

Morphology of high-strength transparent polyethylene prepared under controlled conditions

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Highly oriented transparent polyethylene exhibiting a sixfold improvement in tensile yield strength has been prepared under ordinary pressures by shearing molten polyethylene between two concentric cylinders at rates between 0.4 and 10.0 sec^{-1} and at temperatures between 129 and 135 °C. Our results, based on observed changes in volume and shear stress, show that a transparent polyethylene sample was obtained only when crystallization occurred during the shearing process and further that transparency was greater for samples containing greater fractions of strain-crystallized polyethylene. The major factor controlling the onset of crystallization was found to be the amount of total strain which increased with increasing crystallization temperature. To understand its transparency, electron microscopy and x-ray studies were carried out on polyethylene of various degrees of transparency. Results showed that transparent polyethylene contains perpendicularly well-oriented lamellae (380–400-Å spacing) with limited lateral dimensions (400–2000 Å); whereas polyethylene of increasing opaqueness contains lamellae (285-Å spacing) oriented more or less perpendicular to the flow direction, but with much larger lateral dimensions (1000–10 000 Å).

INTRODUCTION

High-density polyethylene prepared under normal conditions is usually opaque, but recently transparent polyethylene has been prepared by means of special processing techniques.^{1–4} Southern and Porter^{1,2} found that under certain conditions the combined effects of strain and high pressure (1920 atm) near the entrance to the die in a capillary rheometer can result in a polyethylene strand with a transparent crystalline core 0.016 cm in diameter. The transparent polyethylene filament exhibited a high degree of *c*-axis orientation parallel to the capillary flow direction as determined by wide-angle x-ray diffraction. Subsequent morphological studies by Crystal and Southern⁵ have led to the suggestion of an extended chain-type crystalline morphology for these transparent polyethylene filaments.

Kwei *et al.*^{3,4} were able to produce a transparent polyethylene film about 0.0076 cm thick by permitting molten polyethylene to crystallize during rapid quenching at a rate of 10^4 °C/sec between two cold metal rollers rotating at a very high shear rate of about 10^5 sec^{-1} . The resultant polyethylene also exhibited a high degree of molecular orientation in the flow direction. In addition, they reported in comparison to an unoriented compression molded sample a fourfold increase in tensile breaking strength and a tenfold increase in Young's modulus along the rolling direction for their polyethylenes prepared under high-supercooling and high-shear conditions.

The exact cause and the primary processing variable(s) responsible for the transparency of these specially prepared polyethylenes remain unclear at the present time. We have obtained a high-strength transparent polyethylene prepared under normal but well-controlled conditions, thus allowing us to examine more closely the necessary variables responsible for transparent polyethylene and hopefully to study in detail both the morphology and the crystallization kinetics of such transparent materials. Our shearing apparatus also allows precise measurements of shear rate, shear stress, as well as crystallization temperature and changes in specimen volume during crystallization.

In this paper we wish to report the processing variables for the production of transparent polyethylene in a Couette-type shearing device and to describe the morphology responsible for its transparency. Some preliminary values of tensile properties of the transparent poly-

ethylene are also reported; the crystallization-rate studies will be reported elsewhere.

EXPERIMENTAL

The shearing device is shown in Fig. 1. It consists of two concentric cylinders made of beryllium copper. The ends can be sealed by means of silicone rubber O-rings. The specimen cavity has outside and inside diameters of 1.500 and 1.366 in., respectively, making a total sample thickness of about 0.067 in. (0.170 cm), and a length of 3.0 in. This shearing device is capable of subjecting the polymer specimen to a 400-psi hydrostatic pressure by actuating the air cylinder. The polymer can be uniformly sheared at constant rates up to 40 sec^{-1} by rotation of the inner cylinder. With these low shearing rates turbulent flow is generally avoided. Furthermore with this geometry, shear stress can be considered constant across the gap and can therefore be calculated from the measured force required to keep the outer cylinder stationary. End

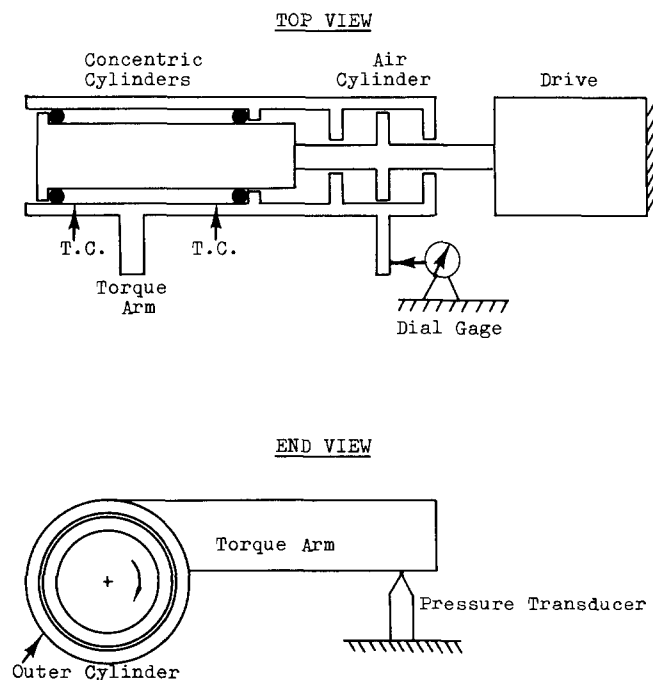


FIG. 1. Shearing device: Top view is a cross-sectional view of the concentric shearing cylinder and air cylinder. End view shows the concentric cylinder and torque arm used for measuring shearing faces.

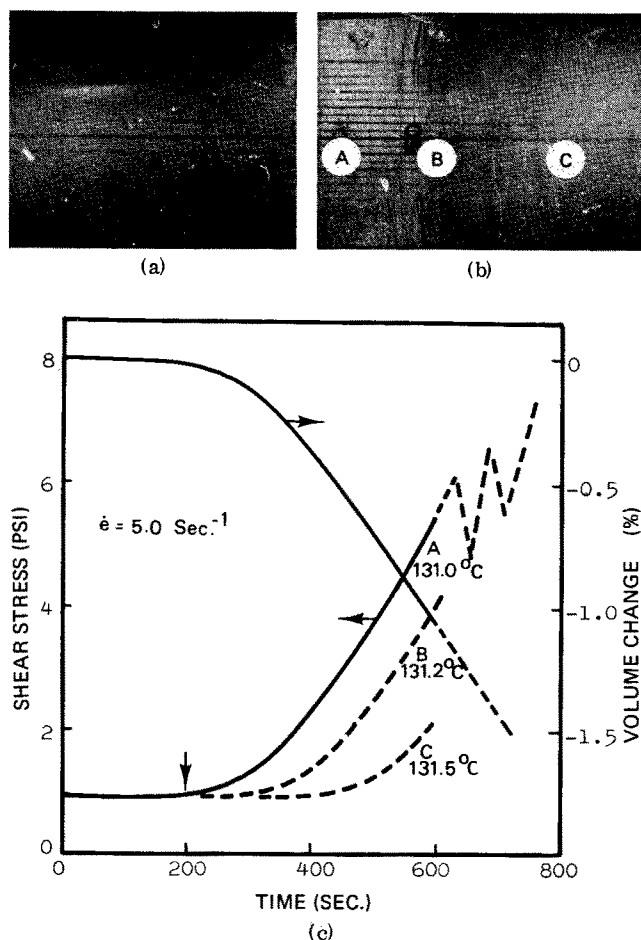


FIG. 2. (a) Compression-molded PE sample viewed lying on graph paper. (b) Strain-crystallized PE sample. Area A was sheared at 131.0°C , area B at 131.2°C , and area C at 131.5°C . (c) Shearing stresses and volume changes that occurred during the processing of the sample shown in (b).

effects were also considered, but calculations⁶ showed that end effects increased the shear stress by 3% at most and therefore were neglected. The volume change of the crystallizing specimen during the shearing process can also be determined with our experimental setup from measurement of the relative axial translation of the cylinders (see Fig. 1).

In a typical run a premolded cylindrical polyethylene sample is first loaded in the shearing device and any air remaining in the cavity is evacuated. The whole device is then inserted in an oven, temperature controlled at 160°C , at which temperature the polyethylene is melted. The shearing device is then quickly transferred to another oven at the desired constant shearing temperature, usually controlled between 129 and $137^\circ\text{C} \pm 0.1^\circ\text{C}$. Upon reaching temperature equilibrium (approximately 15 min) the polymer is sheared at the desired rate while the shear force and volume change are recorded. Although the polymer was sheared immediately upon reaching temperature equilibrium, identical results were obtained even when the polymer was maintained at that temperature for as long as 2 h. After a desirable amount of shearing, the sample is immediately quenched

in a bath of ice water at a cooling rate of approximately $200^\circ\text{C}/\text{min}$.

In order to obtain a clean and undistorted surface for electron microscopic studies, a layered composite of polyethylene and atactic polystyrene was prepared under the same conditions used for pure polyethylene in the following manner: A semicylinder of each polymer was placed in the shearing apparatus and sheared as described above for a single polymer. The laminar flow of the two polymers resulted in a layered transparent composite which could be readily delaminated and either the polyethylene and/or the polystyrene surface (usually both) was replicated for viewing in a JEM-6A electron microscope. Small-angle x-ray diffraction (SAXD) and wide-angle x-ray diffraction (WAXD) patterns were obtained with nickel-filtered CuK_α radiation and recorded photographically with a Rigaku Denki camera capable of $500\text{-}\text{\AA}$ resolution. Tensile tests were carried out on the samples in the flow as well as the transverse directions.

RESULTS

It was found that, with this experimental setup, transparent polyethylene could be easily obtained at shearing rates ($\dot{\epsilon}$) between 0.4 and 10.0 sec^{-1} and at temperatures between 129 and 135°C . A shear rate of 11.0 sec^{-1} was found to be the upper limit because of viscous heating, as observed with the thermocouples in contact with the

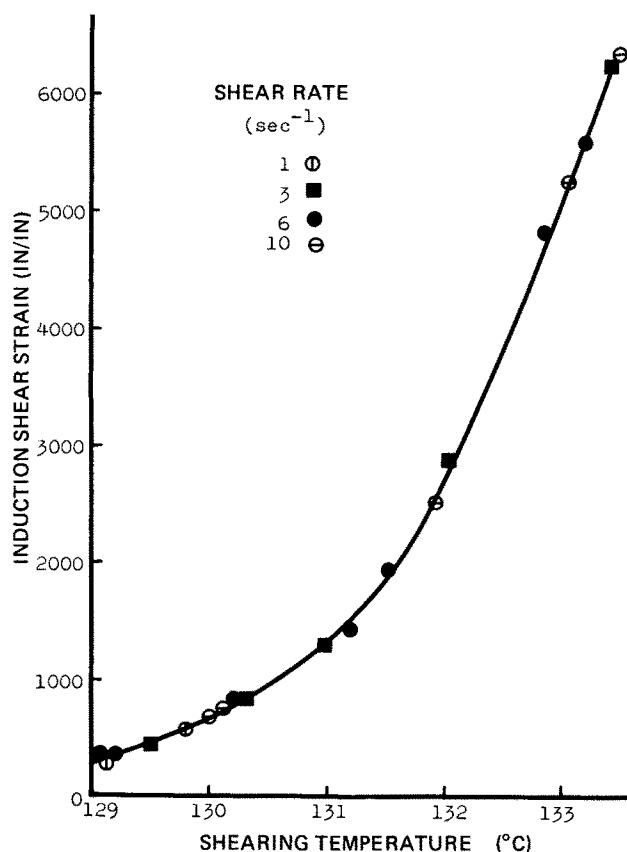


FIG. 3. Induction strain (induction time \times shear rate) vs shearing temperature for shear rates between 1.0 and 10.0 sec^{-1} .

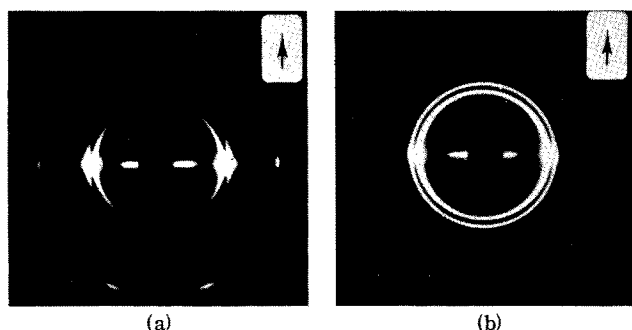


FIG. 4. WAXD patterns of the transparent (A) and translucent (B) areas of the sample shown in Fig. 2(b). In both cases the x-ray beam was directed parallel to the wall thickness of the cylindrical sample with the flow direction vertical.

polymer. At temperatures 135°C and above, the shearing force and volume were found to remain constant for all shearing times (1 h was the maximum time tested) and at all shear rates. This indicates that for all practical purposes crystallization could not be induced in this apparatus above 135°C. However, below 135°C the shear force and volume were found to remain constant for a limited time, after which changes occurred as shown for a typical run in Figure 2(c). This figure shows the results obtained for a sample sheared at 5.0 sec⁻¹ and 131°C. The shearing stress of the molten polyethylene was generally observed to rise immediately to about 1.0 psi and remain constant for 200 sec, after which it began to increase. At about 600 sec the stress began to oscillate, which was later established to be due to some slippage of the solidifying polymer between the concentric cylinders. At about the same time, the shear stress was observed to rise; the volume began to decrease and continued to decrease during the shearing process. Both the stress rise and the volume decrease are indicative that crystallization was occurring under shear. Similar results were obtained for samples prepared at other shear rates and temperatures. The 200-sec time interval was considered to be an induction time t_i for the onset of crystallization. For the sake of consistency, induction time was designated when a 1% stress was observed. This time was reproducible within 3% as determined by four different testings. It was found that the induction time increased with increasing shearing temperature, and with decreasing shearing rates. Moreover, it was found that there existed a unique induction strain ($t_i \dot{\epsilon}$) for the onset of crystallization. This induction strain was *dependent* upon shearing temperature, but *independent* of shear rate. These results are summarized in Fig. 3 which shows that the induction strain increases with shearing temperature.

The polyethylene samples prepared at temperatures above 135°C were opaque [Fig. 2(a)], similar to a compression-molded material, and showed no preferred molecular orientation according to WAXD patterns. However, each sample prepared below 135°C showed varying degrees of clarity; it ranged from being relatively transparent at one end (area A) to translucent (area B) to nearly opaque at the other end (area C) [see Fig. 2(b)]. The transparent region, even at a thickness 10 to 20

times greater than any of the previously reported transparent polyethylenes, appears similar in clarity. The cause for the range (A to C) in transparency in our samples was determined to be due to a $\frac{1}{2}$ °C temperature gradient that existed between the ends of the sample during shearing. The transparent region was always found to correspond to the cooler end where shear-induced crystallization first started. For example, in the sample prepared under conditions shown in Fig. 2(c) and pictured in Fig. 2(b), the transparent end (area A) was sheared at 131.0°C, the center (area B) at 131.2°C, and the least-transparent end (area C) at 131.5°C. Based on this observation it is apparent that once crystallization began the shear stress reported in Fig. 2(c) is only an average stress. Since crystallization starts at one end the large stress increase is due to this region. The stress would be even larger if the true stress of this end region had been recorded. Nevertheless, the stress before the onset of crystallization and the point at which crystallization began are both very well defined. When considering the temperature gradient, the state of stress and induction time at the center of the sample (area B) and at the other end (area C) could be more accurately represented by curves B and C, respectively, in Fig. 2(c), which were obtained in separate runs.

These curves show that the three regions started to crystallize at different times during the shearing process. Thus upon quenching at any instant, area A will have received more strain past the onset of crystallization than either area B or C. This suggests that trans-

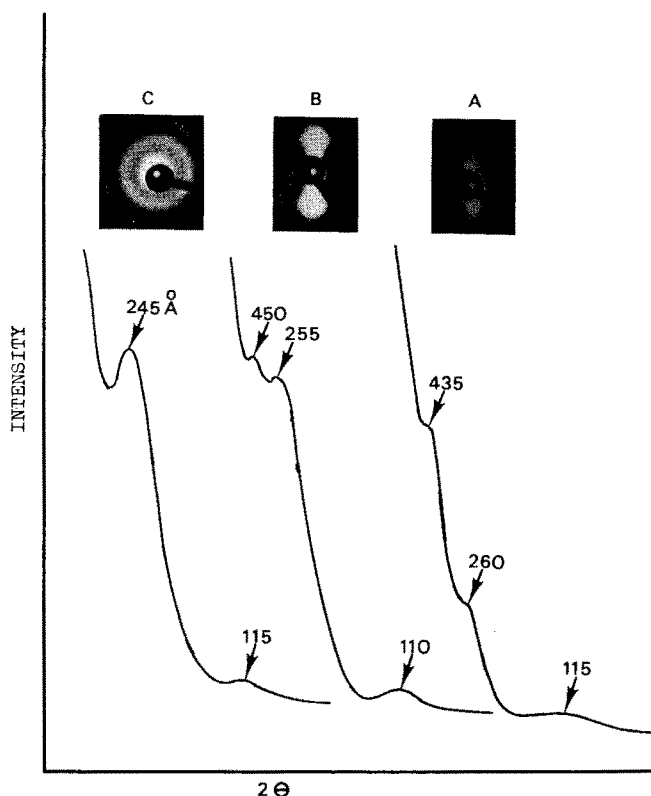


FIG. 5. SAXD patterns and respective densitometer traces of the three areas A, B, and C of the sample shown in Fig. 2(b). (Note curves have been shifted for clarification.)

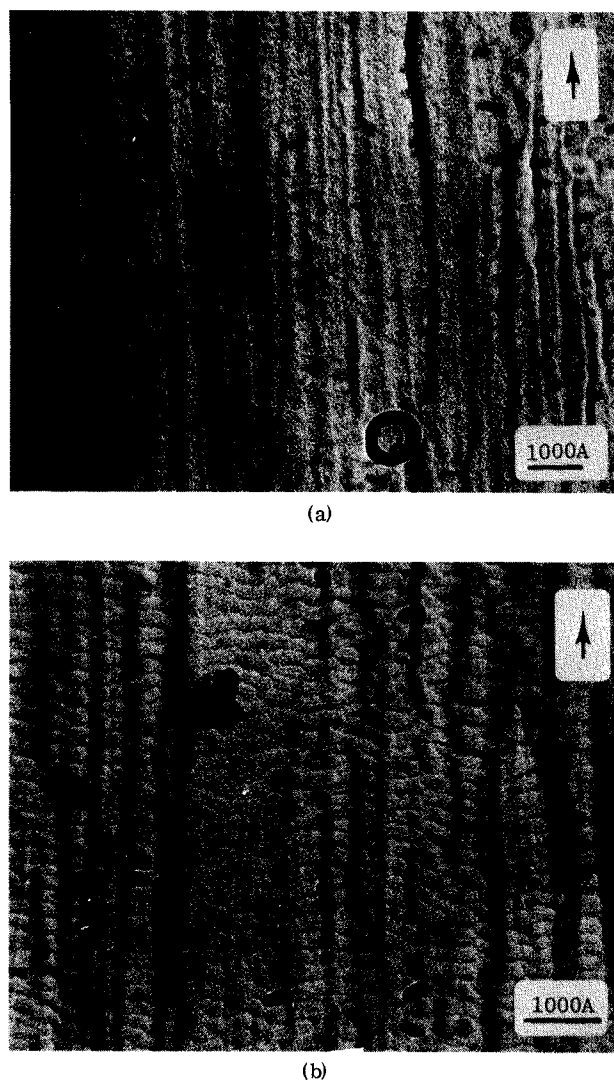


FIG. 6. Electron micrographs of area A and area B of a composite PE/APS sample prepared under conditions similar to the sample shown in Fig. 2(b).

parency is related to the amount of strain the polyethylene samples receives during the crystallization process and therefore related to the amount of strain-crystallized material.

X-ray studies

WAXD results showed that the molecules in the transparent region A are much better oriented with respect to the flow direction [Fig. 4(a)] than those in the less-transparent region B [Fig. 4(b)]. The results from (WAXD) studies are generally in agreement with those reported by Southern and Porter for their transparent polyethylene.

SAXD patterns obtained from the three regions (transparent, translucent, and opaque) are shown in Fig. 5 along with their microdensitometer traces which were obtained with a Joyce-Loebl densitometer. The unoriented pattern from the opaque material is identical to that of an ice-quenched compression-molded sample showing maxima at Bragg spacings at $245 \pm 10 \text{ \AA}$ and 115

$\pm 5 \text{ \AA}$. The translucent or the transparent material also shows these same spacings but in addition shows a $440 \pm 20\text{-\AA}$ spacing in the flow direction. The intensity of the nominal 250-\AA peak, however, is less intense for the transparent than the translucent material, but there is noticeably more arcing in this 250-\AA peak for the translucent than the transparent material.

WAXD and SAXD patterns for the single-polymer samples were identical to the patterns obtained from the composite samples. This suggests that the morphologies (including x ray and EM long periods) are similar, indicating that the electron microscopic studies are also representative of the single-polymer samples.

Electron microscopic studies

Electron micrographs of a polyethylene surface from a translucent and a transparent region are shown in Fig. 6 for a sample prepared under conditions similar to the sample shown in Fig. 2(b). For both regions lamellae were found to be oriented nearly perpendicular to the flow direction and to be about 220 \AA thick. The width of the lamellae ranged between 1000 and $10\,000 \text{ \AA}$ for the translucent material but only between 400 and 1000 \AA for the transparent material. In addition, the lamellae varied from being perpendicular to the flow direction by as much as 35° for the translucent material but varied less than 10° for the transparent material. A long period in the flow direction was obtained by averaging between 50 and 100 periodic striations in well-defined areas. The translucent material showed predominantly a $240\text{--}285\text{-\AA}$ -long period, whereas the transparent material showed predominantly a $380\text{--}460\text{-\AA}$ -long period, although a few regions containing a 285-\AA -long period were evident. These results are summarized in Table I. The "lamellae" were generally not as well defined in the transparent material and they appeared to be aligned into narrow fibrils in the flow direction, although no extended features were observed.

Tensile studies

The transparent material when drawn in the flow direction did not neck but failed in brittle fracture at 22% elongation at $18\,000 \text{ psi}$ and exhibited a modulus of $16 \times 10^4 \text{ psi}$. The tensile strength and modulus are much higher than those obtained from a compression-molded polyethylene, which were measured to have a tensile yield strength of 3000 psi and a modulus of $3.6 \times 10^4 \text{ psi}$.

TABLE I. Morphological features of strain-crystallized polyethylene.

	Area A	Area B
Lamellae width (\AA)	$400\text{--}2000$	$1000\text{--}10\,000$
Lamellae thickness (\AA)	220	220
Maximum lamellae angle from normal to flow (deg)	± 10	± 35
Long-period (\AA)		
electron microscopy	$380\text{--}460^a$	$240\text{--}285^a$
SAXD	$450, 225, 110$	$435, 260, 115$
Comment	Ill-defined lamellae	Distinct lamellae

^aA major portion of the sample shows this long period.

In comparison, Kwei *et al.*⁴ obtained a tensile strength of 15 000 psi for their transparent polyethylene. It was difficult to measure the tensile strength in the traverse direction due to its extreme brittleness in that direction.

DISCUSSION

The results suggest that a necessary, and probably the only, requirement for producing a transparent polyethylene in our concentric shearing apparatus is that crystallization takes place during the shearing process. High pressures, high shearing, and cooling rates were not found to be necessary requirements. Our polyethylene crystallized with a high degree of transparency even at low shear rates approaching 0 sec^{-1} , at constant temperatures approaching the melting point, and at low hydrostatic pressures of less than 400 psi. However, at low shear rates and high temperatures large shearing times, as suggested by Fig. 3, were necessary in order to attain the critical strain required for strain-induced crystallization. Crystallization did not begin until a critical induction strain, which is dependent only on shearing temperatures, was attained. It is interesting to note that the critical strain which brings about a specific crystalline morphology can be met at any shear rate providing the shearing time is such that the critical strain can be reached. The critical strain is the imposed total strain and most probably does not represent molecular strain directly, although the two may be related. Analyses of the critical strain with respect to strain-induced crystallization kinetics will be reported elsewhere.

Our results indicate that the degree of transparency is related to the amount or fraction of material that crystallizes during the shearing action. This was shown by the fact that the most transparent region had essentially completed its crystallization while the less transparent regions had not, but completed its crystallization subsequent to the shearing process. Consequently two morphologies may exist in the final sample; their relative amounts depend on the processing conditions. One morphology develops during the shearing process and is related to transparency; while a second morphology develops during the static cooling process and is responsible for the translucent or opaque appearance.

The two morphologies present in polyethylene samples of varying degrees of clarity were brought clear by our SAXD and electron microscopy results. The SAXD patterns showed a 435-Å Bragg spacing present only in samples that had improved clarity being brought about by at least some partial crystallization during the shearing process. Electron microscopic studies of the transparent samples revealed predominantly a fibrous texture containing well-aligned and oriented lamellae having narrow widths between 400 and 2000 Å and a long period of 380–460 Å in good agreement with the SAXD long period, whereas the less-transparent samples were seen to consist predominantly of less well-aligned, but much better defined, lamellae having widths between 1000 and 10 000 Å and a smaller long period of 285 Å, also in good agreement with SAXD results.

The difference in clarity appears to be directly related to the differences between these two observed morphologies, these differences being the longitudinal periodicity, the lateral size, and the orientation of the lamellae. The transparent material generally consists of anisotropic scattering elements (lamellae) having dimensions [approximately $400 \times (400\text{--}2000 \text{ Å})$] less than the wavelength of light, whereas the less-transparent material also consists of thin lamellae (300 Å thick) but whose lateral dimensions (1000–10 000 Å) are much greater than the wavelength of light. In addition, the narrower lamellae also have much less fluctuation in orientation than the wider lamellae (20° vs 35°). Either (or both) of these observations could account for their transparency. For example, Stein and Prud'homme⁷ had suggested that the transparency in polyethylene prepared by Kwei *et al.* may be accounted for alone by assuming a minimal fluctuation in orientation of anisotropic volume elements of sizes even larger than the wavelength of light. Our studies appear to indicate that the size of the scattering element may also be of a major contributing factor.

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