Production of Super-Tenacity Polypropylene Filaments*

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Synopsis

The effects of the conditions of fiber formation on structural parameters and tensile properties of melt-spun, highly isotactic polypropylene filaments were investigated to determine the feasibility of producing supertenacity polypropylene filaments. Melt-spun polypropylene monofilaments were prepared from five highly isotactic polymers (94% or more by extraction), under different conditions of extrusion, quenching, drawing, and annealing. The molecular weight, molecular weight distribution, crystalline structure, crystallinity, crystallite orientation, and total molecular orientation (as expressed by total draw ratio) of the experimental filaments were determined, and the relationships between these structural parameters and the tensile properties of the filaments are discussed in the paper. Several of the experimental polypropylene filaments produced had tenacities greater than 12 g./den. and one of them had a tenacity of 13 g./den. Polypropylene filaments having tenacities greater than 13 g./den. appear feasible. To produce the super-tenacity polypropylene filaments, a polymer with a weight-average molecular weight of about 470,000 was melt spun into undrawn filaments having the paracrystalline structure, and the filaments were drawn to a maximum and annealed. The tenacity of the polypropylene filaments increased with increasing fiber molecular weight. A narrow molecular weight distribution was beneficial, but was not necessary for obtaining high tenacities. High draw after spinning was important in producing high tenacity. The maximum amount that a fiber could be drawn depended upon its molecular weight, the amount of stretch introduced during spinning, and the drawing time and temperature (filament temperature). Filaments having the paracrystalline structure, which was obtained with proper extrusion and quenching conditions, could be drawn more easily than filaments having the crystalline structure, and hence, under equivalent conditions, the former could be drawn more. The more the filaments were stretched during spinning, the lower were their tenacities. The relationship between crystallite orientation and the tensile properties of drawn and annealed filaments stretched during spinning was different from the relationship for drawn and annealed filaments that were not stretched during spinning. The highly drawn filaments contained voids, but they could be removed by proper annealing conditions, which also increased the tenacity of the filaments.

INTRODUCTION

Empirical data from work in government projects have shown that the resistance of a fabric to penetration by missiles increases with the strength of the fiber used in the fabric. The fibers that are commercially available

today have a maximum tenacity of about 9 g./den., and it is the goal of the Office of Naval Research and the Naval Research Laboratory to have fibers with tenacities of 12 g./den. or more and with elongations at break of at least 8% for use in body armor clothing. The studies described in this paper were undertaken to establish the feasibility of producing super-tenacity polypropylene fibers, while maintaining other desirable properties.

The properties of a polypropylene fiber depend upon its morphological structure, which is constrolled by the methods and conditions of fiber formation. This paper describes the effects of various conditions of melt spinning, drawing, and annealing on structural parameters of experimental polypropylene monofilaments and the relationships between the structural parameters and tensile properties of the filaments. In addition, factors affecting the maximum draw ratio of experimental polypropylene monofila-ments and the tensile properties of filaments drawn to a maximum are considered. The effect of annealing temperature on the tenacities of poly-propylene filaments drawn different amounts is also discussed. The struc-tural parameters considered are molecular weight, molecular weight dis-tribution, crystallinity, and orientation; the tensile properties considered are tenacity, elongation at break, and modulus. The monofilaments were prepared on laboratory melt-spinning and drawing equipment from five highly isotactic polypropylenes of different molecular weights.

MATERIALS AND METHODS

Source of Polymers

The five propylene polymers used in the studies were Pro-fax polymers obtained from Hercules Powder Company.

Characterization of Polymers

The specific viscosities (η_{sp}) of tetralin and decalin solutions of the poly-mers were determined at 135°C. with a Cannon-Ubbelohde semimicro dilu-tion viscometer having a negligible kinetic energy correction. No correc-tion was made for shear dependence. Intrinsic viscosities in tetralin $[\eta]_t$ were calculated by extrapolating η_{sp}/c curves to zero concentration, where c is concentration in grams per deciliter. Intrinsic viscosities in decalin $[\eta]_d$ were determined from a single-point measurement of η_{sp} at a concentration c of 0.1 g./dl. and eq. (1):

$$\log (\eta_{sp}/c) = \log [\eta]_d + k [\eta]_d c \qquad (1)$$

where k has an average value of 0.18.

Weight-average molecular weights $\bar{M}_w$ were calculated with eqs. (2) and (3) given by Moraglio[1] and Chiang,[2] respectively:

$$[\eta]_t = 1.75 \times 10^{-4} \bar{M}_w^{0.74} \qquad (2)$$

$$[\eta]_d = 1.00 \times 10^{-4} \bar{M}_w^{0.08} \qquad (3)$$

The content of isotactic polypropylene in the polymers was determined by extraction and by two methods based on infrared analyses. For the extraction method,[3] the polymers were melt-spun into monofilaments, under conditions that did not significantly degrade them, and the extractions were performed on chopped filaments. A 10-g. sample of chopped filaments was extracted with 350 ml. of n-heptane in a Soxhlet extractor for 48 hr., and the heptane-insoluble fraction was taken as the isotactic polymer.

The infrared methods for determining isotacticities were based on the work of Luongo[4] and Brader.[5] Samples of polypropylene for infrared analyses were prepared by the following procedure to assure maximum crystallinity. A 20-g. portion of the polymer was put into a 50 × 200-mm. test tube, and the sample was heated under nitrogen in an oil bath to 270°C. over a 3-hr. period, and then it was allowed to cool slowly to room temperature in the oil bath. The sample was then removed from the tube, and a specimen about 30 μ thick was sliced from it with a microtome. The infrared spectrum of the specimen was recorded with a Perkin-Elmer Model 21 spectrophotometer, and the ratios of absorbances were determined at 995 and 974 cm.$^{-1}$ and at 1160 and 974 cm.$^{-1}$. The percentage of isotactic polypropylene in the polymer was determined by Luongo's method from the ratio of absorbances at 995 and 974 cm.$^{-1}$, with the aid of a calibration curve obtained by plotting the ratios of absorbances and the isotactic contents of polymers of known composition. The percentage of isotactic polypropylene in the polymer was determined by Brader's method from the ratio of absorbances at 1160 and 974 cm.$^{-1}$. Brader's method assumes that the helical content H_I is a direct indication of the isotactic content and is given by eq. (4):

$$H_I = 141.2(A_{1160}/A_{974}) - 49.0 \tag{4}$$

Values of the melt index were determined with a melt indexer according to ASTM method D 1238-57 T. A temperature of 230°C. and a load for extrusion of 2160 g. were used. The results are reported in grams extruded per 10-min. interval.

Crystalline melting points were determined by birefringence with a Kofler hot-stage microscope equipped with polarizers.

Preparation of Monofilaments

The monofilaments were prepared by extruding the polymers through a monofilament spinneret, with hydraulic pressure applied from metering pumps, and the filaments were taken up by a variable speed godet and wound onto a tube with a Leesona winder. After spinning, the monofilaments were drawn, and, in most instances, the drawn filaments were annealed. The conditions of extrusion, drawing, and annealing that were used are summarized below.

Two sets of extrusion conditions were used. In method A, the polymer was heated for 1.25 hr. at 280°C., which is the maximum temperature at which the Pro-fax polymers are reported to be stable[6]. After heating, the

polymer was extruded at this temperature at a rate of 0.42 cc./min. through a spinneret with a circular orifice having a diameter of 10 mils and a length/diameter ratio of 2.3. No attempt was made to remove the air from the polymer or extrusion pot during the pre-extrusion heating period or during extrusion. In method C, air was eliminated from the polymer and extrusion pot by evacuation of the pot with a rotary oil pump; and while under a vacuum (5–10 mm. Hg pressure), the polymer was heated for 0.75, hr. at 235°C. This is the minimum temperature at which we could extrude the polymers with our equipment. At the end of the heating period, evacuation was discontinued, and the polymer was extruded at a rate of 0.14 cc./min. through a spinneret with a circular orifice having a diameter of 13.5 mils and a length/diameter ratio of 2.3.

Monofilaments extruded by both methods were quenched in air at 25°C. or in a water bath at 10–95°C., with the surface of the bath about 4 in. from the orifice of the spinneret. After quenching, monofilaments extruded by method A were taken up at a speed of 27.3 yd./min. Monofilaments extruded by method C were normally taken up at a speed of 5.3 yd./min. but in one series of experiments, take-up speeds of 10.6, 15.9, and 90.6 yd./min. were used to orient the polymer chain molecules during spinning.

The spun filaments were drawn within a couple of hours after spinning. Normally, they were drawn on our laboratory continuous drawing machine through a heated glycerine bath (50–150°C.) with an immersion time in the bath of 0.6–18.2 sec., which was controlled by adjusting the feed-roll speed. Some experimental filaments were drawn in air (cold drawn) on our laboratory continuous drawing machine; others were cold drawn on an Instron tester, at a draw rate of 0.5 in./min.

In one series of experiments, filaments were drawn in a convection oven with a fixed load in the following manner. Each end of a bundle of about 15 filaments was placed in a clamp with Teflon-lined jaws. One clamp was attached to a support bar on a ring stand, and weights were attached to the other clamp so that each filament was under an average tension of about 0.17 or 0.27 g./den. The ring stand was placed in an oven, and the temperature of the oven was raised to 130–135°C over a 30-min. period. After 1.5 hr. at this temperature, the ring stand was removed from the oven; the fibers were allowed to cool to room temperature, and the weight was removed.

The filaments that were cold-drawn or drawn in an oven were not annealed; those that were machine-drawn at elevated temperatures were annealed by heating them in an oven on the tube on which they were wound. The filaments were annealed at 100°C. for 15 min. except in experiments where the effect of annealing temperature was studied. In these experiments, the filaments were annealed at 100 and at 160°C. for 30 min.

Determination of Filament Properties

Spin-draw ratios, draw ratios, apparent draw ratios, and total draw ratios of the filaments were calculated on the basis of the following definitions.

Spin-draw ratio is the ratio of take-up speed to extrusion speed in the spinning process.

Draw ratio is the ratio of the length of the drawn filament to the un-drawn filament, which is equivalent to the ratio of the denier of the un-drawn filament to the denier of the drawn filament.

Apparent draw ratio is the ratio of draw-roll speed to feed-roll speed in the drawing process.

Total draw ratio is the product of the spin-draw ratio and the draw ratio.

The weight-average molecular weights of the filaments were calculated from intrinsic viscosities of solutions of the filaments in decalin, as described above for the polymer samples. Undrawn samples taken at the beginning (after pre-extrusion heating period) and end of a spinning trial were used for the determinations, and the average values are reported.

The $\bar{M}_w/\bar{M}_n$ ratios of the filaments were calculated with eq. (5):

$$\bar{M}_w/\bar{M}_n = 10([\eta]/[\eta]_0)^{1/a} \tag{5}$$

where $[\eta]$ is the intrinsic viscosity of the extruded polymer in decalin, $[\eta]_0$ is the intrinsic viscosity of the original polymer in decalin, and a is 0.80 from eq. (3). The equation was derived on the assumptions that $\bar{M}_w/\bar{M}_n$ of the Pro-fax polymers, as received, was 10, and that the number-average molecular weight $\bar{M}_n$ of the polymers was the same before and after extrusion. The approximate value of $\bar{M}_w/\bar{M}_n$ reported[7] by the manufacturer was 10 for several of the Pro-fax polymers, and it is the average value of $\bar{M}_w/\bar{M}_n$ reported by Davis and Tobias[8] for isotactic polypropylenes made with triethylaluminum–titanium trichloride catalyst. Davis, Tobias, and Peterli[9] have reported that thermal degradation only slightly changes the value of $\bar{M}_n$ for isotactic polypropylene.

The denier and tensile properties of the filaments were determined at 70° F. and 65% R.H. by ASTM methods D 1577-60 T and D 204-57 T, respectively. All specimens were conditioned under these standard conditions of temperature and relative humidity for at least 24 hr. prior to the determination of their properties. The denier of the filaments was determined with a Vibroscope, and the tensile properties were determined with a Model TM Instron tester adjusted for a 1-in. gage length and a rate of extension of 5 in./min. The values given for these properties are the averages of 10 determinations.

The densities of the polypropylene fibers were determined at 23°C. with a density-gradient column[10] prepared from methanol–water mixtures and calibrated with glass floats ranging in densities from 0.8600 to 0.9500. The densities of the glass floats were known within ±0.0002 g./cc.

The crystallinities of the undrawn polypropylene fibers were calculated from the fiber densities by use of eq. (6), reported by Sobue and Tabata.[11]

$$1/d = x/d_{cr} + (1 - x)/d_{am} \tag{6}$$

In this equation, d is the density of the fiber; x is the crystallinity of the fiber; d_{cr} is the density of 100% crystalline polymer, taken as 0.936;[12] and d_{am} is the density of 100% amorphous polymer, taken as 0.850.[12]

The relative crystallinities of drawn and annealed polypropylene fibers were determined by Ernest F. Fullam, Inc., Schenectady, New York, by the x-ray diffraction method of Weidinger and Hermans.[13] The samples were prepared so that on the average the x-rays were exposed to a mat of fibers 3 to 5 fibers thick. In order to reduce extraneous background as much as possible, the fibers were supported on an open-frame sample holder. The quantity of material used was found to have very little effect on the results. Several materials were examined two or more times in varying amounts without any significant variation in the crystallinity indicated. Only the 110, 040, and 130 peaks were measured with all of the samples. The 111, 131, and 041 peaks were observed only with one fiber sample.

The crystallite orientations of drawn polypropylene fibers were determined from x-ray diffraction patterns made with a General Electric Type XRD instrument, equipped with a copper tube, a nickel oxide filter, and a Laue camera. The samples were bundles of about 30 parallel filaments. They were mounted in the instrument 5 cm. from the camera with their longitudinal axes perpendicular to the x-ray beam and parallel to the film of the camera. The intensities of the x-ray beam were determined from the exposed film. The distributions of intensities along the first three diffraction rings of the x-ray patterns were measured with a microphotometer with the film mounted on a rotating stage, and the distributions were expressed as the width in angular degrees at which half maximum intensity of the peaks occurred. The first three diffraction rings of the x-ray patterns represent the 110, 040, and 130 planes parallel to the c axis of the monoclinic crystal of polypropylene. As fibers are drawn, the crystallites are oriented with the c axis parallel to the fiber axis. Hence, the smaller the angles of the first three diffraction rings, the shorter the rings (or arcs), and the higher the degree of orientation.

POLYMER PROPERTIES

Data on the molecular weights, isotacticities, crystalline melting points, and melt index of the five propylene polymers used in this study are given in Table I.

As shown in Table I, the weight-average molecular weights of the polymers ranged from 250,000 to 355,000, as calculated from intrinsic viscosities of solutions of the polymers in tetralin; and from 245,000 to 470,000, as calculated from intrinsic viscosities of solutions of the polymers in decalin. The reported[7] weight-average molecular weights of the polymers as determined by light scattering ranged from 320,000 to 680,000. The reason for the discrepancies between the molecular weights determined by viscosity and by light scattering is not known. However, the molecular weights of the polymers by the two different viscosity methods were in good agreement, except for the polymer with the highest molecular weight (Polymer 6723). The average molecular weight of this polymer determined by the two viscosity methods was 412,500, with a deviation of about 14%.

TABLE I
Properties of Isotactic Polypropylenes

Polymer	Molecular weight, $\bar{M}_w$			Isotactic content, %			Crystalline melting point range, °C	Melt index, g./10 min.
	Determined in tetralin	Determined in decalin	Reported[a]	Extraction method	Infrared method			
					Luongo[4]	Brader[5]		
6323	250,000	245,000	320,000	94	84	74	164–172	9.37
6423	290,000	285,000	400,000	95	81	74	164–171	7.89
6523	305,000	305,000	450,000	96	84	67	164–172	3.58
6623	335,000	315,000	540,000	97	84	71	164–172	2.71
6723	355,000	470,000	680,000	98	77	67	164–171	0.61

[a] Molecular weights reported by supplier as determined by light scattering.

The melt index of the polymers decreased with increasing molecular weight, as expected, and covered a range of values from 9.37 to 0.61 g./10 min.

The isotactic contents of the polymers as determined by the infrared methods of Luongo and Brader were found to differ from those obtained by extraction, as would be expected from the results of other investigators.[4,5,14] The values obtained by extraction (94–98%) were highest, and those obtained by Brader's method (67–74%) were lowest. The crystalline melting points of the polymers were about the same, ranging from 164 to 171 or 172°C.

The molecular weight distributions of the polymers were not determined, but a skewed molecular weight distribution with a high molecular weight tail is characteristic of isotactic polypropylenes.[8] As noted in the experimental section, the breadth of the molecular weight distribution curve given by $\bar{M}_w/\bar{M}_n$ was reported to be about 10 for Polymers 6323, 6423, and 6523[7] and for isotactic polypropylenes made with triethylaluminum–titanium trichloride catalyst.[8]

EFFECTS OF CONDITIONS OF FIBER FORMATION ON STRUCTURE OF MONOFILAMENTS

The structure of a polypropylene monofilament depends upon the conditions of extrusion, quenching, drawing, and annealing that were used in its preparation. The extrusion conditions affect the molecular weight, molecular weight distribution, crystallinity, and orientation; the quenching, drawing, and annealing conditions affect the crystallinity and orientation of the filament.

Natta, Peraldo, and Corradini[15] have described a three-phase model of the molecular organization of isotactic polypropylene; Wyckoff[16] has corroborated and extended their findings. The model consists of an amorphous phase, a paracrystalline or quasicrystalline phase, and a crystalline phase. The amorphous phase cannot be crystallized or oriented. The paracrystalline phase, like the crystalline phase, can be oriented; and it has some short-range, three-dimensional order, with some similarity to that of the crystal. In the paracrystalline structure, Sobue and Tabata[17] reported the polymer chains are parallel to the fiber axis in a hexagonal arrangement, but they can rotate about their own axes. The crystalline phase contains well ordered regions of varying lateral dimensions and varying thermal stability. The unit cell of the crystal is monoclinic and contains the molecular species in a helical arrangement, as reported by Natta.[18]

Spinning

The effects of spinning conditions on the weight-average molecular weights and the breadths of the molecular weight distribution curve ($\bar{M}_w/\bar{M}_n$) of the five Pro-fax polymers during extrusion by methods A and C are shown by the data in Table II. The data show that the weight-average

TABLE II
Effects of Extrusion on the Molecular Weights and the Breadths of the
Molecular Weight Distribution of the Polypropylenes

Polymer	Extrusion method	Molecular weight, $\bar{M}_w$[a]		Breadth of molecular weight distribution of filament, $\bar{M}_w/\bar{M}_n$[b]
		Polymer	Filament	
6323	A	245,000	67,000	2.5
	C		225,000	9.1
6423	A	285,000	78,000	2.1
6523	A	305,000	88,000	2.1
6623	A	315,000	92,000	3.5
	C		305,000	9.3
6723	A	470,000	110,000	2.1
	C		405,000	8.5

[a] The molecular weights were calculated from intrinsic viscosities of the materials in decalin, estimated from a single-point measurement.

[b] $\bar{M}_w/\bar{M}_n = 10([\eta]/[\eta]_0)^{1.22}$, where $[\eta]_0$ is the intrinsic viscosity of the polymer before extrusion and $[\eta]$ is the intrinsic viscosity of the polymer after extrusion.[14]

molecular-weights of the polymers were lowered 71–77% when extrusion method A (280°C., not air-free) was used; but they were lowered only 3–16% when extrusion method C (235°C., air-free) was used. The molecular weights of the filaments produced were the same at the beginning and end of each spinning run, indicating that the degradation of the polymers occurred during the pre-extrusion heating periods.

Thermal degradation narrows the molecular weight distribution of isotactic polypropylene, and Davis, Tobias, and Peterli[9] have shown that the high molecular weight polymers represented by the tail of the distribution curve of isotactic polypropylene are broken down in the early stages of thermal degradation increasing the amount of polymer in the middle molecular weight range. Since thermal degradation of the Pro-fax polymers was slight with extrusion method C, the molecular weight distribution of the polymers in the filaments was nearly the same as that of the initial polymers, as indicated by M_w/M_n ratios of the filament of 8.5–9.8 and a M_w/M_n ratio of the polymer of 10. With method A, however, extensive thermal degradation occurred, and the molecular weight distribution of each polymer was narrowed considerably. As shown in Table II, the M_w/M_n ratios of the filaments prepared by extrusion method A ranged from 2.1 to 3.5. The M_w/M_n ratio for a polymer having a random distribution is 2.[19]

Figure 1 shows four representative x-ray patterns that we observed for undrawn polypropylene filaments made by spinning the polymers under different conditions of extrusion and quenching. On the basis of published x-ray patterns of isotactic polypropylene,[16, 17, 20] patterns A, B, C, and D in Figure 1 indicate, respectively, the essentially unoriented paracrystal-
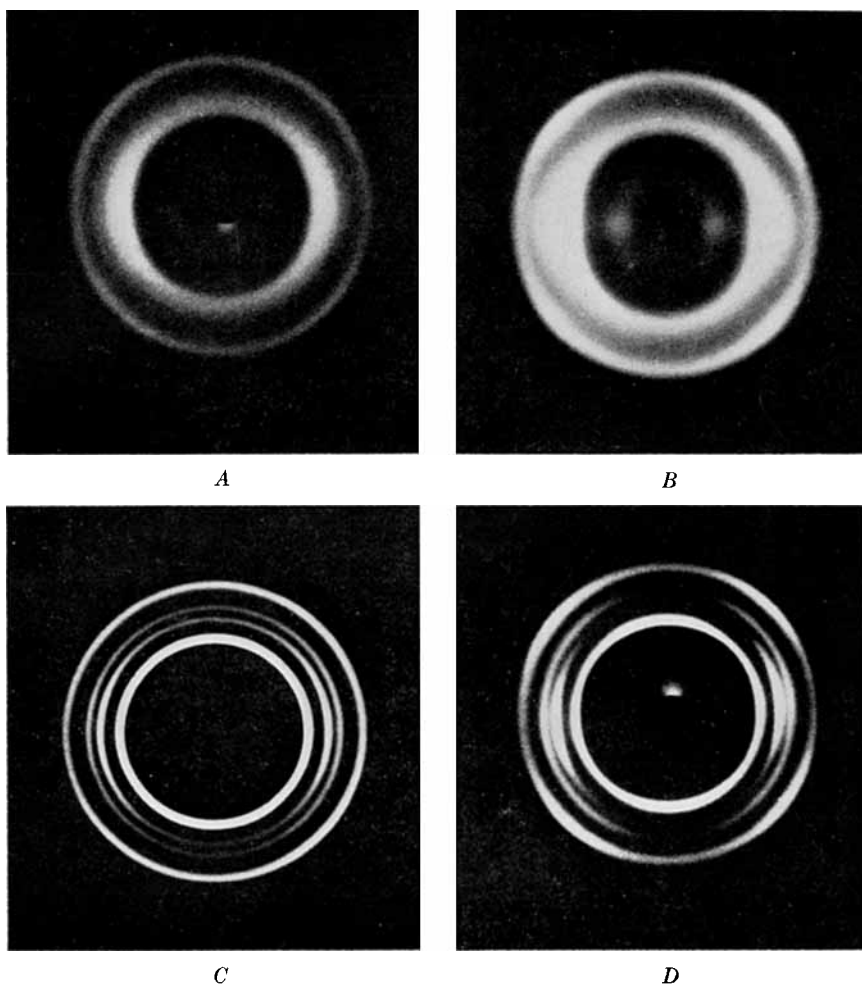
Fig. 1. X-ray diffraction patterns of undrawn polypropylene filaments; (A) essentially unoriented paracrystalline structure; (B) partially oriented paracrystalline structure; (C) unoriented crystalline structure; (D) partially oriented crystalline structure.

line structure, the partially oriented paracrystalline structure, the unoriented crystalline structure, and the partially oriented crystalline structure. In patterns C and D, as well as in most of our x-ray patterns of the crystal structure, the fourth and fifth diffraction rings, which correspond respectively to the 111 and 131/041 planes, appear as one, because of their close proximity. The sixth and seventh diffraction rings of the crystalline structure are always weak and were not observed in unoriented samples. They were visible in the negatives of x-ray patterns of the oriented crystalline structure but were too weak to show up in positive prints.

From an examination of the x-ray patterns of undrawn polypropylene filaments having the oriented crystalline structure, we invariably found

that the c axes of the crystallites were parallel to the fiber axis.   However, it has been reported[20,21] that orientation of the a axes of the crystallites occurs during spinning if the extrusion temperature is too low and the fiber is not properly quenched.

The x-ray patterns of the experimental filaments depended upon the extrusion (melt) and quenching (crystallization) temperature of the polymers, and upon the ratio of the speed of take-up of the filaments to the speed of extrusion (the spin-draw ratio).   For example, when Polymer 6723 was spun at 280°C. into water at 50°C. with a spin-draw ratio of 3.1, pattern A was obtained; but when it was spun at 325°C. into water at 50°C. with a spin draw of 3.1, pattern C, was obtained.   However, pattern A was obtained at a spinning temperature of 235°C. by quenching the filament in water at 10°C. rather than at 50°C.   When the filament was spun with a spin-draw ratio of 3.1 and quenched in air, pattern C was obtained at an extrusion temperature of 280°C.; and pattern D was obtained at an extrusion temperature 235°C.   Pattern D was also obtained when Polymer 6723 was spun at 235°C. into water at 90°C. with a spin-draw ratio of 3.1.   Patterns B and D were also obtained in undrawn filaments prepared under the conditions that normally gave patterns A and C, when the spin-draw ratio exceeded a value of about 3.

In addition to the crystallization temperature and the initial temperature of the melt, the crystallinity of an undrawn polypropylene fiber depends upon the time the polymer is held at the melt temperature.   If the crystalline regions in the polymer are not completely destroyed by melting, they act as nuclei for crystallization upon cooling and increase the rate of crystallization.   The original crystalline order of each of the polymers discussed above was presumably completely destroyed during spinning, since heating propylene polymers for 1 hr. above 220°C. is reported[20] to completely destroy any previous crystalline order.

Drawing

Drawing studies included investigation of: (1) the preferential orientation of the different planes of the crystallites on drawing, (2) the relationship between the degree of orientation of the c axes of the crystallites and total draw ratio, and (3) the effect of drawing on crystallinity.   The experimental polypropylene filaments used in the studies were prepared from the five Pro-fax polymers with the extrusion conditions of methods A and C, a spin-draw ratio of 3.1, and a water quench bath at 50°C.   The crystallinities of the undrawn filaments, as determined by density measurements, ranged from 48 to 53%, with an average value of 51%.   The filaments were drawn in glycerine at 135°C. with a feed-roll speed of 14.8 yd./min., and the drawn filaments were annealed at 100°C. for 15 min.   Measurements were made on the annealed samples.

The function of the drawing operation is to orient the molecules and crystallites of the polymer in the direction of the fiber axis.   During the drawing of the experimental polypropylene filaments, a preferential orien-
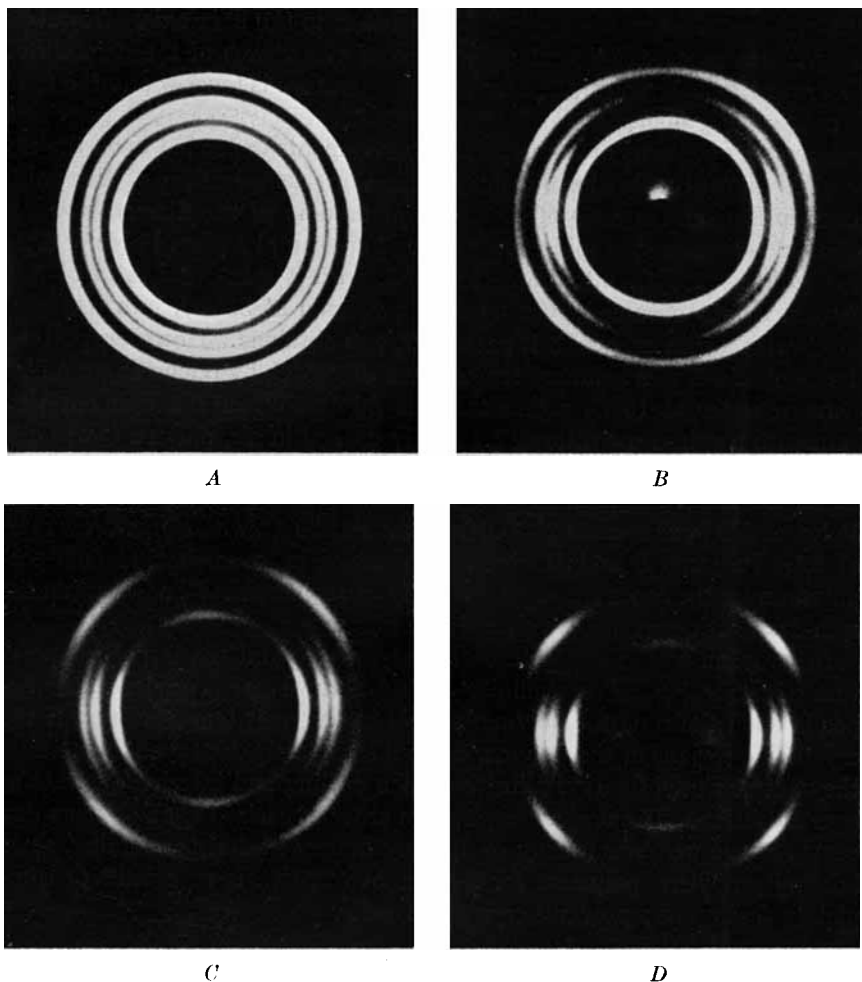
Fig. 2. X-ray diffraction patterns of annealed polypropylene filaments with different amounts of orientation (numbers refer to approximate total draw ratio): (A) 3.1×; (B) 4.7×; (C) 5.7×; (D) 10.4×.

tation of the different lattice planes of the crystallites occurred, as shown by the series of x-ray patterns in Figure 2. The orientation of the 040 plane (second diffraction ring) was predominant in the initial stage of drawing, followed by orientation of the 130 plane (third diffraction ring). On further stretching, the 110 and 111 planes (first and fourth diffraction rings) began to orient and soon all planes were equally oriented.

Figure 3 shows the relationship between the degree of orientation of the c axes of the crystallites (110 plane) along the filament axis and the total draw ratio, for filaments having different molecular weights and different initial (before drawing) crystalline structures. The rate of crystallite
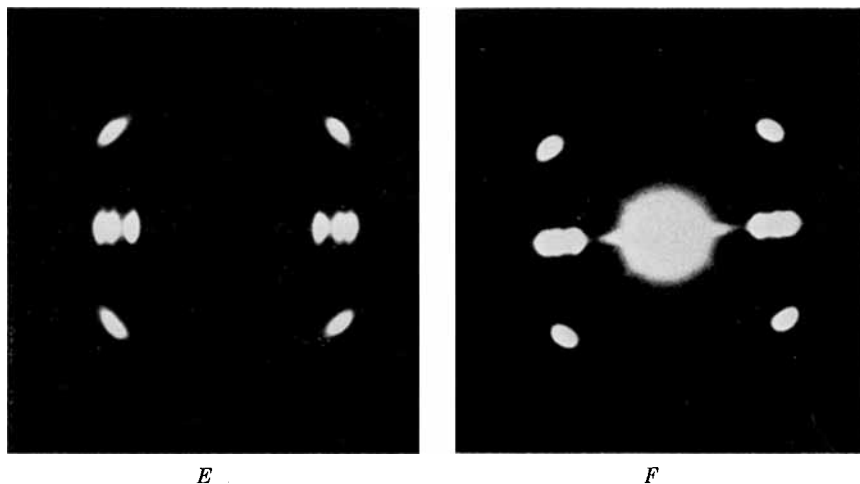
E   F

Fig. 2 (continued). (E) 21.4×; (F) 24.8×.

orientation on drawing was very rapid for undrawn filaments having the partially oriented crystalline structure. Filaments with the paracrystalline structure oriented more rapidly than filaments with the monoclinic crystal structure, which is in agreement with the findings of Compostella, Coen, and Bertinotti.[20]   It is apparent from the curves in Figure 3 that the crystallites were completely oriented at a total draw ratio of about 25, regardless of the type of crystalline structure (crystalline or paracrystalline), the crystallite orientation (unoriented or partially oriented), or the molecular weight of the undrawn polypropylene filaments.

Although the main function of the drawing operation is to orient the crystallites in the direction of the fiber axis, it also decreases the crystallinity of polypropylene fibers. As shown in Figure 4, the relative crystallinity of the drawn and annealed experimental filaments decreased with increasing draw up to a total draw ratio of about 25, and then it became constant.   Cappuccio et al.[21] also found that the crystallinity of polypropylene fibers decreases with increasing amounts of draw, the decrease being less the higher the draw temperature (in the range of 65–120°C.).   However, they did not investigate the effects of high draw ratios on the crystallinity of polypropylene fibers, and therefore, they did not observe the leveling off in crystallinity that we observed.

Sobue and Tabata[17] observed that on drawing completely oriented isotactic polypropylene filaments in water at room temperature to about 70°C., the crystalline structure is transformed to the paracrystalline structure. No statement was made by Sobue and Tabata concerning the crystal–paracrystal transformation at draw temperatures above 70°C.   However, since they investigated draw temperatures up to 150°C., we assume they observed no transformation.   Wyckoff[16] has also observed the complete conversion of the crystalline state to the paracrystalline state on cold drawing isotactic polypropylene 7 to 1; but in addition, he noted the partial
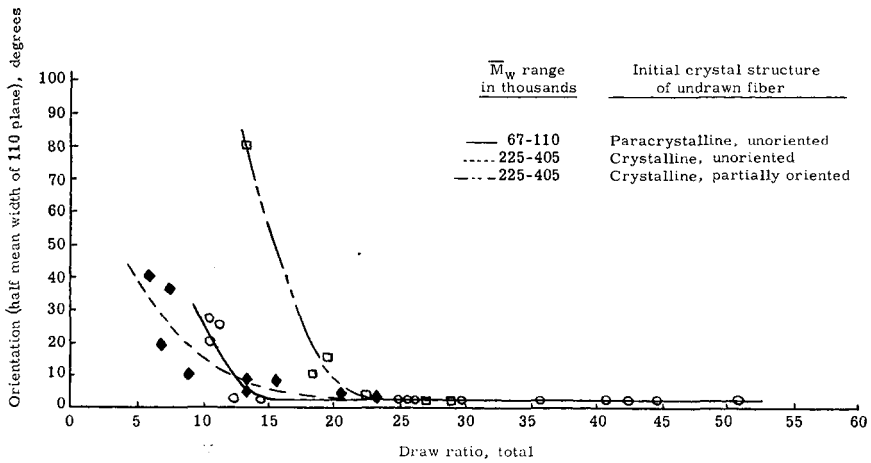
Fig. 3. Relationships between draw ratio and crystallite orientation for annealed polypropylene filaments having different molecular weights and initial crystalline structures.
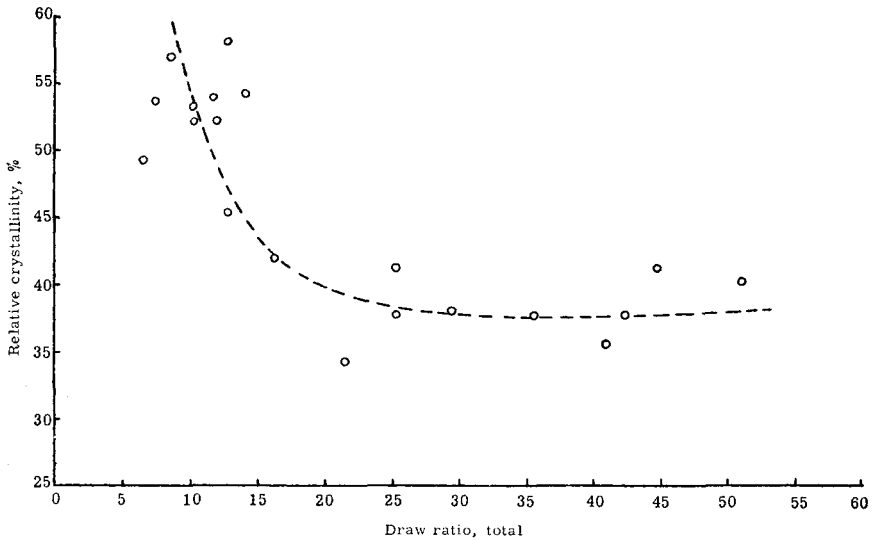

Fig. 4. Relationship between draw ratio and relative crystallinity of annealed polypropylene filaments.

conversion of crystalline to paracrystalline component at lower draw ratios. Changes in crystallinity that occur on hot drawing isotactic polypropylene filaments depend not only on the extent of drawing but also on the temperature and rate of drawing, which can also affect the rate of paracrystalline–crystalline conversion and the rate of crystallization. However, even in hot drawing, at least under the conditions of our experiments, the

mechanical action of drawing was apparently the most important factor in reducing crystallinity.

Annealing

In our initial studies, it was found that drawn filaments elongated if they were not annealed, thus undergoing some structural change.   Therefore, to stabilize drawn filaments, they were generally annealed by heating at 100°C. for 15 min.   No special attempt was made to prevent shrinkage of the filaments during annealing; they were merely wound on tubes under slight tension.   Compostella, Coen, and Bertinotti[20] found that annealing drawn (well-oriented) fibers decreased the orientation of the free polymer chains, but the decrease was less the greater the tension on the fibers during annealing.   Wyckoff[16] reported that annealing highly drawn films did not change the orientation of the crystallites, under the various annealing conditions that he studied, but, if orientation of the crystallites was not complete, marked improvements were brought about by isometric annealing (without shrinkage) but not by atomic annealing (with shrinkage). Crystallinity of the drawn fibers was observed to increase on annealing, and the increase was greater the less the tension on the fibers and the higher the annealing temperature.[16,20]

Wyckoff also reported that conversion of paracrystal to crystal structure proceeded progressively along an S-shaped curve between 70 and 160°C., with a half-way point at 110°C. and with most of the conversion taking place between 100 and 145°C.   Accompanying the paracrystalline–crystalline conversion was an increase in crystal size, and the crystals were larger the higher the temperature.   Small-angle x-ray observations indicated that annealing at progressively higher temperatures progressively closed the voids present in highly drawn samples, with x-ray and visual clarity occurring at about 145°C.

RELATIONSHIPS BETWEEN STRUCTURAL PARAMETERS AND TENSILE PROPERTIES OF MONOFILAMENTS

The effects of molecular weight, molecular weight distribution, total draw ratio (total molecular orientation), crystallite orientation, and crystallinity on the tensile properties of highly isotactic polypropylene filaments are shown in Figures 5–10 and Table III.   The five Pro-fax polymers were spun into filaments by extrusion method A and C or both, and the spun filaments were quenched in a water bath at 50°C. and then drawn in glycerine at 135°C. with a feed-roll speed of 14.8 yd./min.   All of the drawn filaments were annealed for 15 min. at 100°C.

As noted in the previous section, the experimental polypropylene filaments prepared by extrusion method A and quenched in water at 50°C. had weight-average molecular weights ranging from 67,000 to 110,000 (Table II), narrower molecular weight distributions than the original polymers, resulting from thermal degradation, and an unoriented paracrystalline
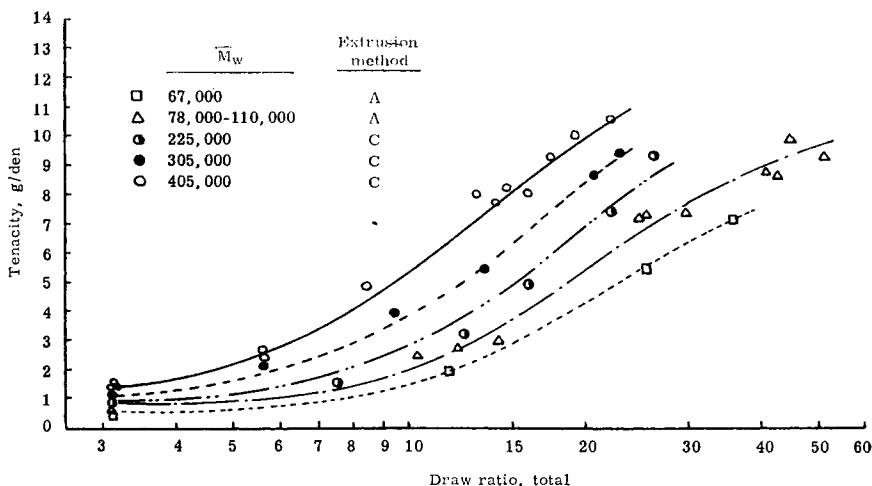
Fig. 5. Relationship between draw ratio and tenacity of polypropylene filaments of different molecular weights.
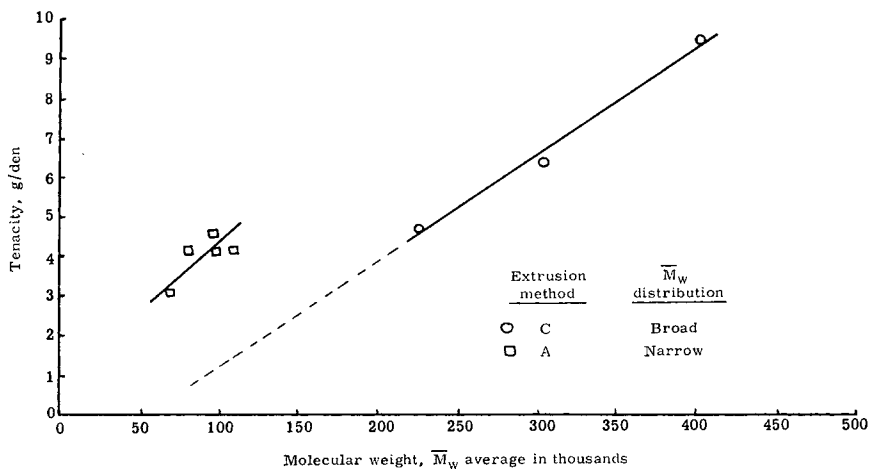

Fig. 6. Relationship between tenacity and molecular weight of polypropylene filaments with a total draw ratio of 15.

structure. Filaments prepared by extrusion method C and quenched in water at 50°C. had weight-average molecular weights ranging from 225,000 to 405,000 (Table II), essentially the same molecular weight distributions as the original polymers, and the unoriented crystalline structure. The absolute crystallinities of the undrawn filaments as determined by density measurements, were nearly the same, with an average value of 51%. All of the drawn and annealed filaments had the monoclinic crystalline structure with relative crystallinities varying from 34 to 58%, as determined by x-ray analyses. The crystallite orientation of the drawn filaments, ex-

pressed as the peak width at one-half maximum intensity in degrees, varied from complete orientation (<2°) to a very low amount (80°), depending on the total amount of stretching of the filaments.

The deniers of the monofilaments ranged from 6.2 to 185, and the densities ranged from 0.8870 to 0.9092. The tenacities, elongations at break, and modulus values were in the ranges of 0.51–9.8 g./den., 2015–11%, and 5–125 g./den., respectively.

The relationships between tenacity and total draw ratio of the filaments of different molecular weights are shown in Figure 5. The tenacity for each filament increased slowly at first, then rapidly, and finally somewhat slower with increasing total draw ratio. The tenacity of the filaments increased as the molecular weight increased from 67,000 to 78,000, but we were unable to detect any significant differences in the tenacities of filaments having molecular weights of 78,000; 88,000; 92,000; or 110,000. Above 110,000, the tenacities again increased with increasing molecular weight.

The increase of tenacity with molecular weight is shown in Figure 6 for filaments with a total draw ratio of 15. Because of the narrow molecular weight distributions of the polypropylene filaments having molecular weights of 110,000 or less, the tenacities of the filaments are probably high in comparison with tenacities of filaments of the same molecular weights having the normally broad distribution of isotactic polypropylene. Suitable low molecular weight polymers were not available to us for preparing filaments for comparison. Therefore, the possible differences in tenacities have been estimated in Fig. 6 by extrapolating to a molecular weight of 67,000 the linear relationship between tenacity and molecular weight of the isotactic polypropylene filaments that were not thermally degraded during extrusion.

In Table III, the tenacities of the polypropylene filaments produced from Polymers 6323, 6623, and 6723 by extrusion method A are compared with the tenacities of filaments produced from the same polymers by extrusion

TABLE III
Molecular Weights, Molecular Weight Distributions, and Tenacities of
Polypropylene Filaments Produced from the Same Polymers
by Extrusion Methods A and C

Polymer	Extruded by method A			Extruded by method C		
	$\bar{M}_w$	Molecular weight distribution $\bar{M}_w/\bar{M}_n$[a]	Tenacity, g./den.[b]	$\bar{M}_w$	Molecular weight distribution $\bar{M}_w/\bar{M}_n$[a]	Tenacity, g./den.[b]
6323	67,000	2.5	3.2	225,000	9.1	4.8
6623	92,000	3.5	3.4	305,000	9.3	6.3
6723	110,000	2.1	3.5	405,000	8.5	8.1

[a] See Footnote b, Table II.
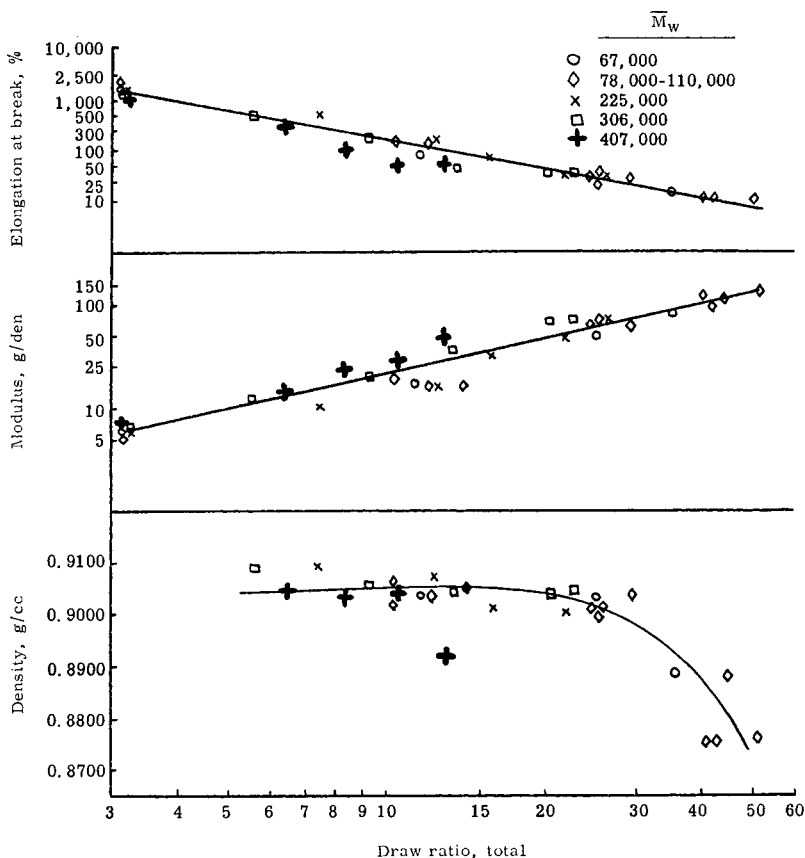[b] Total draw ratio of filaments was 15.

Fig. 7. Relationships between draw ratio and elongation at break modulus, and density of polypropylene filaments of different molecular weights.

method C. The data show that for filaments produced from the same polymer and drawn equivalent amounts, weight-average molecular weight has more influence on the tenacity of polypropylene filaments than molecular weight distribution.   Experiments are in progress to establish the effect of molecular weight distribution on the tenacity of isotactic polypropylene filaments having about the same weight-average molecular weights.

Figure 7 shows the relationships between total ratio and the elongation at break, modulus, and density of the filaments of different molecular weights. The relationships were apparently independent of the molecular weight and molecular weight distribution of the filaments and of the crystalline structure (paracrystalline or monoclinic) of the filaments before drawing.   The log–log plots of elongation at break and modulus against total draw ratio show linear relationships, the elongation at break decreasing and the modulus increasing with increasing total draw ratio.   The density of almost all synthetic fibers usually increases with stretching.   In contrast with this general phenomenon, the density of our drawn polypropylene filaments re-
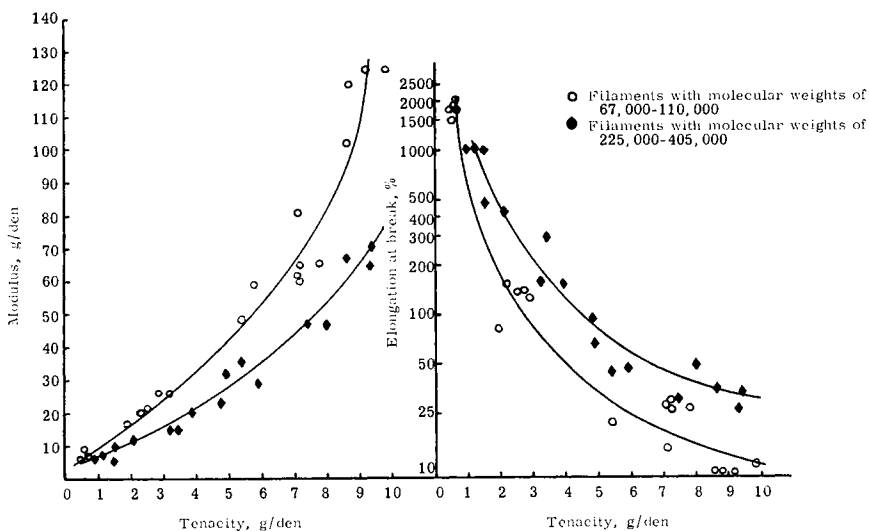
Fig. 8. Relationships between tenacity, modulus, and elongation at break of drawn and annealed polypropylene filaments of different molecular weights.
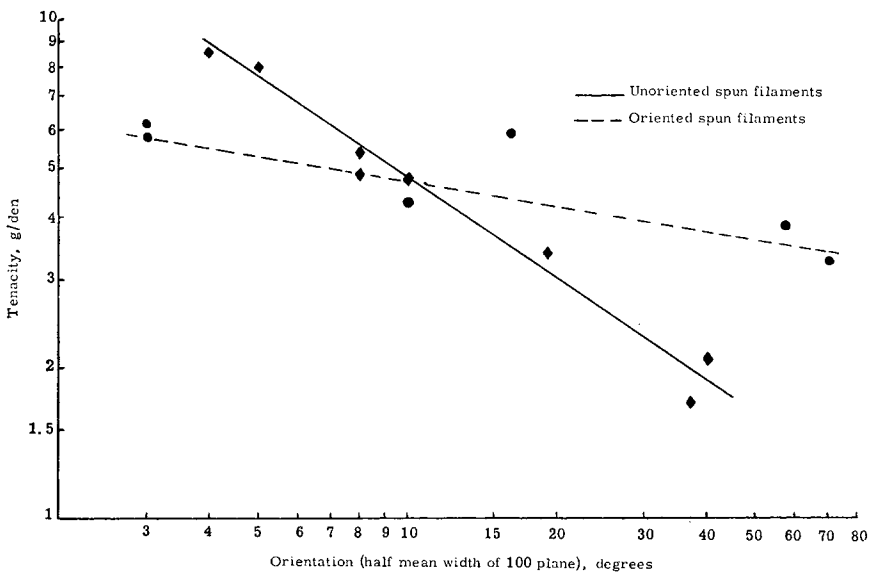

Fig. 9. Relationship between tenacity and orientation of drawn and annealed polypropylene filaments spun by method C.

mained constant up to a total draw ratio of about 25 and then it began to decrease rapidly. It was shown previously (Fig. 4) that filaments that were drawn more than 25× had lower relative crystallinities than those drawn less. Furthermore, we observed a whitening of the filaments at the high draw ratios. Wyckoff[16] has reported this whitening to be due to
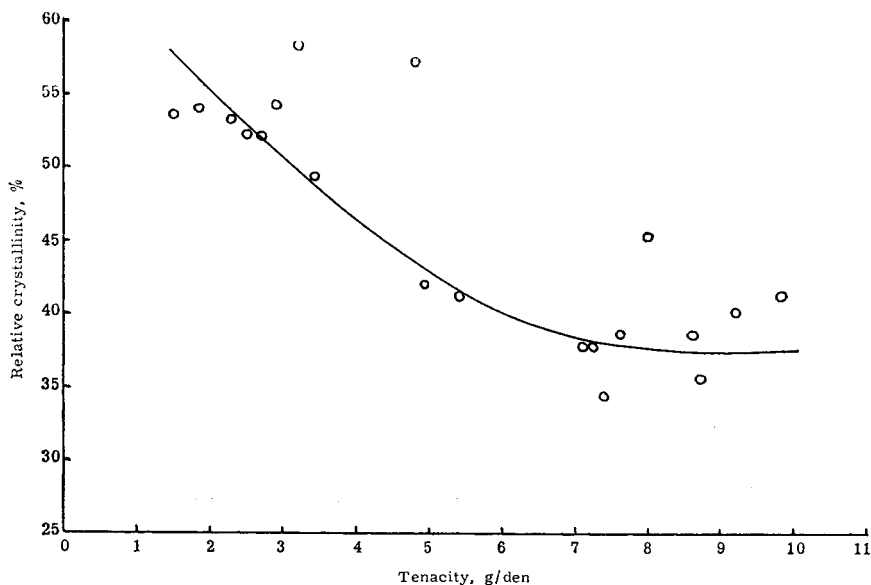
Fig. 10. Relationship between tenacity and relative crystallinity of drawn and annealed polypropylene filaments.

lamella voids elongated in the draw direction. Therefore, we attribute the decrease in the density of the filaments with total draw ratios greater than 25 to both a reduction in the crystallinity of the filaments and the formation of voids. The entire decrease in density with total draw ratio cannot be explained solely on a basis of the decrease in the crystallinity of the filaments, because of the nonlinear relationship between density and relative crystallinity.

The relationships between the tenacity, modulus, and elongation at break of the isotactic polypropylene filaments of different molecular weights are shown in Figure 8. The modulus of the filaments increased and the elongation at break decreased with increasing tenacity. At a given tenacity, the filaments with molecular weights of 225,000–405,000 had a lower modulus and a higher elongation at break than the filaments with molecular weights of 67,000–110,000. The very high modulus values obtained for the filaments with molecular weights of 110,000 or less suggest that polymers having very narrow molecular weight distributions may give polypropylene fibers with improved resiliency.

For the filaments spun by method C, there is a linear log–log relationship between tenacity and crystallite orientation, with tenacity increasing with orientation as shown by the solid line in Figure 9. Sufficient data are not available for establishing the relationship between tenacity and orientation for the filaments spun by method A. These filaments, as mentioned previously, had an unoriented paracrystalline structure before drawing, whereas those produced by method C had an unoriented crystalline struc-

ture. The relationship shown in Figure 10 between tenacity and relative crystallinity of the drawn, highly isotactic polypropylene fibers shows an increase in tenacity with decrease in relative crystallinity from about 58% to about 40%. The tenacity appears to be independent of crystallinity at crystallinity values less than about 45%.

MAXIMUM DRAW RATIO AND TENSILE PROPERTIES

It is evident from the results above that the production of polypropylene filaments with high tenacities requires that the filaments be drawn to a maximum. Therefore, in attempts to prepare experimental polypropylene filaments with tenacities higher than those discussed in the previous section (9.8 g./den.), the effects of filament molecular weight, quenching conditions, and drawing conditions on the maximum draw ratio and tensile properties of the drawn filaments were investigated.

Effect of Molecular Weight

As shown in Figure 11, the maximum amount that a filament could be drawn (135°C., 14.8 yd./min.) depended on the molecular weight and
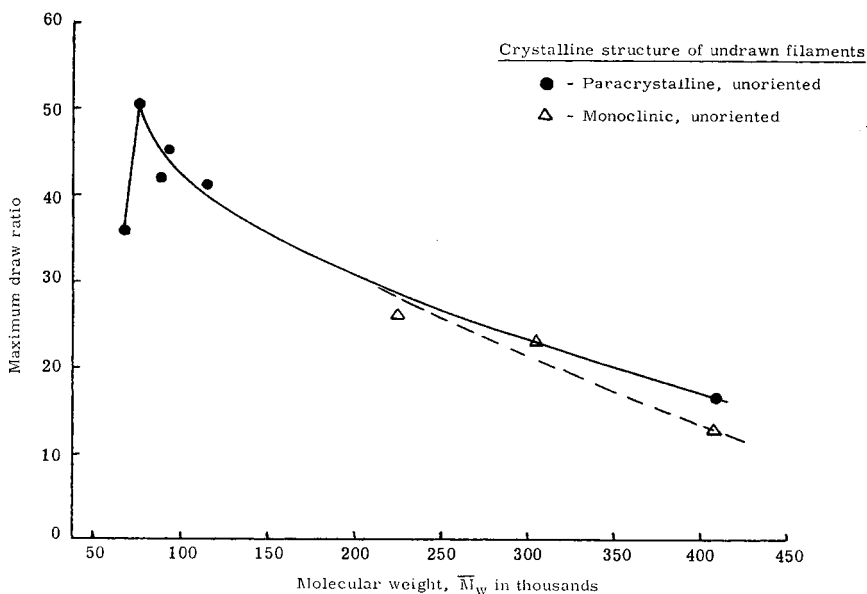

Fig. 11. Relationship between maximum draw ratio and molecular weight of polypropylene filaments, spun-drawn 3.1× and having different initial crystal structures.

crystalline structure of the filaments. The maximum total draw ratio increased as the molecular weight of the filaments increased from 67,000 to about 78,000, and then it decreased with further increases in molecular weight. In addition, under the conditions of drawing used, the maximum

total draw ratio appeared to be greater for filaments having the paracrystalline structure than for filaments having the crystalline structure.

Effect of Quenching Conditions

To determine whether filaments having the paracrystalline structure could be drawn more than filaments having the crystalline structure, filaments having both structures were prepared by extruding Polymer 6723 by method C into water baths at 10 and 50°C. The filaments ($\bar{M}_w$ of 405,000) were drawn to a maximum at 135°C. on our laboratory drawing equipment. Based on machine speeds, the apparent maximum draw ratio was 6X, regardless of the crystalline structure of the undrawn filaments.

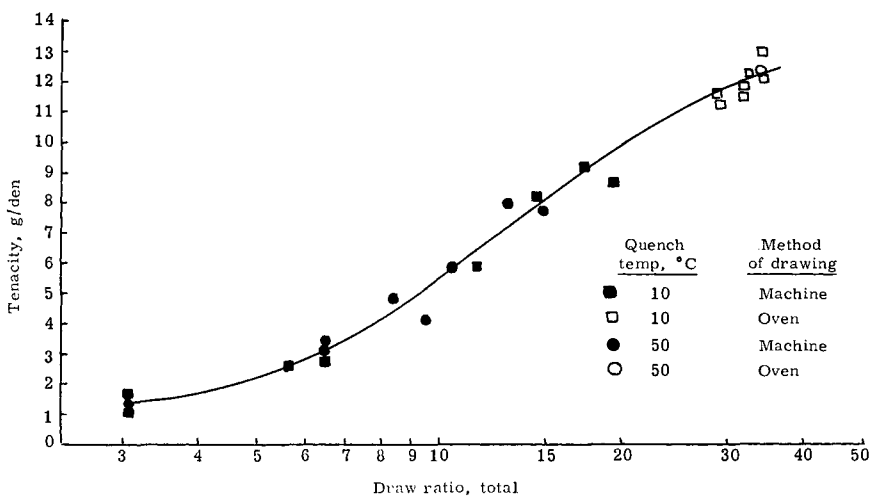|	Quench temp, °C	Method of drawing
◨	10	Machine
◻	10	Oven
●	50	Machine
○	50	Oven

Fig. 12. Relationship between tenacity and draw ratio of filaments prepared from Polymer 6723 by spinning method C, quenched at different temperatures, and drawn under different conditions.

But, based on denier reductions, the real maximum draw ratio of the filament having an initial paracrystalline structure was 6.2, and the maximum draw ratio of the filament having an initial crystalline structure was only 4.8. These results are in agreement with the earlier findings (Fig. 11). However, in drawing the undrawn filaments of different structures in an oven at 135°C. under different tensions, it was found that both could be drawn to the same maximum amount, but more work was required for drawing the filaments having the crystalline structure. For example, it took 0.27 g./den, to draw the filaments with the crystalline structure 12X; whereas it took only 0.17 g./den. to draw the filaments with the paracrystalline structure the same amount. Wyckoff[16] also has reported from his observations on quenched films cold-drawn various amounts with and without preannealing that orientation of the paracrystalline phase is easier to achieve than orientation of the crystallites.

As shown in Figure 12, the tenacities of the drawn filaments prepared in the studies above were independent of the type of crystalline structure of the undrawn filaments. However, if the crystalline structure of the undrawn filament was obtained by quenching the filament in air, the tenacity of the drawn filament was not comparable at equal draw ratios to the tenacity of drawn filaments initially having the paracrystalline structure. The tenacities of filaments quenched in air and in water at 10°C. and at 50°C. and drawn equal amounts are compared in Table IV. The lower tenacities of the drawn filaments prepared from the air-quenched samples are attributed to the partial orientation of the filaments during spinning. Data presented later in this paper show that stretching during spinning is detrimental to the tenacities of drawn polypropylene filaments.

TABLE IV
Physical Properties of Polypropylene Filaments Prepared from Polymer 6723 by Extrusion Methods A and C and Quenched under Different Conditions[a]

Quenching conditions	Crystalline structure	Crystallinity of undrawn filaments, %	Tenacity of drawn filaments, g./den.
Extrusion method A			
Water bath, 50°C.	Unoriented paracrystalline	44	6.5
Air, 20°C.	Slightly oriented crystalline	54	4.8
Extrusion Method C			
Water bath, 10°C.	Unoriented paracrystalline	45	9.5
Air, 20°C.	Slightly oriented crystalline	62	5.5

[a] Filaments prepared by method A had a molecular weight of 110,000. They were hot drawn 8× and annealed. Filaments prepared by method C had a molecular weight of 405,000 and were cold drawn 5×. These filaments were not annealed.

Effect of Drawing Conditions

The effects of variations in the temperature and time of drawing on maximum draw ratio and on filament tenacities were investigated with spun filaments having the unoriented paracrystalline structure. The filaments were prepared from Polymer 6723 by method C, with a quench temperature of 10°C. and a spin-draw ratio of 3.1. The filaments were drawn on our laboratory continuous drawing machine in air at 25°C. or in a glycerine bath at 50, 100, or 135°C. with average bath immersion times ranging from 0.6 to 18.2 sec. In these experiments, the immersion length was 16 in., and the immersion time was varied by changing the feed-role speed. The maximum draw ratios based on denier reductions and the tenacities of the filaments drawn to a maximum are shown in Figure 13 for the various drawing conditions.
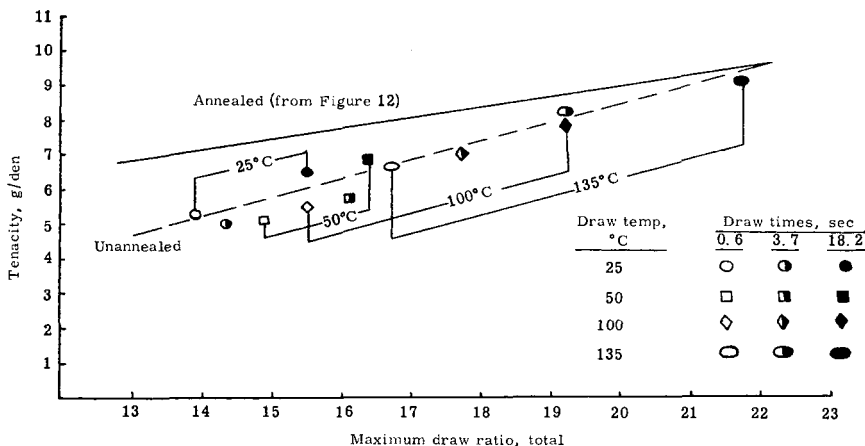
Fig. 13. Effects of drawing conditions on the tenacity of filaments prepared from Polymer 6723 by spinning method C (10°C. quench).

As shown in Figure 13, the maximum total draw ratios increased with increasing stretch-bath immersion time and with increasing bath temperature, which in effect increased the temperature of the filaments. The increase in the maximum draw ratio with increasing filament temperature resulted because of two factors: (1) the increase in filament temperature increased the amount the filament could be stretched during drawing; and (2) it decreased the amount of shrinkage after drawing, apparently by increasing the rate of crystallization, which stabilized the filaments in the stretched state. Figure 13 shows that as the temperature of the draw bath and the time of immersion in the bath were increased, there was a corresponding decrease in the difference between the tenacity of unannealed and annealed (100°C., 15 min.) samples. Therefore, increasing amounts of annealing do apparently take place as the draw-bath temperature or draw time increases.

In the studies above, the highest total draw ratio obtained for the polypropylene filaments was only 22. Since it was observed that the maximum draw ratio depended on the temperature of the filament during drawing, attempts were made to obtain higher draw ratios by drawing bundles of the filaments in an oven. As shown in Table V, total draw ratios ranging from 29 to 34 were obtained. Tenacity and modulus increased with increasing draw ratio, and elongation at break decreased. At the maximum total draw ratio obtained (34), the filaments had a tenacity of 13.1 g./den., an elongation at break of 18%, and a stiffness modulus of 110 g./den.

It appeared possible to obtain higher draw ratios than were obtained by oven drawing by drawing the monofilament during spinning while it was still molten. Therefore, Polymer 6723, extruded by method C, was drawn a maximum amount during spinning. The spin-draw ratio of the filament was 56.8. The unannealed filament had a low tenacity (3.8 g./den.) and stiffness modulus (26 g./den.) and a high elongation at break (167%), con-

TABLE V

Physical Properties of Polypropylene Filaments Drawn Different
Amounts in an Oven at 130–135°C.[a]

Draw ratio, total	No. samples[b]	Properties of drawn fibers		
		Denier	Tenacity, g./den.	Elongation at break, %	Modulus, g./den.
29	2	20.6	11.5	23	88
32	3	19.1	11.5	24	94
33	2	17.6	12.4	17	106
34	1	18.1	13.1	18	110

[a] The filaments were prepared from Polymer 6723 by spinning method C with a quench temperature of 10°C.
[b] Ten specimens per sample.

TABLE VI

Decrease in Tenacity of Filaments Drawn Different Amounts during Spinning[a]

Spin-draw ratio	Total draw ratio = 10		Total draw ratio = 15		Total draw ratio = 20	
	Tenacity, g./den.	Decrease in tenacity from control, %	Tenacity, g./den.	Decrease in tenacity from control, %	Tenacity, g./den.	Decrease in tenacity from control, %
3.1	4.9	Control	7.7	Control	9.3	Control
6.2	2.3	53	3.8	51	4.9	47
9.3	1.9	61	3.0	61	3.9	58

[a] The filaments were prepared from Polymer 6723 by extrusion method C and were quenched in a water bath at 50°C. The filaments were drawn in a glycerine bath at 135°C. and the drawn filaments were annealed for 15 min. at 100°C.

sidering the exceptionally high draw ratio of the filament. For example, a comparable filament drawn to a maximum after spinning (Fig. 13) had a maximum draw ratio of only 21.7, but it had a tenacity of 10.2 g./den., elongation at break of 64%, and a stiffness modulus of 64 g./den. The x-ray diffraction pattern of the unannealed filament with a spin-draw ratio of 56.8 was made shortly after spinning, and the filament was found to have a highly oriented crystalline structure. The crystals were not completely oriented, however, even at the exceedingly high draw; and this, at least partially, explains the unexpected tensile properties of the filament. Apparently there was sufficient time for molecular orientation to relax before the filament crystallized.

On the basis of the poor properties of the polypropylene filament drawn to a maximum during spinning, the effect of different amounts of drawing during spinning on the tenacities of drawn filaments was determined. Polymer 6723 was extruded by method C, quenched in water at 50°C, and taken up at different speeds to give filaments having a weight-average molecular weight of 405,000 and the partially oriented crystalline structure. The data given in Table VI show that at a given total draw ratio of 10, 15,

or 20, the tenacities of the filaments decreased as the amount of drawing during spinning (spin-draw) increased. As can be seen by comparing the lines in Figure 9, the tenacities of the drawn filaments having an unoriented crystalline structure before drawing increased with orientation faster than those of the drawn filaments having an oriented crystalline structure before drawing. These data suggest differences in the crystalline phase of the spun filaments other than degree of orientation. Possibly the spun filaments having the oriented crystalline structure have the a axes rather than the c axes of the crystallites oriented parallel to the axes of the filaments, as observed by Compostella[20] and Cappuccio,[21] even though this was not apparent from the x-ray diffraction patterns of the spun filaments.

EFFECTS OF ANNEALING TEMPERATURE ON TENSILE PROPERTIES

The high tenacities of the oven-drawn filaments of Polymer 6723 (Table V) were attributed to their high draw ratios, since, as shown in Figure 11, the values fit well on the curve for the relationship between tenacity and total draw ratio. However, since the conditions used in oven drawing may have increased the crystallinities of the fibers, which could contribute to strength, the effects of annealing temperature on the properties of the filaments were investigated.

Filaments with an unoriented paracrystalline structure and a molecular weight of about 405,000 were prepared from polymer 6723, and they were drawn different amounts through a glycerine bath at 135°C. with a feed-roll speed of 14.8 yd./min. Samples of undrawn and drawn filaments were annealed in an oven for 30 min. at 100 and 160°C. on the tube on which they were wound. The effects of these annealing conditions on density, tenacity, elongation at break, and modulus are shown in Figure 14. The conditions of annealing that we normally used (100°C., 15 min.) did not appreciably alter the properties of drawn polypropylene filaments.

As shown in Figure 14, annealing at 100 or 160°C. for 30 min. did not significantly change the modulus of undrawn or drawn filaments. Annealing at 100°C. slightly increased the density of the undrawn filaments, but it did not change the density of the drawn filaments. However, annealing at 160°C. greatly increased the density of the undrawn filaments, and significantly increased the density of the drawn filaments. Annealing at either 100 or 160°C. increased the tenacity and decreased the elongation at break of undrawn and drawn filaments, and the changes were about the same for both temperatures.

On the basis of the structural changes that can occur in polypropylene filaments on annealing, which were discussed earlier, the increase in tenacity and decrease in elongation of the experimental filaments on annealing could be due to an increase in orientation, or an increase in crystallinity, or both. The higher densities of the filaments annealed at 160°C. support this conclusion, but the densities of the filaments annealed at 100°C. and

the modulus values of the filaments annealed at both temperatures are too low to support the conclusion. Therefore, it cannot be said, on the basis of these data, that the high tenacities of the oven-drawn filaments are partially due to increased crystallinity. Nevertheless, the beneficial effect
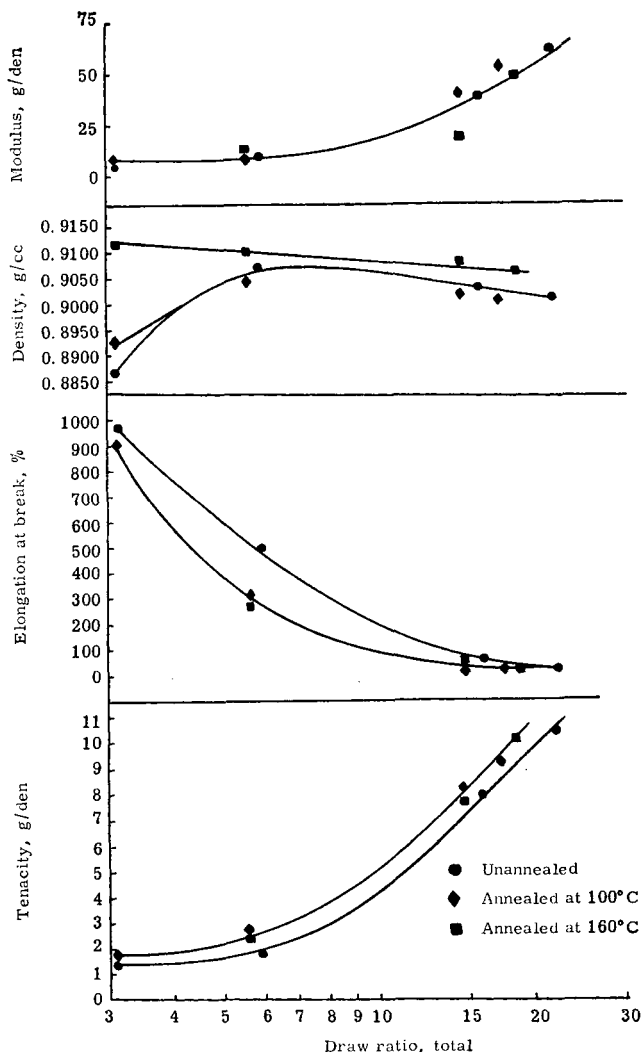

Fig. 14. Effect of annealing temperature on the physical properties of polypropylene filaments drawn different amounts.

that annealing can have on the tenacity of polypropylene filaments is quite apparent, and experiments are now in progress to determine the effect of crystallinity on the tensile properties of annealed polypropylene filaments having the same amount of orientation.

CONCLUSIONS AND SUMMARY

Studies of the structures and properties of melt-spun highly isotactic polypropylene monofilaments prepared under various conditions from five polymers of different molecular weights have led to the production of filaments with exceptionally high tenacities. Several polypropylene filaments were prepared having tenacities greater than 12 g./den. One of these had a tenacity of about 13 g./den. and an elongation at break of 18%, and it appears that higher tenacities are possible.

The following factors were of major importance in producing polypropylene filaments with exceptionally high tenacity.

(1) A polymer (94% or more isotactic) with a molecular weight of about 470,000 was used. It was found that at a given drawn ratio, the higher the molecular weight of the fiber the higher the tenacity. A narrow molecular weight distribution of the polymer was beneficial but was not necessary to produce filaments having tenacities of 12–13 g./den. Filaments with very narrow molecular-weight distributions had unusually high modulus values, which may be of interest in some applications of polypropylene.

(2) The filaments were quenched in water at a low temperature immediately after extrusion to produce undrawn filaments having the para-crystalline structure. The lower the extrusion temperature the lower the quench temperature had to be to produce the desired structure. Filaments having the paracrystalline structure were desired because they could be drawn more easily than filaments having the crystalline structure, and hence under equivalent conditions could be drawn more. However, independent of whether the undrawn filaments had the paracrystalline or crystalline structure, filaments prepared from the same polymer and drawn equal amounts had equivalent tenacities.

(3) The filaments were taken up at a slow enough speed during spinning so that they were not oriented. It was found that the more the filaments were oriented during spinning, the lower were the tenacities of the filaments.

(4) The filaments were drawn to a maximum. It was found that independent of the molecular weight of the filaments, the tenacities of the filaments increased with increasing draw ratio.

(5) The highly drawn filaments contained voids, but they could be removed by proper annealing conditions, which also increased the tenacity of the filaments.

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Résumé

On a étudié l'effet des conditions de formation de la fibre sur les paramètre structuraux et les propriétés mécaniques en extension de filaments de polypropylène hautement iso-tactique filé à partir du polymère fondu. On a entrepris cette étude pour déterminer la possibilité de produire des fils de polypropylène de très haute tenacité. On a préparé des monofils de polypropylène à partir de polymères isotactiques (plus de 94% par extraction). Les fils ont été préparés à partir du polymère fondu et on a varié les conditions d'extrusion, de trempe, d'étirage et de recuit. On a déterminé le poids moléculaire, la distribution des poids moléculaires, la structure cristalline, le taux de cristallinité, l'orientation des cristallites et l'orientation moléculaire totale (exprimée par le rapport d'étirement total) des fils expérimentaux et on discute de la relation entre les paramètres structuraux et les propriétés mécaniques (en extension) des fils. Plusieurs filaments expérimentaux ainsi produits avaient une tenacité supérieure à 12 g/den et l'un d'eux avait même une tenacité de 13 g/den. Ainsi, il s'avère donc possible de produire des fils de polypropylène ayant une tenacité supérieure à 13 g/den. La production de fils de poly-propylène très tenaces exige un polymère d'un poids moléculaire en poids de l'ordre de 470.000, qui est d'abord filé en des filaments non-étirés, qui ont une structure paracristal-line; ensuite les filaments sont étirés jusqu'à leur maximum et recuits. La tenacité des fils de polypropylène augmente avec l'élévation du poids moléculaire. Une distribution étroite des poids moléculaires a une action favorable mais n'est pas indispensable à l'obtention d'une haute tenacité. Un étirage important après le filage est important pour produire une haute tenacité. L'étirage maximum qu'une fibre peut supporter dépend du poids moléculaire, de l'allongement introduit durant le filage, de la durée de l'étirage et de la température (température du fil). On obtient des fils ayant une structure paracristalline en ajustant les conditions d'extinction et de trempe. Ces filaments peuvent s'étirer plus aisément que les filaments ayant une structure cristalline en d'autres termes, on peut dire que, placés dans des conditions identiques, les premières se laissent

étirer plus fortement. Plus on allonge le filament durant le filage, plus la tenacité est basse. La relation liant l'orientation des cristallites et les propriétés mécaniques des fils étirés et recuits est fonction de l'allongement de la fibre durant le processus de filage. Les filaments fortement étirés contiennent des pores mais la recuisson du fil dans des conditions bien déterminées les fait disparaître et augmente en même temps la tenacité.

Zusammenfassung

Der Einfluss der Faserbildungsbedingung auf Strukturparameter und Zugeigenschaften von aus der Schmelze gesponnenen hochisotaktischen Polypropylenfäden wurde zur Bestimmung, ob die Herstellung superzugfester Polypropylenfäden möglich ist, untersucht. Schmelzgesponnene Polypropylenmonofilamente wurden aus fünf hochisotaktischen Polymeren (94% oder mehr durch Extraktion) unter verschiedenen Extrusions-, Abschreck-, Zug- und Temperungsbedingungen hergestellt. Das Molekulargewicht, die Molekulargewichtsverteilung, kristalline Struktur, Kristallinität, Kristallorientierung und Gesamtmolekülorientierung (ausgedrückt durch das gesamte Zugverhältnis) der Versuchsfäden wurde bestimmt, und die Beziehung zwischen diesen Strukturparametern und den Zugeigenschaften der Fäden wird in dieser Arbeit diskutiert. Mehrere der hergestellten Polypropylenversuchsfäden hatten eine Zugfestigkeit grösser als 12 g/den, einer von ihnen hatte eine von 13 g/den. Polypropylenfäden mit einer Zugfestigkeit grösser als 13 g/den scheinen also möglich zu sein. Um diese superzugfesten Polypropylenfäden herzustellen, wurde ein Polymeres mit einem Molekulargewichtsmittel von etwa 470.000 zu ungereckten Fäden mit parakristalliner Struktur schmelzgesponnen; die Fäden wurden bis zu einem Maximum gereckt und getempert. Die Zugfestigkeit der Polypropylenfäden nahm mit zunehmendem Molekulargewicht der Faser zu. Eine enge Molekulargewichtsverteilung war zum Erhalten von grossen Zugfestigkeiten zwar von Vorteil, aber nicht notwendig. Hohe Reckung nach dem Spinnen war zur Erzielung einer hohen Zugfestigkeit wichtig. Der Maximalbetrag, bis zu dem eine Faser gereckt werden konnte, hing von ihrem Molekulargewicht, der Streckung während des Spinnens, der Reckungszeit und -temperatur (Fadentemperatur) ab. Fäden mit durch geeignete Extrusions- und Abschreckungsbedingungen erzielter parakristalliner Struktur konnten leichter als Fäden mit kristalliner Struktur gereckt werden und daher konnten erstere unter sonst gleichen Bedingungen mehr gereckt werden. Je mehr die Fäden während des Spinnens gestreckt wurden, desto geringer war ihre Zugfestigkeit. Die Beziehung zwischen Kristallitorientierung und Zugeigenschaften von gereckten und getemperten, während des Spinnens gedehnten Fäden unterschied sich von der Beziehung für gereckte und getemperte Fäden, die während des Spinnens nicht gedehnt wurden. Die hoch gereckten Fäden enthielten Hohlräume, die jedoch durch geeignete Temperungsbedingungen entfernt werden könnten, was auch die Zugfestigkeit des Fadens verbesserte.