Continuous Polymerization of Caprolactam in a Modular Intermeshing Corotating Twin Screw Extruder Integrated with Continuous Melt Spinning of Polyamide 6 Fiber: Influence of Screw Design and Process Conditions

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SYNOPSIS

The continuous anionic polymerization of caprolactam to polyamide-6 in a modular, intermeshing, corotating twin screw extruder was investigated. Caprolactam was polymerized by anionic polymerization techniques under a range of processing conditions, including different screw configurations, temperature profiles, screw speeds, and throughputs. Studies were also made of melt spinning polyamide 6 into oriented filaments. The polyamide-6 melt spun filaments were characterized using birefringence and wide angle X-ray diffraction. Uniaxial stress measurements of the fibers were obtained and are reported. The results for the melt spun filaments compare favorably with the previous literature. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The use of twin screw extruders for polymerization is credited to the efforts of the I. G. Farbenindustrie[1,2] in the early 1940s, when an intermeshing, corotating twin screw extruder was used to produce polyurethanes and synthetic rubber. Patents for the bulk polymerization of polystyrene and its copolymers in single screw extruders were filed in the 1950s by Dow Chemical[3,4] and American Cyanamid.[5] From the late 1950s, various patents appeared on processes for the continuous polymerization of caprolactam in single screw extruder.[6-9] In 1964, the patent applications of Illing,[10] for free radical polymerization, and of Illing and Zahradnik[11] on caprolactam polymerization, presented a clear discussion of continuous polymerization in a modular intermeshing corotating twin screw extruder. In subsequent years, various patents described the polymerization of polyurethanes,[12-14] polyacetals,[15,16] and polyetherimide[17,18] in modular corotating twin screw extruders. The open literature on polymerization in modular corotating twin screw extruders is limited and there is little study of the influence of modular screw design on process variables on the polymerization process, though some worthy studies have appeared.[19-26] Useful reviews have been presented by Michaeli and Berghaus[27] and Brown.[28]

In this article, we study the continuous polymerization of caprolactam by anionic mechanisms to produce polyamide-6 and its melt spinning to form fibers. Caprolactam was first polymerized in 1938 by Schlack,[29] of the I. G. Farbenindustrie, using an acid catalyst. In 1939, Joyce and Ritter[30] of DuPont described the polymerization of caprolactam using sodium metal. The reaction was slow. In the late 1950s, the catalyzing effect of N-acyl activators was simultaneously discovered by Mottus et al.[31] of Monsanto in St. Louis and by Wichterle et al.[6] and Sebenda and Kralicek[32] at the Institute of Macromolecular Chemistry in Prague. The new systems involved rapid polymerizations, which made possible the above cited reactive extrusion patents of Wichterle et al.[6] and Illing and Zahradnik[11] on the polymerization of caprolactam. Published studies of the anionic polymerization of caprolactam in the twin screw extruder have been presented by Ill-

ing,[19,20] Tucker and Nichols,[34] Menges et al.[21,23] and Berghaus.[24] With the exception of the Menges and Bartilla[21] and Berghaus,[24] consideration of the influence of process variables has been minimal.

The postshaping of anionically polymerized polyamide-6 and other polylactams, emerging from a single screw extruder, is mentioned in a 1959 patent application by Wichterle et al.[6] It was then further developed in subsequent patent applications by Illing and Zahradink,[11] by Reinking, Brassat and their coworkers,[35-38] and by Biensen and Potin.[39] These patents discuss extrusion of rods, profiles, and film casting.

Polyamide-6 has been melt spun into fibers since the 1940s. There is a long history of investigations of melt spinning of polyamide-6 in the literature,[40-51] including one of the current authors.[43-45,49] These articles generally treat crystallization and orientation development. They do not consider continuous melt spinning that is subsequent to polymerization in a twin screw extruder.

In the present article, we describe an extensive experimental investigation of the polymerization of caprolactam in a modular intermeshing, corotating twin screw extruder. We consider the variables of screw configuration, temperature profile, screw speed, and throughput on polymer characteristics. We further consider the drawing down and melt spinning of polyamide-6 filaments from spinnerets at the exit of the twin screw extruder.

EXPERIMENTAL

Materials

The basic materials used in this program were chemicals required for the synthesis of polyamide-6. These include caprolactam, supplied by Allied-Signal as caprolactam flake, sodium metal, supplied by Aldrich as a sodium lump, and N-acetyl caprolactam coinitiator, supplied by Aldrich. Comparisons were often made with a commercial polyamide-6, supplied by Allied-Signal (Capron 8200).

Apparatus

All experiments were carried out on the Werner and Pfleiderer ZSK-30 twin screw extruder, as shown in Figure 1. Three different screw configurations were used in this study. These are shown Figure 2. Screw Configuration 1 is completely based upon right handed screws. In Screw Configuration 2, we introduced two kneading disc blocks in addition to right-
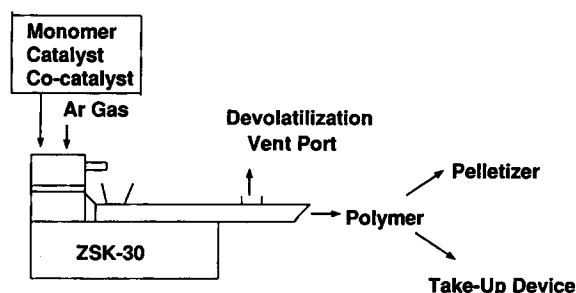

Figure 1   Twin screw extrusion polymerization process.

handed screws. In Screw Configuration 3, we introduced three kneading disc blocks, one left handed screw, as well as right handed screw elements.

Procedure

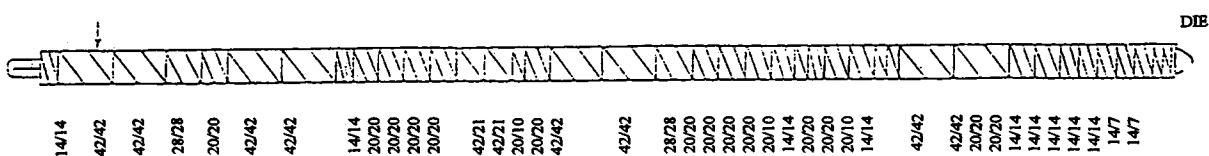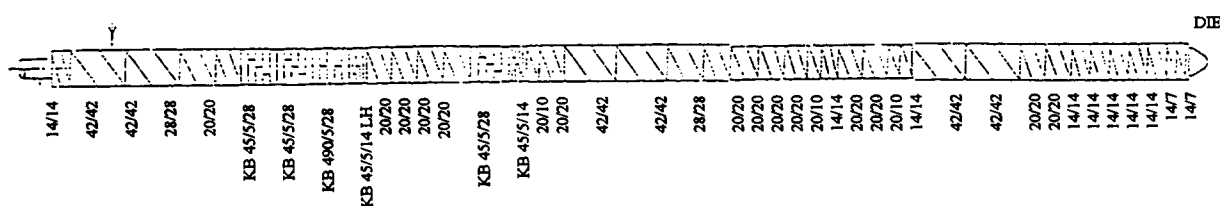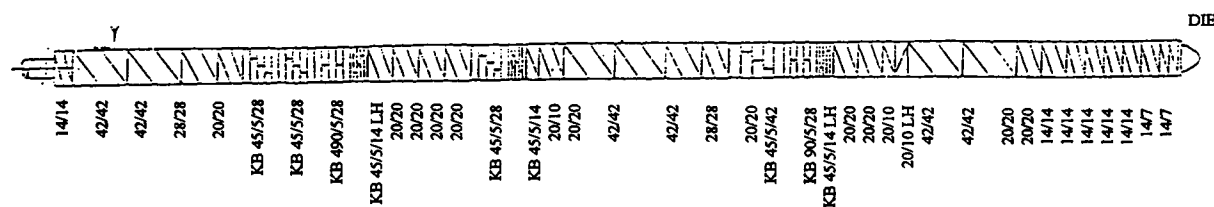### Catalyst/Co-Catalyst Preparation

The first step in our procedure was to prepare the catalyst and cocatalyst. This was carried out in a dry box, purged with argon gas, as follows. First, one mole of caprolactam was melted in a beaker and, subsequently, sodium was added into the molten caprolactam and was agitated until it seemed completely to dissolve or, rather, to react. The product was poured out into a pan. This was cooled down to obtain solid sodium caprolactam. The cocatalyst was prepared in the same manner as the catalyst. After completion of the cooling stage, the product was dry mixed with specific amounts of caprolactam flake. This was subsequently metered into the hopper of the twin screw extruder.

Determination of Residence Time Distribution

The residence time distributions for the different screw configurations were determined using delta functions inputs of carbon black. This was carried out using polyamide-6 as a carrier as follows. We fed 100 mg of carbon black into the hopper at time zero and collected samples every 15 sec. This sample was subsequently dissolved in an m-cresol solvent. The product was filtered using Celite packed glass filter paper. The weight of carbon black, collected in extrudates, was subsequently measured as a function of time.

Twin Screw Polymerization Process

The twin screw extrusion polymerization process was carried out as shown in Figure 1. Caprolactam, catalyst, and cocatalyst were tumble mixed and were

Screw Configuration 1: All right-handed screw elements

DIE

14/14 42/42 42/42 28/28 20/20 42/42 42/42   14/14 20/20 20/20 20/20 20/20   42/21 42/21 20/10 20/20 42/42   42/42   28/28 20/20 20/20 20/20 20/10 14/14 20/20 20/10 14/14   42/42   42/42 20/20 20/20 14/14 14/14 14/14 14/14 14/7 14/7

Screw Configuration 2: Right-handed screw plus two kneading disc blocks

DIE

14/14 42/42 42/42 28/28 20/20 KB 45/5/28 KB 45/5/28 KB 490/5/28 KB 45/5/14 LH 20/20 20/20 20/20 20/20   KB 45/5/28 KB 45/5/14 20/10 20/20 42/42   42/42 28/28   20/20 20/20 20/20 20/10 14/14 20/20 20/20 20/10 14/14   42/42   42/42 20/20 20/20 14/14 14/14 14/14 14/14 14/7 14/7

Screw Configuration 3: Right-handed screw plus one left screw & three kneading disc blocks

DIE

14/14 42/42 42/42 28/28 20/20 KB 45/5/28 KB 45/5/28 KB 490/5/28 KB 45/5/14 LH 20/20 20/20 20/20 20/20   KB 45/5/28 KB 45/5/14 20/10 20/20 42/42   42/42 28/28 20/20 KB 45/5/42 KB 90/5/28 KB 45/5/14 LH 20/20 20/20 20/10 20/10 LH 42/42   42/42 20/20 20/20 14/14 14/14 14/14 14/14 14/7 14/7

Figure 2   Screw configurations used in this study.

subsequently fed into the hopper using a volumetric feeder with argon gas. In these experiments, we used the argon gas instead of nitrogen gas because the argon is denser than nitrogen. One feeding port was used to achieve longer residence times and better mixing.

Different temperature profiles were established using the controllers on the various barrel subsections. In order to feed successfully the caprolactam, catalyst, and cocatalyst, the hopper section has to have a temperature of between 90–170°C, since the melting and boiling points of caprolactam are 80°C and 180°C, respectively. As polyamide-6 has a crys-

talline melting temperature of 215°C, it is necessary that the later barrel section and die have a temperature in excess of this. The temperature must be below the degradation temperature. This is about 290°C. These restrictions led to the following selection of barrel temperature profiles: Temperature profile 1: 170, 230, 230, 230, 230 (°C); temperature profile 2: 170, 240, 240, 240, 240 (°C); Temperature profile 3: 170, 250, 250, 250, 250 (°C).

Devolatilization experiments were carried out using a port near the end of the twin screw extruder barrel, as shown in Figure 1. A vacuum was applied at this position.

Melt Spinning of Continuous Filaments

Spinnerets, with hole diameters of 4 mm and 1 mm, were used. The exit velocities for these diameters was computed to be 1.2 and 10 m/min at a caprolactam feed rate of 2 kg/h. In some of the experiments, the emerging extrudates were drawn down using a Torii winder at various take up velocities up to 550 m/min. This is equivalent to drawdown ratios of 480 and 60, respectively, for the 4 mm and 1 mm die.

Polymer and Fiber Characterization

Polymer Molecular Weight

The polyamide-6 samples produced were characterized in various manners. The primary method was by determining the melt shear viscosity in a capillary rheometer and a Rheometrics RMS-800 at 230°C.

Fiber Characteristics

The birefringence of the fibers was measured with a Leitz polarized light microscope with a Berek

compensator. We measured WAXS film patterns of the melt spun fibers using a General Electric X-ray generator. Tensile mechanical properties of the melt spun fibers were measured using a Monsanto T-10 tensile tester.

RESULTS

Mean Residence Time and Residence Time Distributions

The differential residence time distributions for screw configuration 3 are shown in Figure 3 at screw speeds of 50 to 350 rpm at the same throughput. The residence times were in the range of 1 to 11 min, with mean residence times in the range of 1.5 to 6 min. Mean residence times for the three screws are presented as a function of screw speed in Figure 4. Screw configuration 1 has the shortest residence times and screw configuration 3 has the longest residence times. The effect of feed rate on residence time is shown in Figure 5 for screw configuration 2. Reducing feed rate and reducing screw speed both increase residence time.
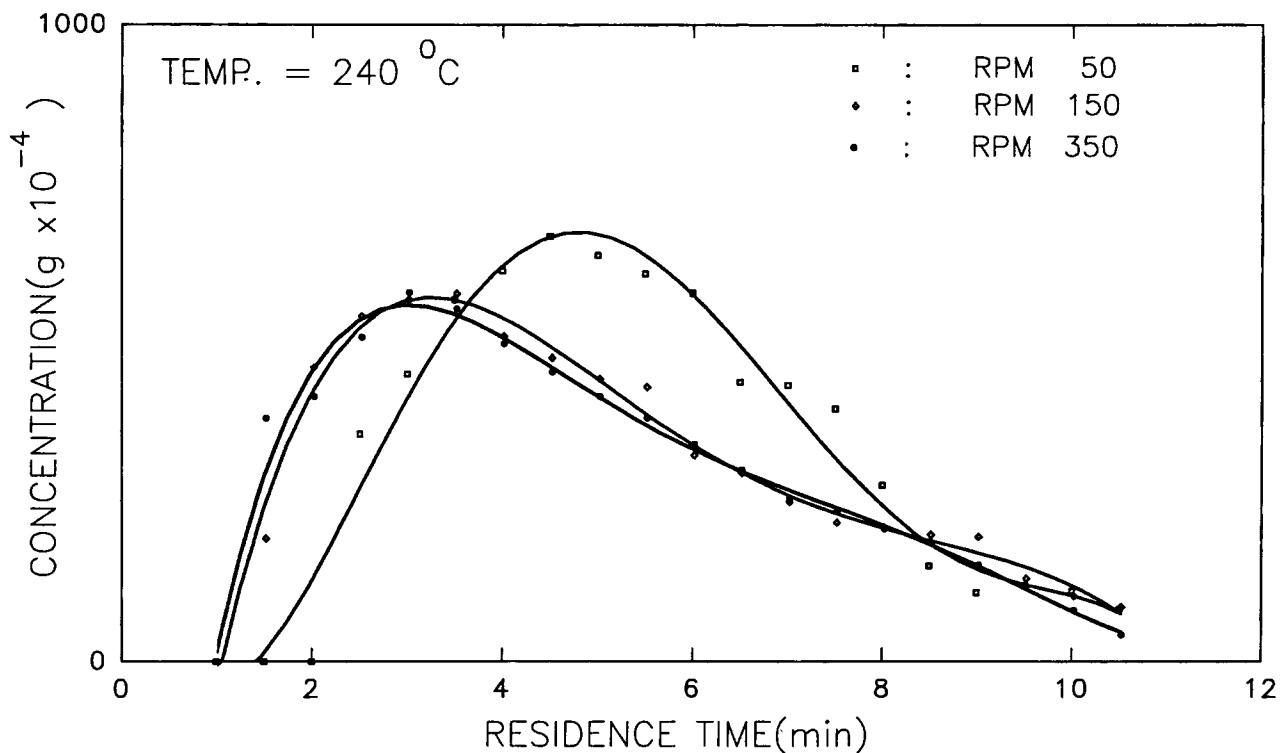

Figure 3   Residence time distributions for screw configuration 3 at N = 50 to 350 rpm, Q = 2 Kg/h.
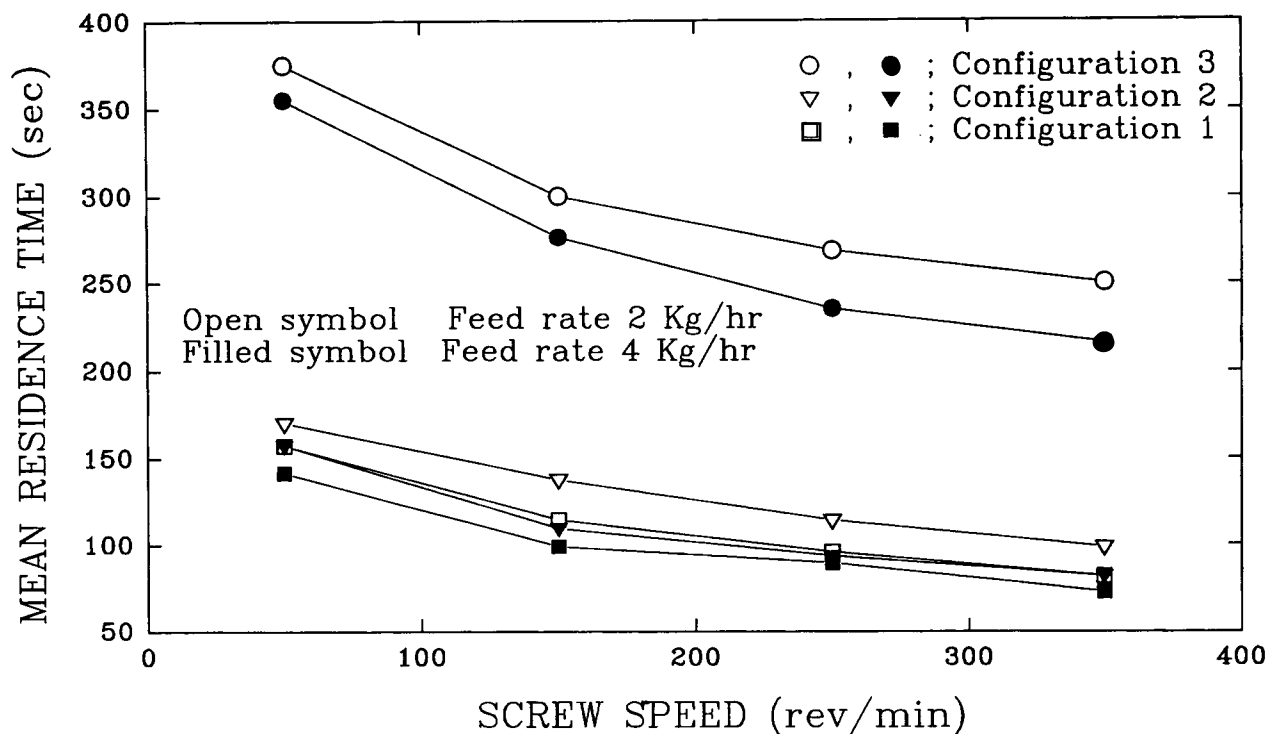
Figure 4   Mean residence time for three screw configurations.

Quantitative Yields of Continuous Polymerization Process

Generally, high yields of polymerized polyamide-6 were obtained in the twin screw extrusion process.
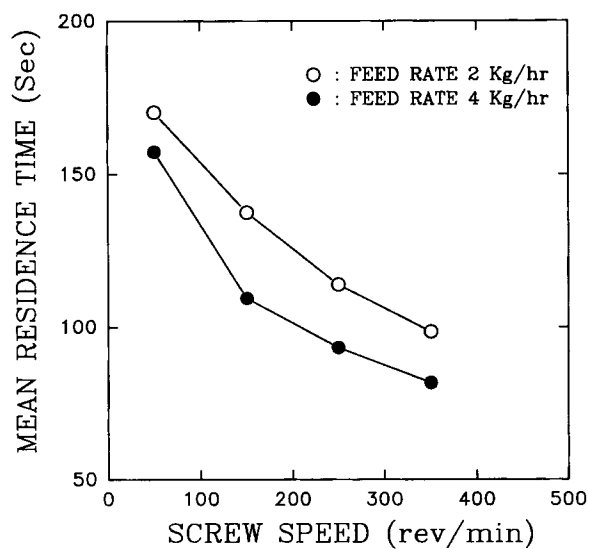

Figure 5   Effect of screw speed on residence time for screw configuration 2.

In Figure 6(a) we show the thermogravimetric analysis (TGA) results extruder for the caprolactam and for the product. The caprolactam monomer has a volatilization temperature of 160°C. The polymerized product volatilizes at 450°C. Figure 6(b) presents a differential scanning calorimeter curve for the product. The material has a crystalline melting point of 215°C and is clearly polyamide-6.

The influence of screw configuration and screw speed on degree of yield is shown in Figure 7. Generally, for screw configuration 1, the yield is on the order of 88 to 92%. Smaller variations are found in screw configurations 2 and 3, where values reach 90 to 95% yield and higher.

The yield is also strongly influenced by the barrel temperature. It is found that reducing the barrel temperature lowers the yield. The results of a study of varying barrel temperatures are summarized in Table I.

Polymer Melt Viscosities

Melt viscosities of various polyamide-6 melts, polymerized in a twin screw extruder, are summarized in Table II. It can be seen that polymers produced
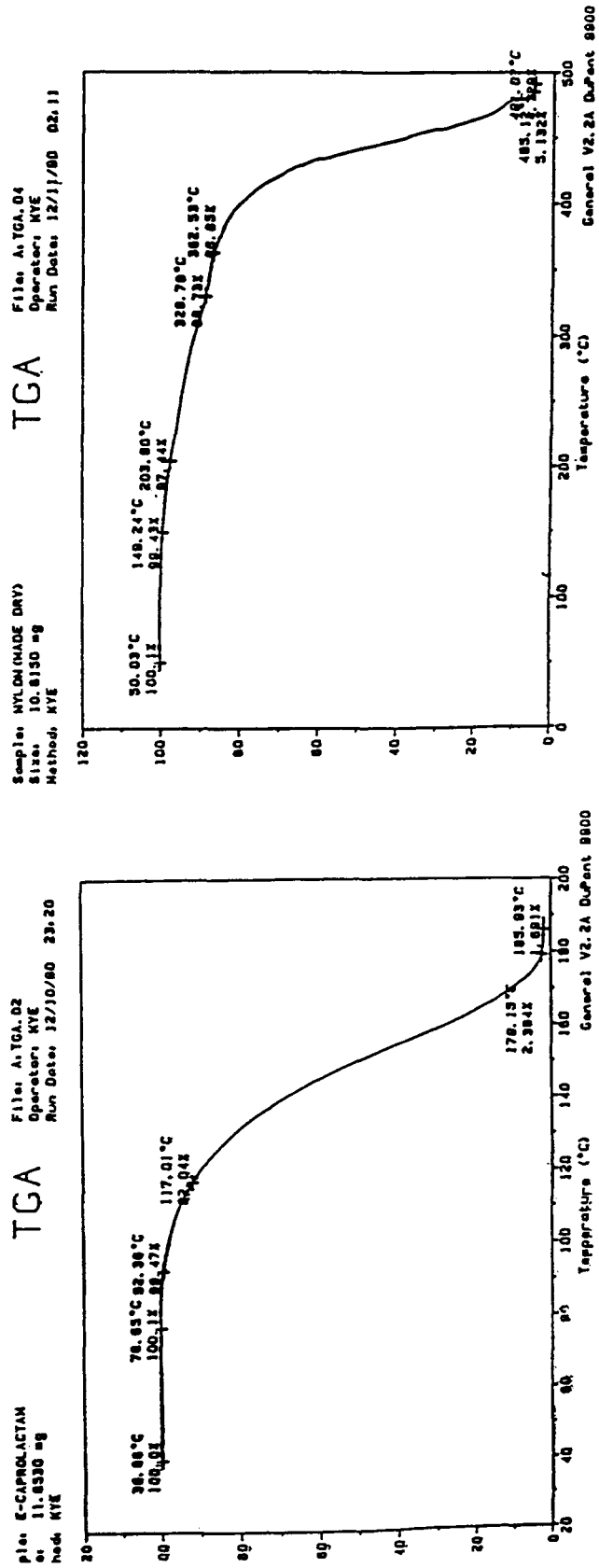
Figure 6 Thermal analysis of caprolactam and polymerization product. (a) TGA and (b) DSC of polymerization products.

Sample: NYLON
Size: 12.5000 mg
Method: H. KYE
Comment: MELTING TEMP.

DSC

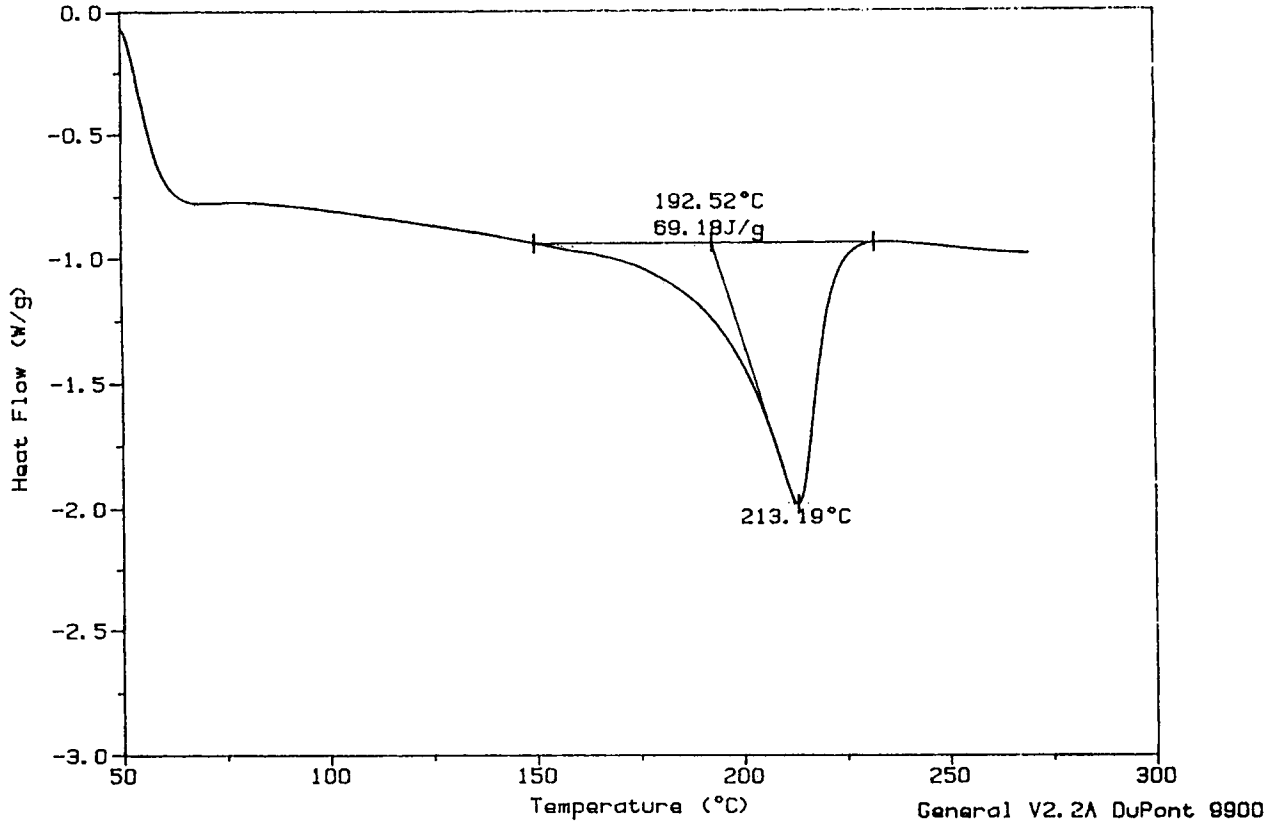File: A:NYLON.01
Operator: H. KYE
Run Date: 11/25/90   16:07

192.52°C
69.18J/g

213.19°C

Heat Flow (W/g)

Temperature (°C)

General V2.2A DuPont 9900

Figure 6   (*Continued from the previous page*)

● : Screw Configuration 3
    (with Devolatilization)
○ : Screw Configuration 3
▼ : Screw Configuration 2
▽ : Screw Configuration 1
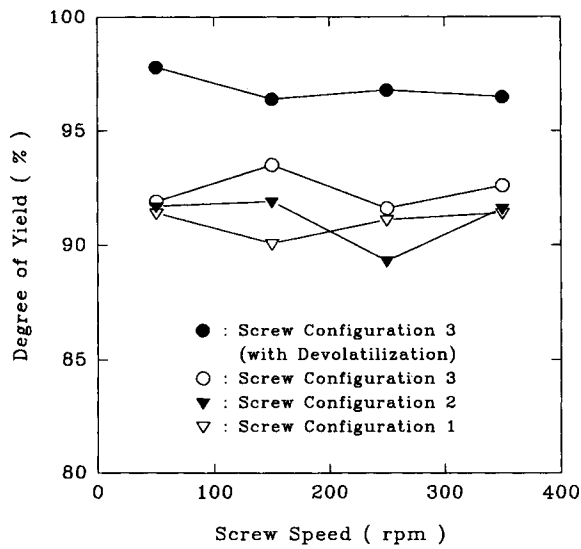
Screw Speed (rpm)

Figure 7   Degree of yield as a function of screw speed for different screw configurations.

in screw configuration 1 possess lower shear viscosities than the products of screw configurations 2 and 3. Lower viscosities are also associated with higher screw speeds.

Material Distributions on Modular Screws

Screws were removed following the continuous polymerization process. Caprolactam was found near the hopper and polyamide 6 near the die. The level of fill increased from screw configuration 1 to 2 to 3, when comparisons were made under different conditions.

The effect of screw speed on the filled region of the screw for different screw configurations is shown in Figures 8 and 9. The behavior is best seen in the region near the die where the caprolactam is polymerized. It clearly shows that increases of screw speed reduce the length of the fully filled region.

Table I   Effect of Barrel Temperature on Degree of Yield

Temperature Profile	Result	Yield %
A. Screw Configuration 1		
170, 170, 170, 170, 230	No polymerization	—
170, 170, 170, 230, 230	Oligomer	43
170, 170, 230, 230, 230	Polymer	76
170, 230, 230, 230, 230	Polymer	85
B. Screw Configuration 2		
170, 170, 170, 170, 230	No polymerization	—
170, 170, 170, 230, 230	Oligomer	64
170, 170, 230, 230, 230	Polymer	85
170, 230, 230, 230, 230	Polymer	90
C. Screw Configuration 3		
170, 170, 170, 170, 230	No polymerization	—
170, 170, 170, 230, 230	Oligomer/polymer	75
170, 170, 230, 230, 230	Polymer	89
170, 230, 230, 230, 230	Polymer	95

Devolatilization

The position of the devolatilization port, relative to filled positions of screw, is shown in Figure 10. Generally, high levels of conversion were obtained with devolatilization in the twin screw extrusion process. This is shown in Table III. The devolatilization port leads to lower levels of residual monomer content. Conversions up to 98% were achieved.

Melt Spun Fibers: Filament Diameter

Melt spun filaments were produced from the 4 mm and 1 mm diameter spinnerets by drawing the melt stream down onto a takeup roll. For the larger diameter spinneret, the filament diameters were in the range of 160–400 μm and for the 1 mm the diameters were in the range of 60–190 μm. Filament diameter decreased with increasing draw down ratio V_L/V_O.

Melt Spun Fibers: Structure

We subsequently measured the birefringence as a function of draw down ratio and obtained WAXS patterns. The birefringence is plotted as a function of draw down ratio in Figure 11. Birefringence increases with draw down ratio, but increases more rapidly with the 1 mm die.

WAXS patterns of spun fibers are shown in Figure 12. In the WAXS patterns, we identify reflections of d-spacing at 8.2 Å and 4.13 Å. With increas-

Table II   Shear Viscosities and Molecular Weight of Polyamide-6 Melts Produced in this Process

Screw Configuration	Temperature (°C)	Feed Rate (Kg/h)	Screw Speed (N)	Shear Visocity ($\times 10^{-3}$, Poise) ($\gamma = 10 \text{ sec}^{-1}$ $T = 230°C$)	$\overline{M_n}$ [a] (calc)
Commercial PA 6				8.17	21,600
1	240	2	50	5.636	19,400
1	240	2	350	4.133	17,640
1	240	4	50	4.093	17,600
1	240	4	350	2.195	14,460
3	230	2	50	7.548	21,088
3	230	2	350	5.452	19,200
3	230	4	50	5.208	18,900
3	230	4	350	3.945	17,400
3	240	2	50	8.450	21,800
3	240	2	350	10.79	23,400
3	240	4	50	7.203	20,800
3	240	4	350	7.871	21,350
3	250	2	50	25.17	30,100
3	250	2	350	22.02	28,900
3	250	4	50	34.28	32,900
3	250	4	350	25.6	30,100

[a] Calculated number average molecular weight is based on G. Pezzin and G. B. Gechele.[56]

TEMPERATURE   240 C
FEED RATE   2 Kg/hr

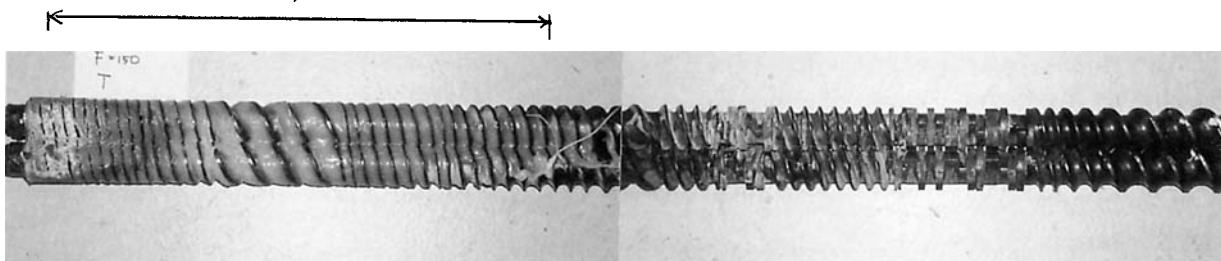A) SCREW SPEED; 50 RPM
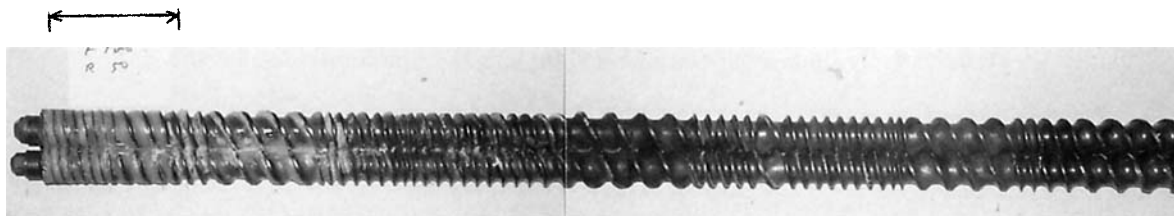
B) SCREW SPEED; 350 RPM

Figure 8   Character of fill in screw configuration 1 at different screw speeds.

TEMPERATURE   240 C
FEED RATE   4 Kg/h

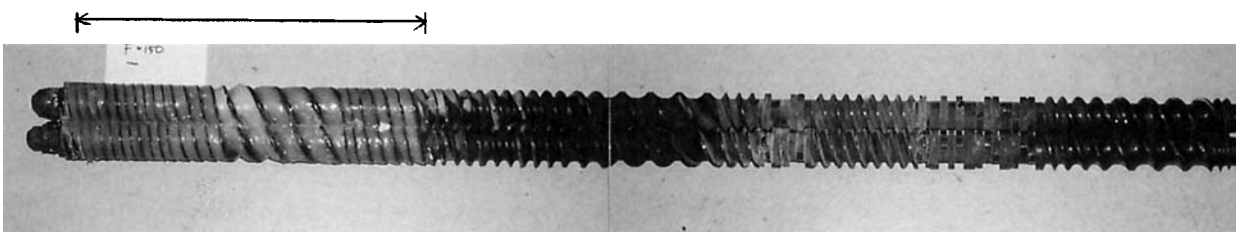SCREW SPEED;   50 RPM

SCREW SPEED;   350 RPM

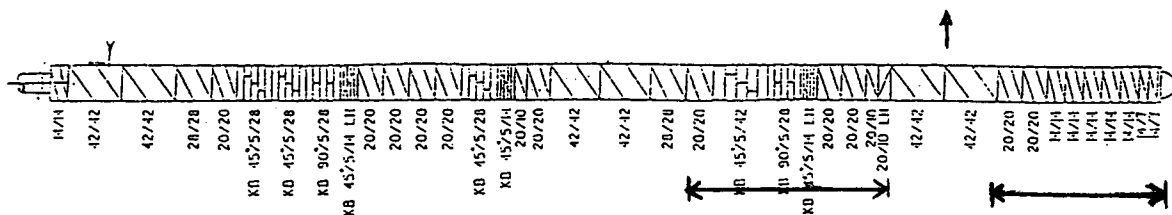**Figure 9**   Character of fill in screw configuration 2 at different screw speeds.

Figure 10   Position of devolatilization port relative to positions of screw fill.

ing draw down, the 8.2 Å reflections become increasing meridional and the reflections at 4.13 Å become equatorial and split into two reflections.

Melt Spun Fibers: Mechanical Properties

We also determined mechanical properties of melt spun filaments. Uniaxial stress–strain curves of the filaments are presented in Figure 13. In general, with an increase in take-up speed, elongation to break decreases while modulus and tensile strength increase. As shown in Figure 13, Young's modulus and tensile strength are increasing functions of filament draw down ratio and the elongation to break is a decreasing function.

DISCUSSION

Residence Time Distribution

Our observations on residence time suggest that introducing kneading disc blocks, and decreasing the

screw speed at constant throughput rate, reduce the residence time. Decreasing the throughput rate at a constant screw speed also increased the residence time. This is similar to what has been observed by earlier investigators.[52-54] The residence time increase is associated with increasing levels of fill. This problem has been considered in some detail by Kim and White,[54] using the University of Akron Akro Co Twin Screw commercial software package of Chen, Montes, and White.[55]

Yield Levels

Based on extraction, about 5–10% of residual monomer and oligomer remain in the product. Screw Configuration 1 shows yields of the order of 88–92%. Screw configurations 2 and 3 show relatively higher yield levels than does screw configuration 1. This is probably because of its lower residence time and poor mixing characteristics. Screw Configuration 1 has a mean residence time of 70 to 160 sec, which is not sufficient to increase the yield levels up to 95%. In

Table III   Influence of Devolatilization on Yield and Polymer Molecular Weight

Feed Rate (Kg/h)	Screw Speed (N)	No Devolatilizating		Devolatilization	
		Yield (%)	M_n (calc)	Yield (%)	M_n (calc)
2	50	91.1	21,800	97.8	31,490
2	150	93.5	25,500	96.4	26,130
2	250	91.6	22,600	96.8	27,110
2	350	92.6	23,400	96.5	26,640
4	50	91.9	20,800	96.7	27,050
4	150	92.6	21,650	95.6	26,100
4	250	90.0	20,210	95.4	25,800
4	350	92.0	21,350	95.8	26,250

[a] All experiments used screw configuration 3 and temperature profile 2.
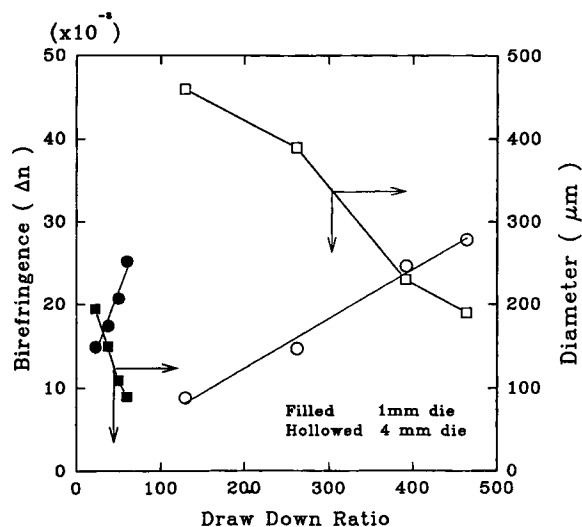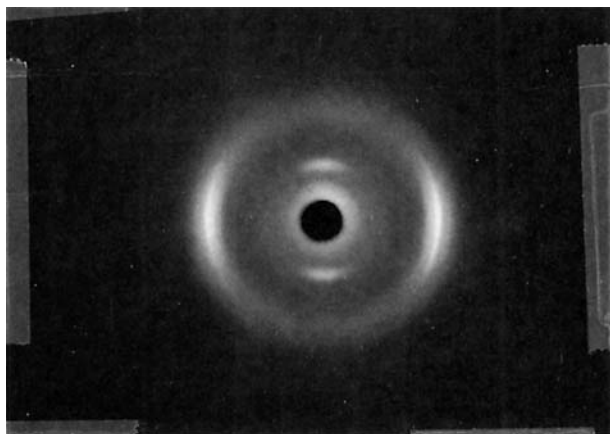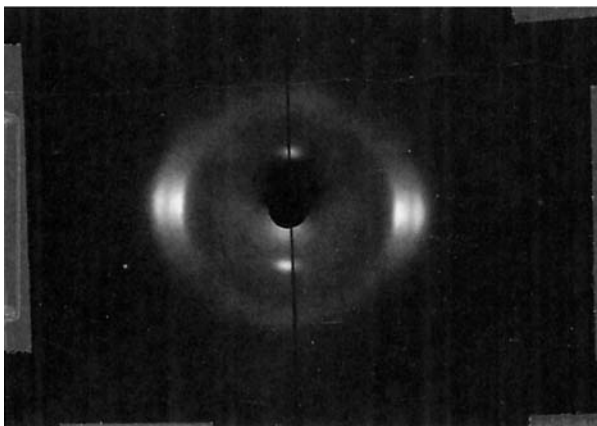

Figure 11   Birefringence and fiber diameter as a function of draw down ratio (V_L/V_O).

A. Draw Down Ratio 60
(1 mm Die)

B. Draw Down Ratio 480
(4 mm Die)

addition, screw configuration 1 has no kneading disc blocks. This leads to low levels of shear mixing during the polymerization. Short residence time and low mixing probably lead to lower conversion and lower molecular weight. On the contrary, screw configuration 3 yields a mean residence time of 220 to 390 sec. As a result, it shows yield levels of 90 to 95% without devolatilization. Screw configuration 3 has three sets of kneading disc blocks. This leads

Figure 13 Uniaxial stress–strain curves for melt spun fibers, taken up at varying velocities.

to greater shear mixing and probably the temperature rises to result in high yields.

We also investigated polymerization temperature effects on yield levels. Polymerization temperatures of 230 and 250°C, in the latter part of the barrel, under same throughput and screw speed, show 90 to 95% yield. However, if the temperature is raised to 290°C, the yield is 70 to 80%. If polymerization temperature is over 300°C, polymerization is not found to occur. High polymerization temperature probably leads to a reduction of yield level because of side reactions.

Generally, investigators found that conversion in reactive extrusion correlates with reduced screw speed and with residence time. A thorough study of such effects was given by Kim and White.[56]
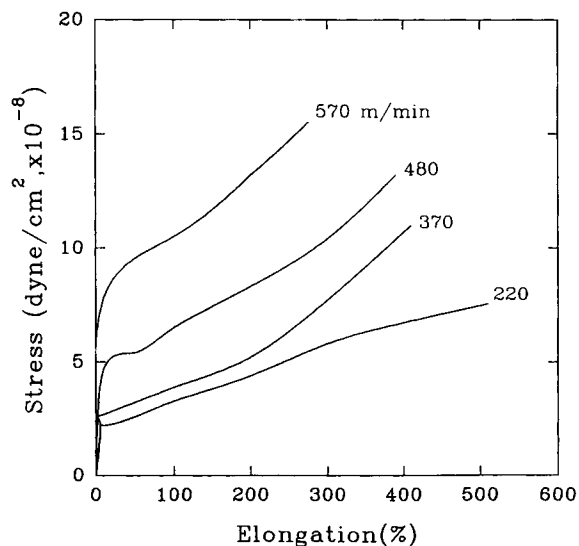
Molecular Weight

Pezzin and Gechel[56] have shown that the shear viscosity, measured at a shear rate 10 sec^{-1}, is proportional to the number average molecular weight of the polymer to the 3.4 power. We have used this method here. Computed molecular weights are shown in Table II. We have also made measurements of molecular weight using gel permeation chromatography, using m-cresol solvent. The numbers obtained correlated with those obtained by the Pezzin and Gechele method.[58]

Molecular weights are in the order of screw configuration 3 > 2 > 1 under the same conditions. As
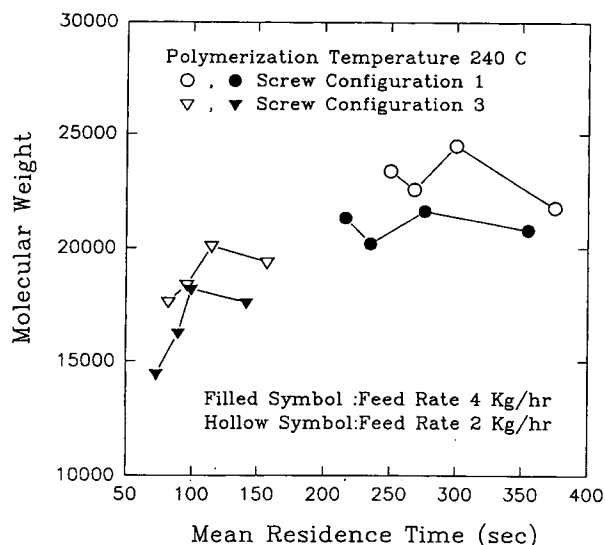
Figure 14   Molecular weight as a function of residence time.

shown in Figure 14, molecular weight is a function of residence time. Increasing residence time, produced by lowering screw speed and by lowering feed rate, leads to increased molecular weight of product. The differences in performance of the three modular screws must, to some extent, represent residence time.

Devolatilization

It is necessary to reduce the monomer contents of the product and the activated catalyst by removal through the vent port, because residual monomer deteriorates the mechanical properties of polymer and is a health hazard to users of polymer. As shown in Table III, applying a devolatilization process reduces the monomer content to under 5% and sometimes to as low as 2%. As a result, the molecular weight of the product increases in the order of 10 to 20%. With slow screw speeds and low feed rates yielding long residence times, with devolatilization, monomer content can be reduced to as low as 2.2%.

Melt Spun Fibers: Structure

The birefringence and WAXS patterns that have been obtained can be contrasted those of earlier investigators, beginning with Ziabicki and Kedzierska.[40]

Filaments were drawn down and the birefringence as a function of draw down ratio was subsequently measured. As shown in Figure 11, birefringence is a increasing function with draw down ratio. The max-

imum birefringence achieved was 29×10^{-3}. This value is higher than that reported by Ziabicki and Kedzierska,[40] Ishibashi et al.[41,42] or Bankar et al.[43] The Herman's orientation factor[43,45,49,51,58-60] may be defined as

$$f = \frac{\Delta n}{\Delta^\circ} \qquad (1)$$

Using a value of Δ° of 89.5×10^{-3}, suggested by the work of Matsumoto,[60] the maximum f achieved was 0.324. In comparison to the work of Shimizu et al.,[47] our maximum birefringence corresponds to a take-up speed of 1000 to 3000 m/min. Our draw down ratios were 20 to 480.

We obtained WAXS patterns for fibers spun from the two different dies with 1 and 4 mm die diameters. These are shown in Figure 12(a,b). In Figure 12(a) is shown the WAXS pattern at low draw down ratios of 60. This is a crude γ form of the type described by Ziabicki and Kedzierska[40] and later investigators.[43-45] Figure 12(b) shows the WAXS pattern of a fiber with a draw down ratio of 480. In Figure 12(b), we identify the appearance of two equatorial reflections, corresponding to 4.42 Å and 3.85 Å. This represents a mixed α and γ-pseudohexagonal structure that is similar to that described by Shimizu et al.[47]

Melt Spun Fibers: Mechanical Properties

The increase of modulus and tensile strength, with draw down ratio and decrease of elongation to break, has been reported by many investigators.[43-45,47-49]
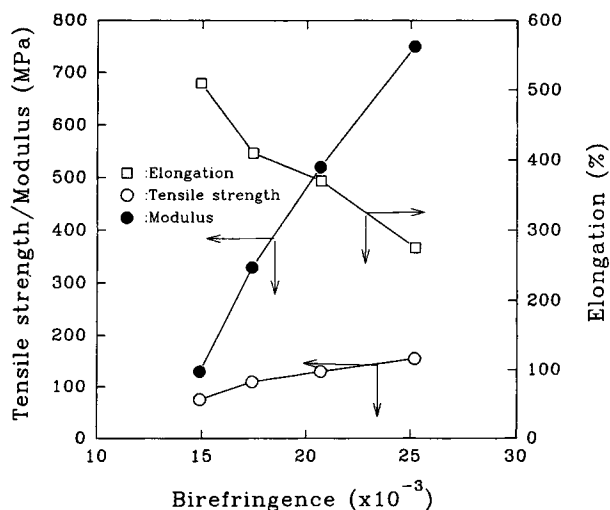

Figure 15   Mechanical properties as a function of birefringence.

We may correlate the mechanical properties of melt spun fibers with fiber birefringence for the small diameter spinneret. The filaments, produced from the 4-mm spinneret, had a much larger diameter and level of radial variation of structural heterogeneity. We thus only consider birefringence to represent orientation in the smaller diameter filaments. As shown in Figure 11, birefringence increases with draw down ratio. Uniaxial stress–strain curves of the filaments are presented in Figure 13. In Figure 15, we plot tensile strength and Young's modulus of the fibers as a function of fiber birefringence, which represents orientation, as indicated in Figure 12. Increasing fiber birefringence increases Young's modulus and tensile strength and decreases elongation to break. Our elongation to break tends to be lower, and Young's modulus higher, than reported in the literature by Bankar et al.,[43] presumably because of the lower moisture content of our fibers. Our data is closer to that of Shimizu et al.[47]

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