high charge ratio of PO to SO_2, then $[B(A)_5B]/[B(A)_6B]$ and $[B(A)_4B]/[B(A)_5B]$ will also be about 1 and 2, respectively.[10]

In general, the expressions for the run-concentration ratios are more involved than eq 21. Figure 3 shows the calculated $[B(A)_2B]/[B(A)_3B]$ and $[B(A)_3B]/[B(A)_4B]$ ratios obtained for $k_{AA^1A} = k_{AA^2A}$ and $\lambda_{21} = 0$ with the other parameters varied to give a reasonable fit to the experimental data ($r_1 = 0.253$, $r_2 = 0.286$, $k_1 = 2.646$, and $[A] + [B] = 0.612$; the sum of [A] and [B] is assumed a constant since no solvent is used in the copolymerization.) Although this simplified model does not give a perfect fit between calculated and observed values of the run-concentration ratios, the essential features are predicted: a nonlinear dependence on the charge ratio with the curvature in the right direction, a slightly stronger charge ratio dependence for $[B(A)_2B]/[B(A)_3B]$, and intercepts for the two ratios which are not reciprocals. The boundary conditions of eq 12 and 13 ensure a tendency for the model to repeat the pair effect with increasing run length, but with a somewhat different charge ratio dependence. The differences are not outside experimental error limits.

The non-Markoffian model presented can account for all of the available $SnCl_4$-catalyzed PO–SO_2 monomer distribution data. Such an agreement does not, of course, constitute a *proof* of the applicability of the model to the real system. Further checks and tests are desirable. Since an equilibrium of catalytic species is an hypothesis of the model, changing the reaction conditions to affect the equilibrium (and so the monomer distribution) in a predictable way would be appropriate. This might be achieved by variation of the polymerization temperature, or perhaps the introduction of an inert solvent. Unfortunately, the danger in this sort of an approach is that any change in conditions which might affect the equilibrium might also change other aspects of the rather involved reaction system[2] so that the same *kind* of polymerization may no longer result.

Polarized Infrared Studies of Amorphous Orientation in Polyethylene and Some Ethylene Copolymers[1a]

B. E. Read[1b] and R. S. Stein

Polymer Research Institute, University of Massachusetts,
Amherst, Massachusetts.
Received November 6, 1967

ABSTRACT: Measurements have been made of the dichroic ratios of a number of infrared bands for uniaxially deformed low-density polyethylene. In order to characterize the amorphous orientation in the polymer, orientation functions have been derived from the results on the conformationally sensitive amorphous bands at 1368, 1352, 1303, and 1078 cm^{-1}. In conjunction with X-ray data and infrared dichroism data on the crystalline 1894-cm^{-1} band, amorphous orientation functions have also been derived from the 2016-cm^{-1} band which appears to contain a normal amorphous component. The results indicate that extended *trans* sequences in the amorphous phase orient to a larger extent than isolated *trans* bonds flanked by *gauche* bonds. Results on the bands at 720 and 730 cm^{-1} appear to show discrepancies when compared with the data from the other bands, and possible reasons for this apparent inconsistency are suggested. Amorphous orientation functions have also been derived from the C≡N stretching band at 2250 cm^{-1} in a copolymer of ethylene and (2 wt %) acrylonitrile. The bands at 2016 and 1894 cm^{-1} have also been analyzed for this copolymer, in addition to a C=O stretching band at 1740 cm^{-1} due apparently to thermal oxidation. Infrared dichroism results are also discussed for a copolymer of ethylene and (4.1 mol %) methacrylic acid in which 70% of the -COOH groups are neutralized with sodium hydroxide.

A considerable amount of work has been reported on the orientation of the crystalline phase of deformed partially crystalline polymers, and the X-ray technique has figured prominently in these investigations.[2–6] Several studies have also been made of the effect of a deformation on the orientation of the amorphous regions. These include studies involving a combination of birefringence and X-ray methods.[2a,4,6] Amorphous orientation has also been investigated by incorporating dye molecules into the amorphous phase and making measurements of visible dichroism.[7–9] In addition, studies of the polarization of fluorescence have been made using samples containing fluorescent molecules in the amorphous regions.[10] The two latter investigations suffer from the disadvantage that the

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(1) (a) Supported in part by grants from the National Science Foundation and the Petroleum Research Fund and in part by a contract with the Office of Naval Research. (b) Work carried out while on leave of absence from the Division of Molecular Science, National Physical Laboratory, Middlesex, England, which is the present address.

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orientation of the added molecules with respect to the amorphous chain segments is generally unknown, so that accurate estimates of amorphous chain orientations have not yet been possible. The polarized infrared method has the advantage that the transition moment directions (with respect to the chain axis) are known to a good approximation for many infrared absorption bands. Furthermore, several polymers exhibit bands associated, either entirely or partially, with the amorphous phase, and in many cases the local chain conformation giving rise to the absorption is known. With the advent of infrared polarizers giving a very high degree of polarization of the incident radiation, more precise measurements of infrared dichroism are now possible. Also, more rapid infrared detection systems are becoming available, making the use of infrared spectroscopy as a rheooptical technique more attractive. Previous studies of molecular orientation by polarized infrared methods include those on stretched natural rubber,[11] polyethylene,[12–15] polypropylene,[4] and polyethylene terephthalate.[16]

In this report polarized infrared results are discussed for some crystalline and conformationally sensitive amorphous bands in uniaxially deformed low-density polyethylene. We also include a discussion of similar data obtained for a copolymer of ethylene and acrylonitrile, and a copolymer of ethylene and methacrylic acid in which 70% of the acid groups have been neutralized by treatment with sodium hydroxide.

For a uniaxially oriented polymer sample, the absorbance ($A_\parallel$) measured with radiation polarized in the stretching direction may differ from the absorbance ($A_\perp$) determined for radiation polarized perpendicular to this direction. The dichroic ratio (D) is given by

$$D = \frac{A_\parallel}{A_\perp} = \frac{\epsilon_\parallel}{\epsilon_\perp} \qquad (1)$$

where ϵ is the absorbance per unit thickness of the stretched sample.[17]

In order to characterize the orientation of polymer chains in the stretched sample, it is convenient to define an orientation function (f) by[18] eq 2, where θ is the

$$f = (3\langle\cos^2\theta\rangle - 1)/2 \qquad (2)$$

angle between the stretching direction and the axis of the chain segments. The relationship between f and the dichroic ratio for a particular absorption band is[19]

$$f = \frac{D-1}{D+2}\,\frac{D_0+2}{D_0-1} \qquad (3)$$

Here D_0 is given by eq 4, where Φ is the angle between

$$D_0 = 2\cot^2\Phi \qquad (4)$$

the chain axis and the transition moment direction for the vibrational mode responsible for the infrared absorption. Measurements of D can thus be used to evaluate f if Φ is known.

For a uniaxially oriented sample we may define an average absorbance (A_{av}) by eq 5. We may note that

$$A_{\mathrm{av}} = (A_\parallel + 2A_\perp)/3 \qquad (5)$$

A_{av} is independent of the state of orientation within the sample and is proportional to the amount of absorbing species within the infrared beam.[15,20] In the undeformed state, we denote the value of A_{av} as $A_{0,\mathrm{av}}$. For a uniaxial extension at constant volume, in which the amount of absorbing species is unchanged, eq 6 must apply. Here the extension ratio λ_1 is equal to

$$\frac{A_{\mathrm{av}}}{A_{0,\mathrm{av}}} = \lambda_3 = \lambda_2 = \lambda_1^{-1/2} \qquad (6)$$

l/l_0, l being the extended length and l_0 the original length of the sample. λ_3 is the extension ratio in the thickness direction and is equal to d/d_0 where d_0 is the undeformed sample thickness. Similarly λ_2 is the extension ratio appropriate to the sample width, and is equal to b/b_0 where b and b_0 are the sample widths in the extended and unextended state, respectively. If the extension produced any changes in the quantity of absorbing species, such as might occur if the per cent crystallinity changed or if there was a change in the relative proportion of *trans* to *gauche* conformations in the amorphous phase, then $A_{\mathrm{av}}/A_{0,\mathrm{av}}$ for the appropriate crystalline or amorphous bands would show deviations from eq 6.

Experimental Section

The infrared measurements were made on a Beckman ir 10 spectrophotometer. For this instrument, the ratio of spectral slit width to absorption band half-width was generally less than 0.1. Hence, errors in the measured absorbance due to the resolving power of the instrument were less than 1% and could be neglected.[20]

For the polarized infrared measurements a Perkin-Elmer wire grid polarizer was employed in the sample beam. This polarizer consists of parallel strips of vapor-deposited gold on a silver chloride substrate. In the wavelength range 4–20 μ, it transmits about 35% of the incident unpolarized radiation, and its efficiency varies from 99% polarization at 4 μ to 99.8% at 20 μ. Errors due to polarizer inefficiency were therefore negligible.[20]

In order to eliminate the effects of machine polarization, it was necessary to orient both the polarizer and the sample with their axes at +45 or −45° to the spectrometer slit.[20] Accordingly, a rotating mount was constructed for the polarizer which enabled the orientation of its polarization axis to be set manually to within 0.5°. This precision was found necessary with the Beckman ir 10 instrument where, in the region of 10 μ, the machine polarization is large.

For extending the samples in the infrared beam, a stretcher has been constructed which enables the sample to be extended from both ends simultaneously so that the same part of the sample is maintained in the infrared beam at all extensions. The stretcher enables the sample to be extended

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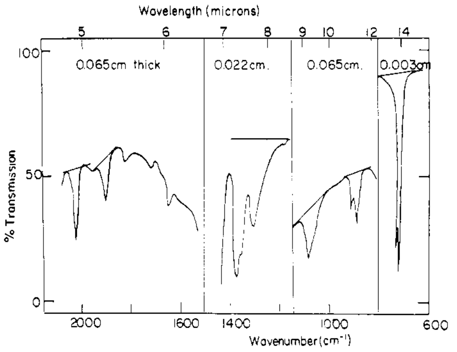

Figure 1. Infrared spectrum of low-density polyethylene. The sample thickness used, and the base lines, are indicated for the different spectral regions.

by about 300–400% and it is oriented in the beam such that the stretching direction is at 45° to the spectrometer slit. The stretcher was mounted in a position such that the infrared beam passed through the sample prior to the polarizer. This arrangement eliminated errors due to sample birefringence which might arise if the sample were located between the polarizer and monochromator.[20] An enclosure has been built around the stretcher enabling the temperature of the sample to be increased to about 200°.

In order to compensate for the intensity loss due to the polarizer in the sample beam, a wire gauze was used to reduce the intensity of the reference beam. The over-all loss in energy required that the gain of the spectrometer be increased from its normal setting of 5 to a setting of 8, and the slowest scanning speed to follow accurately the absorption peaks. The widths and dichroic ratios of the observed peaks were sufficiently large that the slight increase in noise level, due to the increase in gain, was not a serious source of error. However, a double-polarizer technique[11] is being developed for greater precision with the bands having dichroic ratios near unity.

For the dichroic measurements, the samples investigated were in the form of strips measuring (in the undeformed state) about 6 cm long and 2 cm wide and of variable thickness (0.085–0.003 cm). The samples were extended slowly in a stepwise fashion, the recording of both parallel and perpendicular spectra at each extension taking about 1 hr. Extension ratios were determined from the measured distance between lines ruled on the sample about 0.5 cm apart. These lines also served to determine whether the extension was uniform throughout the sample. Although the deformations generally appeared fairly uniform, the actual lines used for the extension ratio determinations were those in a small region near the center of the specimen at which the infrared beam was found to be transmitted.

Low-Density Polyethylene

A. Base Lines. The bands so far investigated in low-density polyethylene are illustrated in Figure 1. In most cases the base line determination is seen not to be ambiguous. For the bands at 1303, 1352, and 1368 cm^{-1}, the base line used (Figure 1) is the one determined by Koenig and Witenhafer.[21]

B. Band Assignments. The following bands have so far been investigated. The terminology used in some of the assignments follows Krimm.[22]

720 Cm^{-1}. This band contains components due to both the crystalline and amorphous phases.[22,23] The crystalline component arises from out-of-phase CH$_2$ rocking modes for the two chains in the unit cell,[24] and in crystals of *n*-paraffins it is polarized along the *b* crystallographic axis[22] $[\gamma_r(\mathrm{CH_2})(\mathrm{B_{2u}})]$. The amorphous component is assigned to CH$_2$ rocking modes of chain segments in the *trans* conformation, and according to Snyder,[25] it is associated with sequences of more than four *trans* bonds. The amorphous component has a transition moment perpendicular to the chain axis.

730 Cm^{-1}. This band arises from the crystalline phase and is assigned to in-phase CH$_2$ rocking modes for the two chains in the unit cell.[24] In *n*-paraffin crystals, it has been found to be polarized along the *a* axis of the crystal[22] $[\gamma_r(\mathrm{CH_2})(\mathrm{B_{1u}})]$.

1078 Cm^{-1}. This band is assigned to a skeletal C–C stretching mode of both *trans* and *gauche* conformations in the amorphous phase.[22] The transition moment direction has been reported to be perpendicular to the chain axis.[26]

1303 Cm^{-1}. This band has been assigned to a CH$_2$ twisting mode of amorphous chain segments in the *gauche* conformation.[22,26] A more recent discussion[25] associates it with a wagging of CH$_2$ groups in a GTG or GTG′ [where G stands for a *gauche* (+), T for a *trans*, and G′ for a gauche (−)] conformation which is antisymmetrical with respect to the center of the *trans* bond. This would have a transition moment parallel to the chain axis (the direction perpendicular to the planes of the two CH$_2$ groups on either side of the *trans* bond).

1352 Cm^{-1}. This band has been assigned to a CH$_2$ wagging mode of amorphous chain segments in the *gauche* conformation.[22] According to Snyder,[25] this band is due to the wagging of a CH$_2$ flanked by *gauche* bonds (GG) and its transition moment should be perpendicular to the plane of the CH$_2$ group.

1368 Cm^{-1}. Snyder[25] assigns this band, like the 1303-cm^{-1} band, to a CH$_2$ wagging in GTG or GTG′ conformation; where now the motion is symmetrical with respect to the center of the *trans* bond. The motion is largely uncoupled with respect to other motions of the polymer. While the motion of each CH$_2$ group is perpendicular to its plane, there will be cancellation of the transition moments of the two CH$_2$ groups so that the transition moment direction of any residual component is uncertain.

It is to be noted that while the above three bands are ones that might be identified with observed polyethylene absorptions, other contributions might be considered which contribute to the band profile in this region. For example, Snyder[25] calculates that CH$_2$ wagging modes of conformational sequences –GTTG– and –GTTG′– are near 1380 and 1336 cm^{-1}, whereas wagging of methylenes in a *trans* sequence is at 1230 cm^{-1}. There is a broad absorption region of 1370–1300 cm^{-1}

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coming from *gauche* isolated *trans* sequences of one, two, or three methylene groups.

It should be noted that because the absorptions do not result from the motions of single CH_2 groups but are modes from groups of CH_2 groups in particular conformations, the assignment of directions of transition moments is, at best, approximate and this limitation should be kept in mind when evaluating the interpretation of the dichroism results in the latter part of the paper.

1894 Cm^{-1}. This band clearly arises from the crystalline phase entirely[17] and has been assigned to a combination between the Raman active $\gamma_r(CH_2)(Ag)$ band at 1168 cm^{-1} and the infrared active 720, 730-cm^{-1} bands.[27] The band is polarized perpendicular to the *c* crystallographic axis,[27] although it is not clear whether the net transition moment lies along the *a* or the *b* axis or along some intermediate direction. Krimm[22] has listed the band as a B_{1u} mode, which corresponds to polarization along the *a* axis, and a similar assignment has more recently been given by Nielsen.[28]

2016 Cm^{-1}. This band is a combination of the Raman active fundamental $\langle\gamma_t(CH_2)(B_{2g})\rangle$ at 1295 cm^{-1} and the 720, 730 cm^{-1} infrared bands.[27] The band has been attributed to both the crystalline and amorphous phases,[22,27] although a recent paper[15] has apparently regarded it as a crystalline band. The crystalline component has a transition moment parallel to the *c* axis (*i.e.*, a B_{3u} mode).[22,27] The nature of the amorphous component has not yet been clearly established. Since the band is a combination involving the 1295- and 720-cm^{-1} fundamentals, it might be expected that the amorphous component is due to extended *trans* sequences. However, Krimm[22] has suggested that the band may also involve some combination between the infrared bands at 1303 and 720 cm^{-1}, indicating that some *gauche* units may be partly involved in the amorphous component. For the amorphous component, the transition moment is parallel to the chain axis.[27]

C. Determination of Orientation Functions. 1. Crystalline. The orientation of the crystallites in uniaxially deformed polyethylene can be studied by the X-ray pole figure experiment[5] which yields the three orientation functions f_α, f_β, and f_ϵ, appropriate to the *a*, *b*, and *c* crystal axes, respectively.[18]

$$f_\alpha = (3\langle\cos^2\alpha\rangle - 1)/2 \tag{7}$$

$$f_\beta = (3\langle\cos^2\beta\rangle - 1)/2 \tag{8}$$

$$f_\epsilon = (3\langle\cos^2\epsilon\rangle - 1)/2 \tag{9}$$

Here α, β, and ϵ are the angles which the *a*, *b*, and *c* axes, respectively, make with the stretching direction. The X-ray technique gives f_α and f_β, from which f_ϵ can be evaluated by means of[18] eq 10. The crystalline

$$f_\alpha + f_\beta + f_\epsilon = 0 \tag{10}$$

infrared and at 730 cm^{-1} should also be capable of yielding f_α since in the orthorhombic *n*-paraffins it is polarized along the *a* axis of the crystal, in agreement with theoretical predictions. It follows from eq 3 and 4, if Φ is now regarded as the angle between the transition moment direction and the *a* axis (*i.e.*, $\Phi = 0$), that

$$f_\alpha = \frac{D_{730} - 1}{D_{730} + 2} \tag{11}$$

where D_{730} is the measured dichroic ratio of the 730-cm^{-1} band. It must be emphasized, however, that for polyethylene it has not yet been confirmed whether the 730-cm^{-1} band is, in fact, effectively polarized along the *a* axis, and experiments would first be necessary to establish this point. As discussed later, the measured dichroism of the 730-cm^{-1} band for polyethylene may be affected by the overlap of the other bands having different transition moment angles. According to some assignments (see above), the crystalline band at 1894 cm^{-1} might also be polarized along the crystal *a* axis. If this fact could be established, then this band could also be used to determine f_α by an equation analogous to eq 11.

2. Amorphous. The complete characterization of the orientation of amorphous regions in polyethylene would require the evaluation of orientation functions for both *gauche* and *trans* units, each of specified sequence length. From the current assignments of the amorphous bands in polyethylene (see above), it is not always possible to state quantitatively the lengths of either *gauche* or *trans* sequence involved in the orientation. The amorphous bands at 1303, 1352, and 1368 cm^{-1} are each reported to have transition moments directed parallel to the chain axis[26,27] and, from eq 3 and 4, amorphous orientation functions can be derived from eq 12–14. The previously mentioned limitations

$$f_{1303}{}^{\mathrm{am}} = \frac{D_{1303} - 1}{D_{1303} + 2} \tag{12}$$

$$f_{1352}{}^{\mathrm{am}} = \frac{D_{1352} - 1}{D_{1352} + 2} \tag{13}$$

$$f_{1368}{}^{\mathrm{am}} = \frac{D_{1368} - 1}{D_{1368} + 2} \tag{14}$$

on assigning directions to these transition moments must be kept in mind. According to current assignments, $f_{1352}{}^{\mathrm{am}}$ should characterize the orientation of amorphous *gauche* conformations. Similarly, $f_{1303}{}^{\mathrm{am}}$ and $f_{1368}{}^{\mathrm{am}}$ should be related to the orientation of amorphous *trans* units, probably those isolated *trans* units flanked by *gauche* units. Since the amorphous band at 1078 cm^{-1} is reported to have a transition moment lying perpendicular to the chain axis,[26] we have from eq 3 and 4

$$f_{1078}{}^{\mathrm{am}} = -2\frac{(D_{1078} - 1)}{D_{1078} + 2} \tag{15}$$

From the present assignments, $f_{1078}{}^{\mathrm{am}}$ probably characterizes some average orientation of both *gauche* and *trans* sequences.

Amorphous orientation functions can also be estimated from the bands at 2016 and 720 cm^{-1} if the orientation functions for the respective crystalline

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components are known from X-ray studies. For the 2016-cm^{-1} band, the amorphous orientation function could be evaluated from dichroic measurements either on the 2016-cm^{-1} band alone or on the 2016- and 1894-cm^{-1} bands.

Using polarized infrared radiation, the absorbance will depend on the average square of the angle between the transition moment direction and the polarization direction.[18] For the 2016-cm^{-1} band, we recall that the crystalline component has a transition moment directed along the crystal *c* axis. For radiation polarized parallel to the stretching direction, we may thus write for the pure crystalline extinction coefficient, $(\epsilon_c)_{2016,\parallel}$

$$(\epsilon_c)_{2016,\parallel} = \epsilon_{c,2016}{}^0\langle\cos^2\epsilon\rangle = \epsilon_{c,2016}{}^0(1 + 2f_\epsilon)/3 \quad (16)$$

where $\epsilon_{c,2016}{}^0$ is the extinction coefficient of perfectly oriented crystals measured with radiation polarized along the *c* axes.

In the case of a uniaxial extension, we obtain the pure crystalline extinction coefficient, $(\epsilon_c)_{2016,\perp}$, for radiation polarized perpendicular to the stretching direction. This follows from eq 17. From eq 16 and 17

$$(\epsilon_c)_{2016,\parallel} + 2(\epsilon_c)_{2016,\perp} = \epsilon_{c,2016}{}^0 \quad (17)$$

we obtain

$$(\epsilon_c)_{2016,\perp} = \epsilon_{c,2016}{}^0(1 - f_\epsilon)/3 \quad (18)$$

The measured parallel, $(\epsilon_{2016})_\parallel$, and perpendicular, $(\epsilon_{2016})_\perp$, extinction coefficients for the 2016-cm^{-1} band may be expressed as the sum of amorphous and crystalline contributions, assuming them to be additive[18]

$$(\epsilon_{2016})_\parallel = X_c(\epsilon_c)_{2016,\parallel} + (1 - X_c)(\epsilon_a)_{2016,\parallel} \quad (19)$$

$$= X_c\epsilon_{c,2016}{}^0(1 + 2f_\epsilon)/3 + (1 - X_c)(\epsilon_a)_{2016,\parallel} \quad (20)$$

where X_c is the volume fraction of crystallinity.

Similarly

$$(\epsilon_{2016})_\perp = X_c(\epsilon_c)_{2016,\perp} + (1 - X_c)(\epsilon_a)_{2016,\perp} \quad (21)$$

$$= X_c\epsilon_{c,2016}{}^0(1 - f_\epsilon)/3 + (1 - X_c)(\epsilon_a)_{2016,\perp} \quad (22)$$

From eq 20 and 22, we obtain for the dichroic ratio of the amorphous component

$$D_{2016}{}^{\text{am}} = \frac{(\epsilon_a)_{2016,\parallel}}{(\epsilon_a)_{2016,\perp}} = \frac{(\epsilon_{2016})_\parallel - X_c\epsilon_{c,2016}{}^0(1 + 2f_\epsilon)/3}{(\epsilon_{2016})_\perp - X_c\epsilon_{c,2016}{}^0(1 - f_\epsilon)/3} \quad (23)$$

$D_{2016}{}^{\text{am}}$ can thus be obtained knowing f_ϵ, X_c, and $\epsilon_{c,2016}{}^0$. Since the transition moment direction for the amorphous component of the 2016-cm^{-1} band is parallel to the chain axis, $f_{2016}{}^{\text{am}}$ follows from the relation

$$f_{2016}{}^{\text{am}} = \frac{D_{2016}{}^{\text{am}} - 1}{D_{2016}{}^{\text{am}} + 2} \quad (24)$$

Another method of obtaining $D_{2016}{}^{\text{am}}$, and hence $f_{2016}{}^{\text{am}}$, involves measurements on both the 2016- and the 1894-cm^{-1} bands. For the crystalline 1894-cm^{-1} band, we can write, by analogy with eq 16

$$(\epsilon_c)_{1894,\parallel} = \epsilon_{c,1894}{}^0(1 + 2f_{1894})/3 \quad (25)$$

where f_{1894} is the crystalline orientation function appropriate to the transition moment direction of the 1894-cm^{-1} absorption. $\epsilon_{c,1894}{}^0$ is the extinction coefficient of perfectly oriented crystals measured with radiation polarized along the transition moment direction. For the 1894-cm^{-1} band, this direction is perpendicular to the *c* crystallographic axis.[27] For a uniaxial extension, it follows that

$$(\epsilon_c)_{1894,\parallel} + 2(\epsilon_c)_{1894,\perp} = \epsilon_{c,1894}{}^0 \quad (26)$$

giving, with the aid of eq 25

$$(\epsilon_c)_{1894,\perp} = \epsilon_{c,1894}{}^0(1 - f_{1894})/3 \quad (27)$$

Since the 1894-cm^{-1} band is assigned entirely to the crystalline phase, we can write for the measured extinction coefficients

$$(\epsilon_{1894})_\parallel = X_c\epsilon_{c,1894}{}^0(1 + 2f_{1894})/3 \quad (28)$$

and

$$(\epsilon_{1894})_\perp = X_c\epsilon_{c,1894}{}^0(1 - f_{1894})/3 \quad (29)$$

From eq 20, 22, 28, and 29 we obtain

$$D_{2016}{}^{\text{am}} = \frac{(\epsilon_{2016})_\parallel - (\epsilon_{1894})_\perp\epsilon_{c,2016}{}^0(1 + 2f_\epsilon)/\epsilon_{c,1894}{}^0(1 - f_{1894})}{(\epsilon_{2016})_\perp - (\epsilon_{1894})_\perp\epsilon_{c,2016}{}^0(1 - f_\epsilon)/\epsilon_{c,1894}{}^0(1 - f_{1894})} \quad (30)$$

where

$$f_{1894} = \frac{D_{1894} - 1}{D_{1894} + 2} \quad (31)$$

D_{1894} being the measured dichroic ratio of the 1894-cm^{-1} band. The value of $f_{2016}{}^{\text{am}}$ can now be obtained from eq 24, 30, and 31 if f_ϵ and the ratio $\epsilon_{c,2016}{}^0/\epsilon_{c,1894}{}^0$ are known. We may note that by this method a knowledge of X_c is not required.

In order to determine $\epsilon_{c,2016}{}^0$ and $\epsilon_{c,1894}{}^0$, measurements could be made of the extinction coefficient, $(\epsilon_c{}^0)_u$, of randomly oriented *n*-paraffin crystals using unpolarized radiation. This method utilizes eq 32 and 33, which follow from eq 17 and 26. Alternatively, extinction

$$\epsilon_{c,2016}{}^0 = 3(\epsilon_c{}^0)_{u,2016} \quad (32)$$

$$\epsilon_{c,1894}{}^0 = 3(\epsilon_c{}^0)_{u,1894} \quad (33)$$

coefficients can be determined, using unpolarized radiation, on a range of polyethylene samples varying in per cent crystallinity. The values of $\epsilon_{c,2016}{}^0$ and $\epsilon_{c,1894}{}^0$ could then be determined from eq 32 and 33 after extrapolating the observed extinction coefficients to 100% crystallinity.

In the case of the infrared bands at 720 and 730 cm^{-1}, it has been observed that the intensity of the crystalline component of the 720-cm^{-1} band is equal to the intensity of the crystalline 730-cm^{-1} band.[23] Furthermore, the band at 730 cm^{-1} should be polarized along the *a* crystal axis, and the crystalline component of the 720-cm^{-1} band should be polarized along the *b* axis. By a procedure analogous to that used in deriving eq 30, it can be shown that the dichroic ratio of the amorphous component of the 720-cm^{-1} band is given by eq 34.

$$D_{720}{}^{\text{am}} = \frac{(\epsilon_{720})_\parallel - (\epsilon_{730})_\perp(1 + 2f_\beta)/(1 - f_\alpha)}{(\epsilon_{720})_\perp - (\epsilon_{730})_\perp(1 - f_\beta)/(1 - f_\alpha)} \quad (34)$$

Since the amorphous component of the 720-cm^{-1} band has a transition moment directed perpendicular to the chain axis, it follows from eq 3 and 4 that

$$f_{720}^{\mathrm{am}} = \frac{-2(D_{720}^{\mathrm{am}} - 1)}{D_{720}^{\mathrm{am}} + 2} \tag{35}$$

Hence it should be possible to evaluate f_{720}^{am} from eq 34 and 35. We may note that eq 34 follows also from equations derived by Stein[18] (using a somewhat different terminology) for the amorphous absorbancies of the 720-cm^{-1} band.

D. Results and Discussion. Unpolarized Radiation Studies. In order to determine the crystal extinction coefficients $\epsilon_{c,2016}^0$ and $\epsilon_{c,1894}^0$ and also to investigate further the nature of the amorphous component of the 2016-cm^{-1} band, extinction coefficients have been measured for a range of polyethylene samples of varying crystallinity using unpolarized radiation. The results of this study are presented in Figure 2 which shows the extinction coefficients of the 1894- (ϵ_{1894}) and the 2016-cm^{-1} (ϵ_{2016}) bands plotted against the extinction coefficient of the amorphous band at 1303 cm^{-1} (ϵ_{1303}). In this figure, sample A is the low-density polyethylene used for the polarization studies which were obtained from the Du Pont Co. Sample B is a sample of medium-density polyethylene obtained from the Monsanto Co. which was prepared by quenching from above the melt into ice–water. Sample C is a sample of very high molecular weight linear polyethylene (less than 1 methyl group per 1000 carbon atoms) supplied by Dr. Allan Gray of the Perkin-Elmer Co. Sample D is Monsanto MPE 220 which is a linear, low-molecular weight ($M_n \approx 15{,}000$; $M_w \approx 70{,}000$) polyethylene. The crosses (×) were derived from the data of Okada and Mandelkern[17] on a linear, low-molecular weight sample of polyethylene which was prepared by isothermal crystallization at 130° for 40 days (sample designated R-4, F-15, HC). For this sample, ϵ_{1894} and ϵ_{1303} were taken directly from Table I of Okada and Mandelkern's paper. In turn, ϵ_{2016} was derived from the ratio $\epsilon_{2016}/\epsilon_{1894}$ which was estimated approximately from Figure 1 of this paper, For our measurements on samples A–D, sample thicknesses ranging from 0.06 to 0.02 cm were employed and the Beckman ir 10 was used with the normal gain setting of five, and on the slow scan.

Figure 2 shows that the plots of ϵ_{1894} and ϵ_{2016} against ϵ_{1303} are each linear and that our data are consistent with those of Okada and Mandelkern[17] on the higher crystallinity samples. The values of ϵ_{2016} and ϵ_{1894} extrapolated to $\epsilon_{1303} = 0$ are 8.1 and 6.4 cm^{-1}, respectively. Since the 1303-cm^{-1} band is associated with the amorphous phase only, these extrapolated values are the extinction coefficients of the pure crystalline phase. Hence, $(\epsilon_c^0)_{u,2016} = 8.1$ cm^{-1} and $(\epsilon_c^0)_{u,1894} = 6.4$ cm^{-1}. It follows from eq 32 and 33 that $\epsilon_{c,2016}^0 = 24.3$ cm^{-1} and $\epsilon_{c,1894}^0 = 19.2$ cm^{-1}. The value of the ratio $\epsilon_{c,2016}^0/\epsilon_{c,1894}^0$ is thus found to be 1.27.

The value of ϵ_{1303} at which ϵ_{1894} extrapolates to zero is 26.6 cm^{-1} and, since the 1894-cm^{-1} band is associated entirely with the crystalline phase, this value is the measured extinction coefficient of the 1303-cm^{-1} band for the wholly amorphous polymer. Extrapolating the values of ϵ_{2016} to the line for which $\epsilon_{1303} = 26.6$ cm^{-1} (Figure 2) yields $(\epsilon_a^0)_{u,2016} = 2.1$ cm^{-1} for the amorphous component of the band at 2016 cm^{-1}.

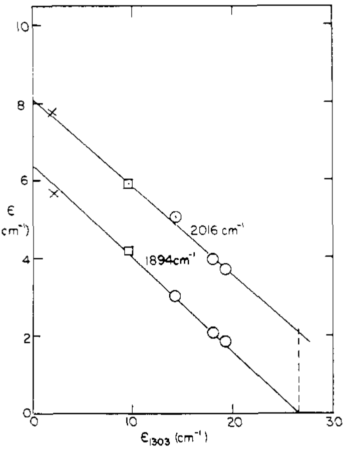

Figure 2. Plots of the extinction coefficients of the 1894-cm^{-1} (ϵ_{1894}) and the 2016-cm^{-1} (ϵ_{2016}) bands against the extinction coefficient of the amorphous band at 1303 cm^{-1} (ϵ_{1303}): □, sample D; ⊙, sample C; ○, samples A and B.

The observation in Figure 2 that the ϵ_{2016} plot is linear and approximately parallel to the ϵ_{1894} plot indicates that the amorphous component of the 2016-cm^{-1} band is, in fact, a normal amorphous phase and that the extinction coefficients of the amorphous and crystalline components are additive. The linearity of the two plots enables a determination of the volume fraction, X_c, of crystallinity

$$X_c = \frac{\epsilon_{1894}}{(\epsilon_c^0)_{u,1894}} = \frac{\epsilon_{1894}}{6.4} \tag{36}$$

or

$$\begin{aligned} X_c &= [\epsilon_{2016} - (\epsilon_a^0)_{u,2016}]/[(\epsilon_c^0)_{u,2016} - (\epsilon_a^0)_{u,2016}] \\ &= (\epsilon_{2016} - 2.1)/6.0 \end{aligned} \tag{37}$$

Equations 36 and 37 each give a value of $X_c = 0.32$ for the low-density polyethylene (sample A) used in the polarization studies.

In order to confirm the above results concerning the amorphous contribution to the 2016-cm^{-1} band, and to explore further the nature of this component, measurements have been made of ϵ_{2016} and ϵ_{1894} for sample C over a range of temperatures extending into the melt. For these measurements, the polymer was molded into a small metal frame of thickness 0.1 cm and silver chloride plates were clamped to the frame on either side of the specimen. The polymer was thus prevented from flowing in the molten state. The results of this experiment are illustrated in Figure 3. We first note that ϵ_{1894} decreases with increasing temperature reaching zero at the melting temperature ($\approx 140°$). This result is expected for a crystalline band and was also found by Okada and Mandelkern.[17] The value of ϵ_{2016} also decreases with increasing temperature up to the melting point, but then levels off to a fairly constant value in the melt comparable with the extrapolated value of $(\epsilon_a^0)_{u,2016} = 2.1$ at room temperature (Figure 2). This result confirms the suggestion that the 2016-cm^{-1} band contains a normal amorphous component. Furthermore, the tendency for ϵ_{2016} to decrease slightly with increasing temperature

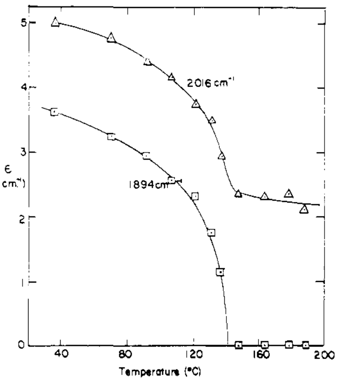

Figure 3. Dependence of the extinction coefficients of the 2016-cm^{-1} band (△) and the 1894-cm^{-1} band (□) on temperature.

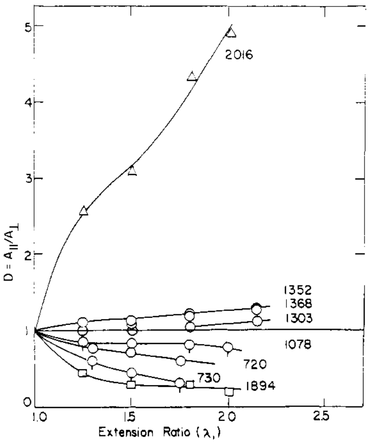

Figure 4. Dichroic ratio *vs.* extension ratio for the bands at 2016, 1894, 1368, 1352, 1303, 1078, 730, and 720 cm^{-1} for low-density polyethylene.

in the melt indicates that the amorphous component may be associated mainly with the lower energy *trans* structures but may result in part from the density decrease upon heating. More precise measurements in the melt would be required to confirm this conclusion.

Polarized Radiation Studies. Results of the polarized infrared studies on low-density polyethylene (sample A, Figure 2) are presented in Figures 4–7. The variation of the dichroic ratio with extension ratio λ is shown in Figure 4. For the bands at 1894, 2016, and 1078 cm^{-1} a sample thickness (in the unstretched state) of 0.065 cm was employed. For the bands at 1303, 1352, and 1368 cm^{-1} a thickness of 0.022 cm was used, and for the bands at 720 and 730 cm^{-1} it was necessary to employ a thickness of 0.003 cm. It will be observed that the largest dichroic effects are exhibited by the bands assigned wholly or partially to the crystalline phase. Of the amorphous bands, the antisymmetric (GTG) band at 1303 cm^{-1} shows a smaller dichroism than the band at 1368 cm^{-1}, which is a symmetric (GTG band). The dichroic effect of the 1303-cm^{-1} band is also smaller than that of the perpendicular band at 1078 cm^{-1} which also contains a contribution from *trans* units. Dichroic ratios of the 1352-cm^{-1} *gauche* band are comparable with those of the 1368-cm^{-1} band. Since these two bands show a considerable degree of overlap, however, it is possible that results for the 1352-cm^{-1} band may be influenced by those for the dominant 1368-cm^{-1} band.

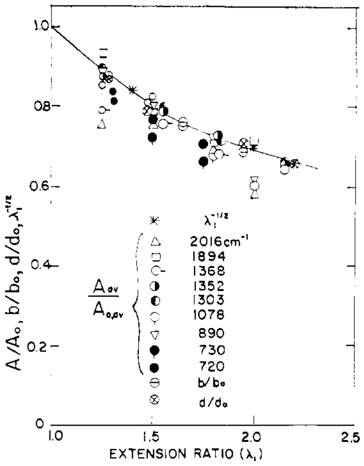

Figure 5. Plots of $A_{av}/A_{0,av}$ *vs.* extension ratio for the bands at 2016, 1894, 1368, 1352, 1303, 1078, 890, 730, and 720 cm^{-1} for low-density polyethylene. Also included are the measured values of b/b_0, d/d_0, and $\lambda_1^{-1/2}$.

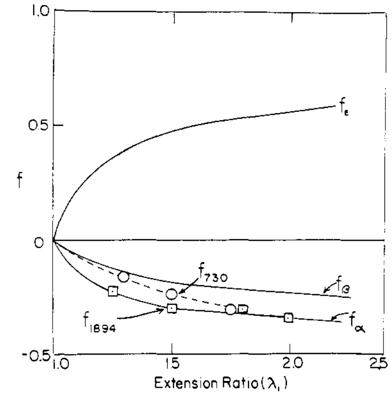

Figure 6. The variation of the crystalline orientation functions (from X-rays[29]) f_α, f_β, and f_ϵ, and f_{730}, and f_{1894} with extension ratio for low-density polyethylene.

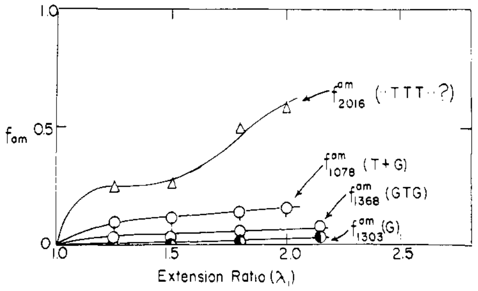

Figure 7. Dependence of the amorphous orientation functions on extension ratio derived from the bands at 2016, 1368, 1303, and 1078 cm^{-1} for low-density polyethylene.

Figure 5 shows plots of $A_{av}/A_{0,av}$ *vs.* λ_1 for the eight bands of Figure 4 and for a band at 890 cm^{-1} (0.065 cm thick sample) which is assigned to vinyl groups and is useful as an internal thickness band. Also shown in Figure 5 are values of b/b_0 and d/d_0 measured for the 0.022 cm thick sample as a function of λ_1. Values of $\lambda_1^{-1/2}$ are also indicated on the plot. The considerable scatter of the infrared points arises from the fact that each point contains the combined errors of four infrared measurements. Despite this scatter, it is apparent that all points in Figure 5 follow the same general curve, and two conclusions from this result are of particular importance. Firstly, the agreement between the measured values of d/d_0, b/b_0, $\lambda_1^{-1/2}$, and $A_{\mathrm{av}}/A_{0,\mathrm{av}}$ for the internal thickness band shows that the deformation is accurately uniaxial. Secondly, the fact that $A_{\mathrm{av}}/A_{0,\mathrm{av}}$ for the crystalline and amorphous bands follows this same curve shows that there is no detectable change in degree of crystallinity or in the concentration of amorphous *trans* or *gauche* segments with elongation.

The crystalline orientation functions, f_α, f_β, and f_ϵ, have been determined for stretched low-density polyethylene by LeGrand[29] using the X-ray method. LeGrand's values are plotted in Figure 6 as a function of extension ratio. Also shown in Figure 6 are values of f_α estimated from our infrared results on the 730-cm^{-1} band with the aid of eq 11. It will be seen that at low extension ratio ($\lambda < 1.5$) there is some discrepancy between the f_α values determined by these two methods. The reasons for this difference are not understood in detail, although its seems likely that quantitative infrared data on the 730-cm^{-1} band may be subject to errors owing to the close overlap of the 720-cm^{-1} component. Furthermore, Snyder[25] has recently studied the shape of the 720-cm^{-1} band in molten (amorphous) polyethylene and observed that it is very broad and asymmetrical on the high-frequency side. He has attributed this observation to the existence of a band at 745 cm^{-1}, assigned to alternating *trans–gauche* sequences. Such sequences might not be expected to orient to such a high degree as the extended *trans* sequences, and the overlap of the 745-cm^{-1} band might give rise to the apparently low dichroic effects for the 720- and 730-cm^{-1} bands. Opaskar and Krimm[30] have also commented on the asymmetry on the high-frequency side of the 720, 730-cm^{-1} bands. These authors have suggested that this effect may partly arise from a coupling between a defect (which may consist of *trans–gauche* sequences of the type considered by Snyder[25]) and the lattice modes. In addition to these possible overlap problems, mention should also be made of the fact that very thin (≈ 0.003 cm) films are required for the infrared analysis of the 720, 730-cm^{-1} bands owing to the strong absorption in this region. Such films are difficult to prepare with a uniform thickness, and, consequently, it is difficult to achieve a uniform sample extension. Furthermore, the accurate measurement of sample thickness becomes a problem so that the determination of accurate extinction coefficients is difficult. Another possibility for the discrepancy between the infrared and X-ray data would be that the state of orientation within the polymer may depend on sample thickness, particularly in the case of very thin films. The determination of X-ray orientation functions on very thin films, combined with simultaneous determinations of f_α from the 730-cm^{-1} infrared band, would be useful in investigating this possibility. Figure 6 also shows values of f_{1894} derived from our data using eq 31. These values compare very well with the f_α values determined by X-rays, suggesting that the 1894-cm^{-1} mode may be polarized along the a crystal axis, and thus lend support to the B_{1u} mode listed by Krimm.[22]

Figure 7 includes the variation with λ_1 of the amorphous orientation functions for the 1303-, 1368-, and 1078-cm^{-1} bands, calculated from eq 12, 14, and 15, respectively. The value of f_{1303}^{am} is very small at all extensions. It is suggested that the difference between this band and that at 1368 cm^{-1} must be a result of the different orientations of the transition moment directions on the two bands, since they both are assigned to the same (GTG) chain conformation. It is difficult to see, however, how the 1368-cm^{-1} band could have a higher dichroism than the 1303-cm^{-1} band since the 1303-cm^{-1} band is believed to have the transition moment parallel to the chain axis which should result in a maximum dichroism. The higher values of f_{am} for the 1078- and 2016-cm^{-1} bands are believed to be due, in part, at least to a greater contribution from *trans* conformations (and may in part be due to differences in ϕ). The very high values of f_{2016}^{am} are a consequence of this band arising from sections of the chain which contain four or more *trans* sequences in a row. Such sequences are considerably stiffer than portions of the chain containing *gauche* conformations, and would be represented in the statistical segment approximation. In this connection, Shindo and Stein[31] have recently considered the problem of amorphous chain orientation in which the chains were considered to comprise a distribution of segment lengths. The analysis was based on an extension of the Kuhn–Grun treatment in which the model of freely jointed, random links was employed. Although this model is clearly very approximate when applied to a real polymer chain, the analysis yielded the interesting result that the longer chain links were oriented to a higher degree than the shorter ones. A complete analysis of the present data would eventually require the consideration of segmental orientation in terms of a more realistic model of the polymer chain. One particularly intriguing feature of the present results concerns the shape of the plot of f_{2016}^{am} against λ_1 and, in particular, the upswing in f_{2016}^{am} values at extension ratios between 1.5 and 2.0. The shape of this curve is reminiscent of the force-elongation plot for amorphous polymers, suggesting that the amorphous regions are behaving in extension like a highly cross-linked amorphous polymer. From the upswing in f_{2016}^{am} values, which occurs in the region of $\lambda_1 = 2$, it may tentatively be estimated, on the basis of the Gaussian random chain model, that the chains in the amorphous phase contain an average of about four equivalent random links.

In Figure 8 we have plotted values of f_{720}^{am} calculated by means of eq 34 and 35. The interesting feature of this plot is that the f_{720}^{am} values are negative at low extensions and cross over to positive values at extension ratios greater than about 1.6. A similar result has

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(29) D. G., LeGrand, Ph.D. Thesis, University of Massachusetts, 1959.

(30) C. G. Opaskar and S. Krimm, *Amer. Chem. Soc., Polym. Preprints*, **8, 2,** 1124 (1967).

(31) Y. Shindo and R. S. Stein, ONR Technical Report No. 91, Project NR 056-378, Contract Nonr 3357(01), University of Massachusetts, Amherst, Mass., July 1967.

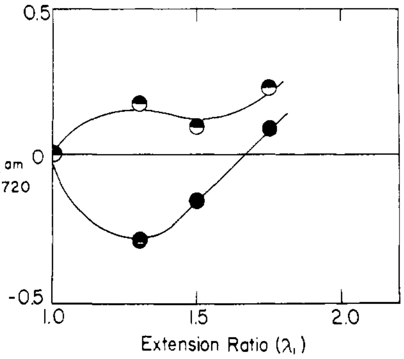

Figure 8. Plots of f_{720}^{am} against extension ratio for low-density polyethylene using the f_β values determined by LeGrand[29] (●) and by Fujino and coworkers[6] (◐).

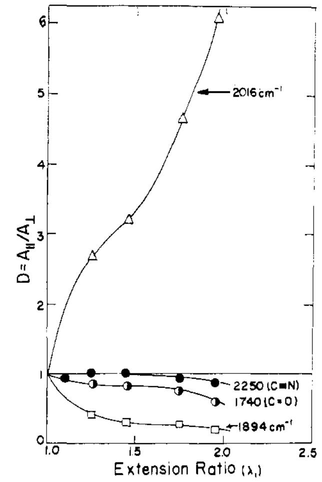

Figure 9. Dichroic ratio *vs.* extension ratio for the bands at 2016 (△), 1894 (⊡), 2250 (●), and 1740 cm^{-1} (◑) for an ethylene–acrylonitrile copolymer.

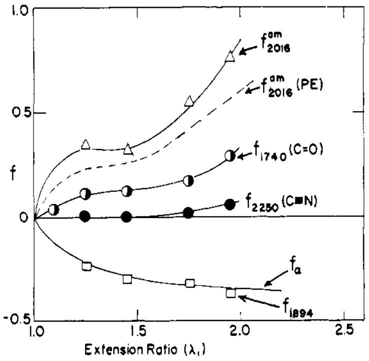

Figure 10. Orientation functions plotted against extension ratio for an ethylene–acrylonitrile copolymer: △, f_{2016}^{am}; ◑, f_{1740}; ●, f_{2250}; ⊡, f_{1894}. Also shown are f_{2016}^{am} (—) and f_α (——) for low-density polyethylene.

already been obtained using this same infrared method,[32] and also from a combination of X-ray and birefringence studies.[2a] The intepretation given was that the amorphous chains are orienting perpendicular to the stretching direction at low elongations. However, this result seems inconsistent with the results obtained on the other infrared bands. Possible reasons for the differences observed between the values of f_{730} and f_α have been discussed above. The apparent inconsistencies in the f_{720}^{am} values may not be entirely related to the discrepancies in f_{730}, since the use of f_{730} values in place of f_α in eq 34 have a fairly small effect on the calculated values of f_{720}^{am}. An additional source of error would seem to involve the X-ray values of f_β which (unlike the f_α values) vary somewhat among different samples[2b] and among different workers,[2b,6,29] and which may depend significantly on the detailed sample morphology. Since the absolute values of f_β are small, these variations give rise to large differences in f_{720}^{am} from eq 34. In fact, as shown in Figure 8, using the f_β values of Fujino and coworkers[6] for low-density polyethylene in place of LeGrand's value yields positive values for f_{720}^{am} at all extensions.

Ethylene–Acrylonitrile Copolymer

The study of infrared dichroism in ethylene–acrylonitrile copolymers was initiated on the grounds that the C≡N stretching mode, which gives rise to an absorption at 2250 cm^{-1}, has a transition moment directed perpendicular to the chain axis.[20] Since it was considered that the –C≡N group would probably be too large to be accomodated in the polyethylene crystal lattice, measurements of the dichroic ratio of the 2250-cm^{-1} band would then enable the determination of an orientation function, f_{2250}, appropriate to the amorphous phase. From eq 3 and 4, f_{2250} is given by

$$f_{2250} = -2\frac{(D_{2250} - 1)}{D_{2250} + 2} \tag{38}$$

The sample of ethylene–acrylonitrile copolymer used in the present work was kindly supplied by the U. S. Industrial Chemicals Co. and contained 2.0 wt % acrylonitrile. From unpolarized infrared studies on the undeformed copolymer, a value of $\epsilon_{1894} = 2.29$ cm^{-1} was obtained corresponding, with the aid of eq 36, to a volume fraction crystallinity of $X_c = 0.36$. Thus the degree of crystallinity of this copolymer is about 4% higher than that of the low-density polyethylene used in this work.

For the dichroic measurements on the bands at 2250, 2016, and 1894 cm^{-1}, compression molded samples about 0.085 cm thick were employed. The molded samples were found to contain a carbonyl stretching absorption at 1740 cm^{-1} which may be due to thermal oxidation, and the strength of which corresponded to about 0.5 wt % carbonyl groups. In order to study the dichroic effects of the carbonyl band, a specimen of about 0.025 cm thickness was employed.

Figure 9 shows the variation of the dichroic ratio with extension ratio for the four bands investigated, and Figure 10 includes derived plots of f_{2250}, f_{2016}^{am}, and f_{1894} according to eq 38, 24, 30, and 31. Also included in Figure 10 is the f_α plot from LeGrand's X-ray results on low-density polyethylene and values of f_{1740} calculated by eq 3 and 4 assuming that the transition moment for the C=O stretching mode is perpendicular to the chain axis. The dashed line in Figure 10 corresponds to f_{2016}^{am} for the low-density polyethylene, reproduced here for comparison.

We first note from Figure 10 that there is again good agreement between the values of f_{1894} and f_α, indicating that the 1894-cm^{-1} mode may be polarized along the *a*

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(32) R. S. Stein and D. G. LeGrand, ONR Technical Report No. 25, Project NR 356-378, Contract Nonr 2151(00), University of Massachusetts, Amherst, Mass., Sept 1, 1960.

crystallographic axis. Secondly, the values of f_{2250} are very small and comparable with the values of $f_{1303}{}^{\mathrm{am}}$ for polyethylene. This result indicates that the –C≡N groups may be associated with coiled segments or GTG conformations in the amorphous phase. Alternatively, there may be some tendency for the acrylonitrile units to exist in blocks. In this case, some phase separation might occur, the rigid acrylonitrile phase showing a relatively small deformation as compared with the polyethylene chains. Regarding the f_{1740} values, it must be emphasized that these are approximations based on the assumption that the transition moment is perpendicular to the chain axis. However, the fairly high values obtained would indicate that the C=O groups may be attached partly to *trans* amorphous bands or perhaps that some of these groups are incorporated into the crystalline phase. The $f_{2016}{}^{\mathrm{am}}$ values are again high, and the plot of $f_{2016}{}^{\mathrm{am}}$ against λ_1 exhibits the upward curvature in the region of $\lambda_1 = 1.5–2$. The $f_{2016}{}^{\mathrm{am}}$ values for the copolymer are higher than the corresponding values for the low-density polyethylene, and the upward curvature is shifted to smaller extension ratios. These results are consistent with the higher degree of crystallinity estimated for the copolymer, indicating that the average chain length in the amorphous phase is smaller for the copolymer than for the low-density polyethylene. It is also of interest to note that samples of the copolymer generally broke at about 100% extension. This observation is in keeping with the very high amorphous orientation estimated from the 2016-cm^{-1} band at this elongation. We may finally add that no evidence of amorphous orientation perpendicular to the stretching direction has been found for this copolymer, suggesting further that the negative $f_{720}{}^{\mathrm{am}}$ values obtained from the 720, 730-cm^{-1} bands in polyethylene may be in error.

Ionized Ethylene–Methacrylic Acid Copolymer. Results have also been obtained for a copolymer of ethylene with 4.1 mol % methacrylic acid in which 70% of the –COOH side groups have been converted into the sodium salt (–COO$^-$ Na$^+$) by treatment with sodium hydroxide. This copolymer was obtained from the Du Pont Co., and for the polarized infrared studies compression molded films of 0.007 cm thickness were prepared. Calorimetric measurements with a differential scanning calorimeter have yielded a value of about 0.07 for the weight fraction of crystallinity for this sample.[33]

Temperature-dependent infrared studies have established that most of the –COOH side groups are linked with –COOH groups on neighboring chains in the form of hydrogen-bonded dimers.[34] At room temperature, it is estimated that only about 1% of these carboxylic acid groups are free. The effect of the hydrogen bonding is to shift the carboxyl stretching band for the –COOH groups to 1700 cm^{-1}. The absorption due to the asymmetric stretching mode of the carboxylate (–COO$^-$) ions is located at 1560 cm^{-1}, and the band due to the methylene rocking mode occurs at 720 cm^{-1}. Owing to the very low degree of crystallinity, the 730-cm^{-1} component is not observed, probably being submerged beneath the high-frequency tail of the 720-cm^{-1} absorption.

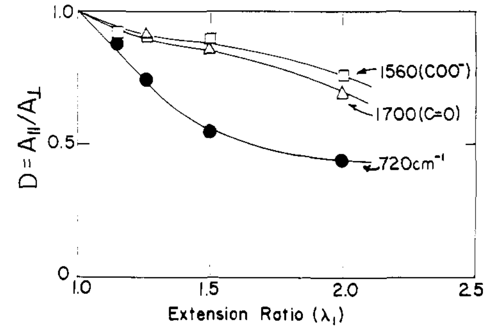

Figure 11. Dichroic ratio *vs.* extension ratio for the bands at 1560 (⊡), 1700 (△), and 720 cm^{-1} (●) for an ionized ethylene–methacrylic acid copolymer.

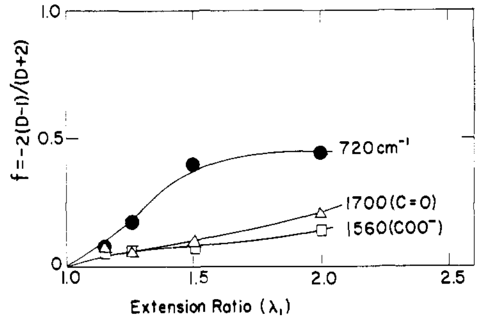

Figure 12. Plots of $-2(D - 1)/(D + 2)$ *vs.* extension ratio for the bands at 1560 (⊡), 1700 (△), and 720 cm^{-1} (●) for an ionized ethylene–methacrylic acid copolymer.

The measured dichroic ratios of the 1700-, 1560-, and 720-cm^{-1} bands are shown as a function of extension ratio in Figure 11, and Figure 12 shows the corresponding plot of $-2(D - 1)/(D + 2)$ against λ_1. From eq 3 and 4 the quantity $-2(D - 1)/(D + 2)$ would be the chain orientation function for each band if the transition moments were perpendicular to the chain axis. For the methylene rocking band at 720 cm^{-1}, the transition moment is, of course, perpendicular to the chain axis and, furthermore, since the crystalline content is extremely low, the amorphous phase should make a large contribution to the observed results. The large dichroic effect observed for this band (Figure 10), and the correspondingly high values of $-2(D - 1)/(D + 2)$ in Figure 12 again indicate a high orientation of amorphous *trans* sequences parallel to the stretching direction. However, X-ray determinations of the crystalline orientation function f_β, and the determination of the extinction coefficient of the pure crystalline phase, would be required to evaluate quantitatively the amorphous orientation for this band (by an equation analogous to eq 23).

The dichroic effects observed for the bands at 1560 and 1700 cm^{-1} must be associated with amorphous orientation since the –COO$^-$ Na$^+$ and –COOH groups are each too large to be accommodated in the polyethylene crystal lattice. The transition moment directions (with respect to the chain axis) are unknown for the modes associated with each of these bands, owing to the possibility for rotation of the side groups around the bonds

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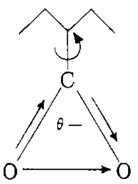
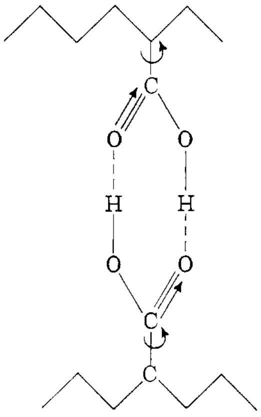
(33) W. J. MacKnight, L. W. McKenna, and B. E. Read, *J. Appl. Phys.*, **38**, 4208 (1967).

(34) W. J. MacKnight, L. W. McKenna, B. E. Read, and R. S. Stein, *Amer. Chem. Soc., Polym. Preprints*, **8**, 1130 (1967).

connecting them to the main chain. For the carboxylate ion, the net transition moment is in the plane of the group as



Hence, the perpendicular dichroism of the 1560-cm^{-1} band suggests that the plane of the carboxylate ion is, on the average, close to perpendicular to the local plane of the main chain. The carboxylic acid dimers also form a planar conformation as



Since the group has a center of symmetry, only the out-of-phase stretching vibrations (as indicated) will be infrared active,[35] and the net transition moment will lie along the C=O bond directions. Rotations around the C–C bonds connecting the acid groups to the main chains would tend to cancel out the parallel components of the transition moment, yielding a net transition moment close to perpendicular to the chain axes. A transition moment perpendicular to the chain axis would also be obtained if the plane of the carboxylic acid dimer was perpendicular to the plane of the local main chain. A comparison of the data for the 1560- and 1700-cm^{-1} bands with the data for the amorphous bands in low-density polyethylene suggests that the side groups orient in a manner similar to that of the *trans* chain bonds in the amorphous phase of low-density polyethylene. Consequently, the portion of the chain to which the side groups are attached behaves as though it were "stiff."

Acknowledgments. We are indebted to Mr. L. D. McCory and Mr. W. F. MacDonald of the U. S. Industrial Chemicals Co. for supplying the acrylonitrile–ethylene copolymer and to Dr. J. W. Brondyke of the Plastics Department of E. I. du Pont de Nemours and Co. for supplying the methacrylic acid ethylene copolymer.

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Dynamic X-Ray Diffraction from Polyethylene[1a]

T. Kawaguchi,[1b] T. Ito,[1c] H. Kawai,[1d] D. Keedy, and R. S. Stein

Polymer Research Institute, University of Massachusetts, Amherst, Massachusetts. *Received December 20, 1967*

ABSTRACT: The technique of dynamic X-ray diffraction is described in which the periodically varying diffracted X-ray intensity is analyzed for a sample of a polymer film subjected to a periodic strain. The intensity change may be resolved into a real part, $\Delta I'$, varying in-phase with the strain and an imaginary out-of-phase component, $\Delta I''$. This resolution is carried out for the amorphous scattering and the diffraction from the {110} and {200} planes of medium density polyethylene at 30° and at frequencies between 0.02 and 1.25 Hz. $\Delta I'$ decreases with frequency and $\Delta I''$ increases with frequency in the range of 1 Hz as a consequence of a crystal orientation process having a relaxation time of the order of 1 sec. Measurements at temperatures of 30, 45, and 60° produce a frequency shift associated with an activation energy of 25 kcal/mol which is close to that for the α_2 process studied mechanically. By integrating the ΔI values over azimuthal angle it is possible to determine the real and imaginary parts of the dynamic orientation function, $\Delta f'$ and $\Delta f''$.

Studies of the rheooptical properties of polyethylene have demonstrated a time-dependent optical response to strain. When a sample is deformed, there is an immediate orientation change followed by a slower change. This latter change may be revealed by measurements of the increase in birefringence during relaxation at constant length, or by the frequency dependence of the strain-optical coefficient during vibration.[2] This is believed to be primarily a result of a two-stage crystal orientation process. The first step is a rapid orientation accompanying the spherulite deformation, which is followed by a slower change in orientation within the deformed spherulite. Of course, the amorphous material also contributes to the bire-

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(1) (a) Supported in part by a contract with the Office of Naval Research and in part by grants from the Army Research Office, the Petroleum Research Fund, and the Monsanto Corporation; (b) Toyo Rayon Co., Shiga, Japan; (c) Kyoto Kogei Seni University, Kyoto, Japan; (d) Department of Polymer Chemistry, Kyoto University, Kyoto, Japan.

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