

The Role of Crystallization Kinetics in the Development of the Structure and Properties of Polypropylene Filaments

F. M. LU and J. E. SPRUIELL*

Center for Materials Processing and Department of Materials Science and Engineering,
University of Tennessee, Knoxville, Tennessee 37996-2200

SYNOPSIS

The processing, structure, and properties of filaments melt spun from three polypropylenes with similar rheology but substantially different crystallization kinetics were studied. The crystallization kinetics of the homopolymer was increased by the addition of a nucleating agent, whereas slower crystallization kinetics was obtained through a small amount of random copolymerization with ethylene. The relative crystallization kinetics of these three polymers was examined under quiescent conditions using differential scanning calorimetry. The technique of on-line diameter and birefringence measurement was used to show the characteristics of the on-line crystallization of the different resins. It was found that changing the quiescent crystallization kinetics by either the addition of a nucleating agent or through copolymerization with ethylene can produce profound effects on the structure and properties of polypropylene as-spun filaments when they are spun under relatively low stress and low takeup velocity conditions. Higher takeup velocities and spinline stresses reduce the effect of differences in quiescent crystallization due to the influence of on-line stress-induced (molecular orientation-enhanced) crystallization. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Fundamental studies of the melt spinning of isotactic polypropylene date back to the 1960s,¹⁻³ when the polymer of commercial significance had just emerged. These and later authors⁴⁻¹⁵ emphasized the importance of processing conditions on filament structure development and the resulting mechanical properties of the spun filaments. In particular, the influence of spinning speed was studied extensively by Shimizu and co-workers¹⁰⁻¹³ and in our own laboratories.^{14,15} The influence of certain resin characteristics such as polymer molecular weight and molecular weight distribution was also examined.^{14,15}

A unifying concept that has emerged from these studies is that factors that increase spinline stress tend to increase on-line molecular orientation and result in a rapid increase in crystallization kinetics, i.e., the so-called stress-induced crystallization,

which plays a major role in establishing the position in the spinline where crystallization occurs. For a given resin, increased spinning speed, decreased mass throughput, decreased extrusion temperature, and an increase in polymer viscosity all lead to increased spinline stress, molecular orientation, and on-line crystallization rates.⁷⁻¹⁵ The increase in crystallization rate results in crystallization closer to the spinneret and at higher temperature. However, the higher molecular orientation in the spinline at the point of crystallization generally leads to filaments with higher as-spun molecular orientation, increased tenacity, and decreased elongation-to-break.

It is clear from these previous studies that the resin crystallization kinetics and its interaction with other parameters is of great importance in controlling the final morphology and properties of polypropylene filaments. To date, however, no studies have been published that establish systematically the influence of the quiescent crystallization rates of different polypropylenes on the resulting filament structure and properties, although Lin et al.¹⁶ ob-

* To whom correspondence should be addressed.

served that certain pigments can exert substantial effects due to their ability to nucleate crystallization. The present paper examines the role of quiescent crystallization kinetics on the structure development and properties of polypropylene filaments. The crystallization kinetics was varied through incorporation of a nucleating agent or copolymerization with ethylene.

EXPERIMENTAL

Materials

Two experimental resin samples, coded HP 35, which is an isotactic polypropylene homopolymer, and CP 35, which is a copolymer of propylene and ethylene, were supplied in the form of pellets by Exxon Chemical Co. The rheology and molecular characteristics of the two resins were matched as closely as feasible. They possess similar MFR (both are nominally 35 MFR resins) and similar molecular weight as well as molecular weight distribution determined by gel permeation chromatography. A summary of the characteristics of the two resins is listed in Table I. A third resin, coded HP 35 NA, was prepared by thoroughly mixing the HP 35 pellets with 0.1 wt % of the nucleating agent powder MIL-LAD 3940, supplied by Milliken Chemical Co., until the powder was spread uniformly on the surface of the pellets.

Melt Spinning

The melt spinning of monofilaments for all three resins was carried out on a Fourne spinning machine at an extrusion temperature of 210°C with a constant throughput of 1.55 g/min. A pneumatic (air drag) device was positioned at 280 cm from the spinneret to draw down the filaments. Air pressures of 2 and 25 psig at the device were maintained, respectively, for obtaining different takeup velocities. In the present case, this resulted in takeup velocities of 1800 and 3500 m/min, respectively. A detailed description of the spinning equipment and procedures can be found in Refs. 15 and 17.

Table I Resin Characteristics

Sample Code	Polymer Type	M_w	M_n	M_w/M_n	Peak MW
CP 35	Copolymer	142,160	61,549	2.31	115,994
HP 35	Homopolymer	143,825	60,330	2.38	115,994

On-line Measurement

On-line diameter and birefringence profiles were obtained as a function of distance from the spinneret, using a noncontact Zimmer diameter monitor and an Olympus polarizing microscope, respectively. The details of the technique were documented elsewhere.^{15,18}

Sample Characterization

Density

A diethylene glycol-isopropyl alcohol density gradient column at 23°C, prepared in our laboratory according to ASTM standard D1505-68, was used to determine the density of as-spun filaments. The crystallinities of the samples were then calculated by the equation

$$X_c = \rho_c(\rho - \rho_{am}) / \rho(\rho_c - \rho_{am}) \quad (1)$$

where ρ is sample density and ρ_c and ρ_{am} are densities of crystalline and amorphous phases, respectively. Contributions of the contents of both the nucleating agent and ethylene component to sample densities were neglected by virtue of their very low percentage.

Diameter and Birefringence

The diameter and optical retardation of as-spun fibers were measured with a Zeiss polarizing microscope and a 5 order Berek compensator. The retardation was then divided by diameter to obtain the birefringence. Thirty measurements of each sample were carried out to better observe statistically the property variations between samples processed under identical conditions.

Crystallinity vs. Crystallization Temperature

A Perkin-Elmer DSC 7 was used to determine the crystallization temperature for the three resins at cooling rates of 40, 20, 10, 5, and 2°C/min, respectively. The crystallinity of each DSC sample was measured by the density technique in order to be directly comparable to the filament density crystallinity measurements.

Crystal Form and Orientation

Information on qualitative features of crystal form and orientation of as-spun fibers were observed through use of wide-angle X-ray diffraction patterns. A Philips Norelco X-ray generator and a flat-plate camera with nickel-filtered $\text{CuK}\alpha$ radiation of 0.1542 nm wavelength were used to obtain the patterns.

Mechanical Properties

The tenacity and elongation-at-break of as-spun fibers were determined with a table model Instron testing machine. According to ASTM standard test method D3822, a gauge length of 25.4 mm and crosshead velocity of 50.8 mm were used. Thirty tests were run on each filament sample. The diameter and birefringence of each filament were measured prior to tensile testing.

RESULTS AND DISCUSSION

Crystallization under Quiescent Conditions

The DSC thermograms of HP 35 NA, HP 35, and CP 35 at a cooling rate $5^\circ\text{C}/\text{min}$ are plotted together for comparison in Figure 1. It is seen clearly that under identical quiescent conditions the onset of crystallization of the resin with a nucleating agent added (HP 35 NA) occurred at 17°C higher than

that of the homopolymer (HP 35). On the other hand, the onset of crystallization for the copolymer (CP 35) was 10°C below that of the homopolymer and 27°C below that of the nucleated resin. These observations indicate that the quiescent crystallization kinetics of the homopolypropylene was substantially increased due to the addition of the nucleating agent, but decreased by the random incorporation of a small amount of ethylene into the polymer chain.

The crystallinity calculated from density measurement of each DSC sample is plotted as a function of the corresponding crystallization onset temperature in Figure 2. These data show that a slower cooling rate and higher crystallization temperature result in higher crystallinity for each resin. For a given cooling rate, the crystallinity of the nucleated homopolymer is higher than that of the neat homopolymer due, presumably, to the greater time available in the temperature range where crystal growth and perfection can occur following the higher temperature crystal nucleation. In this case, the effect of time in the temperature range for rapid crystal growth seems to be more important than the temperature of crystallization per se or the effect that the nucleating agent has on the ultimate crystallinity that the polypropylene resin can reach. This latter statement is based on the observation from Figure 2 that the crystallinity of nucleated samples would be lower than that of the neat homopolymer if the

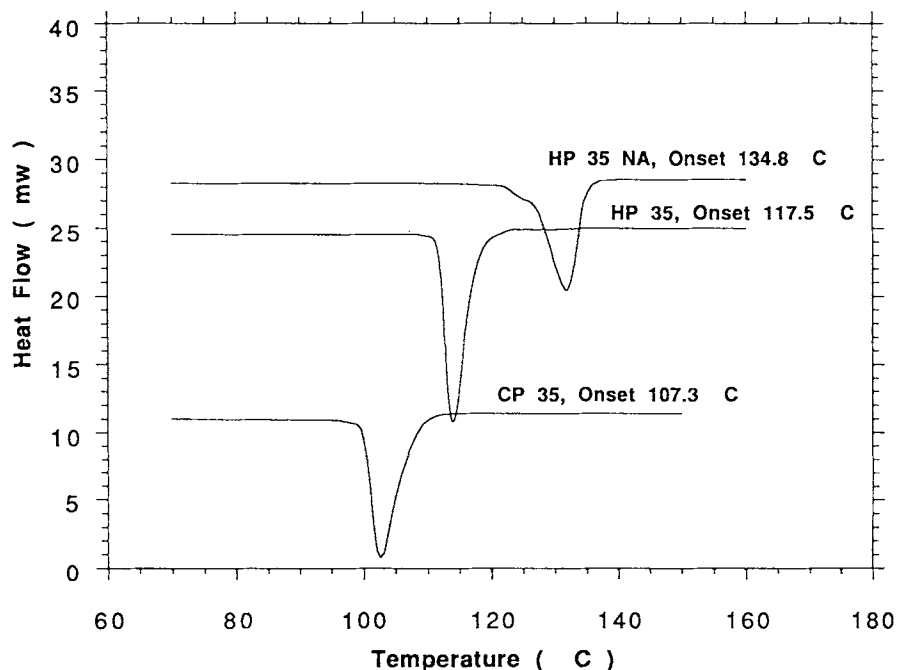


Figure 1 DSC thermogram of HP 35 NA, HP 35, and CP 35 at cooling rate of $5^\circ\text{C}/\text{min}$.

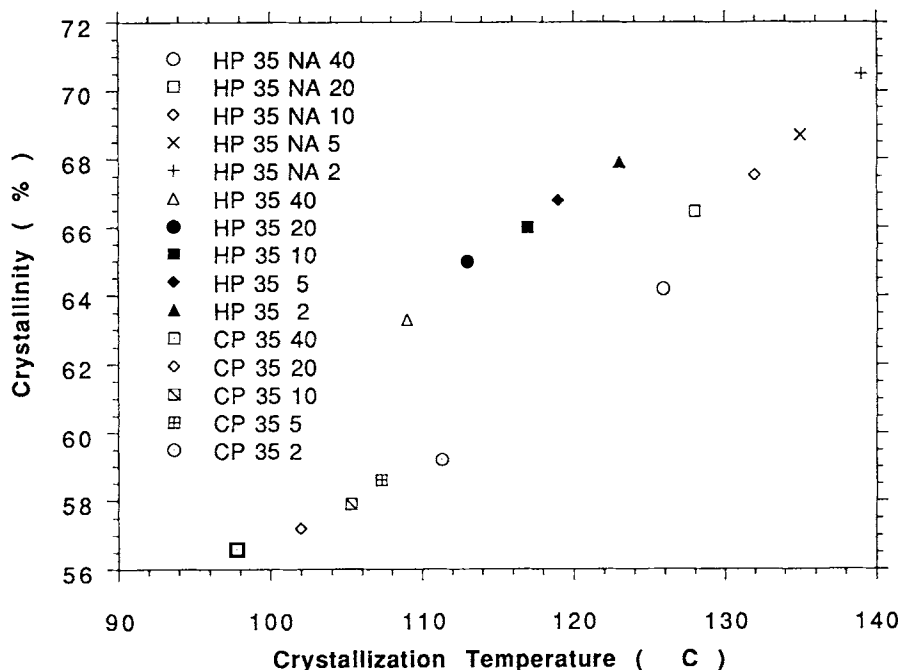


Figure 2 Crystallinity (by density) vs. crystallization onset temperature determined by DSC for HP 35 NA, HP 35, and CP 35 at cooling rate of 40, 20, 10, 5, and 2°C/min.

two samples were crystallized at the same temperature but at necessarily very different cooling rates. On the contrary, the effect of lower ultimate crystallinity for the copolymer is clearly evident from the data, as the crystallinity of the neat homopolymer is higher than that of the copolymer when these two samples are crystallized in the same temperature range by cooling the neat homopolymer much faster than the copolymer. In summary, copolymerization with ethylene clearly reduces both the quiescent crystallization rate and the ultimate crystallinity of polypropylene, whereas the addition of a nucleating agent greatly enhances the overall crystallization rate, but has a much smaller effect on the ultimate crystallinity that can be developed.

On-line Measurements of Diameter and Birefringence Profiles

Figure 3 presents on-line profiles of diameter and birefringence as a function of distance from the spinneret for all three resins spun under identical conditions at the low air pressure of 2 psig at the draw down device (spinning speed about 1800 m/min). Distinct effects due to the crystallization behavior of each resin can be observed in these data. The birefringence of the filament spun from the nucleated resin, HP 35 NA, rises slowly at first and then shoots up rapidly at about 135 cm from the

spinneret. These observations are an indication of oriented crystallization occurring on-line. Note also that the diameter profile becomes relatively flat at this point in the spinline as the diameter approaches its final value. The point at which the birefringence shoots up is about 20 cm farther from the spinneret for the filament spun from the neat homopolymer, HP 35, than for the nucleated resin. For the copolymer filament, CP 35, crystallization appears to begin much further from the spinneret and to develop at a much slower rate. The end of the measurable portion of the spinline (220 cm) is reached before the birefringence is well developed. Further, the filament diameter draws down more slowly than for the other samples, and it has not reached its final value at 220 cm from the spinneret.

The University of Tennessee Melt Spinning Program⁹ was used to estimate the temperature of the spinline as a function of distance from the spinneret for the same spinning conditions as for the data of Figure 3. This provided an estimate of the temperature at the onset of crystallization in the spinline of 61°C for the HP 35 NA filament, which is about 5°C higher than for the neat homopolymer, HP 35. The copolymer appears to have begun crystallization at an even lower temperature of about 50°C.

Figure 4 is analogous to Figure 3 except that the air pressure at the draw down device was 25 psig.

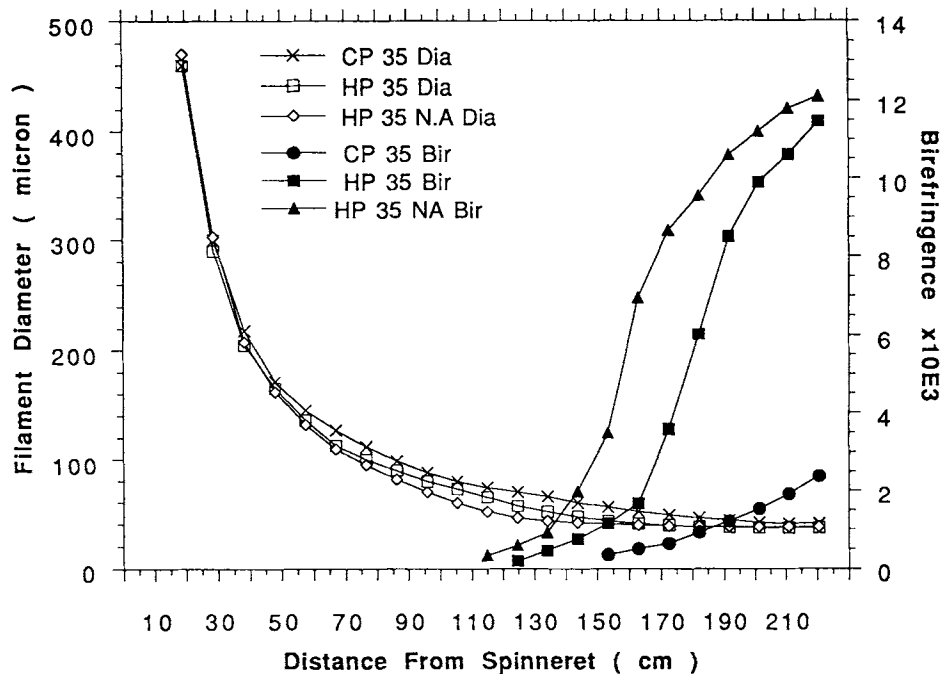


Figure 3 On-line diameter and birefringence profiles for HP 35 NA, HP 35, and CP 35 spun under low air pressure of 2 psig.

Under this higher air pressure, the spinline stress and takeup velocity were substantially higher than for the case of the lower air pressure (Fig. 3). For

the present case (Fig. 4), the takeup velocity reached by the filaments was 3500 m/min. Comparing Figure 4 with Figure 3, it is apparent that under the higher

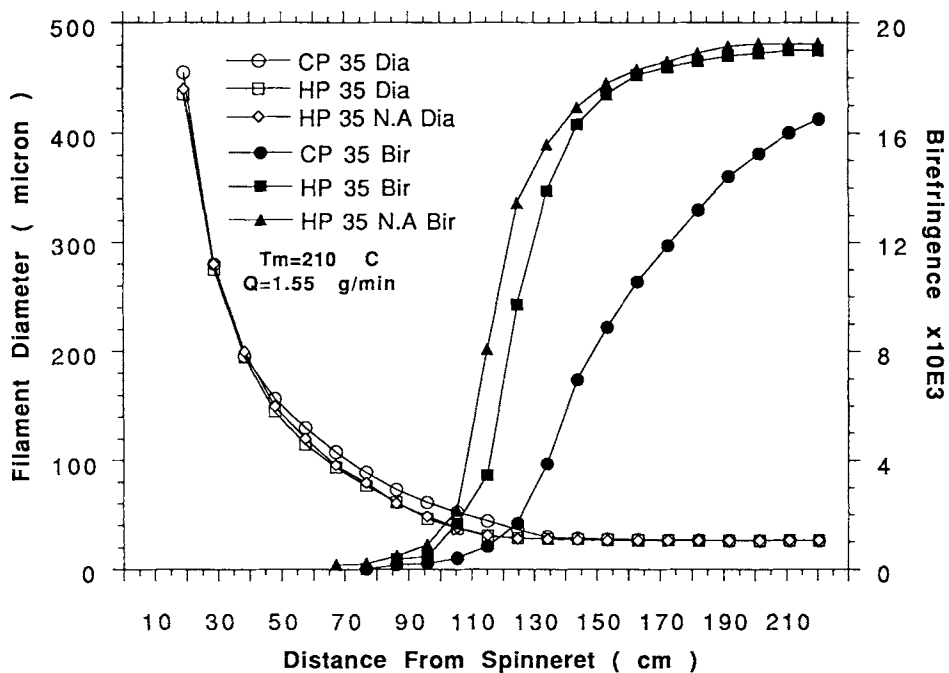


Figure 4 On-line diameter and birefringence profiles for HP 35 NA, HP 35, and CP 35 spun under high air pressure of 25 psig.

spinning velocity imposed by higher air pressure the onset position of on-line crystallization for all three samples was moved to a position closer to the spinneret due to the increased influence of on-line stress-induced crystallization. The effect of increased spinning speed was previously observed by many authors^{10,13,15-19} and is well established. By comparing the data of Figure 4 to the temperature profile provided by our computer simulation, the onset temperature for crystallization for the nucleated resin has moved up to approximately 80°C. Moreover, the on-line birefringence profiles of HP 35 NA and HP 35 in Figure 4 show that the difference of the position of the onset of on-line crystallization between the two resins is reduced from about 20 cm to less than 5 cm as the air pressure increases from 2 to 25 psig. This corresponds to a difference in onset temperature for crystallization of less than 3°C. The onset of crystallization for the copolymer sample moves up to a position about 112 cm from the spinneret, corresponding to a temperature of about 69°C.

The data of Figures 3 and 4 suggest that the relative influence of the nucleating agent within HP 35 NA on the structure and properties of the as-spun filaments is a function of spinline speed (stress). It has a dominant effect when spinline speed is low, but it will be partially offset by the influence of stress-induced crystallization as spinning speed increases. The copolymer also undergoes stress-induced crystallization, which affects the crystallization onset temperature greatly. However, even when high stresses are applied to the spinline, the copolymer continues to crystallize much more slowly in the spinline than does the homopolymer. Copolymerization delays the crystallization onset and slows the rate of development of the final structure as judged by the slope of the birefringence profile: Compare the profile for CP 35 in Figure 4 to that for the homopolymer, HP 35, in Figure 3.

Characteristics of the Structure and Properties of As-spun Filaments

The measured densities and computed crystallinities of the as-spun filaments are presented in Table II. The crystallinity is higher for the higher spinning speed (higher air pressure) for each of the resins. In the low spinning speed case, the sample containing the nucleating agent, HP 35 NA, has the highest crystallinity, whereas the copolymer, CP 35, has a much lower crystallinity. These results are consistent with the crystallization and structure development occurring at very different temperatures for the three different resins when spun at low spinning speed due to the difference in quiescent crystallization rates. For the case of high-speed spinning, the neat homopolymer has crystallinity equal to that of the nucleated resin, a result that is consistent with the structure of these two filaments being developed at nearly the same temperature due to the overriding influence of stress-induced crystallization as described above, plus the fact that the nucleating agent has little effect on the final crystallinity that can be developed in the resin as discussed in relation to the data of Figure 2. Even though the crystallinity of the copolymer increases with increased spinning speed due to the influence of stress-induced crystallization, its crystallinity is still much lower after spinning at high speed than that of the other resins. This is evidently due to the effect of copolymerization on the ultimate crystallinity as well as the crystallization rate.

In Figure 5 are presented X-ray diffraction patterns of the as-spun filaments whose profiles are shown in Figure 3. It is interesting to note from comparison of the pattern for HP 35 NA with that of CP 35 that both the level of crystalline order and the crystalline orientation developed in the fiber are different. The reason for this can presumably be at-

Table II Density and Crystallinity of As-spun Filaments

	Sample					
	HP 35 NA		HP 35		CP35	
	Air Pressure (psig)					
	2	25	2	25	2	25
Density (g/cm ³)	0.8975	0.9028	0.8964	0.9028	0.8871	0.8963
Crystallinity (%)	56.6	63.1	55.2	63.1	43.6	55.1

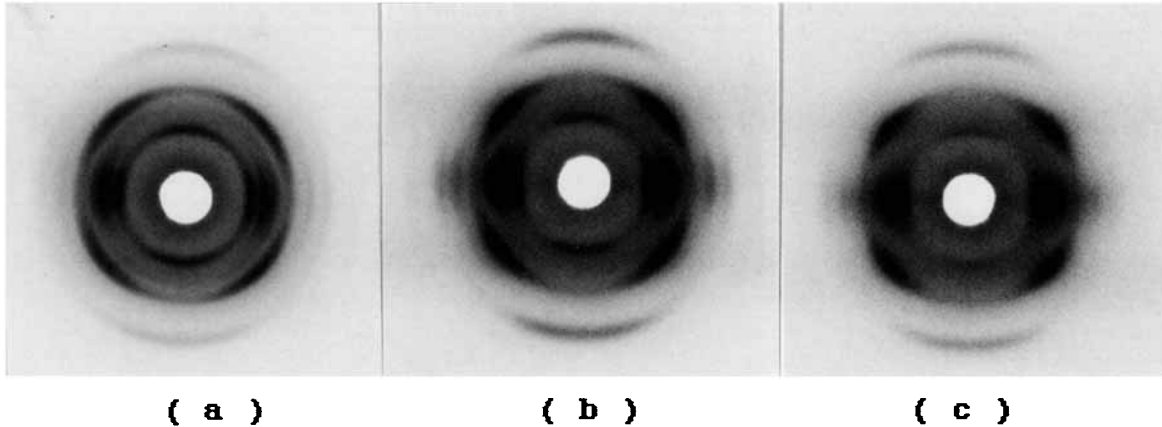


Figure 5 Wide angle X-ray patterns of filaments spun with low spinning speed; (a) HP 35 NA; (b) HP 35; (c) CP 35.

tributed to the fact that the nucleating agent in the HP 35 NA resin causes crystallization to occur closer to the spinneret where the local spinline velocity and molecular orientation in the melt are lower but the temperature is higher, thereby favoring the development of monoclinic crystalline structure with low orientation in the as-spun fiber. On the other hand, the low crystallizability of copolymer CP 35 requires a larger supercooling effect and higher molecular orientation in the fiber before the crystallization can actually start, therefore delaying the onset of crystallization down to around 180 cm from the spinneret, where the temperature is lower and the molecular orientation is higher. The result is a morphology consisting of a less well developed crystalline order, referred to in the literature as the

smectic phase, but with somewhat greater molecular orientation.

The X-ray diffraction patterns are shown in Figure 6 for the filaments spun at higher takeup velocity whose profiles were shown in Figure 4. As expected, these samples all exhibit higher molecular orientation than those spun at the lower speed. Further, all three samples contain the monoclinic crystalline form, consistent with their crystallization at higher temperature.

The average birefringences and filament diameters of the as-spun filaments are given in Table III, along with the coefficient of variation of the measurements. The birefringence values are generally consistent with the X-ray patterns and crystallinity values. The lower birefringence of the nucleated

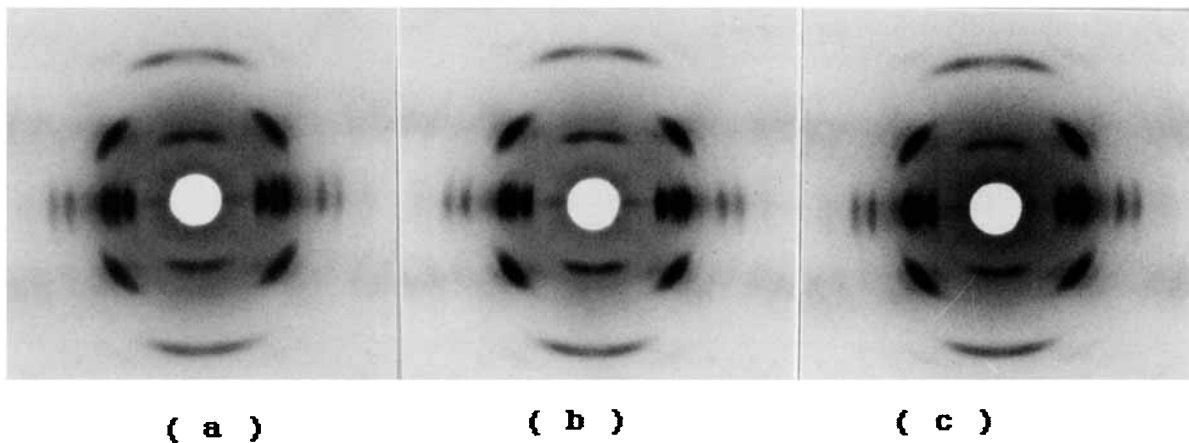


Figure 6 Wide angle X-ray patterns of filaments spun with high spinning speed; (a) HP 35 NA; (b) HP 35; (c) CP 35.

Table III Average Diameter and Birefringence of As-spun Filaments

	Sample					
	HP 35 NA		Hp 35		CP 35	
	Air Pressure (psig)					
	2	25	2	25	2	25
Average diameter (μm)	40	27.3	35.9	27.2	35.8	25.2
Coefficient of variation (%)	8	5.4	2.4	4	2	5
Average birefringence	12.2	19.9	18.7	19.5	19.5	17.1
Coefficient of variation (%)	12	5	4	5	2.7	5.5

resin, compared to the neat homopolymer, for filaments spun at low spinning speed is indicative of the lower molecular orientation accompanying the higher temperature and lower molecular orientation in the melt at the point at which crystallization begins for the nucleated resin. This effect is further illustrated by the high birefringence observed for the copolymer spun at low spinning speed. At high spinning speed, the birefringence of the nucleated and neat homopolymer are equal, within experimental error, as expected. The lower value of the birefringence of the copolymer, compared to the low-speed case, is presumably due to the lower molecular orientation in the amorphous phase because of the higher temperature at which crystallization occurs and due to the smaller crystalline contribution to the birefringence for the copolymer (compared to the homopolymer) because of its lower crystallinity.

Finally, it is worth noting that the coefficient of variation of the birefringence and diameter are much greater for the nucleated resin than for either the neat homopolymer or the copolymer resin in the case of low-speed spinning. This difference is presumably due to the method of mixing the nucleating agent into the polymer and the resulting poor uniformity of the mixture. At high spinning speed, the difference

between the coefficients of variation are negligible. This illustrates again that the nucleating agent can exert a considerable effect at low spinning speeds but stress-induced crystallization tends to control at high spinning speed.

Table IV shows tensile test results for all samples. It is found that the as-spun fibers of HP 35 NA produced at low air pressure possess the lowest tenacity and highest elongation-to-break. This can be attributed to the fact that higher onset crystallization temperature with low molecular orientation due to the effect of the nucleating agent results in higher crystallinity but lower birefringence, thus lower molecular orientation in the amorphous phase of the as-spun fibers to which the tenacity and elongation-to-break are closely related.^{20,21} By the same token, the low crystallinity and high molecular orientation structure of the CP 35 as-spun fibers formed during low-speed spinning due to delay of the on-line crystallization by the effect of copolymer result in the high tenacity and low elongation-to-break of this sample.

At high spinning speed, the effect of the nucleating agent on on-line crystallization, and, hence, the development of structure and properties of as-spun fibers, was dramatically reduced. Therefore, the te-

Table IV Tenacity and Elongation-to-break of As-spun Filaments

	Sample					
	HP 35 NA		HP 35		CP 35	
	Air Pressure (psig)					
	2	25	2	25	2	25
Tenacity (g/d)	1.25	1.97	2.17	1.94	2.3	1.73
Elongation-to-break (%)	386	273	300	236	250	270

nacity of as-spun fibers of HP 35 NA and HP 35 thus obtained were logically expected to be very close. This is clearly seen in Table IV. On the other hand, the lower birefringence of CP 35 as-spun fibers produced under high spinning speed results in lower tenacity and higher elongation-to-break than for the neat homopolymer prepared under the same conditions. These results suggest that the choice of a copolymer might be preferred to the homopolymer whenever spinning is to be carried out at low to moderate speed. For high-speed spinning, there may be a disadvantage of using a copolymer compared to the homopolymer if higher tenacity is the major criterion. Thorough understanding of the interaction of the polymer's quiescent crystallization behavior with the stress-induced crystallization effects is necessary if the properties of as-spun filaments are to be optimized.

CONCLUSIONS

It was found that changing the quiescent crystallization kinetics by either the addition of a nucleating agent or through copolymerization with ethylene can produce profound effects on the structure and properties of polypropylene as-spun filaments. Increasing the quiescent crystallization kinetics by addition of a nucleating agent causes crystallization to occur closer to the spinneret and at higher temperature. This results in lower molecular orientation of the as-spun filaments, lower tenacity, and higher elongation-to-break than for the unmodified homopolymer spun under identical conditions. The effects are most significant when the resins are spun under relatively low stress and low takeup velocity conditions. Higher takeup velocities and spinline stresses reduce the effect of the nucleating agent because of the influence of on-line stress-induced (molecular orientation-enhanced) crystallization. Because copolymerization reduces ultimate crystallinity as well as crystallization rate, the effect of copolymerization is more complex. At low spinning speed, the reduced rate of crystallization allows greater supercooling and greater molecular orientation to develop, producing a filament with high tenacity and lower elongation-to-break than either the nucleated or unnucleated homopolymer. Higher spinning speed produces lower final orientation in the copolymer due to a lower content of oriented crystals and a lower level of orientation in the amorphous regions. This effect produces a lower tenacity

than that obtained from the homopolymer under similar spinning conditions.

The authors thank Exxon Chemical Co. for their financial support of this study and for supplying the resins. The authors also thank Mr. D. Agrawal and Mr. Z. Ding for their help in making part of the on-line diameter measurements and Mr. S. Misra for carrying out the calculations involved in the computer simulation of the spinline temperature profiles.

REFERENCES

1. V. Capuccio, A. Coen, F. Bertinotti, and W. Conti, *Chem. Ind. (Milan)*, **44**, 463 (1962).
2. V. Compostella, A. Coen, and F. Bertinotti, *Angew. Chem.*, **74**, 618 (1962).
3. W. C. Sheehan and T. B. Cole, *J. Appl. Polym. Sci.*, **8**, 2359 (1964).
4. S. E. Ross, *J. Appl. Polym. Sci.*, **9**, 2729 (1965).
5. K. Katayama, T. Amano, and K. Nakamura, *Kolloid Z. Z. Polym.*, **226**, 125 (1968).
6. T. Kitao, S. Ohya, J. Furukawa, and S. Yamashita, *J. Polym. Sci.*, **11**, 1091 (1973).
7. J. E. Spruiell and J. L. White, *Polym. Eng. Sci.*, **15**, 660 (1975).
8. O. Ishizuka and K. Koyama, *Sen-i Gakkaishi*, **32**, T-43 (1976).
9. H. P. Nadella, M. M. Henson, J. E. Spruiell, and J. L. White, *J. Appl. Polym. Sci.*, **21**, 3003 (1977).
10. J. Shimizu, A. Watanabe, and K. Toriumi, *Sen-i Gakkaishi*, **30**, T-53 (1974).
11. J. Shimizu, K. Toriumi, and K. Tamai, *Sen-i Gakkaishi*, **33**, T-208 (1977).
12. J. Shimizu, K. Toriumi, and Y. Imai, *Sen-i Gakkaishi*, **33**, T-255 (1977).
13. J. Shimizu, N. Okui, and Y. Imai, *Sen-i Gakkaishi*, **35**, T-405 (1979).
14. F. Lu and J. E. Spruiell, *J. Appl. Polym. Sci.*, **34**, 1521 (1987).
15. F. Lu and J. E. Spruiell, *J. Appl. Polym. Sci.*, **34**, 1541 (1987).
16. Y. Lin, J. Zhou, and J. E. Spruiell, in *Proceedings SPE ANTEC*, 1991, Vol. 37, p. 1950.
17. K. F. Zieminski and J. E. Spruiell, *J. Appl. Polym. Sci.*, **35**, 2223 (1988).
18. J. H. Bheda and J. E. Spruiell, *J. Appl. Polym. Sci.*, **39**, 477 (1990).
19. R. M. Patel, J. H. Bheda, and J. E. Spruiell, *J. Appl. Polym. Sci.*, **42**, 1671 (1991).
20. R. J. Samuels, *J. Polym. Sci. A-2*, **6**, 1101 (1968).
21. R. J. Samuels, *Structured Polymer Properties*, Wiley, New York, 1974.

Received September 8, 1992

Accepted September 25, 1992