

Effect of Molecular Weight on High-Speed Melt Spinning of Nylon 6

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Synopsis

An extensive experimental study of the structure and properties developed in as-spun nylon 6 filaments is reported. Five polymers representing different molecular weights in the range 25,000–73,000 g/mol (viscosity average) were studied. These polymers were melt spun over a range of spinning speeds using an air drag type of drawdown device. Maximum take-up velocities achieved were in the neighborhood of 4000 m/min. The structure and properties of the as-spun filaments were characterized using density, DSC, WAXS, SAXS, birefringence, and tensile tests. The structural characteristics and properties of the filaments are strongly dependent on molecular weight. Generally, higher molecular weight leads to higher modulus and filament tenacity and lower elongation to break in the as-spun filaments. The structural changes with molecular weight are rather complicated; the complications are explained in terms of changes of crystallization rate and attainable crystallinity.

INTRODUCTION

Because of its importance as a commercial synthetic fiber, many studies have been devoted to the melt spinning of nylon 6.^{1–16} Ziabicki and Kedzierska^{2,4} studied the structure of as-spun nylon 6 filaments equilibrated with the ambient conditions using birefringence and x-ray diffraction. They showed that the birefringence increased with take-up stress. The x-ray data exhibited a broad equatorial reflection, which was interpreted to indicate the presence of a poorly developed pseudohexagonal crystal form whose diffraction pattern is much different from that of the stable α -phase.¹⁷ Hamana et al.,^{5,6} Ishibashi et al.,⁷ Hiramani and Tanimura,¹² and Bankar et al.,¹¹ made on-line birefringence or wide-angle x-ray scattering (WAXS) measurements. It was concluded that, in the low take-up velocity regime investigated, as-spun nylon 6 filaments are initially amorphous and crystallization to the pseudohexagonal form takes place on the bobbin. This point was further investigated by Gianchandani et al.,³ who predicted from their results that strain-induced crystallization will occur on the threadline at sufficiently high drawdown ratios (i.e., high take-up velocities).

Gianchandani et al.¹³ also reviewed the literature concerning phases observed in nylon 6 and suggest an appropriate nomenclature to help clarify the various notations used in the literature. The reader is referred to their paper for a detailed discussion of this problem. Briefly, they suggest that in addition to the stable α phase of Holmes et al.¹⁷ and the metastable γ

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phase of Arimoto,¹⁸ there exist poorly crystallized pseudo-hexagonal forms of both α and γ type as well as paracrystalline monoclinic α . They also found that the relative amounts of phases in conditioned nylon 6 filaments depend upon the molecular orientation developed during melt spinning. Low orientation resulted in higher amorphous and pseudo-hexagonal α -phase fractions; higher orientation resulted in greater pseudo-hexagonal γ -phase fractions.

There has been much recent interest in high-speed spinning because of its potential for high productivity and because of the special properties developed in filaments spun at high speeds. Most of the published studies on high-speed spinning relate to poly(ethylene terephthalate) (PET).¹⁹⁻²⁹ Shimizu et al.^{19,21-23} and Heuvel and Huisman²⁰ report that PET filaments are highly crystalline when spun at speeds greater than 4000 m/min, but they are amorphous at speeds below about 3000 m/min. Studies on high-speed melt-spun nylon 6 filaments were carried out by Shimizu et al.¹⁵ and Heuvel and Huisman.¹⁴ Both research groups observed increasing crystallinity and high orientation with increased take-up velocity results that were rather similar to the results for high-speed spinning of PET.^{19,23} Both groups also reported an increase in γ phase with increasing take-up speed. Heuvel and Huisman¹⁴ proposed that, at take-up velocities greater than 2500 m/min, γ crystals were mainly generated from orientation-induced nuclei and α crystals grew slowly after moisture pickup.

The molecular weight effect on the melt spinning of nylon 6 was investigated by Ishibashi and Ishii⁸ who carried out on-line temperature and diameter measurements. They found molecular weight independence of the temperature and diameter profiles over the number-average molecular weight range from 18,500 to 24,100. Gurato et al.³⁰ investigated the annealing effect on nylon 6 filaments for two different molecular weights ($M_n = 4700$ and 17,000). They found lower crystallinity for the higher molecular weight nylon 6. The molecular weight dependence of shear viscosity of nylon 6 melt was investigated by Kemblowski and J. Torzecki.³¹ They obtained a good correlation between molecular weight and melt viscosity.

In this paper we explore the high-speed spinning of a series of nylon 6 samples with varying molecular weight. Density, differential scanning calorimetry (DSC), birefringence, wide-angle x-ray diffraction (WAXS), and small-angle x-ray scattering (SAXS) were used to characterize the effect of molecular weight on the structure of filaments spun over a range of spinning speeds. Mechanical properties of the as-spun filaments were also measured and related to the molecular weight, spinning conditions, and structural characterization. A new model for structure development during melt spinning is suggested to explain the observed results.

EXPERIMENTAL DETAILS

Materials

The nylon 6 polymers used in this study were of five different molecular weights. The two nylon 6 polymers with lower molecular weight were supplied by the American Enka Company, and the remaining three polymers

of higher molecular weight were supplied by Allied Fibers and Plastics. Their basic characteristics are summarized in Table I and Fig. 1.

The relative viscosities given in Table I were determined by a solution of 1.0% nylon 6 in 85% formic acid at 20°C. Intrinsic viscosities were obtained by extrapolation of inherent viscosity versus concentration data to zero concentration. The intrinsic viscosity values were converted to viscosity-average molecular weight using the expression³²

$$M_v = \left(\frac{[\eta] \times 10^5}{75} \right)^{1/0.7} \quad (1)$$

The shear viscosities of nylon 6 melt were determined at 260°C using an Instron capillary rheometer. Residence time in the molten state was in the range from 20 to 40 min. The shear stress σ_{12} was determined by

$$P_T = 4\sigma_{12} \frac{L}{D} + \Delta P_e \quad (2)$$

where P_T is the total pressure and ΔP_e the end pressure loss. The shear rate was determined using Weissenberg's relationship³³

$$\dot{\gamma} = \frac{3n' + 1}{4n'} \frac{32Q}{\pi D^3} \quad (3)$$

where

$$n' = \frac{d \log \sigma_{12}}{d \log (32Q/\pi D^3)}$$

Figure 1 shows that all the viscosities are decreasing functions of shear rate and the viscosities increase with an increase in molecular weight at any shear rate. The viscosity for the highest molecular weight nylon 6 is almost 10 times as large as that for the lowest molecular weight nylon 6 at low shear rate.

TABLE I
Summary of Solution Viscosity Data

Material	Relative viscosity at 1.0 g/dl	Intrinsic viscosity	M_v
CN 9984	2.090	0.905	25,250
CN 0002	2.124	1.007	29,400
LBS	2.490	1.170	36,440
BHS	2.692	1.525	53,210
HMW	3.104	1.901	72,900

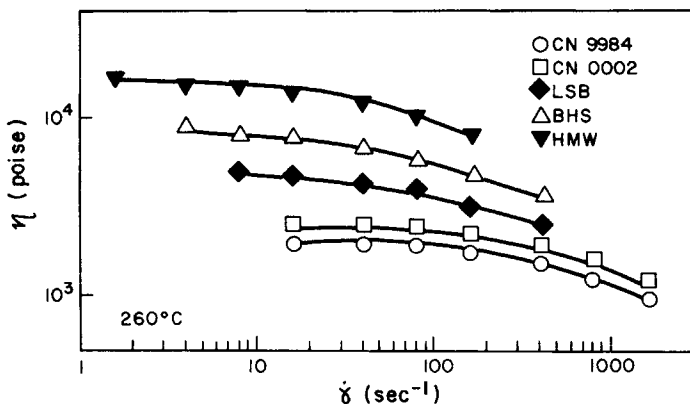


Fig. 1. Shear viscosity of nylon 6 melt as a function of molecular weight at 260°C.

Melt Spinning

The filaments were melt spun from a Fourne Associates screw extruder with a 1.3-cm diameter screw. At one end it is connected to a N_2 -purged hopper through which dry nylon pellets were fed. At the other end of the extruder, polymer is metered through a gear pump to a single-hole spinneret with a capillary of diameter 0.0762 cm and length-diameter ratio of 5. Two different extrusion rates, 3.55 and 5.55 g/min, were used. All except the highest molecular weight polymer were spun at 260°C. The highest molecular weight sample was spun at 265°C.

The filaments were spun into ambient air at a temperature of 25°C. No cross blow was used. Under such cooling conditions, the surface temperature of the filaments typically decreased by about 15°C for each 10 cm of spinline (within 50 cm of the die exit) for a mass flow rate of 5.55 g/min and a take-up velocity of 1000 m/min. The temperature profile was relatively insensitive to changes in take-up velocity at constant mass throughput. The spinline was 150 cm long for all experiments.

The filaments were drawn down in the present study using a pneumatic type drawdown device supplied by Rhone Poulenc Fibres. This device is a form of aspirator that uses high-velocity air to apply drag forces to the filament and draw it down. The final velocity of the filaments was controlled by the air pressure supplied to the aspirator and the properties of the nylon 6 melt. Filaments were spun at aspirator air pressures of 2, 20, 40, 60, 70, and 85 psig. The aspirator was located at a distance of 400 cm from the spinneret. The final filaments were collected and conditioned for at least 24 h at 65% relative humidity in a conditioned room. The take-up velocities for various samples as a function of air pressure supplied to the aspirator are presented in Fig. 2 for an extrusion rate of 3.55 g/min. In general, the take-up velocity that can be achieved at a given air pressure is lower the higher the molecular weight of the nylon 6. This is expected due to the higher melt viscosity of the higher molecular weight samples and consequent higher spinline stress required to achieve a particular velocity. This behavior is further illustrated in Fig. 3, which shows a cross plot of spinline stress versus molecular weight at three different take-up velocities and a mass throughput of 5.55 g/min.

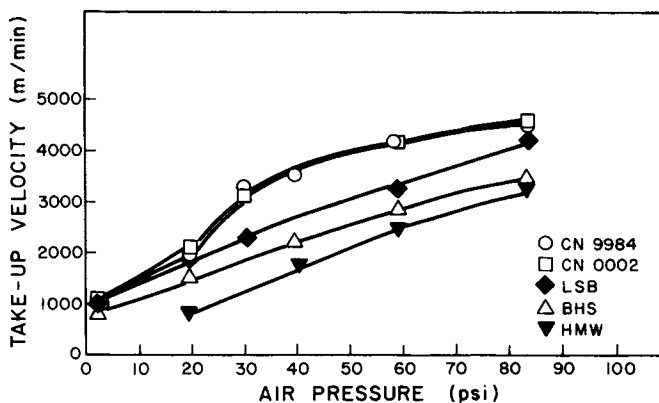


Fig. 2. Plots of take-up velocity versus air pressure in the aspirator. Throughput is 3.55 g/min.

Tension produced in the filaments during spinning was measured using a Rothschild tensiometer with a 4-g measuring head. The tensiometer was located 70 cm above the inlet to the aspirator.

Characterization of Spun Filaments

Structural characterizations of spun and conditioned nylon 6 filaments were carried out by density, DSC, WAXS, SAXS, and birefringence measurements. The densities of the sample were determined using a density gradient column prepared from a mixture of carbon tetrachloride and toluene.

Thermal analysis of nylon 6 filaments were performed on a Perkin-Elmer DSC model II. The heating rate was 20°C/min for the determination of

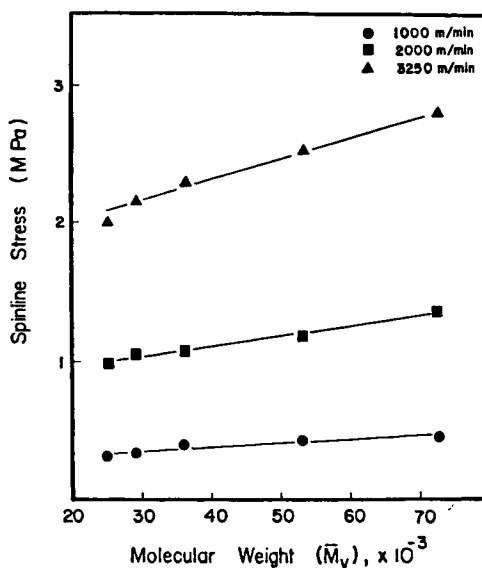


Fig. 3. Spinline stress of nylon 6 filaments as a function of molecular weight (mass throughput is 5.55 g/min).

melting point T_m and heat of fusion. After the initial heating process a constant temperature of 240°C was kept for 10 min, and then a cooling experiment was carried out at 10°C/min in order to obtain crystallization temperature and heat of crystallization. Prior to the DSC experiments, some filaments were dried by heating to 100°C under vacuum.

WAXS patterns of the spun filaments were made using a flat plate-type camera and nickel-filtered $\text{CuK}\alpha$ radiation. A Rigaku X-ray Diffractometer was used to obtain both the 2θ scans to evaluate the presence of the different phases and the azimuthal scan to evaluate the orientation function. Graphite crystal-monochromatized $\text{CuK}\alpha$ radiation was used for intensity measurements.

The birefringence measurements were carried out by the usual method using a Berek compensator in conjunction with an optical microscope.

The crystal orientation was estimated from the meridional (020) reflection after Herman's definition.³⁴

The relative amounts of α , γ , and amorphous phases were evaluated by the method of Gianchandani et al.¹³ This method uses a combination of density and WAXS data to evaluate the relative proportions of α , γ , and amorphous phases present in the sample.

Shrinkage was examined by heating the as-spun and conditioned filaments for 5 min in air at 175°C without applied restraint (free shrinkage). The shrinkage was computed as

$$\text{Shrinkage (\%)} = \frac{\Delta l}{l_o} \times 100 \quad (4)$$

The tensile mechanical properties were measured using a table model tensile testing machine located in a room controlled at 65% relative humidity and 20°C. The samples were conditioned in this same room for at least 24 h prior to testing. A gage length of 25.4 mm and a crosshead speed of 25.4 mm/min were used to obtain the force-versus-elongation data. Tensile strength, initial (tangent) modulus, and elongation at break were evaluated in the usual manner from the force-versus-elongation data and the initial fiber diameter.

EXPERIMENTAL RESULTS

Crystallinity and Phases Present in as-Spun Filaments

Figure 4 shows the density of as-spun filaments as a function of take-up velocity for five different molecular weight nylon 6 filaments. The results for the lowest molecular weight nylon 6 are consistent with data reported previously¹⁵; the filaments spun at low take-up velocity exhibit low density. These filaments increase in length ("grow") with time after take-up. It is explained that the crystallization of as-spun filaments occurs during conditioning after spinning and the crystallinity developed is quite low. The densities increase with increasing take-up velocity. Shimizu et al.¹⁵ and Heuvel and Huisman²⁰ suggest that the higher densities result from higher crystallinities resulting from orientation-induced crystallinity increases. At

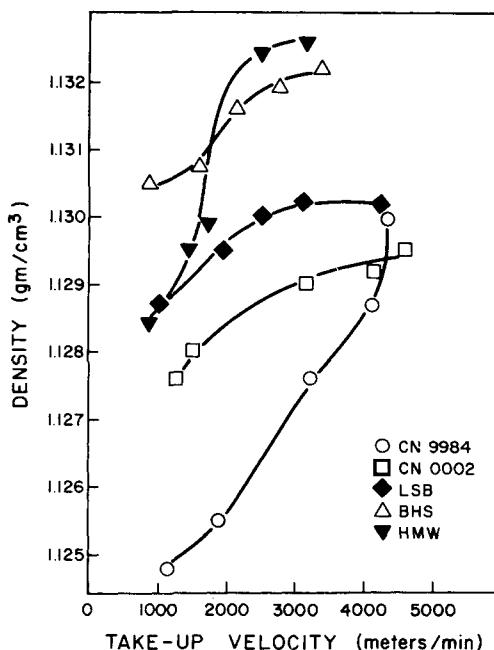


Fig. 4. Variation of density with take-up velocity for five different molecular weight nylon 6 filaments spun at a throughput of 3.55 g/min.

the highest take-up velocities, it is suggested that crystallization begins on the spinline.

On the other hand, our measurements show that the densities of higher molecular weight nylon 6 filaments have higher values than that of lower molecular weight samples at any take-up velocity. This suggests that increasing molecular weight leads to higher crystallinity or a change in the crystalline phases present.

The overall crystallinity is also characterized by using DSC measurements. The results of constant heating and cooling experiments are listed in Table II for dried and undried samples. Although melting temperatures

TABLE II
Effect of Molecular Weight on Melting Temperature, Heat of Fusion, Crystallization Temperature, and Crystallization Heat of Nylon 6 Filaments

Sample condition	Sample	Take-up velocity (m/min)	T_m (°C)	Q_h (cal/g)	T_c (°C)	Q_c (cal/g)
Dried	HMW	3180	495	13.2	448	13.2
Dried	BHS	3300	493	13.5	448	13.5
Dried	LSB	4230	493	14.6	450	13.5
Dried	CN0002	4600	494	15.0	453	14.3
Dried	CN9984	4325	494	15.1	453	14.3
As spun and conditioned	HMW	3180	492	12.8		
As spun and conditioned	CN9984	4325	492	15.0		
As spun and conditioned	HMW	870	491	11.8		
As spun and conditioned	CN9984	1880	491	14.7		

of dried nylon 6 filaments are higher than those of undried filaments, the molecular weight dependence of melting temperature is not clear. Heat of fusion, which can be related to the crystallinity, shows a strong dependence on molecular weight. The heat of fusion decreases with increasing molecular weight for both dried and undried samples. The results of DSC measurements have molecular weight effects on the overall crystallinity opposite to those suggested by the density measurements at first glance. This discrepancy will be discussed below and is related to a change in the crystal structure of the dominant crystalline phase. The heat of crystallization shows dependencies on molecular weight similar to the results for the heat of fusion, although the samples in melting measurements have various crystallization conditions and those in crystallization experiments are considered to have the same melting conditions for different molecular weight samples. The higher crystallinity of low-molecular-weight nylon 6 is compatible with the data of annealing experiments reported by Gurato et al.³⁰

The crystallization temperature, which is defined as an exothermic peak temperature, in the constant cooling rate experiments decreases with increasing molecular weight. The results suggest that the crystallization rate constant decreases with increasing molecular weight; that is, the low-molecular-weight nylon 6 crystallizes more quickly.

Typical x-ray diffraction patterns and equatorial intensity profiles are shown in Figs. 5 and 6. The equatorial profiles of low-molecular-weight

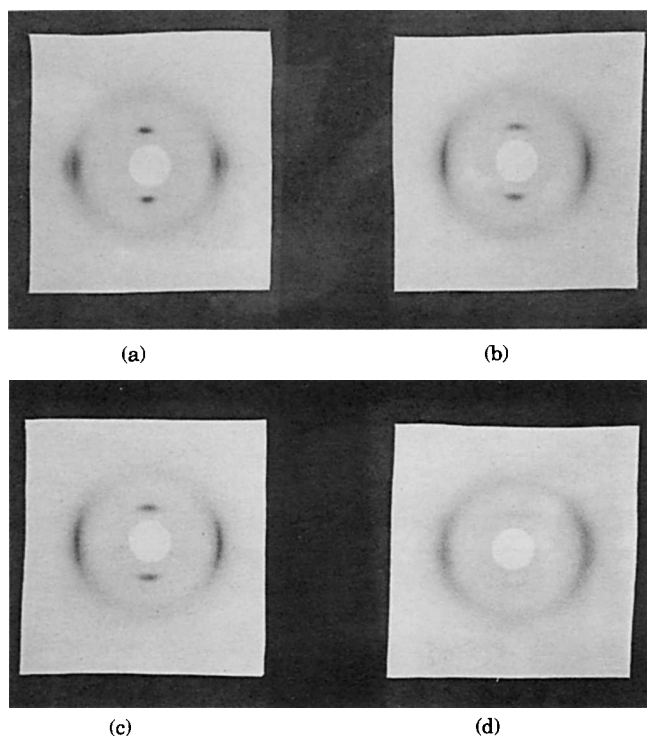


Fig. 5. Typical WAXS patterns of as-spun and conditioned nylon 6 filaments spun at a throughput of 3.55 g/min: (a) HMW, 3180 m/min; (b) HMW, 870 m/min; (c) CN9984, 4325 m/min; (d) CN9984, 1880 m/min.

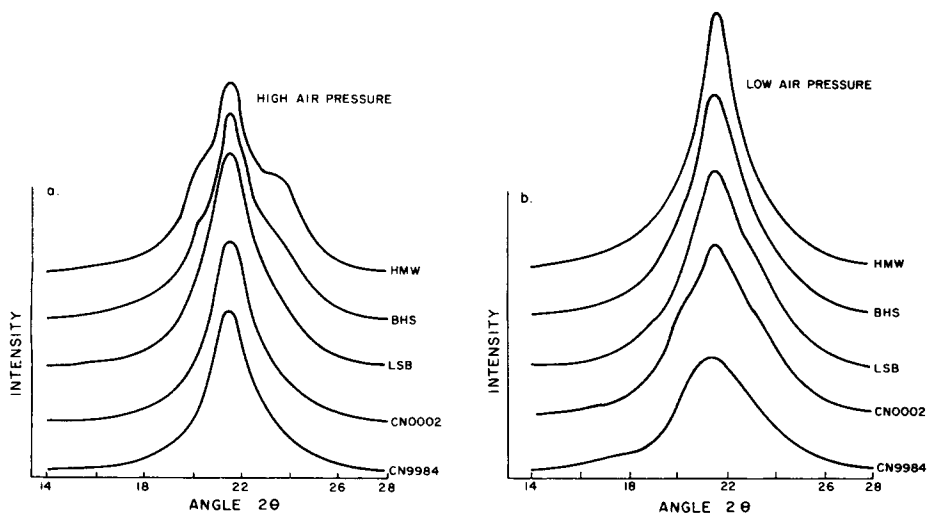


Fig. 6. Equatorial diffractometer scans for nylon 6 filaments as a function of molecular weight. Throughput is 3.55 g/min: (a) 85 psig air pressure; (b) 20 psig air pressure.

nylon 6 filaments spun at low take-up velocity show a relatively broad peak; the profiles of both low-molecular-weight samples spun at high take-up velocity and high-molecular-weight samples spun at low take-up velocity show a sharp peak characteristic of the γ -crystal form. The x-ray diffraction pattern of the high-molecular-weight filaments spun at high take-up velocity shows two weak but moderately sharp spots assigned to the α -crystalline form as well as a strong sharp γ spot. The two sharp spots of the α form correspond to shoulders in the intensity profiles in Fig. 6 for the high-molecular-weight sample spun at high take-up velocities. The sharpness of x-ray reflections is often controlled by crystallite size. Small crystallites result in line broadening, and larger crystallites result in sharper reflections.

Figure 7 shows the fraction of γ phase calculated from the equatorial and meridional intensities after the method of Gianchandani et al.¹³ The fractions of α -phase and total crystallinity estimated from combinations of the x-ray data with the density are shown in Figs. 8 and 9. Variation of the crystallinity is similar to that of the γ fraction; the major portion of the variation of the crystallinity with take-up velocity and with molecular weight is contributed by that of γ -phase fraction. The degree of change of the α -phase, γ -phase, and total crystalline fraction with take-up velocity decreases with increasing molecular weight. At high take-up velocity, the γ -phase fraction and crystallinity of the high-molecular-weight nylon 6 are smaller than those of the low-molecular-weight samples. The molecular weight dependence of total crystallinity is related to the heat of fusion measured by the DSC technique. The high density of high-molecular-weight filaments, which have small crystallinity, results from the higher fraction of α phase present in these samples because the crystal density of α form ($\rho_{\alpha} = 1.23 \text{ g/cm}^3$) is much higher than that of the γ form ($\rho_{\gamma} = 1.17 \text{ g/cm}^3$).³⁵

The effect of cooling rate can be examined using the melt-spinning ex-

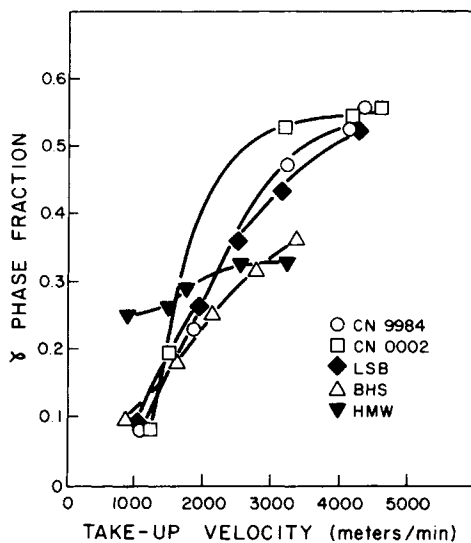


Fig. 7. Variation of γ -phase fraction with take-up velocity for different molecular weight filaments spun at a throughput of 3.55 g/min.

periments with different mass throughput rates. The crystallinities of the filaments spun at two different throughput rates ($Q = 5.55$ and 3.55 g/min) are plotted in Fig. 10 against the spinline stress for the highest molecular weight sample and the lowest molecular weight samples. If the cooling rate had little effect on the total crystallinity developed, the crystallinity would be expected to correlate with spinline stress independent of

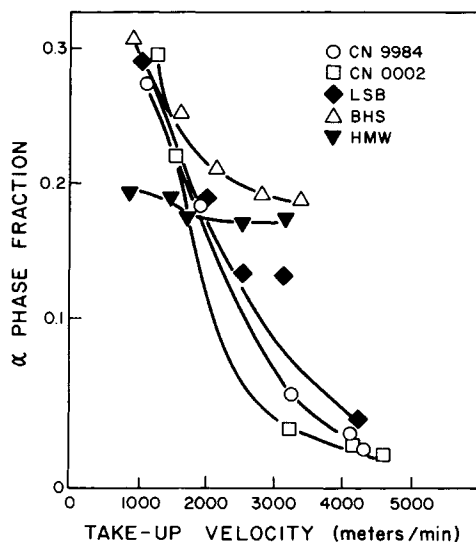


Fig. 8. Variation of α -phase fraction with take-up velocity for different molecular weight filaments spun at a throughput of 3.55 g/min.

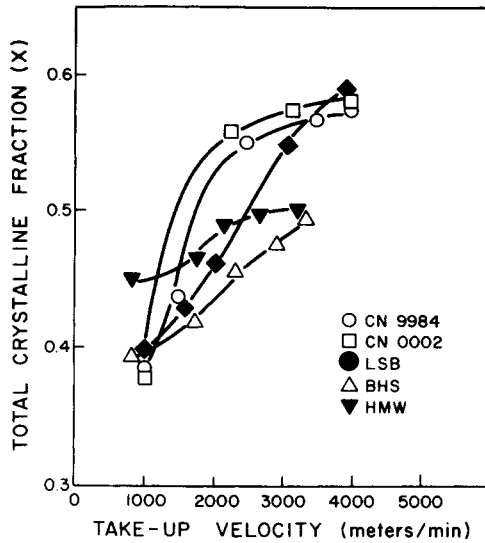


Fig. 9. Variation of total crystallinity with take-up velocity for different molecular weight filaments spun at a throughput of 3.55 g/min.

throughput rate. This seems to be the case for the high-molecular-weight sample. The crystallinity of the low-molecular-weight sample varies with both stress and mass throughput, indicating strong dependence on cooling rate. The slowly cooled filaments ($Q = 5.55$ g/min) of the low-molecular-weight nylon 6 have higher crystallinity than the more rapidly cooled filaments ($Q = 3.55$ g/min) at the same spinline stress.

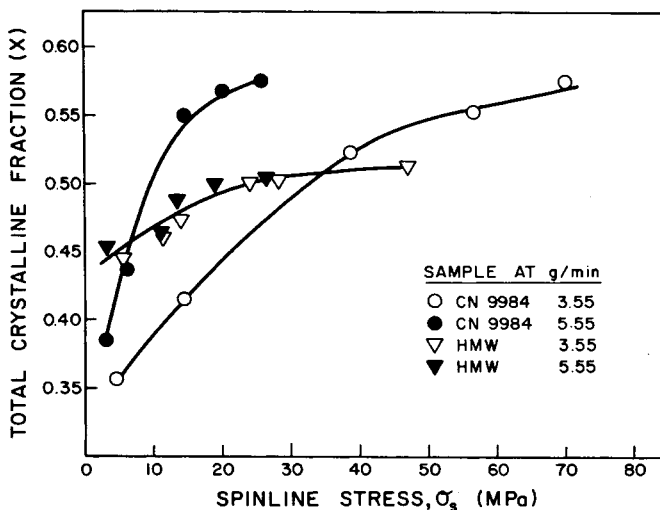


Fig. 10. Relationship between crystallinity and spinline stress for two different molecular weight filaments spun at two throughputs.

Orientation of Spun Filaments

The values of birefringence measured for the different molecular weight filaments are shown in Fig. 11 as a function of take-up velocity and a fixed throughput rate of $Q = 3.55$ g/min. The data for a throughput rate of 5.55 g/min exhibit similar trends. Birefringence values increase rapidly with take-up velocity up to 2000 m/min and then tend to saturate for the low-molecular-weight nylon 6. Similar results are reported by Shimizu et al.¹⁵ The behavior of the low-molecular-weight filaments seems to be related to the initial rapid rise in crystallinity and γ -crystal content and subsequent saturation with increase in take-up velocity. The birefringence values are higher for the high-molecular-weight samples and continue to increase rapidly at 3000 m/min. This continued increase in birefringence with take-up velocity contrasts with the small increase in crystallinity and γ fraction for the high-molecular-weight nylon 6.

The birefringence values for the lowest and highest molecular weight polymers are plotted versus the spinline stress in Fig. 12. Results are compared at two different mass throughput rates for each polymer. The relationship between birefringence and spinline stress is independent of mass throughput for a given molecular weight sample. The same result, in which the birefringence of spun filament is governed by spinline stress at the solidification point, was earlier reported for polypropylene.³⁶⁻³⁸ In the present data, however, there is no single correlation of the birefringence developed with the spinline stress independent of molecular weight in nylon 6 as was observed for polypropylene by Nadella et al.³⁸ This is probably due to complications associated with the development of crystallinity in

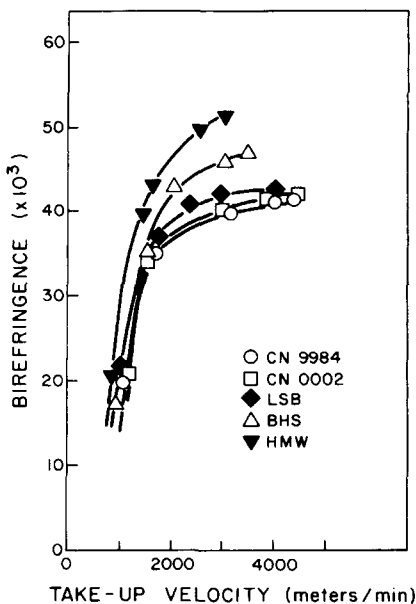


Fig. 11. Variation of birefringence with take-up velocity for different molecular weight filaments spun at a throughput of 3.55 g/min.

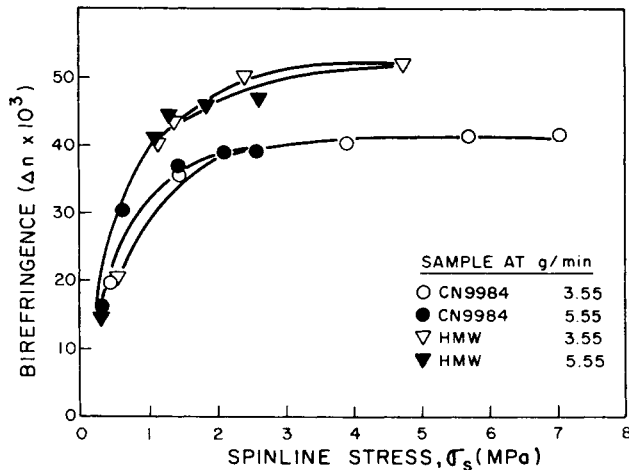


Fig. 12. Relationship between birefringence and spinline stress for two different molecular weight filaments spun at two throughputs.

nylon 6. The variation in molecular weight produces changes in both crystallization rate and resulting crystalline form in the case of nylon 6. Some samples may crystallize on the threadline and others crystallize during conditioning.

The chain axis orientations of the crystallites present in the filaments spun with a throughput rate of 3.55 g/min are shown in Fig. 13. The chain axis orientation for the high-molecular-weight filaments is consistently higher than for the low-molecular-weight filaments in the range of take-up velocities below about 3000 m/min. The highest molecular weight sample has already reached a saturation value at 2000 m/min, which is only reached by the lowest molecular weight sample at take-up velocities ap-

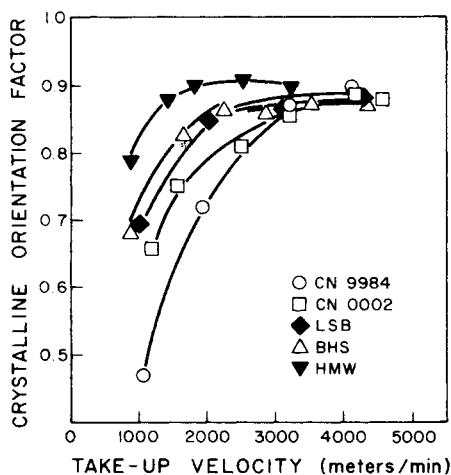


Fig. 13. Variation of crystalline chain axis orientation with take-up velocity for different molecular weight filaments spun at throughput of 3.55 g/min.

proaching 4000 m/min. The molecular weight independence of the chain axis orientation of crystallites at high take-up velocity contrasts with the overall molecular orientation as measured by the birefringence, which increases with an increase in molecular weight.

Small-Angle X-ray Scattering Patterns

SAXS patterns are shown in Fig. 14 at two take-up velocities for both the high-molecular-weight and low-molecular-weight nylon 6 samples. All samples exhibit discrete scattering maxima that allow calculation of a long-period spacing. The long-period values are given in Table III, where it is seen that the low-molecular-weight samples have long periods in the 60–68 Å range, consistent with prior results in the literature for melt-spun low-molecular-weight filaments.¹¹ The high-molecular-weight filaments have significantly larger long periods. The long periods increase with increasing take-up velocity, this effect being more pronounced for the high-molecular-weight samples.

The SAXS patterns also exhibit other differences. The low-molecular-weight samples show a substantial difference in lamellar orientation between the low and high take-up velocity samples, but there is essentially no change in lamellar orientation with take-up velocity for the high-mo-

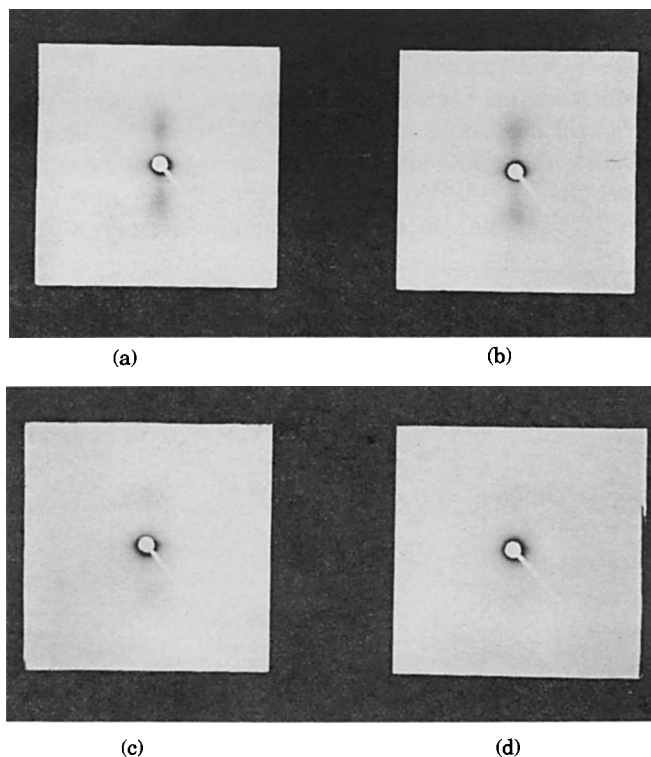


Fig. 14. Typical SAXS patterns of as-spun and conditioned nylon 6 filaments spun at a throughput of 3.55 g/min: (a) HMW, 3180 m/min; (b) HMW, 870 m/min; (c) CN9984, 4325 m/min; (d) CN9984, 1880 m/min.

TABLE III
Values of Long Period as a Function of Drawdown Rate and Molecular Weight

Sample	Take-up velocity (m/min)	Long Period (Å)
HMW	3180	93
HMW	870	81
CN9984	4325	68
CN9984	1880	60

molecular-weight samples. These observations are consistent with the WAXS crystalline orientation measurements. Finally, the discrete two-point maxima for the high-molecular-weight samples tend to be elongated in the meridional direction, especially at the highest take-up velocity. This may indicate some variation of the long period within the filaments.

Birefringence Changes with Conditioning Time

In order to establish whether molecular weight has a major effect on the crystallization process during spinning and whether crystallization is occurring on the threadline or during conditioning after take-up, the birefringence was measured as a function of conditioning time for all five molecular weight samples at a single take-up velocity of 1000 m/min. As has been previously established by several investigators,^{11,13,15} our lowest molecular weight sample would be expected to crystallize as it conditions not on the running threadline at this relatively low take-up velocity. This was in fact the case, as shown in Fig. 15. The birefringence of the lowest mo-

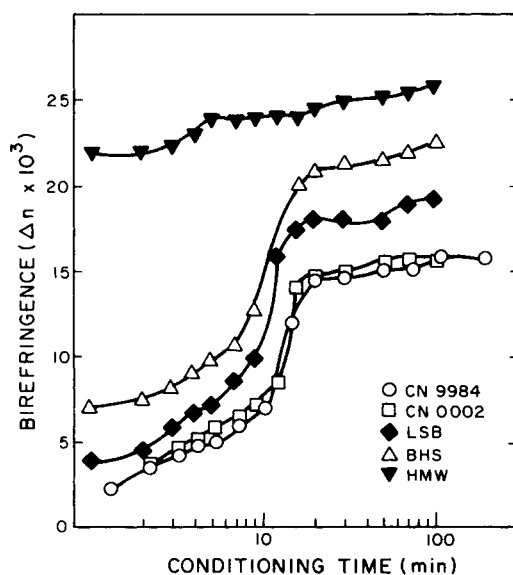


Fig. 15. Variation of birefringence with conditioning time for different molecular weight filaments spun at 1000 m/min at 3.55 g/min.

lecular weight filaments rapidly increases in the conditioning time range from 10 to 20 min after take-up. These data are consistent with the data reported by Shimizu et al.¹⁵ and Gianchandani et al.¹³ These previous authors also showed that the elapsed conditioning time prior to the rapid rise in birefringence decreases with increased take-up velocity. Our results presented in Fig. 15 show that the elapsed conditioning time prior to the rapid rise also decreases as the molecular weight of the polymer increases at constant take-up velocity. Moreover, the highest molecular weight nylon 6 sample exhibits a relatively high birefringence even at 1 min after take-up (the shortest elapsed time for which a measurement could be made) and a small gradual change in birefringence with further elapsed time. It should be noted that no change in sample length was observed after take-up for the highest molecular weight sample, but the other four samples were observed to undergo self-extension, which we attributed to crystallization aided by the absorption of moisture. These experiments prove that, for given spinning conditions, the crystallization kinetics of nylon 6 during or after melt spinning are greatly affected by the molecular weight of the polymer. Furthermore, the highest molecular weight samples studied can crystallize on the threadline during melt spinning within the range of take-up velocities available in our experiments.

Shrinkage of Melt-Spun Filaments

The shrinkage results are presented in Fig. 16 for the lowest and highest molecular weight samples. All samples were conditioned prior to the shrinkage experiments. The high-molecular-weight samples exhibit a very slight shrinkage when exposed to air for 5 min at 175°C, and there is a very small but observable increase with increased take-up velocity. The low-molecular-weight samples spun at take-up velocities below about 4000 m/min grow rather than shrink when exposed to these conditions. But when the low-molecular-weight sample is spun at higher speeds, it behaves in a manner similar to that for the high-molecular-weight samples. This again suggests that the morphology of low- and high-molecular weight samples are quite different when both are spun at low spinning speeds, but they may be similar

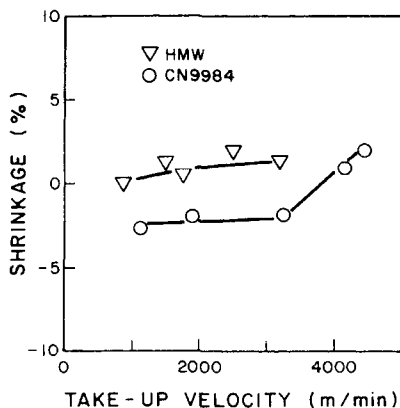


Fig. 16. Variation of shrinkage with take-up velocity for different molecular weight filaments spun at a throughput of 3.55 g/min.

when the low-molecular-weight sample is spun at sufficiently high spinning speed.

Tensile Properties of Melt-Spun Filaments

Typical engineering stress-versus-elongation curves are shown for the high- and low-molecular-weight samples at two different take-up velocities and a mass throughput of 3.55 g/min in Fig. 17. The variation of tangent modulus, tensile strength, and elongation to break as a function of take-up velocity and molecular weight are shown in Figs. 18, 19, and 20 for a mass throughput of 3.55 g/min. The properties, especially the modulus and elongation, also vary with mass throughput, with other variables held constant, although the trends with other variables at each throughput are similar. The effect of molecular weight and take-up velocity on the modulus of samples prepared with a throughput of 5.55 g/min is shown in the cross plot presented in Fig. 21. The data of Figs. 17 through 21 show that the modulus and tensile strength increase with increasing take-up velocity but elongation to break decreases with increasing take-up velocity. Generally, higher molecular weight results in higher modulus and tensile strength and lower elongation to break at any given take-up velocity and mass throughput. Figures 19 and 21 also show that the sensitivity of modulus to changes of molecular weight is greater at high speeds (about 3000 m/min) than at low speeds (about 1000 m/min).

Attempts to correlate the mechanical properties with spinline stresses or orientation (as measured by birefringence) failed. This is illustrated for the case of modulus plotted versus birefringence in Fig. 22. At low birefringences the modulus is quite sensitive to molecular weight, being much greater for the high-molecular-weight samples. For a given molecular weight and mass throughput, the birefringence tends to saturate at high take-up velocities (Fig. 11) and the modulus continues to steadily increase

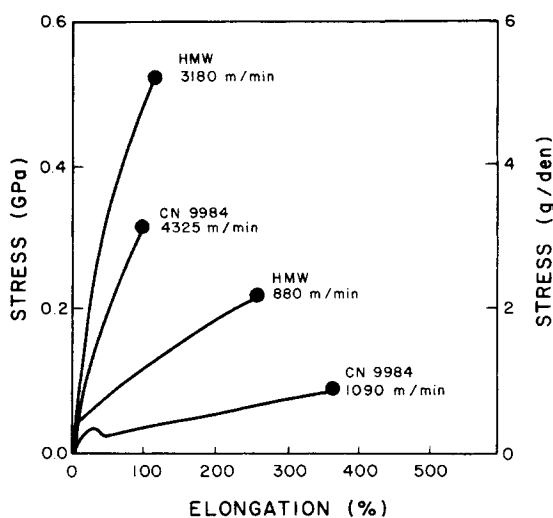


Fig. 17. Stress versus elongation of spun and conditioned nylon 6 filaments spun at a throughput of 3.55 g/min.

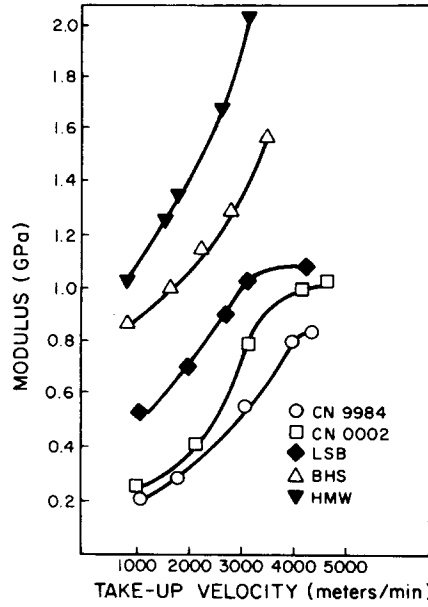


Fig. 18. Modulus of nylon 6 filaments spun at a throughput of 3.55 g/min as a function of take-up velocity.

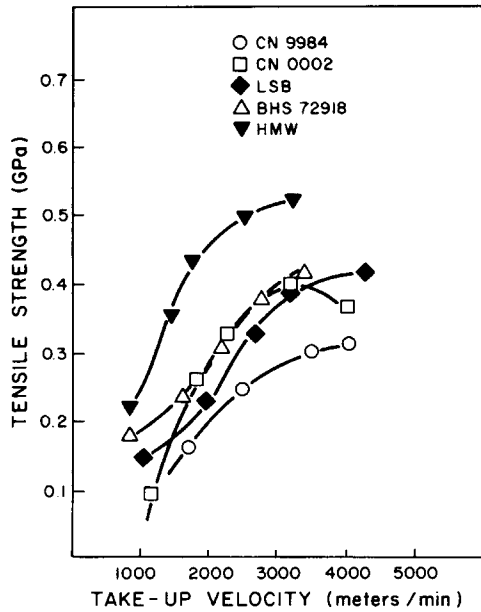


Fig. 19. Tensile strength of nylon 6 filaments spun at a throughput of 3.55 g/min as a function of take-up velocity.

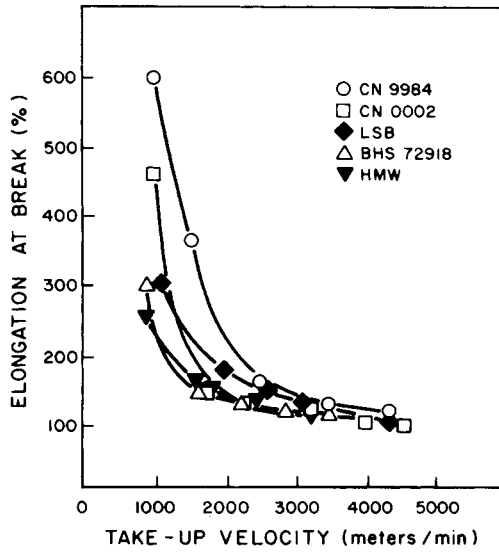


Fig. 20. Elongation at break of nylon 6 filaments spun at throughput of 3.55 g/min as a function of take-up velocity.

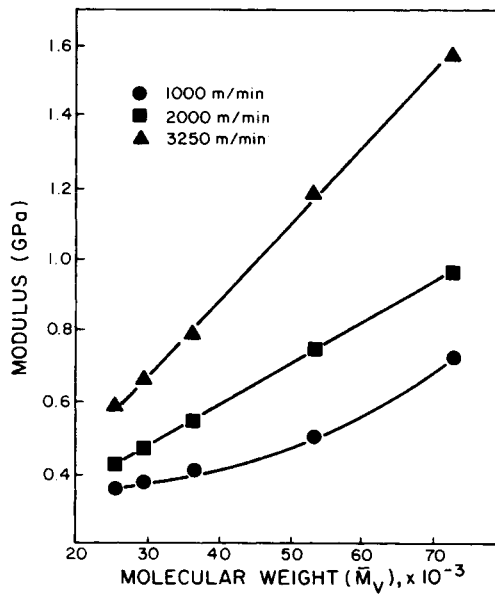


Fig. 21. Modulus of conditioned nylon 6 filaments spun at throughput of 5.55 g/min as a function of molecular weight.

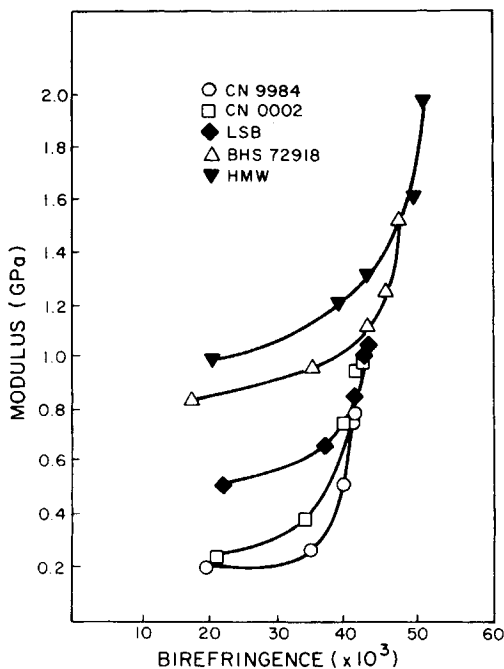


Fig. 22. Relationship between modulus and birefringence for different molecular weight filaments spun at throughput of 3.55 g/min.

with take-up velocity (Fig. 18). These effects combine to produce the results shown in Fig. 22, where the modulus of all samples tends to merge and rise rapidly with further increase of birefringence.

Figure 23 shows a plot of true strength of the filaments plotted versus birefringence of the spun and conditioned filaments. The true strength is defined as the force at break in the tensile test divided by the cross-sectional area at break. The change in cross-sectional area during tensile testing was computed from the elongation ratio using a constant volume assumption. The results in Fig. 23 show true strength generally increases with increase in the molecular weight of the polymer. True strength also increases slightly as the birefringence increases.

DISCUSSION

Structure Variations

The on-line studies of Bankar et al.¹¹ showed that nylon 6 filaments are amorphous on the threadline at spinning speeds up to 1000 m/min. The filaments were found to crystallize on the bobbin during "conditioning." Conditioning involves allowing the filament to come to equilibrium with the ambient conditions, which are nominally at room temperature ($\sim 20^\circ\text{C}$) and 65% relative humidity. The molecular weight studied by Bankar et al. was similar to the lowest molecular weight polymer of the present samples.

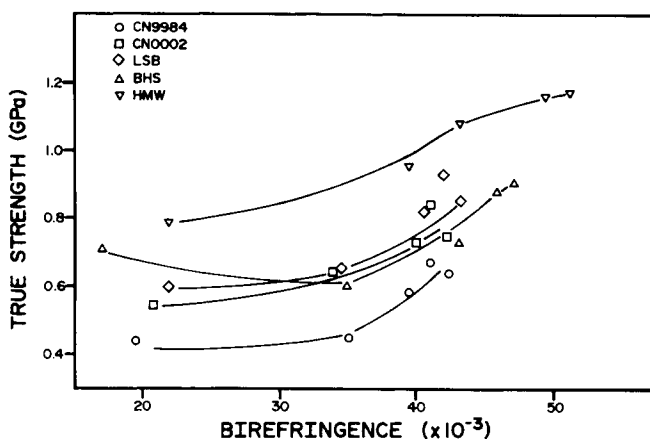


Fig. 23. Relationship between true strength and birefringence for different molecular weight filaments spun at throughput of 3.55 g/min.

The WAXS patterns of the present samples show well-defined peaks indicating the existence of crystallinity in the as-spun and conditioned filaments. Combination of the WAXS data with density showed that the crystallinity increases in all samples as the take-up velocities increase. Lower molecular weight filaments reach crystallinities of up to 60% with an increase in the spinline stress. The crystallinities of higher molecular weight filaments are lower than those of lower molecular weight filaments at high take-up velocities, but the reverse is true at low take-up velocities. Previous investigations^{13,15} studying low-molecular-weight nylon 6 found that the crystallization rate increased with an increase in take-up velocity. At sufficiently high take-up velocity (> 4000 m/min), Shimizu et al.¹⁵ found that nylon 6 crystallizes on the threadline rather than the bobbin. These changes would seem to be involved in the increase in crystallinity with increased take-up velocity.

The present data imply that these changes are also sensitive to molecular weight effects. It is observed that the higher molecular weight samples have higher crystallinity at low spinning speeds, but the low-molecular-weight samples tend to have higher crystallinity at high spinning speeds. It is necessary to explain the crossover of the total crystallinity curves of the low- and high-molecular weight materials with increasing take-up velocity. In order to do this, we first consider the effect that changing the molecular weight might have on quiescent crystallization (in the absence of stress and deformation). Then we consider the effect of stressing and elongating the melt as in the melt-spinning experiments.

Under quiescent conditions it is expected that the crystallization rate of a polymer and its ultimate crystallinity will both decrease somewhat with increasing molecular weight.^{39-41,46} The molecular weight dependence of the crystallization rate is understood in terms of the molecular entanglement in the polymer melt; the greater entanglement in the higher molecular weight polymer will reduce the rate of incorporation of crystallizable chains

into the crystals. A similar argument involving incorporation of part of a polymer molecule into more than one crystal and the subsequent prevention of its complete incorporation into either of the crystals during the final stages of the crystallization process explains the molecular weight effect on the final attainable crystallinity. This picture is consistent with the present DSC results, which indicate that the higher molecular weight polymer has slower quiescent crystallization kinetics (lower crystallization temperature) and lower final crystallinity (lower crystallization heat) under given cooling conditions. Further support for this view of the behavior of nylon 6 comes from the work of Garato et al.,³⁰ who investigated the attainable crystallinity by annealing at high temperature. They reported that the density of high-molecular-weight nylon 6 is lower than that of a low molecular weight nylon 6 under the same annealing conditions.

During melt spinning the presence of stresses and elongational deformation, with the accompanying molecular orientation, would be expected to enhance the crystallization kinetics of each of the nylon 6 samples. But since higher molecular weight polymer has the higher melt viscosity, it would be expected to have higher spinline stress than a lower molecular weight polymer under equivalent spinning conditions (i.e., same kinematics and cooling conditions). Under these conditions, the trend in the rate of crystallization with molecular weight would likely be reversed; for a given set of spinning conditions the higher molecular weight polymer would crystallize faster. This would explain the higher crystallinity in the high-molecular-weight material of relatively low take-up velocity (~ 1000 m/min) and is confirmed by the measurements of birefringence as a function of conditioning time. These results clearly indicate increased crystallization rates with increasing molecular weight following low-speed spinning. The large differences in crystalline orientation observed in Fig. 13 in the samples spun at low speeds and the differences in lamellar orientation observed in the SAXS patterns of the two samples spun at low speeds (Fig. 14) are also consistent with this interpretation.

With increase in spinning speed the spinline stresses increase for each molecular weight polymer. This increase in spinning stress should enhance the crystallization rate still further compared with the low spinning speed case. The effect is more noticeable in the low-molecular-weight samples, for two reasons. First, the low-molecular-weight polymers are just reaching spinline stress levels at the higher spinning speeds where they develop enough molecular orientation to induce on-line crystallization. The prior work of Shimizu et al.¹⁵ demonstrates this fact. This results in the rapid rise in the crystallinity of the low-molecular-weight polymers. Our results show that our highest molecular weight sample has already reached this condition at a take-up velocity of 1000 m/min. The crystallinity of the high-molecular-weight polymer increases much more slowly with further increase in spinning speed. This would seem to be a saturation effect. The high-molecular-weight sample cannot reach the same ultimate level of crystallinity as the low-molecular-weight sample for the same reasons cited for the quiescent crystallization case. Thus, although the high-molecular-weight polymer can crystallize more rapidly than the low-molecular-weight

polymer at low spinning speeds, it cannot reach the same level of crystallinity at high spinning speeds.

The situation is further complicated by the presence of the α - and γ -crystalline forms and their changes with spinning conditions. The present and previous data¹³⁻¹⁵ indicate the presence of a greater fraction of γ form with increasing take-up velocity. Heuvel and Huisman¹⁴ studied a low-molecular-weight polymer similar to our lowest molecular weight sample in the take-up velocity range from 700 to 5500 m/min. These authors suggested that γ crystals are mainly generated from orientation-induced nuclei at speeds in the neighborhood of 2500 m/min and above. The present data for the low-molecular-weight sample and the data of Shimizu et al.¹⁵ are qualitatively in agreement with this interpretation. Shimizu et al.¹⁵ further show from their birefringence versus conditioning time data that their polymer largely crystallizes on the running threadline prior to reaching the winding device at speeds in excess of about 4000 m/min. Our results again indicate that an increase in molecular weight is similar to increasing the spinning speed for the low-molecular-weight sample. The γ content is greater in the high-molecular-weight polymer at low take-up velocities (Fig. 7). However, at higher spinning speeds the saturation effect described above occurs for the γ form. In addition, some of the γ formed in the high-molecular-weight sample at high take-up velocities may transform to α phase, as discussed below. The net effect is that there is a crossover of the γ contents in the high- and low-molecular-weight samples with increasing take-up velocity.

Heuvel and Huisman¹⁴ suggest that the α crystals present in their low-molecular-weight nylon 6 filaments grow slowly at room temperature after moisture absorption during conditioning. This is similar to the suggestion of Gianchandani et al.,¹³ who use this argument to explain the presence of α -type pseudo-hexagonal crystals at low to modest spinning speeds. The crystals of such α -phase material would be very small and imperfect and exhibit highly broadened diffraction profiles. Shimizu et al.¹⁵ further showed that fairly sharp well-developed α reflections start to appear in the equatorial profiles at spinning speeds in the neighborhood of 7000 m/min. The present results (Figs. 5 and 6) show that similar sharp α reflections appear at low spinning speeds (about 3000 m/min) for our high-molecular-weight nylon 6. These sharp α reflections may be interpreted in terms of on-line crystal transformation from γ to α form (or, perhaps, a very high stress, high temperature nucleation of α phase directly). Because these α -phase crystals form at higher temperature on the threadline, they are larger and more ordered. The increased long period observed for the high-molecular-weight sample also suggests that the structure was formed at a higher temperature than the corresponding low-molecular-weight sample. Crystal transformation from γ to α form at high temperature has been observed in the isothermal crystallization experiments from the melt by Kyotani and Mitsuhashi.⁴² Although this suggests that the α crystals giving rise to the relatively sharp reflections were formed by transformation from the γ crystals, it does not seem possible to rule out direct nucleation of α crystals from the stressed melt. The net effect of these phenomena is that the high-

molecular-weight polymer has more α phase than the low-molecular-weight polymer after spinning at speeds in the neighborhood of 2000 m/min and above.

Tensile Properties

In general we would expect that a property such as the initial modulus could be described as some combination of the modulus of the crystalline phase and the modulus of the noncrystalline, amorphous phase. The modulus of the crystalline phase is normally much greater than that of the amorphous phase; thus the filament modulus increases with crystalline content. The modulus of the crystal varies with direction within the crystals and is much greater along the polymer chain direction than in other directions. This should produce a dependence of filament modulus on crystalline orientation. In the case of nylon 6 the crystal modulus in the chain direction will be greater for the α phase than for the γ phase because of the different chain conformation in these two phases. Thus, the modulus should also be sensitive to the ratio of α -phase content to γ -phase content. The modulus of the noncrystalline phase should be affected by molecular orientation and the degree to which the molecules are cross-linked into a network structure. For a semicrystalline polymer there are no chemical cross-links but the crystals serve as physical cross-links. There is also the question of hydrogen bonding in the case of nylon 6.

The data of Fig. 18 show a very strong dependence of the initial modulus on both molecular weight and take-up velocity. The behavior observed for the low-molecular-weight polymer with increasing take-up velocity is similar to that observed by previous investigators.^{13,15} These changes would seem to be related to the increased crystallinity and orientation produced by the increased spinning speed.

The changes with polymer molecular weight are more complicated. The modulus increases monotonically with molecular weight for any given set of spinning conditions, but the structure changes vary in a complex fashion. At low take-up velocity the high-molecular-weight polymer has higher crystallinity than the low-molecular-weight polymer, but at high take-up velocity the reverse is true. On the other hand, the α -phase fraction is greater for the high-molecular-weight polymer in the high take-up velocity range. Increasing the molecular weight would be expected to increase the connectivity in the network structure by increasing the number of tie molecules that connect two crystal blocks together. This should clearly increase the filament modulus and may be the overriding effect controlling the observed modulus. The higher melt viscosity of the high-molecular-weight polymer may also promote higher molecular orientation in the noncrystalline fraction of the high-molecular-weight filaments. Preliminary attempts to estimate the amorphous orientation factors in the manner of Samuels⁴⁷ do indicate this to be the case. However, there are numerous difficulties of quantitatively applying this approach to nylon 6 as-spun filaments. In general, we can qualitatively rationalize the observed variation of the modulus with molecular weight through the effect that molecular weight has on the noncrystalline orientation and molecular connectivity and the changes in

crystallinity and crystal type, but a detailed quantitative treatment is not available at the present time.

The lack of correlation of the initial modulus with birefringence when comparing samples of varying molecular weight, shown in Fig. 22, would seem related to large differences in morphology in filaments with the same birefringence. Although birefringence is a measure of average orientation of the filaments, samples with markedly different morphologies can be expected to have very different moduli.

The situation is even more difficult to analyze for the ultimate properties, such as tensile strength and elongation at break. It is clear from Figs. 19, 20, and 23 that molecular weight has a strong influence on these properties, but the situation is too complicated for quantitative interpretation. Another major concern in dealing with structure-property relations of as-spun filaments is the possibility of variations in the morphology with radial position within the filaments. This effect is known to exist in large filaments at low spinning speeds and in relatively fine-denier filaments at very high spinning speeds.^{15,48}

SUMMARY AND CONCLUSIONS

A study was carried out of the high-speed melt spinning of filaments from nylon 6 polymers having different molecular weights. The molecular weight ranged from a viscosity average of about 25,000 to 73,000 and corresponded to a variation of zero shear melt viscosity from 2×10^3 to 1.8×10^4 poise at the melt-spinning temperature. The structure of the as-spun filaments depended markedly on spinning speed (take-up velocity) and on molecular weight. Although crystallinity and γ fraction both increase with increasing take-up velocity, these quantities show an intricate dependence on molecular weight. The crystallinity at high take-up velocity (~ 3000 m/min) decreases with increasing molecular weight. At low take-up velocity (~ 1000 m/min) the opposite trend was observed, with the high-molecular-weight polymer having the higher crystallinity. This crossover in the behavior of the crystallinity was attributed to the fact that increasing either take-up velocity or molecular weight increases the crystallization rate but the final attainable crystallinity decreases with increasing molecular weight. The increase in crystallization rate of the spun filaments with increased molecular weight was confirmed by measurements of birefringence as a function of conditioning time; the filaments of the highest molecular weight nylon 6 crystallized in less than 1 min of conditioning at a take-up velocity of only 1000 m/min.

In general, the data were consistent with previous suggestions that the γ phase forms from orientation-induced nuclei. It was observed, however, that high-molecular-weight samples spun at high speeds contained a larger proportion of α -phase crystals than did low-molecular-weight samples. These α -phase crystals were relatively large and well ordered compared with α -phase crystallites present in low-molecular-weight as-spun samples. It was concluded that this likely resulted from transformation of γ to α phase at elevated temperature on the running threadline.

The tensile properties of the filaments were strong functions of both take-

up velocity and molecular weight. The initial modulus and tensile strength increased and elongation to break decreased with increase of take-up velocity or molecular weight. The true strength at fracture was also found to increase with increase of molecular weight. The variation in initial modulus could be rationalized in terms of the structure changes with take-up velocity and molecular weight, but quantitative interpretation has not yet been achieved.

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