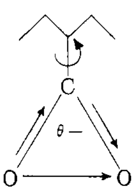
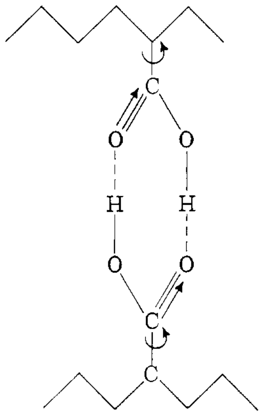
connecting them to the main chain. For the carboxylate ion, the net transition moment is in the plane of the group as



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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(35) M. M. Davies and G. B. B. M. Sutherland, *J. Chem. Phys.*, 6, 755 (1938).

Dynamic X-Ray Diffraction from Polyethylene[1a]

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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.

(2) (a) R. S. Stein, S. Onogi, K. Sasaguri, and D. A. Keedy, *J. Appl. Phys.*, 34, 80 (1963); (b) R. Yamada and R. S. Stein, *ibid.*, 36, 3005 (1965).

fringence, but it is thought that the crystal orientation change is the prime contributor, because (a) high-density polyethylene shows a larger birefringence change than low-density polyethylene, even though it has less amorphous material, and (b) the birefringence change is much too large to be accountable in terms of even a complete change in amorphous orientation from that of complete disorder to perfect orientation.

Thus, it is believed that the process of orientation of crystals in a crystalline high polymer takes a finite time and may occur in a number of ways such as interlamellae slip and crystal deformation involving intracrystalline migration of dislocations. The direct proof of this hypothesis is best accomplished by X-ray diffraction techniques. This is difficult, however, because of the times of seconds or less involved with these processes.

A method for X-ray study was described[3] in a previous article involving an X-ray "stroboscopic" technique. The sample was vibrated in tension in the X-ray beam at frequencies from 0.01 to 30 cps with a dynamic amplitude of 2.5% superimposed on a static strain of the order of 22.5%. This 22.5% static strain was necessary in order that the sample remain taut during vibration. A detector was set at a Bragg angle of 21.6° corresponding to the 110 reflection. The preamplified output of the detector was distributed among four counting channels by a rotating cam which operated microswitches. Each channel was activated during a small part of the period of strain so that counts could be repetitively accumulated at a particular strain interval over many cycles of straining. Each channel accumulated counts during a different interval of strain. The diffracted intensity could then be compared for different parts of the cycle. It was found that at low frequencies, the change in diffracted intensity with strain was essentially the same as that found during a static experiment whereas differences appeared at straining frequencies of the order of 10–20 cps. The effect was small, however, but the results indicated that crystal orientation times for the medium-density polyethylene studied were of the order of 0.1 sec in agreement with the birefringence results.

In an effort to improve the precision of the study, two modifications in technique were made which have been described in detail elsewhere.[4–6]

A. The mechanical commutator was replaced by an optical commutator in which a rotating sector synchronized with the sample stretching intercepted the light beam falling on a bank of four photocells which drove gating circuits such that when light fell on a photocell the corresponding counting circuit was activated. The program of activation of scalers was determined by the pattern out on the rotating sector. This arrangement was not limited by the finite time of operation of the cam and microswitches of the mechanical commutator.

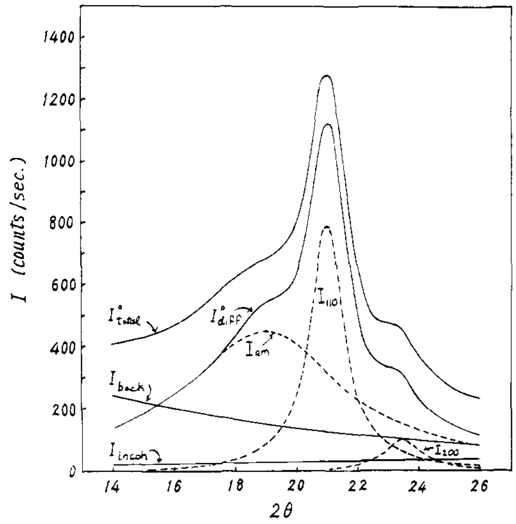

Figure 1. The resolution of the total equatorial scattering into contributions from the background, incoherent scattering, amorphous scattering, and diffraction from the {110} and {200} planes for a 22.5% stretched sample at $\phi = 0°$.

B. Rather than accumulating counts over only a small interval of the strain cycle, a given channel would accumulate over a larger part of the strain cycle and the integrated intensities over different parts of the strain cycle would be compared. This technique is capable of giving a measurement of both the real and the imaginary parts of the crystal orientation–strain coefficient.

Sample Preparation. Samples were prepared from an experimental Monsanto medium density polyethylene identical with that used in other experiments in this laboratory.[7] Films were molded with a laboratory press at 160° using a 0.5-mm thick spacer between aluminum foil and copper sheets. After 10 min in the press, they were quenched in a Dry Ice–ethanol bath. The films were then remolded using the same press conditions but a thinner spacer (0.3 mm) and quenching in an ethanol–Dry Ice bath. X-Ray examination of samples prepared in this manner revealed no orientation.

Measurements of Static Diffraction. The experimental variation of the diffracted intensity was resolved into components as has been described.[4–6,8] An example of such a resolution into contribution from the amorphous {110} and {200} components is shown in Figure 1 for the equatorial scan of a 22.5% stretched sample. The dependence of the total diffracted intensity upon azimuthal angle is shown in Figure 2 at the 2θ corresponding to the peaks of the {110} and {200} scattering at elongations of 20 and 25%. The azimuthal angle is the angle of rotation of the polymer film about its normal, and is zero when the stretching direction is vertical. The variation of intensity in the dynamic experiment at 2.5% strain amplitude about the static strain of 22.5% is within this small interval between the 20 and 25% static curves. It is the study of

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(3) H. Kawai, T. Ito, D. A. Keedy, and R. S. Stein, *J. Polym. Sci., Part B*, 2, 1075 (1964).

(4) T. Kawaguchi, ONR Report No. 86, Project NR 056-378, Contract Nonr 3357(01), Polymer Research Institute, University of Massachusetts, Amherst, Mass., April 1966.

(5) T. Kawaguchi, T. Ito, H. Kawai, D. A. Keedy, and R. S. Stein, ONR Report No. 97, Project NR 056-378, Contract Nonr 3357(01), Polymer Research Institute, University of Massachusetts, Amherst, Mass., Dec 1967.

(6) T. Ito, T. Oda, H. Kawai, T. Kawaguchi, D. A. Keedy, and R. S. Stein, *Rev. Sci. Instr.*, in press.

(7) S. Hoshino, J. Powers, D. G. LeGrand, H. Kawai, and R. S. Stein, *J. Polym. Sci.*, **58**, 185 (1962).

(8) C. R. Desper, ONR Report No. 80, Project NR 056-378, Contract Nonr 3357(01), Polymer Research Institute, University of Massachusetts, Amherst, Mass., Oct 1965.

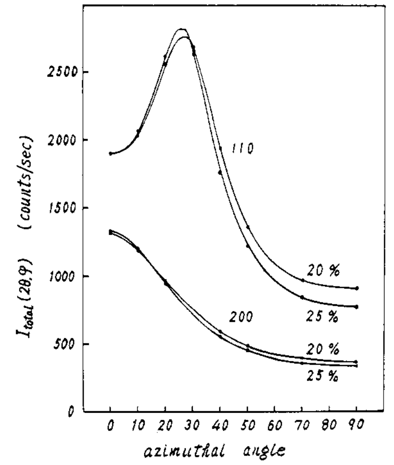

Figure 2. The variation of I_{total} with azimuthal angle at 2θ values corresponding to the positions of the {110} and {200} diffraction at static strains of 20 and 25%.

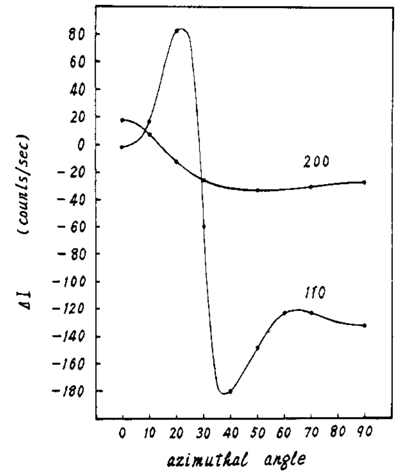

Figure 3. The variation of ΔI (difference in scattered intensity between 25 and 20% static strain) with azimuthal angle at 2θ values corresponding to the positions of the {110} and {200} diffraction.

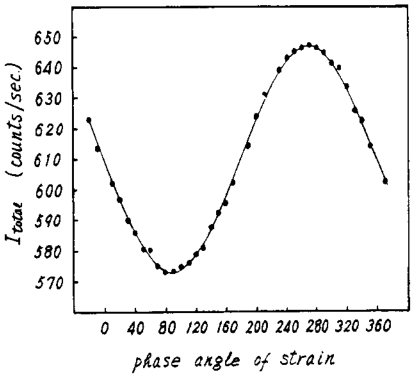

Figure 4. The change in total diffracted intensity at the position of the {110} peak at ϕ = 90° with strain as the strain is varied sinusoidally in a stepwise fashion between 20 and 25%.

this small difference which is the purpose of this work. The {200} diffraction concentrates at the equator, while the {110} diffraction concentrates at a ϕ of 20–30° from the equator. The difference in intensity ΔI between the static 20 and 25% curves is shown in Figure 3 as a function of azimuthal angle. At small azimuthal angles, ΔI is positive, representing an increase of number of diffracting crystal with strain, whereas at larger azimuthal angles ΔI is negative representing a decrease in number of diffracting crystals. Thus the change of intensity which is observed in the dynamic experiment represents a change in orientation of the diffracting crystals rather than a change in number of crystals. For small strains, ΔI is found to vary linearly with strain so that a sinusoidal variation of strain produces a sinusoidal variation of the diffracted intensity (as is required by the theoretical analysis). This is demonstrated in Figure 4 in which the intensity of the {110} peak is measured as the strain is varied in a stepwise fashion between 20 and 25%. It is expected that during dynamic vibration, the diffracted intensity also changes sinusoidally in this manner. However, the amplitude of the intensity change depends upon the frequency and temperature, and the intensity is no longer in phase with the strain but is shifted through the phase angle χ.

Dynamic Diffraction Measurements. Samples were mounted in the dynamic apparatus and given as before a static strain of 22.5%. They were then subjected to a 2.5% dynamic strain and were vibrated at the highest frequency of measurement for at least 0.5 hr prior to taking data. When the sample was vibrated, part of the mechanical energy was converted into heat resulting in a temperature rise. This could be avoided by circulation of air over the sample, in which case the diffraction by the sample was independent of the time during which the sample was vibrated.

The strain, λ, was sinusoidal and may be represented by eq 1. The vibrating sample then gave a sinusoidally varying diffracted intensity given by eq 2,

$$\lambda(t) = \lambda_0 - (\Delta\lambda)\cos\omega t \qquad (1)$$

$$I_{diff} = I_0 - \Delta I_{diff}\cos(\omega t - \chi) \qquad (2)$$

where I_0 is the static diffracted intensity at static strain λ_0, and ΔI_{diff} is the amplitude of the periodic variation in intensity which lags the strain by phase angle χ.

This may be also expressed using complex notation giving

$$I_{diff} = I_0 - \Delta I_{diff}'\cos\omega t - \Delta I_{diff}''\sin\omega t \qquad (3)$$

where

$$\Delta I_{diff}' = \Delta I_{diff}\cos\chi \qquad (4)$$

is the component of ΔI_{diff} which is in-phase with strain, and

$$\Delta I_{diff}'' = \Delta I_{diff}\sin\chi \qquad (5)$$

is the component which is out-of-phase.

The subscript (total) is used to designate the experimentally measured ΔI which is uncorrected. Values of $\Delta I_{total}'$ and $\Delta I_{total}''$ were obtained using the semicircular sector technique as previously described.[4-6] These were calculated using the equations

$$\Delta I_{total}' = [N_{(-\pi)-\pi} - N_{(\pi/2)-(3\pi/2)}]/2\tau \qquad (6)$$

and

$$\Delta I_{total}'' = [N_{\pi-2\pi} - N_{0-\pi}]/2\tau \qquad (7)$$

where, for example, $N_{(-\pi)-\pi}$ is the number of counts recorded by the scaler in the counting channel which was activated during the part of the period of vibration in the phase interval between $-\pi$ and π radians with respect to the sample strain. τ is the time interval for one cycle of vibration.

For example, the result of the measurement of $\Delta I_{\text{total}}'$ and $\Delta I_{\text{total}}''$ for the {110} peak at 30° at different azimuthal angles at frequencies between 0.02 and 1.25 Hz is shown in Figure 5. In accordance with the static results, $\Delta I_{\text{total}}'$ is positive at $\phi = 20°$ but is negative at the higher azimuthal angles. The absolute values decrease with increasing frequency. $\Delta I_{\text{total}}''$ increases in absolute value with increasing frequency as a result of the increasing phase angle between the diffracted intensity change and the strain. The phase angle itself could be obtained from the relationship

$$\tan \chi_{\text{total}} = \frac{\Delta I_{\text{total}}''}{\Delta I_{\text{total}}'} = \frac{\Delta I_{\text{total}} \sin \chi_{\text{total}}}{\Delta I_{\text{total}} \cos \chi_{\text{total}}} \qquad (8)$$

The measured intensities were corrected for thickness change during vibration and for background, incoherent scattering, polarization, and absorption as discussed. The curves were resolved into amorphous, {110} and {200} contributions as in Figure 1 for each azimuthal angle, assuming that the resolution of the dynamic data into these components was the same as that of the static data.

After these corrections and resolutions, the resulting frequency dependence of $\Delta I'$ and $\Delta I''$ for the {110} and {200} peaks are given in Figures 6 and 7. The trends are the same as for the uncorrected intensities where the absolute values of $\Delta I_k'$ are positive at small azimuthal angles and negative at large corresponding to a tendency for these planes to orient equatorially with strain. The tangents of the phase angles between the variation of the diffracted intensity and strain for the corrected {110} and {200} peaks are plotted as a function of frequency in Figures 8 and 9. These are negative at all frequencies characteristic of the diffracting intensity variation lagging strain. The phase lag is small at 0.02 Hz, but increases with frequency.

It is seen from Figures 8 and 9 that the frequency dependence of the loss tangent is dependent upon azimuthal angle, being greater for the smaller azimuthal angles. This indicates that the ability of the more highly oriented crystals to follow higher frequency strains is less than that for more poorly oriented crystals. This may be consistent with the postulate that the more highly oriented crystals are larger and more perfect, and consequently less mobile.

Amorphous Orientation. Plots of the azimuthal angle variation of $\Delta I_{\text{am}}'$ and $\Delta I_{\text{am}}''$ for the corrected amorphous orientation are given in Figure 10. This is independent of frequency and may be compared with the azimuthal angle variation of $\Delta I_k'$ and $\Delta I_k''$ for the corrected {110} and {200} peaks in Figures 11 and 12. The variation of $\Delta I_{\text{am}}'$ is only about one-eighth that of the {110} peak indicating a degree of amorphous orientation change that is comparable with the amount of amorphous orientation estimated by such methods as birefringence and sonic modulus. The lack of frequency dependence of $\Delta I_{\text{am}}'$ and the negligible value of $\Delta I_{\text{am}}''$ is significant. This shows that the variation

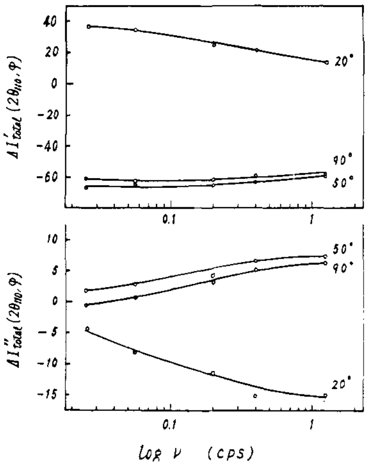

Figure 5. The variation of $\Delta I_{\text{total}}'$ and Δ_{total}'' with frequency at the position of the {110} peak at different azimuthal angles at 30°.

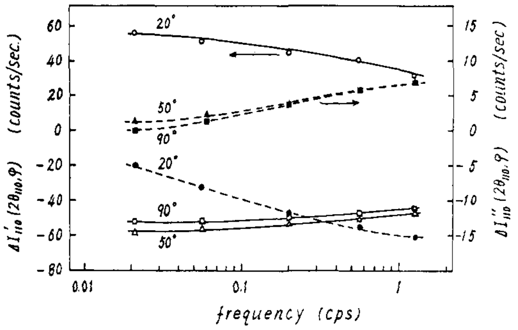

Figure 6. The variation of the corrected values of $\Delta I_{110}'$ and $\Delta I_{110}''$ with frequency for different azimuthal angles at a temperature of 30°.

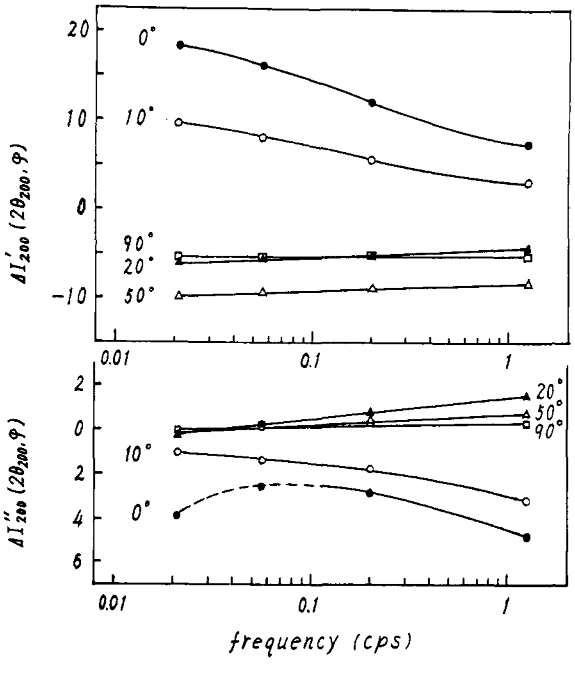

Figure 7. The variation of the corrected values of $\Delta I_{200}'$ and $\Delta I_{200}''$ with frequency for different azimuthal angles at a temperature of 30°.

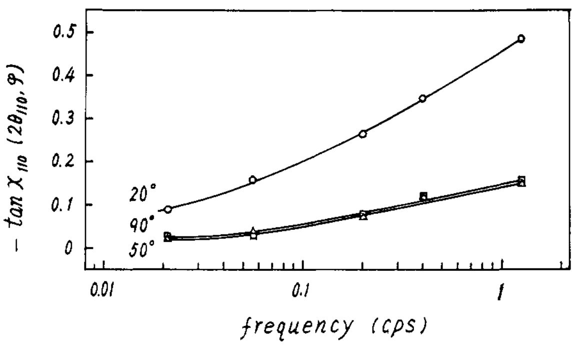

Figure 8. The variation of the loss tangent, tan χ_{110}, for the 110 peak with frequency at a number of azimuthal angles at 30°.

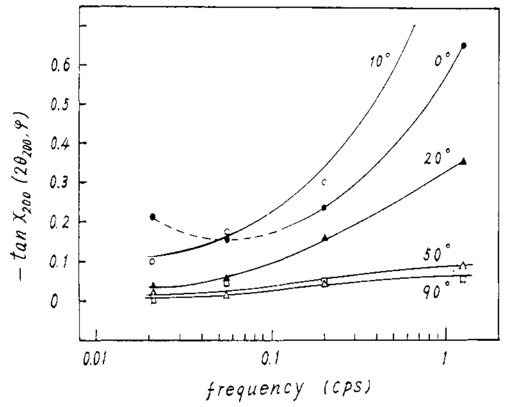

Figure 9. The variation of the loss tangent, tan χ_{200}, for the 200 peak with frequency at a number of azimuthal angles at 30°.

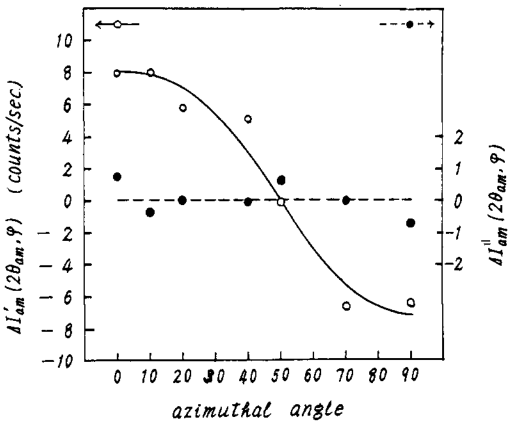

Figure 10. The variation of the variation of $\Delta I_{\text{am}}'$ and $\Delta I_{\text{am}}''$ for the corrected amorphous peak with azimuthal angle at 30°.

in amorphous orientation is in phase with the strain at all frequencies at least to within the precision of about ±25% for the measurement of the small values of $\Delta I'$ possible here. It is not likely that this observed variation is an artifact arising from the lack of complete separations of overlapping crystalline peaks, since such contributions would be frequency dependent and would make an observable contribution to $\Delta I_{\text{am}}''$.

Determination of Dynamic Orientation Function. The state of orientation of the $\{hkl\}$ plane of a crystal is often conveniently described by the Hermans orientation function[9,10] (eq 9) where α_{hkl} is the angle between

$$f_{hkl} = [3\langle\cos^2\alpha_{hkl}\rangle - 1]/2 \tag{9}$$

the normal to the $\{hkl\}$ crystal plane and the principal axis of strain. The value of $\langle\cos^2\alpha\rangle$ may be determined

$$\langle\cos^2\alpha_j\rangle = \frac{\int_0^{\pi}\sin^2\phi\, I_j(\phi)\cos\phi\, d\phi}{\int_0^{\pi} I_j(\phi)\cos\phi\, d\phi} \tag{10}$$

from the diffracted intensity by eq 10 where the incident X-ray intensity falls on the sample at an angle θ_j to the film normal.

It is recalled that f_{hkl} is a measure of the state of orientation of the $\{hkl\}$ plane and ranged from +1 when the normal to the plane is parallel to the strain direction to $-1/2$ when the normal is perpendicular to this direction. For random orientation, $f_{hkl} = 0$.

When the sample is strained periodically, the orientation function will oscillate periodically at the straining frequency, and its change may be resolved into a real and imaginary part (eq 11) where f_j^0, $\Delta f_j'$ and $\Delta f_j''$

$$f_j = f_j^0 - \Delta f_j'\cos\omega t - \Delta f_j''\sin\omega t \tag{11}$$

are the orientation function for the static strain and the portion of the change in orientation function varying in-phase and out-of-phase with the strain, respectively. It may be shown[4] that these may be given by

$$f_j^0 = \frac{1}{2}\left[3\frac{I_j^{11}}{I_j^{21}} - 1\right] \tag{12}$$

$$\Delta f_j' = \frac{3}{2}\frac{I_j^{11}}{I_j^{21}}\left[\frac{I_j^{12}}{I_j^{11}} - \frac{I_j^{22}}{I_j^{21}}\right] \tag{13}$$

and

$$\Delta f_j'' = \frac{3}{2}\frac{I_j^{11}}{I_j^{21}}\left[\frac{I_j^{13}}{I_j^{11}} - \frac{I_j^{23}}{I_j^{21}}\right] \tag{14}$$

where the I_j^{kl} terms are integrals over the azimuthal angle, ϕ, defined by

$$I_j^{11} = \int_0^{\pi/2}\sin^2\alpha\, I_j^0(\phi)\cos\phi\, d\phi \tag{15}$$

$$I_j^{12} = \int_0^{\pi/2}\sin^2\phi\,\Delta I_j'(\phi)\cos\phi\, d\phi \tag{16}$$

$$I_j^{13} = \int_0^{\pi/2}\sin^2\phi\,\Delta I_j''(\phi)\cos\phi\, d\phi \tag{17}$$

$$I_j^{21} = \int_0^{\pi/2} I_j^0(\phi)\cos\phi\, d\phi \tag{18}$$

$$I_j^{22} = \int_0^{\pi/2}\Delta I_j'(\phi)\cos\phi\, d\phi \tag{19}$$

$$I_j^{23} = \int_0^{\pi/2}\Delta I_j''(\phi)\cos\phi\, d\phi \tag{20}$$

These integrals may be evaluated numerically using the experimental values of I_j^0, $\Delta I_j'$, and $\Delta I_j''$ evaluated as a function of ϕ.

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(9) J. J. Hermans, P. Hermans, D. Vermaos, and A. Weidinger, *Rec. Trav. Chim.*, **65**, 427 (1946).

(10) R. S. Stein, *J. Polym. Sci.*, **31**, 327 (1958).

The values of $\Delta f_{110}'$, $\Delta f_{110}''$, $\Delta f_{200}'$, and $\Delta f_{200}''$ obtained in this way are plotted as a function of frequency in Figure 13. The in-phase components, $\Delta f_k'$, are negative indicating that the {110} and {200} plane normals tend to orient perpendicularly to the direction of strain upon increasing the strain. The magnitude of $\Delta f_k'$ decreases with increasing frequency indicating that less change of orientation of these crystal planes occurs at higher frequency. The out-of-phase components $\Delta f_k''$ increase in magnitude with increasing frequency. This corresponds to a negative phase angle between the orientation function change and the strain, again indicating that the crystal orientation lags strain by an increasing amount with increasing frequency.

From these values of $\Delta f_k'$ and $\Delta f_k''$ it is possible to calculate the crystalline contribution to the real and imaginary strain–optical coefficient K' and K''. This is discussed elsewhere[11] where it is shown that the crystalline contribution can account for most of the observed strain–optical coefficient.

Temperature Dependence. A temperature control chamber was constructed for the dynamic X-ray diffraction apparatus which permitted circulating heated air about the sample. Temperatures could be maintained to ±1° in the range of 25–150°. Prior to measurements the sample was mechanically conditioned by vibrating at 10 Hz for 1 hr at 60°. The variation of $\Delta I_{\text{total}}'$ and $\Delta I_{\text{total}}''$ (uncorrected) with frequency for the {110} peak at $\phi = 90°$ are given in Figure 14 at 30, 45, and 60°. It is apparent that the decrease in $\Delta I_{\text{total}}'$ and increase of $\Delta I_{\text{total}}''$ occurs at higher frequency at higher temperature, the change occurring at about 0.2, 0.8, and 7 Hz at 30, 45, and 60°, respectively. A plot of the logarithm of this frequency (where the out-of-phase component reaches a value of 1 count/sec) against the reciprocal of absolute temperature is given in Figure 15. These points give a straight line with a slope giving an apparent activation energy of 25 cal/mol, a value also found from the temperature dependence of dynamic birefringence.[12]

Discussion of Results

Several investigators have reported[13–15] that the high temperature or α dispersion region of mechanical loss for polyethylene actually consists of two or more dispersions. Nakayasu,[13] *et al.*, reported "that the α dispersion could be decomposed into two mechanisms designated α_1 and α_2 with activation energies of 28 and 46 kcal/mol, respectively." Takayanagi[16,17] found that for polyethylene single crystals, the lower temperature side of the α_c dispersion had an activation energy of 25 kcal/mol. Hideshima[18] examined the

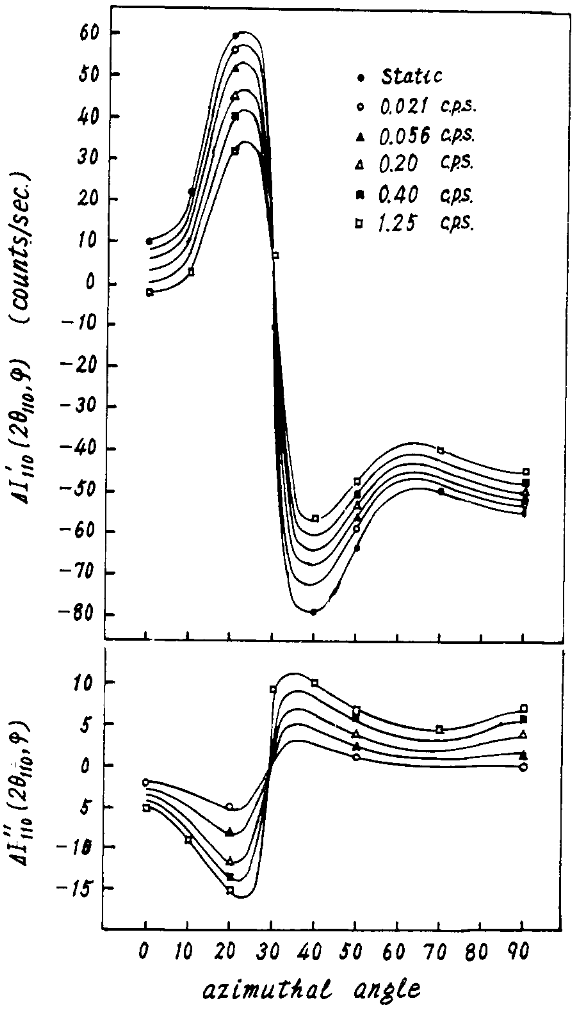

Figure 11. The variation of the corrected $\Delta I_{110}'$ and $\Delta I_{110}''$ with azimuthal angle at a number of frequencies at 30°.

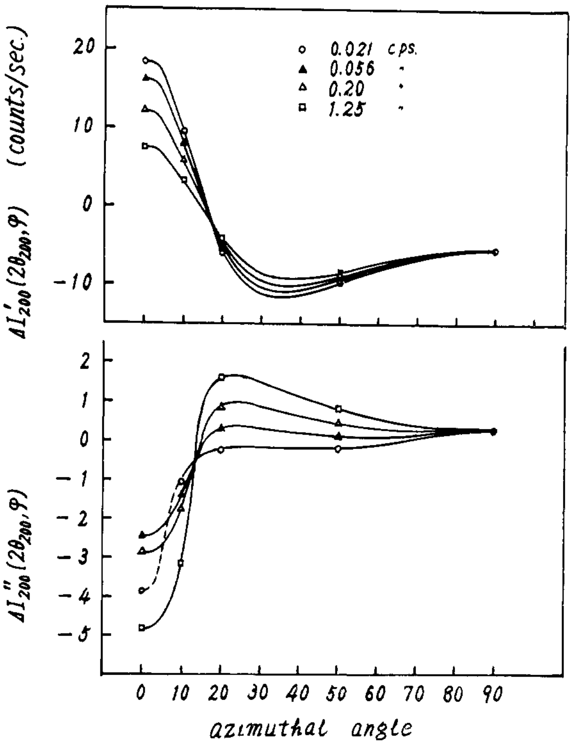

Figure 12. The variation of the corrected $\Delta I_{200}'$ and $\Delta I_{200}''$ with azimuthal angle at a number of frequencies at 30°.

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(11) T. Kawaguchi, I. Kimura, A. Takeuchi, and R. S. Stein, *J. Polym. Sci., Part B*, **5**, 339 (1967).

(12) A. Takeuchi and R. S. Stein, *ibid., Part A-2*, **5**, 1079 (1967).

(13) H. Nakayasu, H. Markovitz, and D. J. Plazek, *Trans. Soc. Rheol.* **5**, 261 (1961).

(14) S. Iwayanagi in "Solid State Physics," Vol. 14, F. Seitz and D. Turnbull, Ed., Academic Press Inc., New York, N. Y., 1963, p 458.

(15) Y. Wada and K. Tsunge *J. Appl. Phys. Jap.*, **1**, 64(1962).

(16) M. Takayanagi, *Proc. Intern. Congr. Rheol., 4th Providence* **1963**, Part I, 1965.

(17) T. Aremaki, S. Minami, F. Nagatoshi, and M. Takayanagi, *Rept. Progr. Polym. Phys. Jap.*, **7**, 237 (1964).

(18) T. Hideshima, *Progr. Polym. Phys. Jap.*, **9**, 279 (1966).

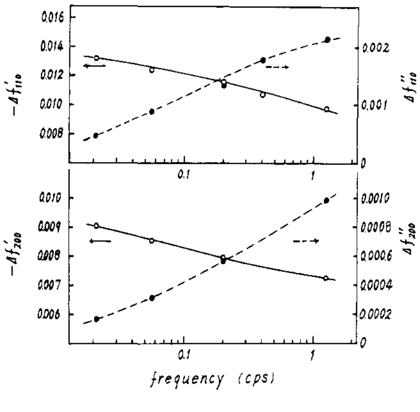

Figure 13. The variation of $\Delta f_{110}'$, $\Delta f_{110}''$, $\Delta f_{200}'$, and $\Delta f_{200}''$ with frequency at 30°.

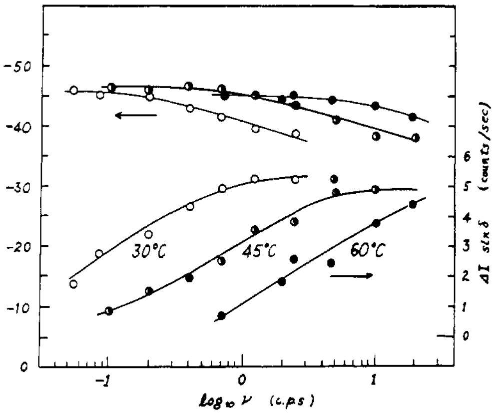

Figure 14. The variation of Δ_{total}' and Δ_{total}'' (uncorrected) with frequency at the position of the {110} peak at $\phi = 90°$ at temperatures of 30, 45, and 60°.

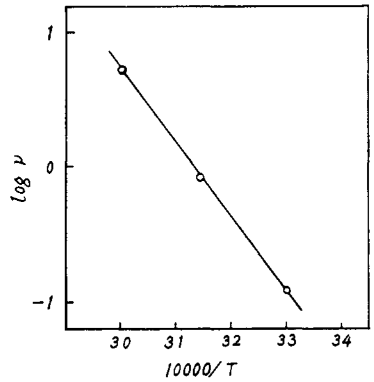

Figure 15. The variation of $\log \nu$ for the frequency at which $\Delta I_{\text{total}}''$ reaches 1 count/sec with the reciprocal of the absolute temperature.

effect of absorption of diluent and pointed out that this caused a shift in the α_1 dispersion toward lower temperatures, while the α_2 dispersion is unaffected. Thereby, he concluded that the α_1 dispersion is related to the amorphous regions whereas the α_2 dispersion is concerned with processes within the crystals.

Studies by McCrum and Morris[19] on the α loss peak of high-density polyethylene indicate two crystalline contributions which he designates α and α' for the low (70°) and high (110°) temperature components, respectively. He attributes the α component to intracrystalline phenomona and the α' component to interlamella slip in contrast to the assignments of α_1 and α_2 by Takayanagi. The α' assignment is based upon the dependency of this peak upon anisotropy, irradiation, and crystallization temperature while the α peak has no dependency upon crystallization conditions. Activation energies of the order of 25–30 kcal/mol were found for both of these peaks.

Illers[20] has reported mechanical relaxation studies on single crystals of the *n*-paraffins while Sinnott[21,22] has reported results of such studies on polyethylene single crystals. Sinnott reports a single α loss peak at a frequency which increases with annealing temperature (and crystal thickness) but with an area which decreases with annealing temperature. On the basis of this observation, he has assigned the α loss peak as being due to motion of the chain in the folds of single crystals.

In a recent review, Hoffman, Williams, and Passaglia[23] have considered these data along with dielectric data and concluded that the α peak consists of two components, one of which decreases in area with increasing crystal thickness and is due to fold motion, while the other has an area independent of thickness and is related to a combined rotation–translation of chains within the crystals.

Recently, Takayanagi[24] has reported that for isothermally crystallized single crystals, a single α loss peak is observed with an area which increases with increasing growth temperature. He believes this to be related to rotational motion within the lattice and which represents the temperature at which the crystals become internally viscoelastic.

The studies reported here are not at present adequate to distinguish between the various proposals for the α peak but do require that it be associated with a process in which the orientation of the crystals reversibly changes with vibration of the sample. Three possibilities might be considered. (1) The peak is the α' peak described by McCrum and is related to interlamella slip. (2) The peak is the component of the α peak described by Hoffman, Williams, and Passaglia which is related to fold motion. This fold motion allows crystals to slip over each other more easily. (This does not seem too likely an explanation in view of the fact that our measurements were on polyethylene containing considerable amorphous material, residing principally in the interlamella regions and which would become mobile at the lower temperature of the β peak.) (3) The X-ray dispersion corresponds to the component of the α peak at which motion within the crystal lattice becomes possible. This onset of intracrystalline motion itself would not be sufficient to account for the orientational change found by the dynamic X-ray and birefringence techniques. It is likely, however, as suggested

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(19) N. G. McCrum and E. L. Morris, *Proc. Roy. Soc.* (London), **A292**, 506 (1966).

(20) K. H. Illers, *Rheo. Acta*, 3, 202 (1964).

(21) K. M. Sinnott, *J. Appl. Phys.*, 37, 3385 (1966).

(22) K. M. Sinnott, *J. Polym. Sci.*, *Sect. C*, No. 14, 141 (1966).

(23) J. C. Hoffman, G. Williams, and E. Passaglia, *ibid.*, 173 (1966).

(24) M. Takayanagi, private communication.

by Takayanagi,[23] that when internal motion commences, the crystal becomes viscoelastic and can undergo orientational changes more easily. In this way, the onset of internal motion is reflected in the increase in the dynamic orientation function with temperature.

It is desirable, in order to obtain better comparison with dynamic mechanical spectra, to determine the variation of the dynamic orientation function (as determined by X-ray diffraction) with temperature at a fixed frequency and to compare this result with the corresponding variation of dynamic birefringence and modulus. Such studies are presently in progress.

An Entropic Repulsion Theory for Random Copolymer Dispersant Action[1]

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ABSTRACT: An entropic repulsion theory is applied to random copolymer dispersants, where the possibility exists of adsorption of the macromolecule in a flattened conformation. To do this a computer program has been devised which simulates the movements of adsorbed model macromolecules as they undergo Brownian motion with progressive attachment of polar groups to the adsorbing surface. The implications of the configurational behavior results with respect to the dispersancy performance have been calculated.

A recent quantitative theory of polymeric dispersant action[2] considers that the repulsion necessary to prevent particle adhesion arises from the reduction in configurational entropy of the adsorbed polymer molecules when they are compressed on close approach of the dispersant-covered surfaces. The theory was developed in detail for the terminally adsorbed, block copolymer type of dispersant which is the simplest to treat theoretically, since it remains unequivocally in randomly coiled configuration on the surface.

In the present work this theoretical treatment has been extended to cover the more complex case of the random copolymer type of dispersant where, because of the polar adsorbing units distributed at random along the length of the polymer chain, the possibility exists that the adsorbed macromolecule could tend to settle down flat on the surface with progressive attachment of these polar units, rather than retain its original coiled configuration. It is important that the treatment of such changes in adsorbed configuration should be able to take into account the realistic possibility that a polymer molecule, arriving at the adsorbing surface in its coiled "solution configuration," could be greatly hindered in its progress to the thermodynamic equilibrium state of a flattened configuration with virtually every polar group adsorbed, and may well achieve a metastable thick film state. One may readily visualize that this could happen because of appreciable loss of freedom of the polymer chain as soon as some of its polar units are strongly adsorbed, because of entanglement of the adsorbed polymer chain with itself and, at the higher surface coverages, because of entanglement with a neighboring adsorbed chain. Any examination of this possibility by an extension of existing theoretical treatments of such polymer adsorption appeared to be out of the question, since they employ analytic techniques which cannot as yet deal satisfactorily with the self-avoiding random walk problem involved here. A direct computer simulation of the adsorption process seemed most practicable, in which the adsorption of macromolecules of different structure would be followed, and their height, number of adsorbed units, and other quantities of interest would be recorded at intervals. Thus a computer program was devised which simulates the movements of model random copolymer molecules as they arrive at an adsorbing surface, undergo Brownian motion and progressive attachment of polar groups, and approach a limiting adsorbed film thickness. The implications of the configurational behavior differences with respect to the resulting dispersancy performance of random copolymers were then calculated. In this work, it was evident that the number of samples that would be obtained in any reasonable time would hardly be sufficient to give a high degree of precision to the results. Even the generation of random walks with a computer is a relatively lengthy process, and here the generation of a random walk is merely the preliminary to a much longer operation. The work was thus expected to provide broad indications, rather than to show up any statistically significant differences in configurational behavior associated with small changes in conditions.

Method

Outline of Computer Simulation of Adsorbed Behavior. A nonintersecting random chain with 90° bond angles is generated on a simple cubic lattice.[2b] It may be of any length up to 1024 chain elements and polar groups may be introduced, either regularly at specified intervals or at random with a specified average frequency;

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[1] Paper presented at the Colloid and Surface Chemistry Symposium, 154th National Meeting of The American Chemical Society, Chicago, Ill., Sept 10–15, 1967.

[2] (a) E. J. Clayfield and E. C. Lumb, *J. Colloid Sci.*, 22, 269 (1966); (b) *ibid.*, 22, 285 (1966).