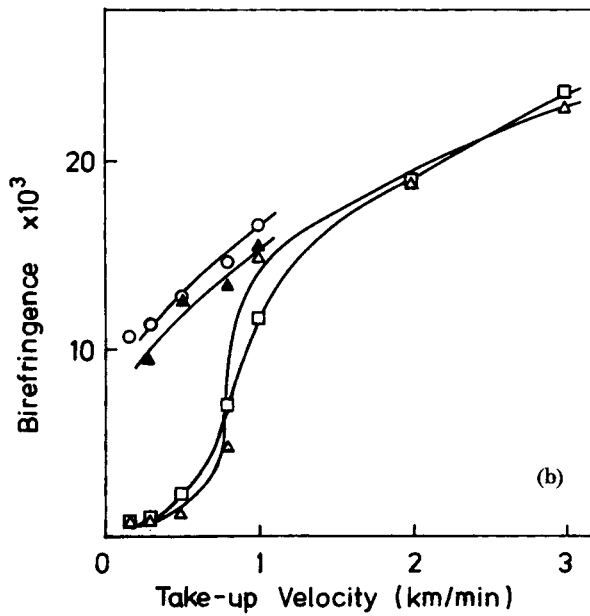
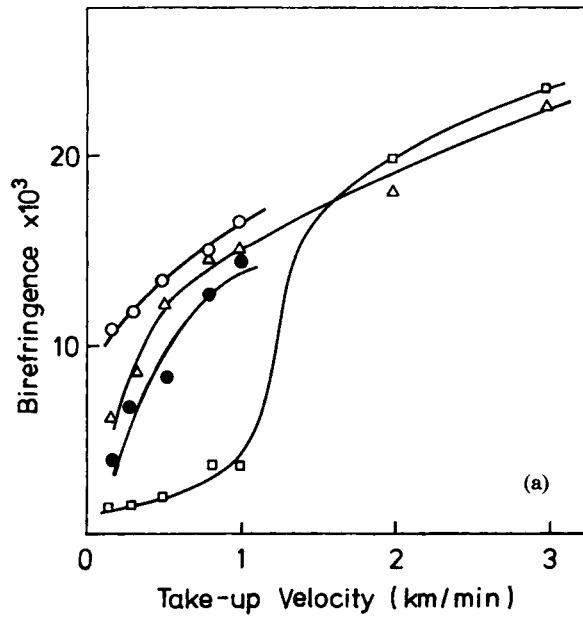


Fig. 1. Birefringence of as-spun filaments vs. take-up velocity at various spinning temperatures ($^{\circ}\text{C}$): (a) MI15: (○) 210; (△) 250; (●) 270; (□) 290. (b) MI30: (○) 210; (▲) 230; (△) 250; (□) 290.

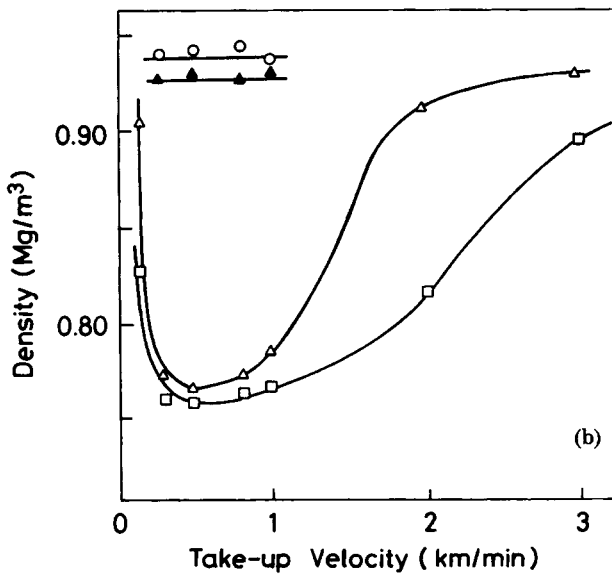
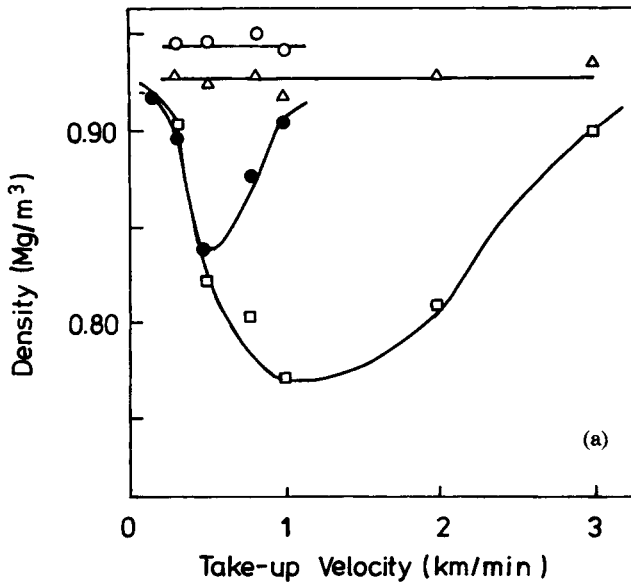


Fig. 2. Density of as-spun filaments vs. take-up velocity at various spinning temperatures ($^{\circ}\text{C}$): (a) MI15: (○) 210; (△) 250; (●) 270; (□) 290. (b) MI30: (○) 210; (▲) 230; (△) 250; (□) 290.

(a)

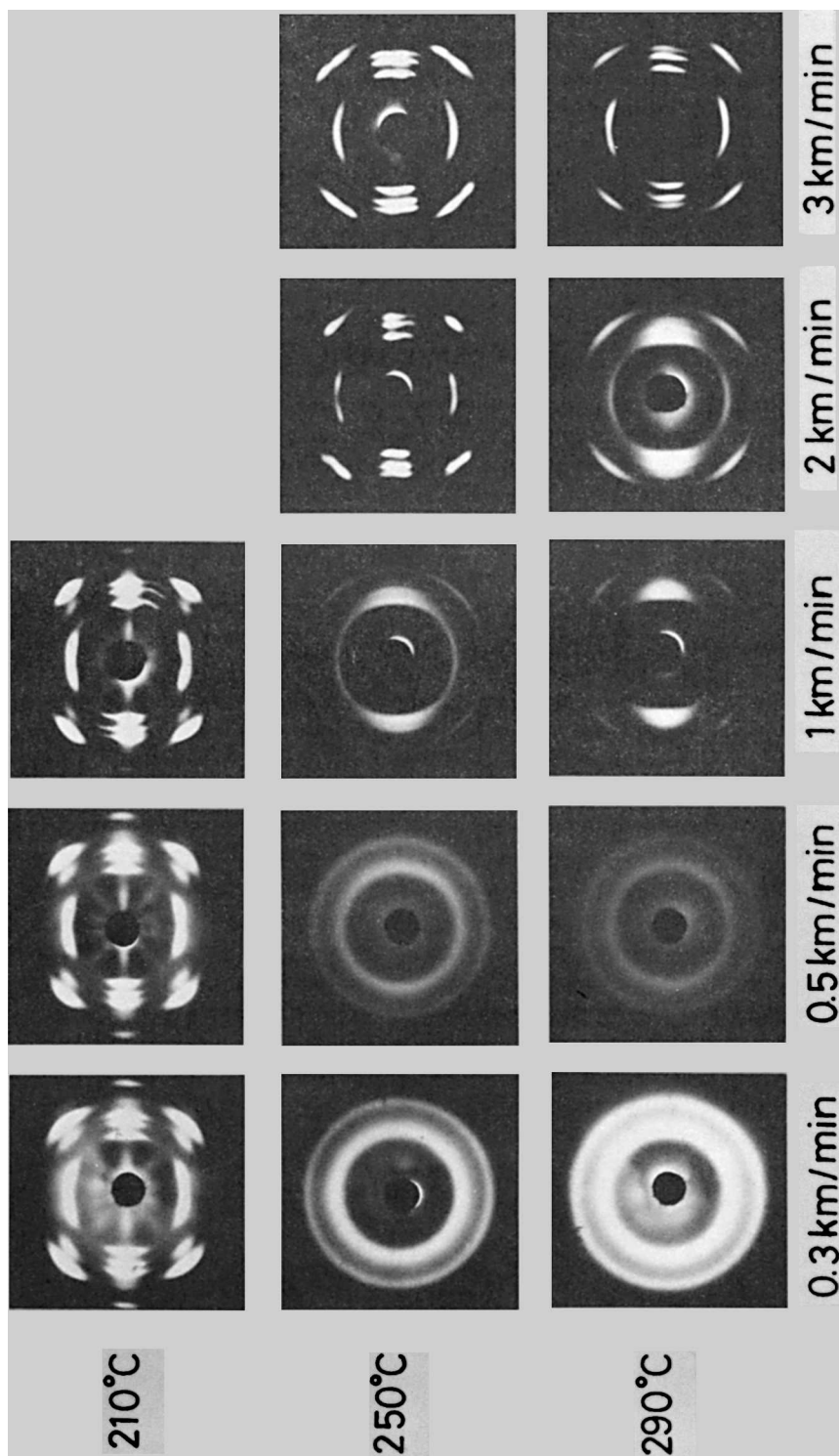


Fig. 3. Wide-angle X-ray diffraction patterns of as-spun filaments. Spinning temperature and take-up velocity are indicated: (a) MI15; (b) MI30.

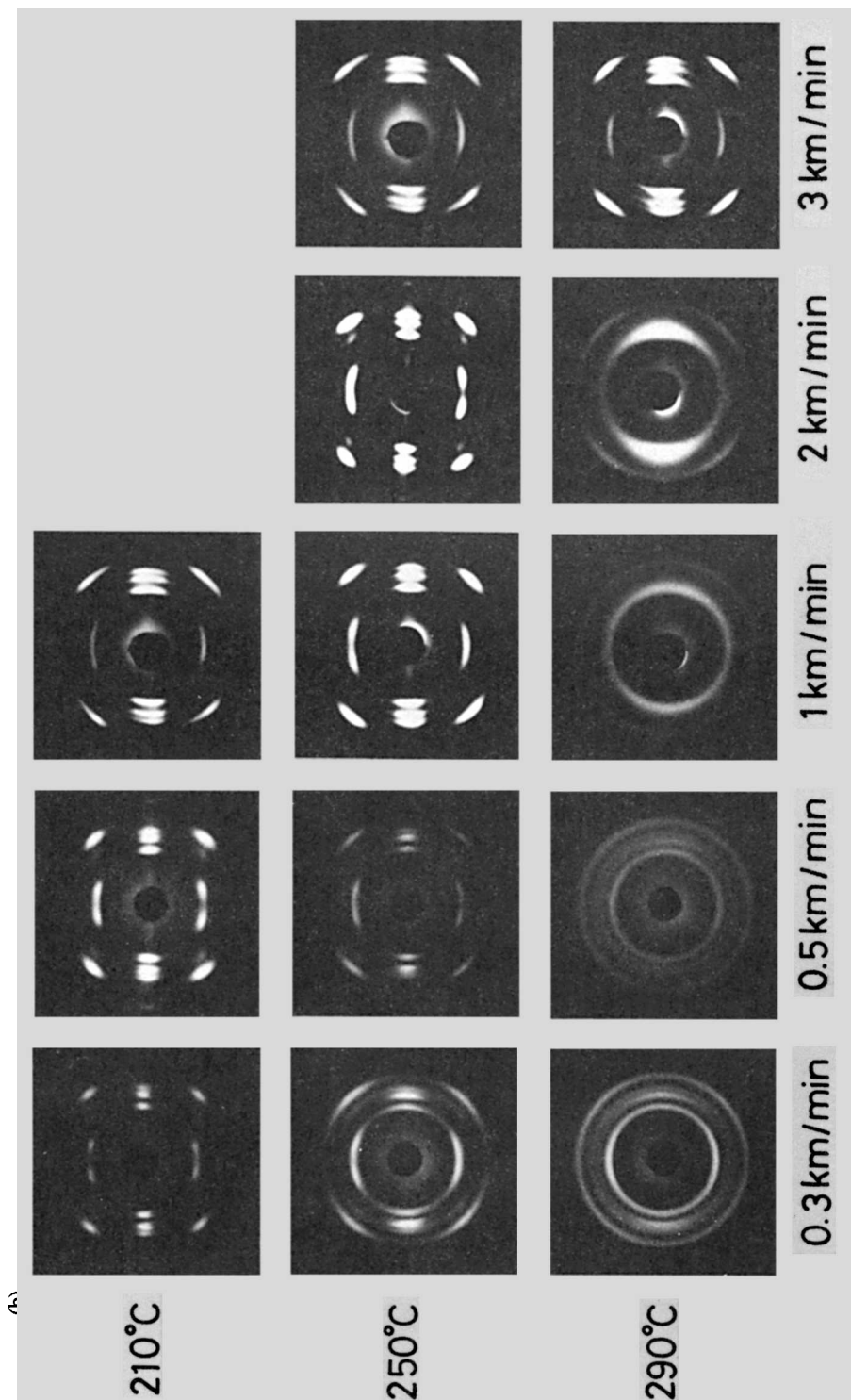


Fig. 3. (Continued from the previous page.)

velocities both for MI15 and MI30 filaments. At 250°C, highly oriented monoclinic crystal was observed for MI15, while in the case of MI30, crystal orientation increased and crystal form changed from pseudo-hexagonal to monoclinic with increasing take-up velocity. A similar result was observed for MI30 filaments spun at 290°C. More notable were the WAXD patterns of MI15 filaments spun at 290°C. Crystal structures of slightly oriented monoclinic, slightly oriented pseudo-hexagonal, highly oriented pseudo-hexagonal, and highly oriented monoclinic were observed successively with increasing take-up velocity.

Dependence of Crystal Modification on Temperature

In order to discuss more detail of the mechanism of crystal structure formation in the spinning process, dependence of crystal modification on temperature was investigated.

Figure 4(a) is the change in equatorial intensity profile of MI15 filaments spun at 250°C, 0.5 km/min. The filament had oriented monoclinic crystals. Three strong peaks were assigned to the reflections from (110), (040), and (130) planes. No crystal modification was observed with increasing temperature up to 155°C; however, the position of each reflection moved to lower Bragg's

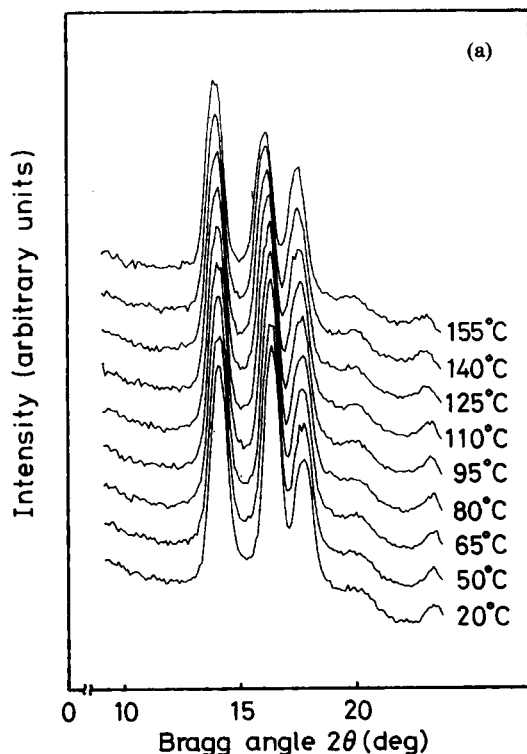


Fig. 4. Changes of equatorial wide-angle X-ray diffraction profile with increasing temperature for filaments spun at 250°C, 0.5 km/min: (a) MI15, oriented monoclinic crystal; (b) MI30, oriented pseudo-hexagonal crystal.

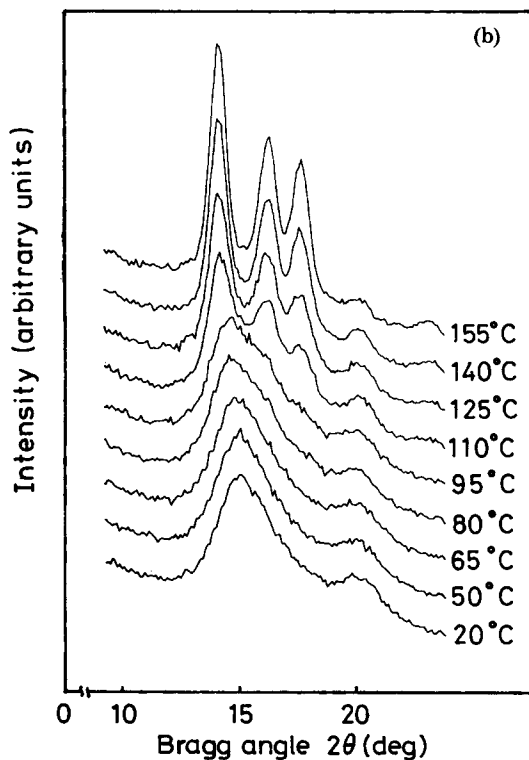


Fig. 4. (Continued from the previous page.)

angle and the intensity of (040) reflections decreased markedly. The increase in the spacing of crystal planes may be because of the heat expansion of crystal lattice. Since selective intensity reduction of (040) reflection was not observed in unoriented monoclinic crystal filaments, preferential orientation relaxation presumably took place. In this filament, a^* -axis-oriented crystals coexist with c -axis-oriented crystals. If it is only a^* -axis-oriented crystals which experience relaxation, the intensity of (040) reflections decrease selectively since both a^* -axis- and c -axis-oriented crystals contribute to the intensity of (040) peaks on the equator whereas only c -axis-oriented crystals contribute to the equatorial intensity of (110) and (130) peaks.

Figure 4(b) shows the intensity profile change of MI30 filaments spun at 290°C, 1 km/min. The as-spun filament had oriented pseudo-hexagonal crystals. The intensity profile remained unaltered up to 95°C. Reflections of monoclinic crystals appeared at 110°C and became sharper and stronger with increasing temperature.

Ishizuka⁸ and Stein⁹ have reported that pseudo-hexagonal crystals of PP can be changed to monoclinic crystals by 2 h annealing at 110°C. From these results, it is evident that pseudo-hexagonal crystals are metastable. If we can assume that crystal structure formed in melt spinning process was influenced by crystallization temperature, the changes of crystal structure with take-up velocity can be interpreted as follows.

At low take-up velocity, crystallization occurs at relatively high temperature because of low cooling rate, and monoclinic crystals are formed. With increasing take-up velocity, cooling rate increases, and crystallization temperature decreases. Consequently, pseudo-hexagonal crystals are formed. With further increase of take-up velocity, crystallization rate increases because of significant molecular orientation. When the increase of crystallization rate becomes comparable to that of the cooling rate, crystallization temperature rises again, and oriented monoclinic crystals are formed.

From the temperature dependence of crystal modification, it was concluded that pseudo-hexagonal crystals cannot exist at temperatures higher than $\sim 110^\circ\text{C}$. However, it is not clear whether monoclinic crystals can be formed below this temperature or not. In addition, the crystal transition temperature possibly changes with molecular orientation. Glass transition temperature of PP is lower than room temperature. Therefore, PP can crystallize after the polymer passes through the spinline (e.g., on a take-up bobbin). In this case, a certain amount of pseudo-hexagonal crystal may be formed.

Simulation of the Melt Spinning Process

To describe the mechanism of crystallization and the formation of different kinds of crystal modification, numerical simulation of melt spinning process was performed. The steady-state spinning process can be described by the following equations^{10,11}:

Equation of continuity:

$$W = \rho V \pi D^2 / 4 \quad (1)$$

Equation of momentum balance:

$$dF/dx = W(dV/dx - g/V) - \pi D \tau_f \quad (2)$$

Equation of energy balance:

$$dT/dx = -(\pi Dh/WC_p)(T - T_s) \quad (3)$$

Constitutive equation:

$$F\rho V/W = \eta(dV/dx) \quad (4)$$

where F , V , D , and T denote the spinline tension, axial velocity, diameter, and temperature of the filament at a distance x from the spinneret, W is the extrusion mass outflow rate, ρ , η , and C_p are the density, elongational viscosity, and specific heat of the polymer, g the acceleration of gravity, τ_f the shear stress on the surface of the filament related to the air friction, h the heat transfer coefficient, and T_s the air temperature.

These parameters for PP and air can be expressed as follows^{11,12}:

$$\rho = 0.912 - 4.8 \times 10^{-4}T \quad (\text{Mg/m}^3) \quad (5)$$

$$C_p = 2.60 \quad (\text{MJ/kg deg}) \quad (6)$$

$$\text{Nu} = Dh/\kappa^* = 0.42\text{Re}^{0.334} \quad (7)$$

$$\tau_f = 0.5\rho^*V^2C_f \quad (\text{Pa}) \quad (8)$$

$$C_f = 0.37 \text{Re}^{-0.61} \quad (9)$$

where ρ^* and κ^* are the density and thermal conductivity of air, C_f the air friction coefficient, Nu the Nusselt number, and Re the Reynolds number based on filament diameter.

Diameter and temperature profiles along the spinline and spinline tension at the take-up position were measured for the spinning condition of 250°C, 0.5 km/min, and the elongational viscosity was calculated.¹³ The results were plotted against the reciprocal of the absolute temperature in Figure 5. MI15 obviously has higher viscosity than MI30.

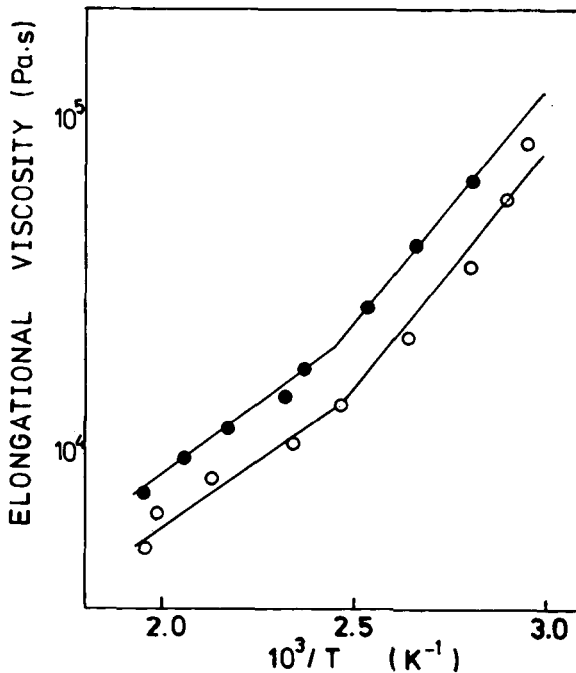


Fig. 5. Elongational viscosity for MI15 and MI30 polymers vs. reciprocal of the absolute temperature.

Elongational viscosities can be expressed as follows:
MI15:

$$\begin{aligned} \eta &= 228 \exp[1670/(T + 273)] \quad (\text{Pa s}), \quad T \geq 141^\circ\text{C} \\ &5.38 \exp[3190/(T + 273)] \quad (\text{Pa s}), \quad 141 > T > 64^\circ\text{C} \end{aligned} \quad (10)$$

MI30:

$$\begin{aligned} \eta &= 201 \exp[1890/(T + 273)] \quad (\text{Pa s}), \quad T \geq 133^\circ\text{C} \\ &6.16 \exp[3190/(T + 273)] \quad (\text{Pa s}), \quad 133 > T > 64^\circ\text{C} \end{aligned} \quad (11)$$

There was a break point for each sample as was shown in the earlier work.¹⁴ When temperature was lower than 64°C, elongational viscosity could not be evaluated since diameter change was not detectable.

Calculated diameter profile along the spinline, which was obtained from Eqs. (1), (2), (3), and (4) by the finite difference technique, was compared with the experimental results in Figure 6. The consistency of the calculated and measured diameter profiles suggests the validity of the numerical analysis. Calculated filament temperature, spinline stress and residence time are also shown in Figure 6.

If quasistatic approximation is introduced for nonisothermal orientation-induced crystallization, crystallinity X_c can be expressed as follows^{15,16}:

$$X_c(t)/X_\infty = 1 - \exp\left(-\left\{\int_0^t K[T(\tau), f_a(\tau)] d\tau\right\}^n\right) \quad (12)$$

where X_∞ is the degree of ultimate crystallinity, K the crystallization rate function, and f_a the amorphous orientation. The crystallization rate of PP with no orientation $K(T, 0)$ was formulated by Ziabicki¹⁷ based on Magill's

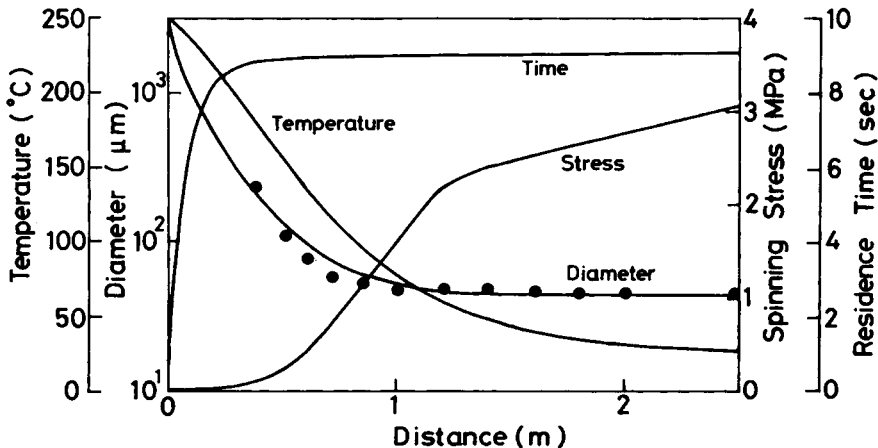


Fig. 6. A typical example of calculated diameter, temperature, spinning stress, and residence time profiles in spinline of MI15 at 250°C, 0.5 km/min. Measured diameter is also indicated.

experimental result.¹⁸ The effect of molecular orientation on the crystallization rate was also formulated by Ziabicki. Crystallization rate function of oriented PP can be expressed as follows¹⁷:

$$K(T, f_a) = 0.55 \ln 2 \exp\left(-4 \ln 2(T - 65)^2/3600 + A(T)f_a^2\right) \quad (13)$$

where $A(T)$ is a positive temperature dependent parameter.

Taking into account the latent heat of crystallization, the equation of energy balance [eq. (3)] must be replaced by

$$dT/dx = -(\pi Dh/WC_p)(T - T_s) + (\Delta H/C_p)(dX_c/dx) \quad (14)$$

where ΔH denotes the heat of fusion for PP (209 kJ/kg).¹⁹

Results of Calculation

Numerical calculations on the crystallization process in melt spinning were performed by combining eqs. (1), (2), (4), (13), and (14). For the estimation of amorphous orientation, the linear relationship between spinning stress and amorphous orientation, $f_a = C\sigma$, was assumed,⁵ where C is a constant. The parameter $A(T)$ was assumed to be independent of temperature and an arbitrary value of 1 MPa^{-2} was chosen for $A(T)C^2$. Avrami index n and the degree of ultimate crystallinity X_∞ in eq. (12) were assumed to be unity and 0.5, respectively.

Figure 7 shows the dependence of take-up velocity on crystallinity. Broken lines represent the results obtained without considering the effect of molecular orientation. Crystallinity decreased with increasing take-up velocity; however, it is obvious that PP can crystallize to some extent without the effect of molecular orientation at take-up velocities up to ca. 0.3 km/min. Solid lines are results of calculation with the effect of orientation-induced crystallization. Calculated crystallinities with and without the effect of molecular orientation

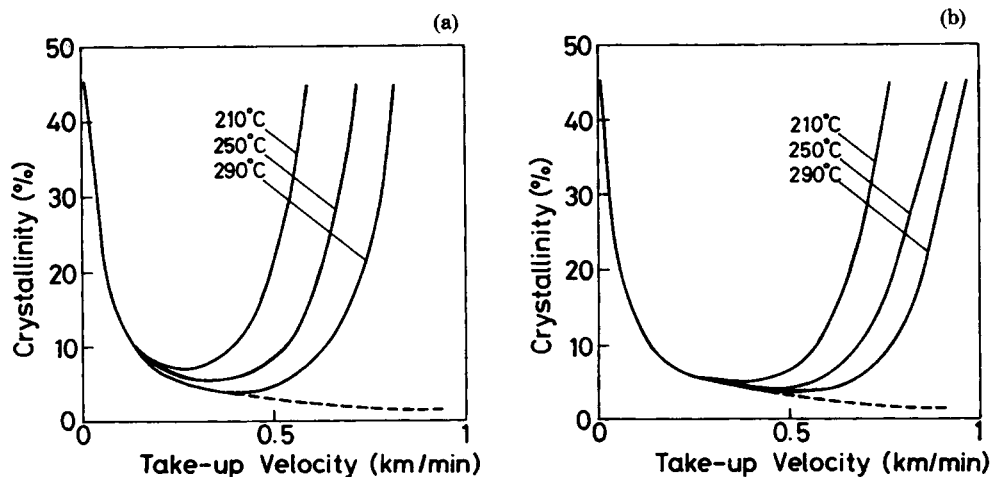


Fig. 7. Changes of calculated crystallinity with (solid line) and without (broken line) the effect of molecular orientation vs. take-up velocity: (a) MI15; (b) MI30.

change in the same manner at low take-up velocities. Crystallinity took a minimum at around 0.3–0.5 km/min and started increasing with take-up velocity. The minimum was shifted to higher take-up velocity with increasing temperature and decreasing molecular weight. This tendency coincides with experimental results, however it can be noticed by comparing Figures 2 and 7 that the dependence of crystallinity on spinning temperature is more significant in the experimental result.

From the numerical analysis, it was reaffirmed that crystallinity of as-spun filaments takes a minimum at a certain take-up velocity due to the competitive effects of cooling rate and crystallization rate. However, quantitative estimation of crystallization behavior is difficult to achieve at the present moment because of the lack of detailed information on the mechanism of molecular orientation, the crystallization kinetics under molecular orientation and the effects of molecular orientation and crystallization on viscoelastic properties of polymer fluids.

CONCLUSIONS

Two kinds of polypropylene with different molecular weights were melt spun under various spinning conditions. Birefringence of as-spun filaments increased with increasing take-up velocity. At a constant take-up velocity, birefringence increased with decreasing spinning temperature and increasing molecular weight. When spinning temperature was low, density of as-spun filament was high, and no take-up velocity dependence was observed. At spinning temperatures of 270 and 290°C for MI15 and 250 and 290°C for MI30, density took a minimum with increasing take-up velocity at 0.5–1 km/min. This result suggests the competitive effects of cooling rate and crystallization rate. Slightly oriented monoclinic, slightly oriented pseudo-hexagonal, highly oriented pseudo-hexagonal, and highly oriented monoclinic crystals were successively observed with increasing take-up velocity. The change of crystallization temperature may result in different kinds of crystal modification.

Numerical simulation of melt spinning process was performed. Calculated results of the change of crystallinity with spinning temperature and molecular weight showed qualitative agreement with experiment.

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