

Orientation in Extruded Polyethylene Films

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INTRODUCTION

Polyethylene film prepared by extrusion of the molten polymer through a die, followed by quenching in air or water, shows an unexpected orientation of the crystalline regions. One might expect that as the melt issues from a die, the polymer chains would become at least partially oriented in the direction of flow (commonly referred to as the machine direction, M.D.). Then, after crystallization had occurred, the crystalline regions would be preferentially oriented with the *c*-axis of the crystals parallel to the machine direction, since this axis is parallel to the polymer chains. This simple supposition has been found incorrect for extruded polyethylene film or for samples prepared under similar conditions of flow and crystallization.

Concurrent with our studies on orientation of the crystalline and amorphous regions in extruded polyethylene films, results were reported which show that in extruded polyethylene films the crystalline regions are preferentially oriented with their *c*-axes perpendicular to the machine direction; the *a*-axes of the crystallites are preferentially oriented parallel to the machine direction.¹ Also, observations by the same investigators on the dichroism of the infrared absorption bands at 13.70 and 13.88 μ and optical birefringence were interpreted to mean that the polymer chains in the amorphous regions are oriented perpendicular to the orientation of the chains in the crystalline regions. In other words, while the *a*-axis orientation of the crystallites makes the orientation of polyethylene chains in the crystalline regions perpendicular to the machine direction, chains in the amorphous region are oriented parallel to the machine direction. It was further inferred that a higher degree of orientation of the crystallites is accompanied by a higher degree of orientation of the amorphous regions, and that in addition to *a*-axis orientation of the crystalline regions the *c*-axes of the crystallites show also a preference to lie in the plane of the extruded film. The simultaneous orientation of the *a*- and *c*-axes of crystallites in polyethylene films are termed "double orientation."

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Herein are reported the results of our studies on orientation of the crystalline and amorphous regions in extruded polyethylene films, and in films which have been cold drawn about 200%. These studies support the *a*-axis orientation in extruded polyethylene film, but show that the amorphous regions are either unoriented or possess only slight orientation; furthermore, in the latter case, the chains are also oriented perpendicular to the machine direction. We have found no evidence for double orientation in extruded polyethylene films. In films which have been stretched about 200% after extrusion, both the crystalline and amorphous regions are oriented. In the stretched film samples, the polymer chains in both the crystalline and amorphous regions are preferentially oriented parallel to the stretching direction. A possible mechanism by which *a*-axis orientation in extruded polyethylene film may arise and a convenient x-ray diffractometer method for determining the relative degree of *a*-axis orientation are given.

EXPERIMENTAL

Materials

All of the polyethylene films used in this study were made by commercial melt extrusion equipment from high-pressure polyethylene, DYNH-3, supplied by the Bakelite Company, Division of Union Carbide Corporation. Polyethylene film samples made by both blown tubular extrusion² and flat film extrusion³ methods were chosen for study. The thickness of the film samples varied from 1.5 to 2.0 mils. The stretched film samples were made by slowly extending to about 200% a rectangular extruded film sample clamped between the jaws of an Instron tensile tester (manufactured by the Instron Engineering Corp. of Quincy, Mass.).

Techniques for Studying Orientation in Polyethylene Films

(A) Orientation of Crystallites in Polyethylene Films

The two important techniques that may be used for establishing the orientation of the crystalline regions are x-ray diffraction and dichroism of in-

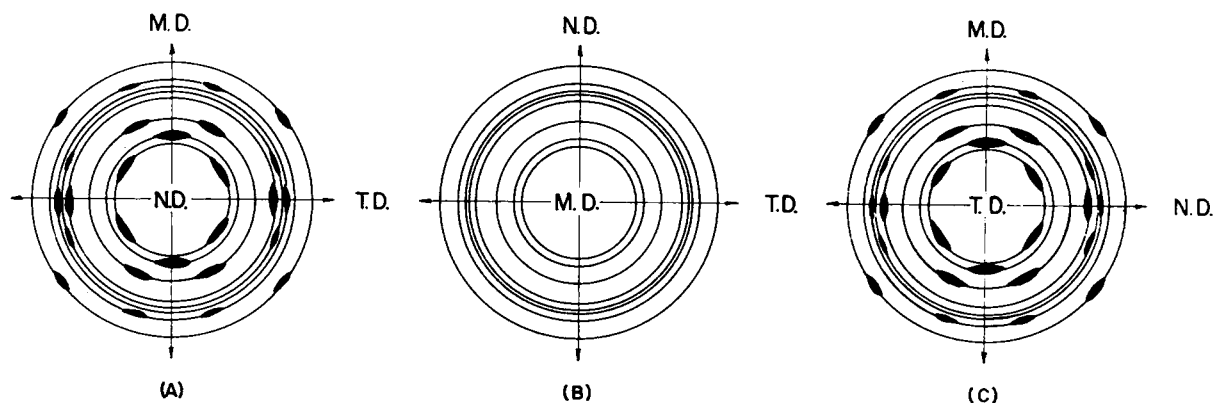


Fig. 1. X-ray diffraction patterns for *a*-axis orientation of polyethylene crystallites. X-ray beam (A) normal to the plane of the film (N.D.), (B) parallel to the machine direction (M.D.), (C) parallel to the transverse direction (T.D.). The reflections from the center are from (110), (200), (210), (020), (120), (011), (310), and (220) planes.

frared absorption. To appreciate the interpretation of the results from these methods in terms of the orientation, it is helpful to consider two limiting cases of orientation in polyethylene films: (1) *a*-axis orientation, according to which the *a*-axes of the crystalline regions are preferentially oriented parallel to the machine direction, with the *b*- and *c*-axes in a plane perpendicular to the machine direction; and (2) *c*-axis orientation, according to which the *c*-axes of the crystallites are preferentially oriented parallel to the machine direction (or to the stretching direction in the study of stretched films). The expected x-ray diffraction patterns for the *a*- and *c*-axis orientations are shown in Figures 1 and 2, respectively, for the cases in which the x-ray beam is (A) normal to the plane of the film, (B) parallel to the machine direction, and (C) parallel to the transverse direction (the direction perpendicular to the machine direction in the plane of the film).

The use of polarized infrared radiation for the study of orientation is particularly suitable for

polyethylene films. Of special importance for this purpose is the doublet with absorption peaks at 13.70 (730 cm^{-1}) and 13.88 μ (721 cm^{-1}) in the absorption spectrum of polyethylene.⁴⁻⁷ When polyethylene melts, the doublet is replaced by a broad band centered at 13.88 μ .⁴⁻⁶ The absorption band at 13.88 μ observed in molten polyethylene has been assigned to the rocking of hydrogen atoms in the methylene groups of polyethylene chains.⁸ This vibration was found to be perpendicular to the polymer chain axis from studies by polarized infrared radiation.^{9,10} On crystallization, splitting of the single absorption band at 13.88 μ into a doublet absorbing at 13.88 and 13.70 μ occurs because of the interaction of the methylene groups in the crystalline regions.^{11,12} Thus, the absorption at 13.70 μ is from the crystalline regions alone, while both the crystalline and amorphous regions contribute to the absorption at 13.88 μ .

The absorptions at 13.70 and 13.88 μ from the crystalline regions of polyethylene have been shown to correspond to the dipole change vectors which

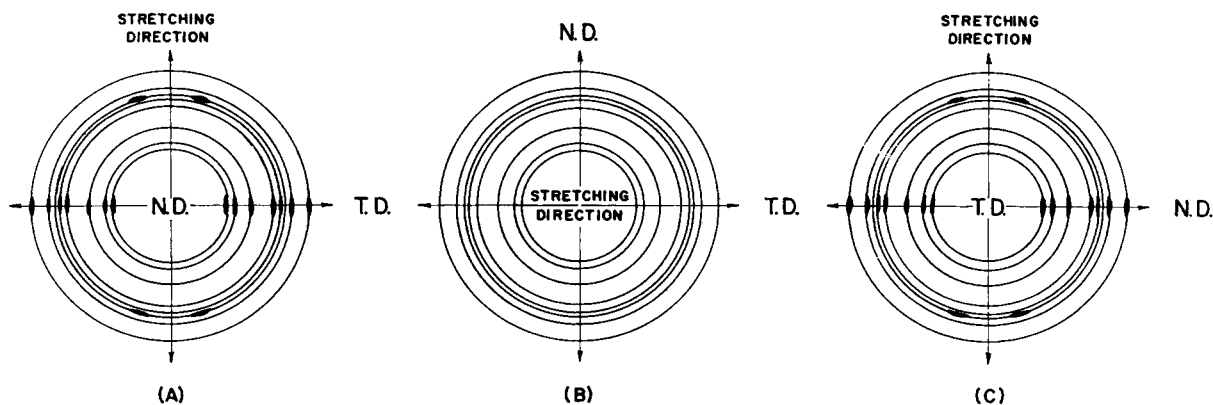


Fig. 2. X-ray diffraction patterns for *c*-axis orientation of polyethylene crystallites. X-ray beam (A) normal to the plane of the film (N.D.), (B) parallel to the stretching direction, (C) parallel to the transverse direction (T.D.). The reflections from the center are from (110), (200), (210), (020), (120), (011), (310), and (220) planes.

TABLE I
Dichroism of the Absorption Bands at 13.70 and 13.88 μ
for a - and c -Axis Orientations of Polyethylene Crystalline Regions

Orientation in crystalline regions	Electric vibration vector \vec{E} with respect to machine or stretching direction	Absorption at 13.70 μ	Absorption at 13.88 μ	Type of dichroism
a -Axis parallel, b - and c -axes perpendicular to machine direction	\vec{E} parallel to machine direction	Maximum	Minimum	Parallel for 13.70 μ band, and perpendicular for 13.88 μ band
	\vec{E} perpendicular to machine direction	Minimum	Maximum	
c -Axis parallel to machine or stretching direction; a - and b -axes distributed about c -axis	\vec{E} parallel to stretching or machine direction	Minimum	Minimum	Perpendicular dichroism for both 13.70 and 13.88 μ bands
	\vec{E} perpendicular to stretching or machine direction	Maximum	Maximum	

are parallel to the a - and b -axes of the crystal unit cell, respectively.^{5,11-14} The absorption of infrared radiation is proportional to the scalar product of the vectors, \vec{E} and \vec{D} , where \vec{E} is the electric vibration vector of the polarized infrared radiation and \vec{D} is the dipole change vector corresponding to the molecular motion which gives rise to the absorption. Therefore, when the orientation is such that the crystalline regions are preferentially oriented with their a -axes parallel to the machine direction, the 13.70 μ band will exhibit maximum absorption for the radiation which has its vibration vector parallel to the machine direction, as compared to the absorption for the radiation which has its vibration vector perpendicular to this direction. Therefore, for a -axis orientation of the crystalline regions in the film, the 13.70 μ band will exhibit parallel dichroism. From similar considerations it can be shown that the 13.88 μ band will show perpendicular dichroism for the a -axis orientation of the crystallites, i.e., maximum absorption will occur for radiation having the electric vibration vector perpendicular to the machine direction. The perpendicular dichroism of the 13.88 μ absorption band thus does not necessarily imply orientation of the chains in the amorphous regions of polyethylene, but can arise from a -axis orientation of the crystallites alone. The conclusion in the studies mentioned previously,¹ based on the perpendicular dichroism of the 13.88 μ band, that the chains in the amorphous regions are oriented parallel to the machine direction, i.e., perpendicular to the orientation of the chains in the crystalline regions of the film, seems therefore of doubtful validity.

For the c -axis orientation of the crystalline regions, the a - and b -axes will be perpendicular to the machine direction, and both the 13.70 and 13.88 μ bands will exhibit perpendicular dichroism. In Table I are summarized the dichroic properties of the 13.70 and 13.88 μ bands for the a - and c -axis

orientation of the crystalline regions in polyethylene film.

(B) Orientation of Chains in the Amorphous Regions

The infrared absorption band at 13.88 μ is not well suited for the study of orientation of chains in the amorphous regions, since both the amorphous and crystalline regions contribute to absorption at this wavelength. This is particularly true if there be appreciable orientation of the crystalline regions and only slight orientation of the chains in the amorphous regions. There are, however, other absorptions in the infrared spectrum of polyethylene which arise from the amorphous regions alone. These absorptions are at 7.68 μ (1300 cm.^{-1}), 7.45 μ (1340 cm.^{-1}), and 7.39 μ (1355 cm.^{-1}). These absorptions have been assigned to the deformation of methylene groups. Of these, the bands at 7.39 and 7.45 μ show parallel dichroism,^{11,15} i.e., if the chains in the amorphous regions are oriented, the absorption for radiation polarized parallel to the direction of the polymer chains will be a maximum.

Optical birefringence is another method which may be used for obtaining information regarding the orientation of chains in the amorphous regions. As discussed below, however, optical birefringence is of little help when only a small degree of orientation of the amorphous regions is present. In any case, the contributions to birefringence from the orientation of the crystalline regions is a complication which has to be taken into account before birefringence results can be used to obtain information regarding the orientation of the amorphous regions.

RESULTS AND DISCUSSIONS

(A) Orientation in Extruded Polyethylene Films and in Films Stretched Approximately 200%

Figure 3 is an x-ray diffraction picture of an extruded polyethylene film, and Figure 4 is the cor-

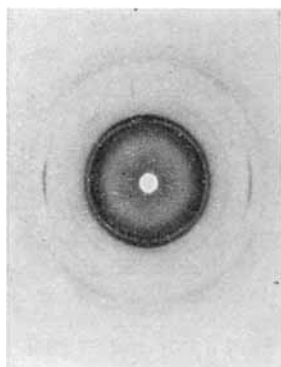


Fig. 3. X-ray diffraction picture of polyethylene film (x-ray beam perpendicular to the plane of the film sample, and machine direction vertical in the figure).

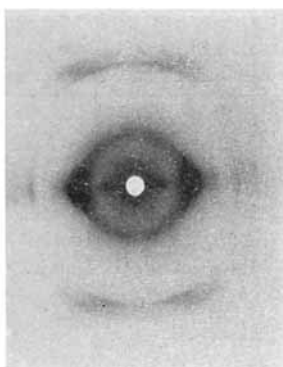


Fig. 4. X-ray diffraction picture of polyethylene film stretched 200% in the machine direction (x-ray beam perpendicular to the plane of the film sample, and machine direction vertical in the figure).

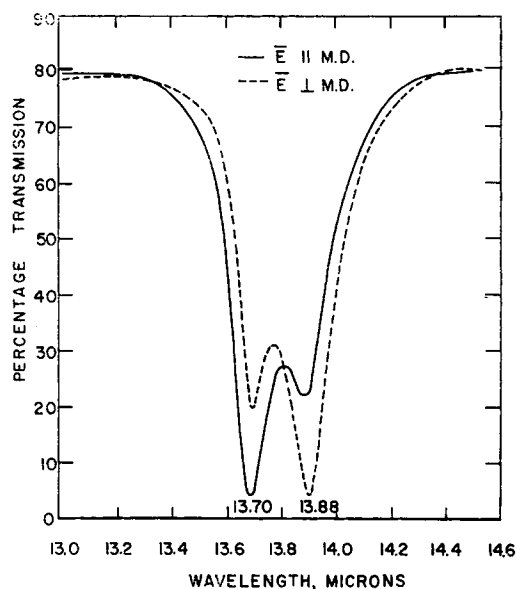


Fig. 5. Polarized infrared spectra of extruded polyethylene film, 13–14.6 μ .

responding picture of the same film after having been stretched approximately 200% in the machine direction. These pictures were taken with a flat-

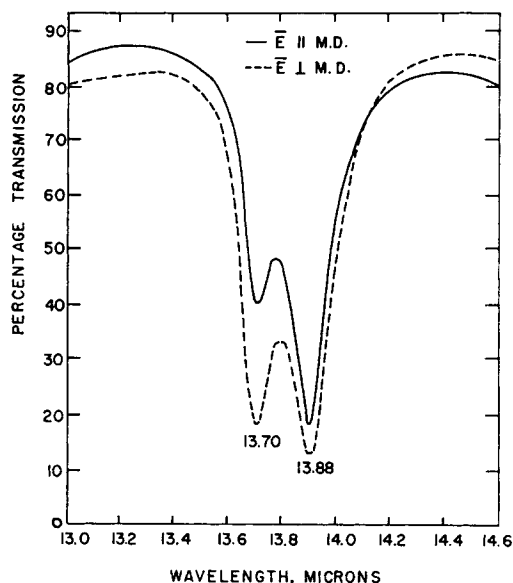


Fig. 6. Polarized infrared spectra of stretched polyethylene film, 13–14.6 μ .

plate camera, with the x-ray beam normal to the plane of the film. The diffraction patterns with the x-ray beam parallel to the transverse direction (T.D.) were similar to Figures 3 and 4 for the extruded and stretched films, respectively. The diffraction patterns with the x-ray beam parallel to the machine direction in the case of extruded films, and to the stretching direction in the case of stretched films, had complete rings for the various reflections.

Figures 5 and 6 are respectively the infrared spectra obtained with polarized radiation in the 13 to 14.6 μ region for an extruded polyethylene film, and for the same film after having been stretched approximately 200%.

The x-ray diffraction photograph, Figure 3, and the dichroism of the 13.70 and 13.88 μ infrared absorption bands, Figure 5, show that in the extruded polyethylene film the crystallites are oriented with their *a*-axes parallel to the machine direction. In polyethylene films which have been stretched about 200% in the machine direction, both the x-ray

TABLE II
Dichroism of Absorption Bands at 7.39 and 7.45 μ
for Extruded and Stretched Polyethylene Films

Polyethylene film	Absorbance at 7.39 μ		Absorbance at 7.45 μ	
	\bar{E} parallel to machine or stretching direction	\bar{E} perpendicular to machine or stretching direction	\bar{E} parallel to machine or stretching direction	\bar{E} perpendicular to machine or stretching direction
As extruded	0.191	0.200	0.114	0.120
Stretched	0.117	0.084	0.070	0.055

diffraction pattern, Figure 4, and the dichroism of the 13.70 and 13.88 μ bands, Figure 6, show that the crystallites are oriented with their c -axes parallel to the stretching direction. Thus, during the stretching of extruded polyethylene film, the a -axis orientation of the crystallites in the film changes to c -axis orientation. The intermediate stages involved in going from the a -axis orientation to c -axis orientation on stretching extruded polyethylene films will be discussed in a subsequent paper.

To study the orientation of chains in the amorphous regions of the films, infrared absorption spectra with polarized radiation were obtained in the 7–8 μ region. In Table II are given the absorbance ($\log I_0/I$) at 7.39 and 7.45 μ for an extruded and a stretched polyethylene film calculated from the spectra obtained with infrared radiation polarized parallel and perpendicular to the machine (or stretching) direction. The extruded films show a slight perpendicular dichroism for both the 7.39 and 7.45 μ absorptions. For the stretched film, the 7.39 and 7.45 μ absorptions show parallel dichroism. Thus, in extruded films, the chains in the amorphous regions, contrary to earlier studies,¹ are oriented perpendicular to the machine direction. This orientation of the amorphous regions in extruded polyethylene films is only slight, as evidenced by the small difference in the values of absorbance with infrared radiation polarized parallel and perpendicular to the machine direction. In stretched films there is appreciable orientation of the amorphous regions, and the chains in these regions are oriented parallel to the stretching direction.

(B) Comparative Study of Crystalline Orientation of Polyethylene Films

The crystalline orientation and optical birefringence of ten polyethylene films were studied to establish: (1) whether the same type of crystalline orientation is present in all samples of melt-extruded polyethylene films; (2) whether there are any differences in the extent (degree) of orientation in the films; and (3) the dependence of birefringence on the degree of crystalline orientation. Of the films studied, seven were obtained by the blown tubular extrusion method and three were obtained by the flat film extrusion method.

All of the extruded films gave x-ray diffraction photographs characteristic of a -axis orientation. Also, all films showed parallel dichroism of the 13.7 μ band and perpendicular dichroism of the 13.88 μ band.

To determine the relative degree of a -axis orientation in these film samples, the ratio of the merid-

ional intensities from the (200) and (110) planes, and the dichroism of the 13.7 μ absorption band were measured.

The ratio of the x-rays diffracted from the (200) and (110) planes was determined for each sample by the Norelco x-ray diffractometer (equipped with scanning Geiger tube and goniometer, supplied by the North American Philips Company, Inc., Mount Vernon, New York). The sample holder in the diffractometer was clamped in a position 90° from the position ordinarily used for reflection of x-rays from powder samples. The film samples of 10–15 mils thickness (made by stacking film pieces of 1.5 mil thickness) were clamped with the machine direction aligned vertically with respect to the sample holder. Times for 3200 counts were measured with the scanning goniometer set at the diffraction angles (2θ) corresponding to the (110) and (200) reflections from polyethylene. The times required for 3200 counts were proportional to the meridional intensities of the x-rays diffracted from the (110) and (200) planes in the diffraction pattern with the x-ray beam perpendicular to the plane of the film and the machine direction parallel to the meridian of the diffraction pattern. The higher the ratio of the meridional intensities from the (200) and (110) reflections, the higher is the degree of orientation of the a -axes of the crystallites parallel to the machine direction.

The dichroism of the 13.70 μ band was measured by obtaining the absorption curves of the films with polarized infrared radiation. Absorption curves in the region of 12.9–14.50 μ were made with infrared radiation polarized both parallel to the machine direction and perpendicular to the machine direction. The doublet in this region was resolved into peaks with maxima at 13.70 and 13.88 μ , assuming the bilateral symmetry of the 13.88 and 13.70 μ peaks and the background as continuous from 12.90 to 14.50 μ . Taking account of the variation in the background, a symmetrical absorption band with absorption peak at 13.88 μ was first constructed, and the contribution of this band to the absorption between 12.90 and 13.70 μ was then subtracted. The ratio of the specific absorption coefficients, k_{\parallel}/k_{\perp} , at 13.70 μ , measured from the resolved curves obtained with infrared radiation polarized parallel to and perpendicular to the machine direction, is a measure of the parallel dichroism of the 13.70 μ band. The higher the dichroic ratio, k_{\parallel}/k_{\perp} , the higher is the degree of orientation of the a -axes of the crystalline regions in the film. The ratio of the specific absorption coefficients at 13.88 μ , from the resolved curves obtained with the infrared radiation perpendicular and parallel to the

TABLE III
Comparative Evaluation of Crystalline and Molecular Orientation in Polyethylene Films
by X-Ray Diffraction, Polarized Infrared Absorption, and Optical Birefringence

Sample No.	Extrusion method and nominal thickness, inch	Ratio of intensities at meridian, of (200) and (110) reflections (I_{200}/I_{110})	Dichroism of infrared absorption		Birefringence $\times 10^3$
			Parallel at 13.7 μ	Perpendicular at 13.9 μ	
1	Tubular, 0.0015	3.60	2.50	2.41	+0.2
2	Tubular, 0.0020	2.48	1.47	1.82	+3.0
3	Tubular, 0.0020	2.87	1.55	1.76	+2.3
4	Tubular, 0.0015	3.76	2.35	2.97	+0.4
5	Tubular, 0.0020	2.39	1.48	1.43	+2.1
6	Tubular, 0.0020	2.90	2.07	2.48	+0.9
7	Tubular, 0.0015	2.03	1.74	1.55	+1.7
			2.26	1.63	
8	Flat film, 0.0015	0.92	1.31	1.33	+0.6
9	Flat film, 0.0015	0.66	1.15	1.35	+2.1
10	Flat film, 0.0015	0.48	1.17	1.12	+0.3

machine direction, was also measured for each film to obtain the perpendicular dichroism of the absorption at 13.88 μ . Though the perpendicular dichroism of each of the polyethylene films indicates a -axis orientation of the crystallites, it is not a measure of the degree of a -axis orientation because of the additional contribution to absorption at 13.88 μ by the amorphous regions.

The optical birefringence of the films was obtained by measuring the optical retardation (in millimicrons) by means of the polarizing microscope, using a calibrated quartz wedge and dividing the retardation by the thickness of the film (also in millimicrons). Birefringence measured with the incident polarized light normal to the plane of the film is the difference in refractive indexes along the two perpendicular directions in the plane of the film. All the films showed positive birefringence, i.e., the direction of higher refractive index was parallel to the machine direction. In some films, however, there were microscopic areas which showed negative birefringence (higher refractive index perpendicular to the machine direction in the plane of the film).

Table III presents the x-ray diffraction, polarized infrared absorption, and birefringence data. It will be noted from the results in Table III that considerable variation with respect to relative degree of a -axis orientation is present among these polyethylene films. The ratio of the intensities of x-rays diffracted from (200) and (110) planes of polyethylene samples showing no orientation of crystallites is approximately 0.25. In Table III the ratio of the intensities at the meridian from the (200) and (110) planes is greater than 0.25, signi-

fying a -axis orientation in all film samples. The values of this ratio range from 0.48 to 3.76 for different films. The higher this ratio, the higher is the degree of a -axis orientation. The dichroic ratios at 13.70 μ show a similar variation among films with respect to the degree of a -axis orientation. Higher values of the dichroic ratio at 13.70 μ signify greater a -axis orientation. The dichroic ratios for the films reported in Table III range from 1.15 to 2.93. Higher ratios of the x-ray intensities at the meridian from (200) and (110) reflections are, within experimental error, associated with higher dichroic ratios of the 13.70 μ absorption band.

Optical birefringence, on the other hand, seems to show no correlation with the degree of crystalline orientation in these films. Also, all films showed positive birefringence, i.e., the higher of the two refractive indexes in the plane of the films was parallel to the machine direction. This seems to be in contradiction to the a -axis orientation of crystallites present in a matrix of amorphous regions which are either unoriented or show only slight orientation with chains perpendicular to the machine direction. The c -axis of the polyethylene crystals is the axis of greatest polarizability, and the polymer chains in the amorphous regions also have their greatest polarizability along the chain direction.¹⁶⁻¹⁹ In polyethylene films in which the a -axes of the crystalline regions are preferentially oriented parallel to the machine direction, and chains in the amorphous regions are either unoriented or show slight orientation perpendicular to the machine direction, it would be expected that a lower refractive index would be exhibited

parallel to the machine direction than in the transverse direction; that is to say, extruded polyethylene films would be expected to show negative birefringence. Thus the positive birefringence observed in polyethylene films appears to contradict this expectation. However, the small positive birefringence observed should be interpreted with caution before concluding that optical birefringence evidence is contrary to that shown by x-ray diffraction and polarized infrared absorption, because of the multiplicity of effects that may contribute to the birefringence of films. Some of the factors, other than orientation, that may affect birefringence of films are: (1) form birefringence^{20,21} which arises purely from the anisotropic shape of regions of one refractive index embedded in a matrix of another refractive index; (2) the introduction of stresses, microvoids, or microcracks during crystallization of the films; and (3) the branched structure of polyethylene. Branch points are sites where discontinuity in the ordering of chains into crystallites occurs. When the chains in the crystallites pack preferentially perpendicular to the machine direction, the short branches containing the methyl groups may be aligned parallel to the machine direction. The polarizability of the methyl group is large, and even a small degree of alignment of the methyl groups parallel to the machine direction will tend to make the birefringence of the films positive.

(C) Double Orientation of Crystallites in Polyethylene Films

X-ray diffraction and infrared studies discussed above show only that in the melt-extruded films the *a*-axes of the crystallites are preferentially aligned parallel to the direction of extrusion (machine direction), but leave unanswered the question whether the *b*- and *c*-axes are randomly oriented about the machine direction or show preference for certain positions with respect to the plane of the film. This additional orientation of *b*- and *c*-axes about the machine direction may be termed secondary or double orientation. The latter term is preferred because the word secondary conveys the impression that this type of orientation is not so important as the orientation of the *a*-axes, and this need not be true. In fact, any preferential orientation of the *b*- and *c*-axes may have important effects on the properties of the films. A careful study to establish the presence of any double orientation in the polyethylene films was deemed necessary, not only to determine the exact type of orientation of the crystallites, but also to study any differences with respect to double orientation be-

tween polyethylene films obtained from the flat and tubular extrusion methods.

The Weissenberg moving film method²² offers a suitable technique for the study of double orientation in polyethylene films. Samples for the Weissenberg camera studies were made by stacking polyethylene films and cutting a rectangular parallelepiped such that the long edges of the sample were parallel with the machine direction and the cross section was square. (Ideally the cross section should be circular to avoid any absorption errors from a sample of square cross section, but this could not be accomplished in the case of samples prepared from polyethylene films.) The samples were made approximately 2 cm. in length with square cross sections of approximately 2×2 mm. The samples were mounted so as to make the machine direction (the length of the sample) the axis of rotation. The Weissenberg pictures were made between 0 and 180° of rotation. Reflections from zero, first, and second layers were obtained. The intensities were found to be uniform for all reflections from both the flat and tubularly extruded films. If any double orientation had been present, discontinuities in the intensities of various reflections should have been observed. The absence of any such variation in the intensities of the various reflections shows that no double orientation is present either in the flat or tubularly extruded films.

(D) Possible Mechanisms of the a-Axis Orientation in Melt-Extruded Polyethylene Films

It is not yet clearly understood how the *a*-axis orientation in extruded polyethylene films is brought about. It has been suggested that this orientation may arise from the stretching and relaxation of polyethylene film during extrusion. This conclusion was based on the results and interpretation of studies of stretching and relaxation of polyethylene filaments.^{23,24} Unfortunately, in the interpretation of the results,²³ the crystal direction was interchangeably used with reciprocal lattice direction (refer to the discussion of the geometry of the reciprocal lattice^{25,26}). This confusion, in spite of the subsequent correction in the value of the angle between (001) and (011) reciprocal lattice directions,^{27,28} has made quite ambiguous the discussion of the orientation effects during stretching and relaxation of polyethylene. Thus, the mechanism for the *a*-axis orientation in films of polyethylene, based on the published results concerning stretching and relaxation of filaments, is open to question.

Two other plausible mechanisms are conceivable

by which *a*-axis orientation of polyethylene crystallites may be achieved.

In the molten polyethylene, the polymer molecules are tangled and intertwined, but because of the shearing stresses present during extrusion, some alignment of chain segments may occur. As the polymer melt cools there will be no tendency for the crystals to grow in the direction of extrusion, because it is unlikely that any appreciable lengths of chains of neighboring molecules will be present in the exact spatial arrangement necessary for crystallization. Crystal growth along the direction of

of a bottle brush. The length of the brush in this analogy is in the machine direction. Figure 7A shows schematically the growth of crystallites in flowing molten polyethylene. Since these needle-like crystallites are formed in a flowing matrix, they will tend to become aligned with the longer dimension parallel to the direction of flow. Thus, the crystallites which initially grew at right angles to the direction of flow may now slue round in the flowing matrix and line up with their long dimension parallel to the direction of flow. Schematically, the crystallites shown in Figure 7A will at-

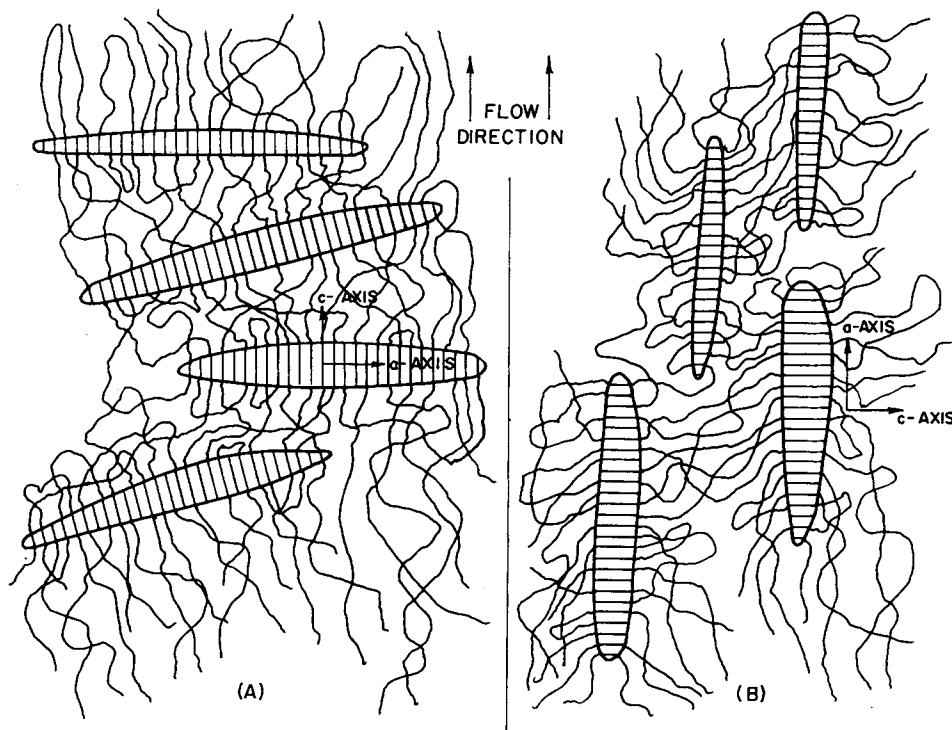


Fig. 7. (A) Schematic representation of growth of crystallites with long dimension perpendicular to flow direction of the melt. (B) Alignment of crystallites with long dimension parallel to direction of flow, resulting in chains in the crystalline regions perpendicular to the machine direction of extruded polyethylene film.

extrusion will thus be inhibited because of some previous alignment of the molecules in the melt and the inability of the molecules along appreciable chain lengths to be in exact spatial arrangement with respect to each other. Such a requisite spatial arrangement over short lengths of the neighboring molecules in the melt is quite likely, however. These small regions where the chains are in favorable proximity form nuclei for growth in a direction perpendicular to the machine direction. The crystallites in the cooling melt will thus have a tendency to grow in needle-like form with long dimensions of these needles perpendicular to the direction of flow. In this stage of incipient crystallization, these radiating needles will be like bristles

tain a position in the final film as shown in Figure 7B. As a result, the preferential orientation of polymer chains in the crystalline regions will be perpendicular to the direction of extrusion, i.e., with the *c*-axis of the crystallites perpendicular to the machine direction.

Another possibility by which *a*-axis orientation of crystallites in polyethylene films may be achieved is through a tendency of the polyethylene crystals to form with their *c*-axes perpendicular to the direction in which the molten polyethylene is stretched. No special reason why this should be so can be advanced at this time. It has been shown, however, that crosslinked molten polyethylene, when allowed to crystallize in a stretched condition,

results in orientation of crystals with their c -axes perpendicular to the direction of stretching of the amorphous material.²⁹ A similar situation may prevail during extrusion of film, since during extrusion the issuing melt is under tension before crystallization and solidification. This would result in the structure shown schematically in Figure 8. The orientation changes during stretching and

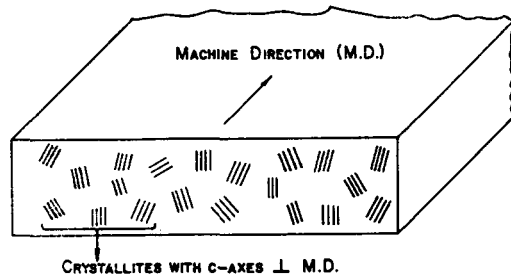


Fig. 8. Schematic representation of a -axis orientation of crystallites showing the tendency of crystals to form with their c -axes perpendicular to stretching direction of molten polyethylene.

relaxing of polyethylene films, discussed in a subsequent paper, suggest that the crystallites of polyethylene seem to be formed by the stacking of platelets with the b - and c -axes lying in the plane of the platelets.

(E) Row Orientation in Polyethylene

It is pertinent to discuss briefly here another oriented structure that has been proposed for samples prepared under conditions which are in many respects similar to those present during commercial extrusion of polyethylene film. This oriented structure is the so-called "row orientation."³⁰⁻³² According to this structure, the unit which lies parallel to the stretching direction of the melt (which would correspond to the machine direction in the case of commercially extruded films) is a cylinder. Within this cylinder a helical arrangement of polyethylene crystallites exists. The axes of the helices, along which crystallites are arranged, lie randomly in planes perpendicular to the axis of the cylinder. The crystallographic b -axes of the crystallites are parallel to the helical axes. Further, the helical angle of the helices along which the polyethylene crystallites are arranged is assumed to be quite small, and thus the helices have been postulated to be closely coiled.

It is difficult to the point of uncertainty to distinguish between the row orientation and a -axis orientation in polyethylene films on the basis of x-ray diffraction and dichroism of infrared absorption at 13.70 and 13.88 μ . The x-ray reflections, on the basis of which one may be able to distinguish

between row orientation and a -axis orientation, are weak and are close to other reflections which tend to confuse the information. The x-ray diffraction and infrared dichroism data on polyethylene films discussed in the preceding can be satisfactorily explained on the basis of row orientation. Based on the following considerations in extruded polyethylene films, however, we prefer the presence of a -axis orientation of crystallites over row orientation.

According to the row orientation model, one expects the values of E_{\perp}/E_{\parallel} (ratio of intensities of the bands with infrared radiation polarized perpendicular to the machine direction to that for radiation polarized parallel to the machine direction) to be 0.5 for the 13.70 μ band and approximately 1.73 for the 13.88 μ band. As shown in Table III, in the case of extruded polyethylene films, there are deviations from these values greater than the experimental error. These deviations can be accounted for by introducing deviations of the helices from the perpendicular direction and of the rows from parallelism to the machine direction. But under these conditions it becomes difficult to explain the x-ray diffraction patterns shown by the samples.

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Synopsis

A discussion of the methods for studying orientation of crystalline and amorphous regions in polyethylene films is given. Extruded polyethylene films and films after having been stretched approximately 200% were studied by the methods of x-ray diffraction and absorption of polarized infrared radiation. It is shown that in extruded polyethylene films the *a*-axes of the crystallites are oriented parallel to the extrusion direction. The amorphous regions in these are either not oriented or show only to a slight degree the orientation of chains perpendicular to the extrusion direction. When the polyethylene films are stretched, both the crystallites and the amorphous regions become oriented. In stretched films, the orientation of the crystallites is with *c*-axis parallel to the stretching direction, and the chains in the amorphous regions are also oriented parallel to the stretching direction. Two mechanisms by which *a*-axis orientation may arise during extrusion of polyethylene films, and a convenient method for determining the relative degree of *a*-axis orientation in polyethylene films are given. The relative degrees of *a*-axis orientation as determined by x-ray diffraction and dichroism of absorption at 13.70 μ are compared for a number of film samples.

Résumé

Une discussion des méthodes pour étudier l'orientation des régions cristallines et amorphes dans les films de polyéthylène est faite. Des films de polyéthylène comprimés et des films ayant été étirés environ 200% sont étudiés par la méthode de diffraction aux rayons-X et absorption de rayons infra-rouges polarisés. On voit que dans les films de polyéthylène extrudés, les axes-*a* des cristallites sont orientés parallèlement à la direction d'extrusion. Les régions amorphes dans ces films sont soit non orientées ou montrent seulement à un faible degré une orientation de chaînes perpendiculaires à la direction d'extrusion. Quand les films de polyéthylène sont étirés, les régions cristallines et amorphes deviennent orientées. Dans les films étirés, l'orientation des cristaux est parallèle à l'axe *c* de la direction d'étirement, et les chaînes dans les régions amorphes sont aussi orientées parallèlement à la direction d'étirement. Deux mécanismes par lesquels l'orientation suivant l'axe *a* peut être causée pendant l'extrusion des films de polyéthylène et une méthode adéquate pour déterminer le degré relatif d'orientation de l'axe *a* dans les films de polyéthylène sont donnés. Les degrés relatifs de l'orientation de l'axe *a* déterminés par la diffraction aux rayons-X et le dichroïsme de l'absorption à 13,70 μ sont comparés pour un certain nombre d'échantillons de films.

Zusammenfassung

Eine Diskussion der Methoden, die zur Untersuchung der Orientierung kristalliner und amorpher Bereiche in Polyäthylenfilmen anwendbar sind, wird durchgeführt. Gespritzte Polyäthylenfilme, sowie Filme, die um etwa 200% gestreckt wurden, wurden nach der Röntgenbeugungsmethode und der Methode der Absorption im polarisierten Infrarot untersucht. Es wird gezeigt, dass in den gespritzten Polyäthylenfilmen die *a*-Achsen der Kristallite parallel zu der Spritzrichtung orientiert sind. Die amorphen Bereiche sind bei diesen Filmen entweder überhaupt nicht orientiert oder zeigen nur eine schwache Orientierung der Ketten senkrecht zur Spritzrichtung. Bei der Streckung der Polyäthylenfilme werden sowohl Kristallite als auch amorphe Bereiche orientiert. Bei den gestreckten Filmen erfolgt die Orientierung der Kristallite mit der *c*-Achse parallel zur Streckungsrichtung und auch die Ketten in den amorphen Bereichen werden parallel zur Streckungsrichtung orientiert. Zwei Mechanismen werden für die Orientierung nach der *a*-Achse während des Spritzens der Polyäthylenfilme angegeben und eine bequeme Methode zur Bestimmung des relativen Grades dieser Orientierung in Polyäthylenfilmen wird entwickelt. Die relativen Beträge der Orientierung nach der *a*-Achse, wie sie sich aus der Röntgenbeugung und dem Dichroismus der Absorption bei 13,70 μ ergeben, werden für eine Anzahl von Filmproben verglichen.

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