

The Properties of Polyethylene Crystallized Under the Orientation and Pressure Effects of a Pressure Capillary Viscometer

JOHN H. SOUTHERN and ROGER S. PORTER, *Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01002*

Synopsis

High-density commercial polyethylenes have been crystallized under the combined orientation and pressure effects available in the Instron capillary rheometer. The samples so formed were found to have a high degree of crystal perfection and crystal orientation in combination with the unusual property of transmitting visible light. The procedure for forming the crystal structure is elucidated. X-Ray and differential scanning calorimetry techniques were utilized to initiate a study of the structure. Evidence is presented that is consistent with the presence of an extended chain component in the crystal structure.

INTRODUCTION

This is a study of crystallinity induced in a high-density polyethylene under the influence of orientation and pressure effects in an Instron capillary rheometer.¹⁻³ The crystal structures so produced are found to be unusual in terms of melting point, orientation, modulus, and transparency. The instrumentation used in analyzing the crystal structures included a Perkin-Elmer differential scanning calorimeter Model 1-B (DSC), wide-angle x-ray equipment, and the $\bar{T}o\bar{Y}o$ Vibron instrument for dynamic tensile modulus measurements.

CRYSTALLIZATION PROCEDURE

All tests were performed on a single polyethylene, du Pont Alathon 7050, unless noted otherwise. It has a density of 0.978 g/cm³ and a melt index of 2.1. Gel permeation chromatography and light scattering provided number- and weight-average molecular weights for this polymer of 18,400 and 52,500, respectively.

In the procedure used for inducing crystallization, the Instron capillary rheometer was operated at a series of constant plunger velocities. The effect of certain plunger speeds in combination with test temperatures of 130°C to 145°C was such that the recorded Instron pressure trace failed to attain a steady state or even an average value over long times. The pres-

sure required to move the plunger at a constant velocity was observed to increase to the maximum value attainable in the rheometer (1900 atm), with accompanying cessation of extrudate flow. This is contrary to the usual observations concerning the extrusion of high-density polyethylenes and was suggestive of crystallization in the rheometer.

The specimen of interest consisted of the strand that crystallized in the rheometer capillary. After cessation of flow, the pressure was maintained in the vicinity of 1900 atm in order to prevent the structure from returning to the melt state. This is accomplished under such a pressure since the equilibrium melting point of the polyethylene will be approximately 180°C,⁴ a value that is much higher than the ambient rheometer temperatures (130–145°C). It can be assumed that no melting occurs in the crystallized material once it has formed in the high pressure segment of the capillary length adjacent to the capillary entrance. A pressure drop exists over the length of the capillary, and the polyethylene in the capillary adjacent to the exit is subject to reorganization due to the lower pressure value.

The rheometer was cooled after cessation of flow at a rate of 1°C/min, while maintaining the 1900 atm of pressure. On cooling to 110°C, it was assumed that no additional changes would occur in the crystal structure at atmospheric pressure; hence, the pressure was released and the capillary removed from the rheometer. The polyethylene strand in the capillary was sufficiently cohesive to retain its cylindrical shape on being forced from the capillary. The capillary used to form the strands was of the following dimensions: 0.0508 cm diameter, 2.56 cm length, and 90° entrance angle. It is to be emphasized that only the segment that is adjacent to the capillary entrance contains the crystal structure formed under pressure and orientation. The crystallinity in the segment adjacent to the capillary exit is formed during the cooling cycle. This report is primarily concerned with the properties of the transparent segments near the entrance of the capillary that are under sufficient pressure to prevent reorganization during the cooling cycle.

EFFECT OF PLUNGER VELOCITY AND RHEOMETER TEMPERATURE

As has been explained in greater detail in a previous publication,¹ the crystallization process initially occurs in the entrance region of the capillary as the consequence of both pressure and orientation. For a given plunger velocity, it is reasonable that the influence of both pressure and orientation on the flowing melt is a function of the rheometer temperature. An example of this temperature effect is presented in Figure 1, in which a 0.5-cm/min plunger velocity was utilized. At 139°C, the pressure trace is observed to attain an equilibrium value of 373 atm. The general shape of this pressure trace is typical of those obtained for a fully melted polyethylene.

Figure 1 also contains a pressure trace at a 138°C rheometer temperature. Never leveling off as in the 139°C example, the pressure during extrusion at

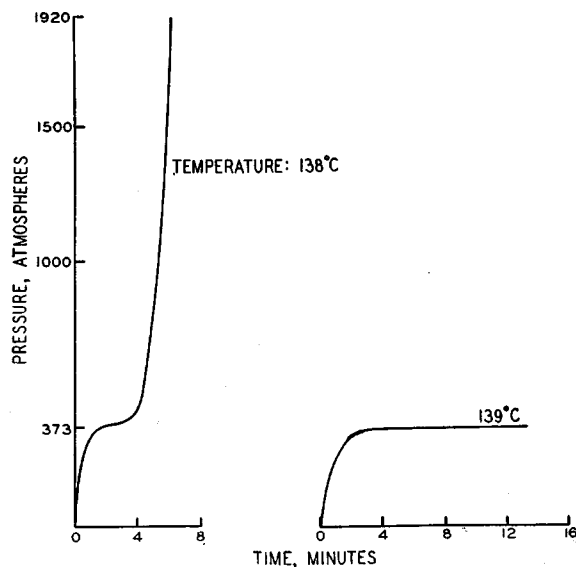


Fig. 1. Instron pressure traces using a capillary of diameter 0.0508 cm and length 2.56 cm and a plunger velocity of 0.5 cm/min.

138°C increases to the 1900-atm limit with accompanying cessation of extrudate flow. Thus, a temperature drop of about 1°C was sufficient to result in massive crystallization in the rheometer. Due to temperature gradients existing in the barrel and capillary, the accuracy of the temperature in the rheometer was limited to $\pm 0.5^\circ\text{C}$. It should also be noted that the pressure traces presented in this report represent uncorrected data. Such factors as pressure losses in the barrel, elastic energy effects, and entrance corrections are of negligible importance to the conclusions derived here.

Rheometer temperature is critical not only in obtaining crystallization in the capillary but also in determining crystal structure within the strand. For a constant plunger velocity of 5.0 cm/min, Table I shows the melting points from peak maxima of DSC fusion curves for the 4-mm strand segments adjacent to the capillary entrance crystallized at various rheometer temperatures. These melting points, ranging from 137.6°C to 140.1°C, are indicative of an extended-chain crystal structure and/or a chain-folded structure with a relatively long fold period. The brief time for crystallization under the combined influence of pressure and orientation is consistent with the formation of a crystal structure containing an extended chain component, since lengthy annealing times are usually required to form long fold periods. However, low-angle x-ray studies are necessary for more definitive crystal structure determinations. It is interesting to note that the maximum melting point in Table I has the relatively high value of $140.1 \pm 0.4^\circ\text{C}$. For crystallization temperatures below 136°C, and also for those above 139°C, the melting points are notably lower. The implications

TABLE I
Melting Point as a Function of Rheometer Crystallization Temperature
by Differential Scanning Calorimetry^a

Rheometer crystallization temp, °C	Melting point, ±0.4°C
132	137.6
134	139.6
136	140.1
137	140.0
138	140.0
139	140.0
140	138.8
142	139.0
144	138.8

^a The samples were the 4-mm segments adjacent to the capillary entrance crystallized at a plunger speed of 5.0 cm/min; scan rate, 5°C/min.

of these results to the crystal morphology will be discussed in conjunction with the orientation data obtained from wide-angle x-ray equipment. It is also of interest to point out, for comparative purposes, that the initial melting point of the Alathon 7050 (prior to processing in the Instron) was approximately 132–133°C.

A wide-angle x-ray photograph of the high melting point portion of a strand produced at 136°C is shown in Figure 2. The presence of arcs, rather than concentric circles, in the reflections is evidence for crystal orientation in this segment. A quantitative measure of the orientation was obtained by performing an azimuthal scan to determine the average angle between each axis of the crystallite unit cell and the direction of flow in the capillary.⁵⁻⁷ The orientation functions presented in Table II as a function of crystallization temperature were obtained from the average angle values (ϕ) using the following equation:

$$f_x = \frac{3 \langle \cos^2 \phi \rangle - 1}{2}$$

where x refers to either the a -, b -, or c -axis of the unit cell. An orientation function value of $-\frac{1}{2}$ corresponds to a particular axis of the unit cell being perpendicular to the flow direction, and a value of $+1$ indicates that the axis is aligned parallel to the flow direction. In all cases presented in Table II, the x-ray beam was targeted on the strands at a point approximately 4 mm from the capillary entrance.

TABLE II
X-Ray Orientation Data as a Function of Crystallization Temperature

	Orientation functions, ±0.05					
	132°C	134°C	136°C	138°C	140°C	142°C
a -Axis	-0.4	-0.4	-0.4	-0.4	-0.3	-0.3
b -Axis	-0.5	-0.5	-0.5	-0.5	-0.4	-0.3
c -Axis	+0.9	+0.9	+0.9	+0.9	+0.7	+0.6

The *c*-axis of the unit cell is the axis down the length of the polymer chain. The *c*-axis orientation function is approximately +0.9 for crystallization temperatures of 132–138°C. This is conclusive evidence that the polymer chains are significantly aligned in the crystal structure in the direction parallel to the flow axis. It is of interest to note that the orientation functions presented in Table II conform to the model for crystallization from a flowing melt that was postulated by Keller and Machin.^{8,9} The model is

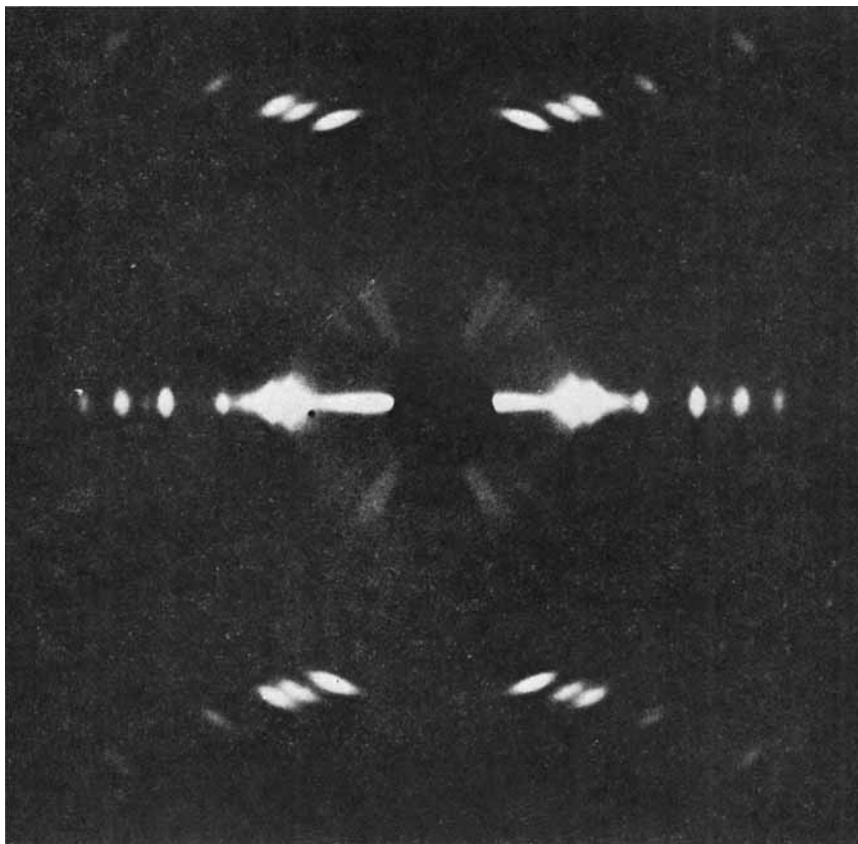


Fig. 2. Transparent segment formed at 5.0 cm/min and 136°C (flow axis perpendicular to equator).

characterized by lamellar crystal growth occurring in planes perpendicular to a central nucleation axis. Such a crystallization model would require cylindrical subunits for crystallization in a capillary. A scanning electron micrograph, noted in previous research,¹ clearly indicates that each strand consists of many such cylinders, all aligned parallel to the flow direction. The Keller and Machin model is one of several requiring both chain folded and extended chain crystalline units that can be used to adequately describe the data so far obtained. Additional studies are

necessary in order to clearly define the correct model for the structure produced in the rheometer.

It was also observed that *c*-axis crystal orientation decreased with increasing crystallization temperatures above 138°C (see Table II). Sieglaff and O'Leary² have provided a qualitative confirmation of this effect using a technique for the crystallization of polypropylene that is similar to the one

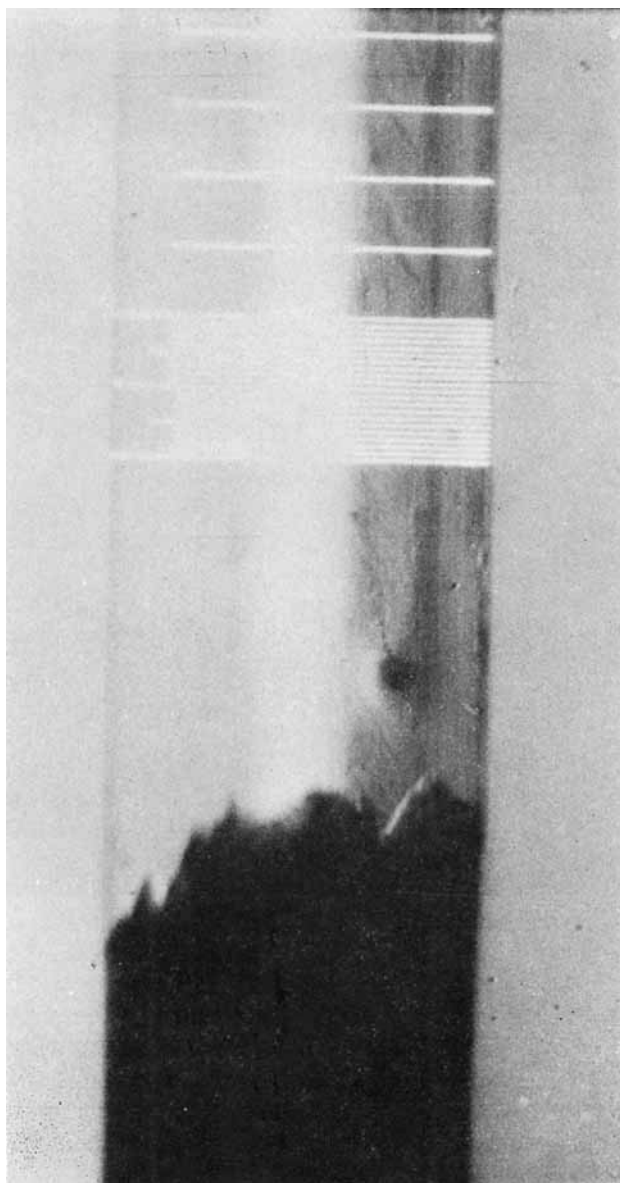


Fig. 3. Transmission photograph showing clear scale observed through 0.0508-cm-diameter strand.

described in this report. For polypropylene crystallized over the range of 170°C to 195°C, they reported that crystal orientation generally decreased with increasing rheometer temperature. For polyethylene, the data presented in Table II shows that *c*-axis orientation decreases above 138°C; however, below this temperature down to 132°C, the orientation does not change significantly as a function of crystallization temperature.

The drop in orientation in the structure crystallized at 140°C relative to that crystallized at 138°C is also accompanied by a decrease in the melting point. Specifically, the data in Tables I and II show that, as the melting point dropped from 140.0°C to 138°C, the orientation function also dropped from +0.9 to +0.7 on going from the 138°C to the 140°C crystallization temperature. This comparison constitutes supporting evidence for a correlation of increasing crystallite perfection, as measured by increasing melting point, with increasing *c*-axis orientation. It is of interest to note that an increased importance of extended chains in the crystal structure would result in the observed melting point increasing with increasing *c*-axis orientation.

An entirely different effect was observed in comparing the strands crystallized at 132°C and 134°C. As shown in Tables I and II, crystal orientation did not change significantly for the two strands, but the melting point increased from 137.6°C to 139.6°C on going from a crystallization temperature of 132°C to 134°C. A possible explanation for this observation is an annealing of the internal defects in the crystal structure that is more easily accomplished at higher temperatures. Such an annealing process does not, in general, have a significant effect on the orientation function, hence the approximately constant orientation data for crystallization temperatures from 132°C to 138°C.^{10,11}

Perhaps the most remarkable property of the strands crystallized at temperatures from 132°C to 138°C is their transparency to visible light. They are extremely clear, as can be seen in the transmission photograph shown in Figure 3, which contains a transparent segment crystallized at 136°C. It is possible to look through the 0.05-cm-diameter segment and observe the scale markings on a clear ruler that has been placed *beneath* the strand. The strand in this photograph has been immersed in an oil of similar refractive index in order to reduce the lens effect due to its cylindrical shape. The opaque segment seen adjacent to the transparent one was crystallized during the cooling cycle. As a point of comparison to show the distinct differences in the crystal structure, the melting point of the transparent segment (adjacent to the capillary entrance) is 140°C, while that of the opaque segment (adjacent to the capillary exit) is 134°C.

It must be emphasized that light is being transmitted through segments that are highly crystalline. Using a value of 69.2 cal/g as the heat of fusion of the perfect extended chain crystal,¹² the experimental DSC heats of fusion of 57.2 cal/g ($\pm 2\%$) for the transparent segment shown in Figure 3 indicate 83% crystallinity. A density measurement for per cent crystallinity gave a value of 86%, using 1.001 cm³/g as the specific volume of the

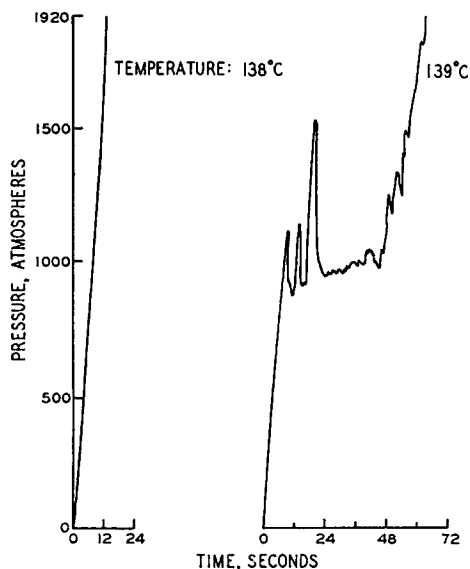


Fig. 4. Instron pressure traces during crystallization using a capillary of diameter 0.0508 cm and length 2.56 cm and a plunger velocity of 5.0 cm/min.

perfect crystal and $1.173 \text{ cm}^3/\text{g}$ as that of the completely amorphous unit.¹² It is not required that density and specific heat measurements should give an identical value for the crystalline content; they are based on different calibrations for crystallinity determination.

It was found that the temperature in the Instron rheometer is a critical factor in obtaining transparent segments. This is emphasized by the observation that a plunger velocity of 5.0 cm/min resulted in a translucent segment for crystallization at 139°C , whereas a transparent segment was obtained at 138°C . As indicated in Figure 4, the pressure traces for 138°C and 139°C that accompanied the formation of these segments were distinctly different. A possible explanation for the irregular pressure oscillations at the higher temperature could involve an alternating formation and destruction of a crystalline network in the flowing polyethylene.¹ Evidence obtained from extrudate weight and plunger volume displacement gave effective density data which implied that a density increase was occurring in the material remaining in the rheometer barrel during these oscillations. The observed density increase is evidence for the existence of a critical density requirement at a given temperature that must be met in order to induce stable crystallites from the flowing melt. It is of interest that transparent segments, formed at rheometer temperatures below 139°C , were accompanied by pressure traces during crystallization that were similar in form to the 138°C trace shown in Figure 4.

The physical change from transparent to translucent as a function of increasing crystallization temperature has been observed previously on an industrial type of extrusion apparatus.¹³ Similar in principle to the

Instron capillary rheometer, the apparatus produced a transparent polyethylene tube at temperatures near the atmospheric melting point of the polyethylene. A temperature gradient, maintained down the barrel, is necessary in order to produce a continuous extrudate. The gradient prevents the solidification of the material in any region other than that at the die exit.

It is of interest to note that, for a given rheometer temperature, the plunger velocity has little effect on the clarity of the strand. An increase in the plunger speed from the 5 cm/min value that resulted in the pressure traces in Figure 4 to a value of 10 cm/min at the 139°C temperature still resulted in the formation of a translucent strand accompanied by pressure oscillations. This reinforces the earlier assertion that the temperature is the critical factor in producing transparency. Additional evidence supporting this conclusion was obtained from the crystallization of Marlex 6009. For Alathon 7050 and Marlex 6009, the melt indices of 2.1 and 0.9, respectively, are indicative of differences in the average molecular weight of the two polymers. The strands produced from both polymers exhibited the previously described change from transparency to translucency at 139°C. The lack of influence of plunger velocity and molecular weight on the transparent-to-translucent change may indicate that 138°C is a maximum temperature for the formation of transparent polyethylene by means of pressure and orientation techniques available in an Instron rheometer. The translucent quality observed in strands crystallized at temperatures greater than 139°C may be the result of a partial melting of the structure, an effect that can be attributed to the pressure drop which occurs in the capillary.

SUPERHEATING OF THE TRANSPARENT SEGMENTS

Other studies¹⁴ have shown that extended-chain crystals are more superheatable than chain-folded crystals. With this superheating effect in mind, a series of DSC scans at different heating rates were obtained on transparent segments produced at 136°C and on translucent segments produced at 140°C.¹ These results are compared in Figure 5. Note that the apparent melting points (from maxima in fusion curves) for the transparent segments rise from 137.5°C to 146.7°C at scan rates of 0.625°C/min and 20°C/min, respectively. This constitutes a 9.2°C rise in the apparent melting point largely attributed to superheating. Over identical scan rates, the translucent strands exhibited only a 6.5°C melting point increase. The conclusion is that the transparent segments are significantly more superheatable than the translucent segments, and hence it is probable that extended chains form a more important element in the overall crystal structure of the transparent segments.

In Figure 5, the shapes of the two curves at scan rates below 2.5°C/min are of some importance. The curve for the translucent segments goes through a minimum which is lacking in the curve for the transparent seg-

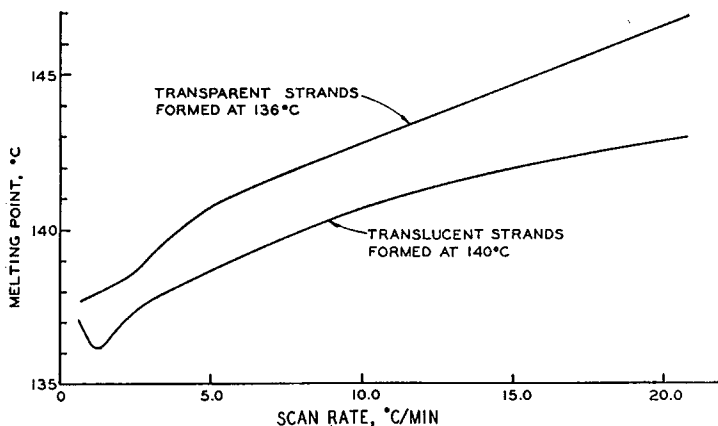


Fig. 5. Comparison of superheating for strands formed at 136° C and 140° C.

ments. A minimum value suggests that the material is reorganizing into a more perfect crystal structure at sufficiently low heating rates. Such observations are the norm for chain-folded structures that increase their fold period as well as anneal out the irregularities in the crystal structure.¹⁴ The model described previously of a chain-folded structure in combination with an extended-chain structure is one possible crystal scheme that can account for the observed superheating and annealing of the translucent segments.

EFFECT OF TIME AT 136°C ON TRANSPARENT SEGMENT LENGTH

When the cooling cycle was not immediately initiated on cessation of extrudate flow, it was found that the length of the transparent segment could be increased as a function of time at the constant crystallization temperature. Figure 6 shows the transparent segment length as a function of time at 136°C. The transparent segment formed after 30 min at 136°C prior to initiating the cooling cycle was found to extend 16 mm into the capillary from the entrance, as compared with the 10-mm-long segment formed in zero minutes before cooling (maintaining approximately 1900 atm until the cooling cycle was finished).

Extrusion continued very slowly after crystallization had occurred. From Figure 6, this extrusion rate was computed to be approximately 0.2 mm/min. As there was no detectable effect of time on either the crystal perfection or crystal orientation (the entire transparent segment length had a *c*-axis orientation function of +0.9 and a melting point of 140°C), the advancing crystal structure can be assumed to be moving down the capillary as a solid plug. The implication of these observations is that only a very slow flow rate at the 1900 atm of pressure is required to produce the oriented, transparent crystal structure. Hence, the orientation produced in the

structure may not be due to the magnitude of the flow rate, but only to the magnitude of the change in the flow rate occurring in the conical capillary entrance region. This longitudinal change in velocity per unit distance through the entrance region is, in all probability, the critical factor in producing the oriented, transparent structure. In future experiments using glass capillaries, it is hoped that it will be feasible to conclusively determine

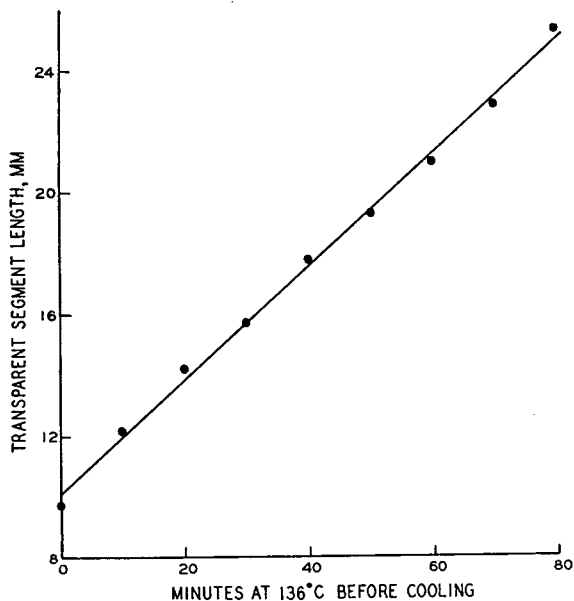


Fig. 6. Transparent segment length as a function of time at 136° C under a maximum pressure of 1900 atm.

whether the final crystal structure is either induced directly from an oriented melt or produced from "cold drawing" a crystal structure that forms in the rheometer barrel.^{13,15}

ELASTIC MODULUS OF A TRANSPARENT SEGMENT

The strand annealed for 80 min at 136° C before cooling was transparent throughout its 25-mm length (see Fig. 6). This strand was tested on the Vibron at 30° C, and the results were compared with those of an unoriented strand of similar length that was formed by simply cooling polyethylene in the melt state at 1° C/min. The data are presented in Table III together with the data of Takayanagi et al.¹⁶ obtained on a drawn polyethylene, Marlex 50, having an orientation function +0.98, an 86% crystallinity, and a melting point of 137° C. The tensile storage modulus attained the largest value for the strand crystallized under the pressure and orientation conditions existing in the Instron rheometer. This modulus value of 6.6×10^{10} dynes/cm² is more than four times that of the unoriented, thermally

TABLE III
Moduli of Polyethylene Crystallized Under Various Conditions
Measured on the Vibron^a
(30°C, 110 cps)

	Modulus, dynes/cm ²		
	Instron at 136°C	Unoriented, thermally formed	Drawn Marlex 50 ^b
Tensile storage modulus	6.6×10^{10}	1.5×10^{10}	4.0×10^{10}
Tensile loss modulus	6.6×10^8	3.7×10^8	2.8×10^8

^a 30°C, 110 cps.

^b Data from Takayanagi et al.¹⁶

crystallized strand. This high modulus is due to both the high crystalline content and the orientation of these crystals.

CONCLUSIONS

Evidence has been presented to show that strands can be formed in the Instron rheometer that have a relatively high melting point, high modulus, and high oriented crystal content, combined with the property of being transparent. The distinctive engineering possibilities of these transparent strands indicate the need for additional research in this field. Our own work continues with the goals of developing a process for the production of a continuous strand with such properties as well as determining more about the crystal structure.

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