Deformation Mechanisms of Polyethylene

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Polyethylene is a typical semicrystalline polymer, a class of materials which are useful for fibers, films, and materials of construction.[1] Such polymers possess the fortunate blend of high strength, imparted by strong interactions between molecules within crystalline regions, and toughness and ductility, imparted by the rubberlike nature of the amorphous chains. It has become increasingly apparent that the mechanical properties of these materials depend not only upon the amount of polymer which is crystalline but on details of chain topology and morphology and the degree of crystal perfection.[2]

The mechanical properties of cross-linked rubbery polymers[3] and linear amorphous polymers above their glass transition temperatures[4] are understood relatively well. The presence of some crystalline structure sufficiently complicates the response to stress so as to permit only very approximate theories of mechanical behavior.[5] In the absence of a complete theory, an experimental approach was taken in an attempt to define the deformational processes.

As an idealization, crystalline polymers may be represented as two-phase systems where perfect crystals are interconnected by rubberlike amorphous phases.[6] Earlier considerations involved the fringed micelle concept of structure in which most amorphous chains passed from one crystal to another. However, observations of the structure of polymer single crystals grown from dilute solution demonstrate the existence of lamellae composed of regularly folded chains.[7] It appears likely that such structures persist in the solid state, where crystals are imperfect and contain defects such as chain ends, kinks, and folds. The amorphous phase is far from rubberlike and involves chain ends (cillea), regular and irregular folds, and tie chains of various lengths.

Deformation of the polymer produces both a change in orientation and a deformation of the crystals themselves. For highly crystalline polymers the crystals participate in superstructures such as spherulites (Figures 1 and 2), the stress being transmitted directly from crystal to crystal without an intervening amorphous phase. Consequently the stress distribution and mechanical properties depend upon the arrangement of crystals and their size and number. The latter depend upon the conditions of nucleation and growth. For example, crystallization carried out at a lower temperature results in higher nucleation rates, and thus a larger number of small spherulites.[6]

Deformation processes are rate dependent. A finite time is required for crystal orientational changes to take place. Thus, if a polymer is stretched at a high rate so that crystal orientation cannot follow the strain, large strains will concentrate on intercrystalline tie chains and cause the polymer to be brittle. However, if the polymer is stretched slowly, the strain may distribute itself more uniformly over the sample which may then deform in a more ductile manner. The rate of structural response and the resulting mechanical properties depend upon the size, perfection, and organization of the crystalline and amorphous regions.

It is evident that the macromechanics of the polymer as a whole depend upon the micromechanics of the structural entities of which the polymer is composed. Since present theory cannot interrelate the two, we have chosen to utilize various experimental techniques to study the kinds and rates of the various structural changes which accompany the deformation of polymers.[8-12]

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In 1961 he helped found the Polymer Research Institute, of which he is Director, within the Department of Chemistry at the University of Massachusetts. Together with his group, Dr. Stein has developed methods for the study of properties of plastic films, fibers, and rubbers, employing X-ray diffraction, infrared dichroism, birefringence, low- and wide-angle light scattering, gas scattering, phase and electron microscopy, and laser techniques. He is the 1972 recipient of the American Chemical Society Award in the Chemistry of Plastics and Coatings, sponsored by Borden Foundation, Inc.

(1) R. A. V. Raff and J. B. Allison, "Polyethylene," Interscience, New York, N. Y., 1956; K. W. Doak and R. A. V. Raff, "Crystalline Olefin Polymers," Vol. I and II, Wiley, New York, N. Y., 1964.

(2) S. Matsuoka, *Polym. Eng. Sci.*, **5**, 142 (1965); M. Takayanagi in "Proceedings of the Fourth International Conference on Rheology," Part 1, E. H. Lee and A. L. Copley, Ed., Interscience, New York, N. Y., 1961, p. 161.

(3) L. R. G. Treloar, "The Physics of Rubber Elasticity," 2nd ed, Oxford Press, London, 1958.

(4) J. D. Ferry, "Viscoelastic Properties of Polymers," Wiley, New York, N. Y., 1961.

(5) F. Bueche, *J. Polym. Sci.*, **22**, 113 (1956).

(6) L. Mandelkern, "Crystallization of Polymers," McGraw-Hill, New York, N. Y., 1964.

(7) P. Geil, "Polymer Single Crystals," Interscience, New York, N. Y., 1903.

(8) R. S. Stein, *SPE (Soc. Plast. Eng.) Trans.*, **4**, 1 (1964).

(9) R. S. Stein, *Polym. Eng. Sci.*, **8**, 2501 (1968).

(10) R. S. Stein, *J. Polym. Sci., Part C*, **4**, 185 (1966).

(11) R. S. Stein, *Polym. Eng. Sci.*, **9**, 320 (1969).
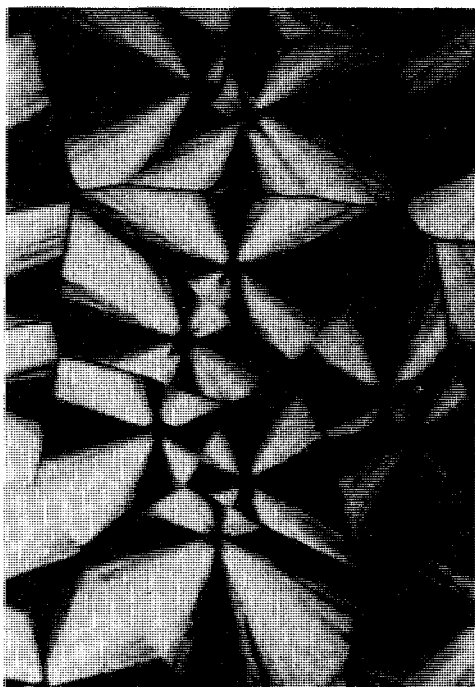
(12) R. S. Stein, *Rheology*, **5**, 297 (1969).

Figure 1. A photograph of polyethylene spherulites between crossed polaroids in a microscope (reprinted from R. S. Stein and C. Picot, *J. Polym. Sci., Part A-2*, **8**, 2127 (1970)). (Figures 1–7 are reprints through the courtesy of the copyright holders.)

Microscopic Observations

The deformation of a spherulitic polymer may be directly studied using a polarized light microscope. One observes that the spherulite deforms in much the same way as the macroscopic dimensions of the sample.[13] If the fractional change in macroscopic and microscopic dimensions is the same, the deformation is said to be "affine." As might be expected from the anisotropic structure of the spherulite as shown in Figure 2, it might not deform uniformly, but may exhibit greater strain in its equatorial part (along the plane perpendicular to the stress) where the effect of the stress is to separate crystalline lamellae. This tendency is opposed by the somewhat weak force of occasional tie chains and van der Waals forces. Such locally anisotropic deformation of spherulites has been described for polyethylene by Hay and Keller[14] and for polybutene-1 by Yang and Stein.[15]

Light-Scattering Studies

The photographic light-scattering technique was developed in our laboratory for the study of spherulitic and other superstructures.[16,17] A polarized monochromatic light beam, obtained from a gas laser, is passed through a thin film of the polymer sample, then through

(13) K. Sasaguri, M. B. Rhodes, and R. S. Stein, *J. Polym. Sci., Part B*, **1**, 571 (1963).
(14) I. L. Hay and A. Keller, *Kolloid-Z. Polym.*, **204**, 43 (1965).
(15) R. Yang and R. S. Stein, *J. Polym. Sci., Part A-2*, **5**, 939 (1967).
(16) R. S. Stein and M. B. Rhodes, *J. Appl. Phys.*, **31**, 1873 (1960).
(17) R. S. Stein in "Proceedings of the Interdisciplinary Conference, Potsdam, N. Y., 1962," M. Kerker, Ed., Pergamon Press, Oxford, 1963, p 439.
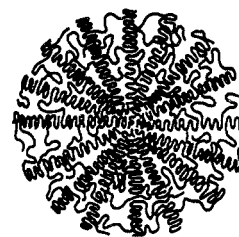

Figure 2. A schematic diagram of the arrangement of chains in a spherulite (reprinted from ref 12).
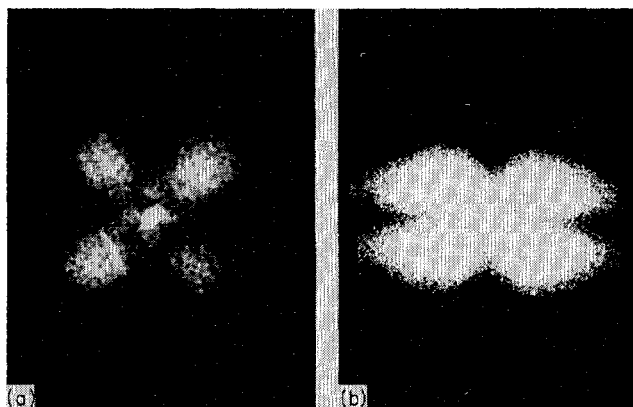

Figure 3. Photographic light-scattering patterns for an unstretched (a) and an 80% stretched (b) polybutene-1 sample (reprinted from ref 12).

an analyzing polaroid, and subsequently recorded on a photographic film, or else measured with a photomultiplier photometer. Typical light-scattering patterns of unstretched and stretched polybutene-1 are shown in Figure 3. These are designated as "H_v patterns" and are obtained when the incident light is vertically polarized and the scattered light is passed through an analyzing polaroid which transmits horizontally polarized light.

The patterns may be interpreted theoretically in terms of the scattering from spherical structures (spherulites) where the refractive indexes in the radial and tangential directions are different. As seen from Figure 3, the change upon stretching results from a deformation of spherulites from spheres to ellipsoids,[18–21] and is related to the manner in which the optic axes of the spherulites change their orientations with deformation. Satisfactory agreement between the measured and theoretical scattering patterns has been obtained.

A great advantage of light scattering is its ability to follow rapid changes. A high-speed light-scattering motion picture technique has been used to follow the rapid deformation of polyethylene and polybutene-1.[21,22] An observation for polyethylene is that the spherulite

(18) S. Clough, J. J. van Aartsen, and R. S. Stein, *J. Appl. Phys.*, **36**, 3072 (1965).
(19) R. J. Samuels, *J. Polym. Sci., Part C*, **4**, 37 (1966).
(20) J. J. van Aartsen and R. S. Stein, *J. Polym. Sci., Part A-2*, **9**, 295 (1971).
(21) P. F. Erhardt and R. S. Stein, *J. Polym. Sci., Part B*, **3**, 553 (1965).
(22) P. F. Erhardt and R. S. Stein, *J. Appl. Polym. Sci.*, No. 5, 113 (1967).
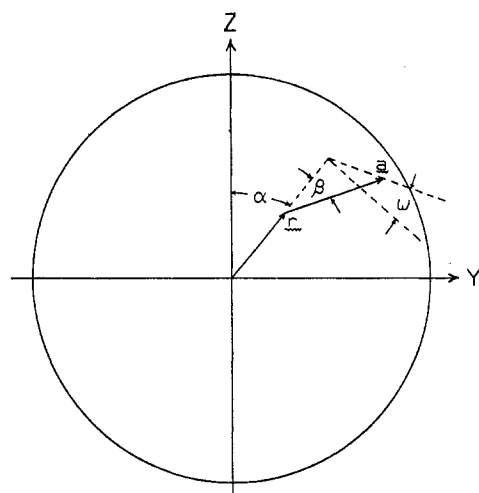
Figure 4. The angles β and ω defining the orientation of the optic axis within a spherulite (from ref 25).

shape change occurs essentially simultaneously with the sample deformation. In retrospect, this should be obvious since spherulites are volume filling and if their shape did not change along with the change in shape of the sample, failure would occur at the spherulite boundaries.

As pointed out later, crystal and amorphous chain orientation changes occur over much longer time intervals than required for the spherulite shape change. Such orientation changes imply that the direction of the optic axis within the spherulite changes. In the undeformed state the optic axis is oriented at some fixed angle, β_0, to the spherulite radius (Figure 4). The twist angle, ω, is usually random but may vary helicoidally with the distance away from the center of the spherulite. For a purely, affine deformation, (a) the coordinates of all points within a spherulite are displaced in the same ratio as are the external dimensions of the sample so that the local strain, λ_l, is equal to the macroscopic strain, λ, (b) the angle β remains fixed at β_0, and (c) the angle ω remains random.

The actual deformation may deviate from the above in several respects. Even though the overall length of the spherulite in the stretching direction may change in a manner paralleling the change in length of the sample, the local deformation may not. The spherulite is often found to deform more near its equator than elsewhere.[14,15] This gives rise to a density depletion in this part of the spherulite, possibly associated with the formation of microvoids between separating lamellae. With H_v polarization, this density change does not produce much effect on light scattering. However, when the polarization directions of the incident light and the analyzing polaroid are both parallel to the stretching direction (V_v polarization) or both perpendicular to the stretching direction (H_h polarization), theory predicts and experiments confirm that excess scattering occurs. This excess scattering proves to be time dependent, so that in short times the spherulite deformation is less uniform than in long times.

A second deviation from pure affine deformation is

the change of the angle β with strain. For polyethylene, the local optic axis direction of the spherulite lies in the direction of the polymer chain within the crystal (the c-axis direction) at $\beta_0 = 90°$. If β_0 remained at 90° during the affine deformation of the spherulite, chains would approach an average orientation perpendicular to the stretching direction. This effect is indeed seen at small strains in short times and at low temperatures. However, it is a well documented and intuitively obvious observation that stretching a polymer orients chains parallel to the stretching direction. This must mean that β changes with strain in a manner described by a parameter K.[18,20,23,24] When $K = 0$, β is restricted to β_0, and with increasing values of K, β is permitted to decrease more with elongation in a manner such that the change is greater at smaller α. As will be discussed later, this change of β is time dependent and lags the change in shape of the spherulite itself.

Upon elongation of the sample, the randomness of the twist angle ω is lost, especially in the equatorial part of the spherulite. As ω approaches 0°, optic axes tend to lie in the plane containing the stretching direction. A second parameter, η, is introduced to express this tendency of ω to assume a preferred value. This twist process is also time dependent.

One may associate the crystalline contribution to these processes with changes in the orientation of lamellae within the spherulite. The change in β is related to bending of lamellae and tilting of chains with respect to the lamellae planes (involving a shear of the crystal itself), whereas the change in ω is related to the twisting of the lamellae about the spherulite radius. As might be expected, a rapidly crystallized sample possesses smaller and more disordered spherulites characterized by larger values of K and η.

These descriptions are useful at relatively low strains of the order of a few per cent where the integrity of the spherulite is preserved. At larger strains, irreversible structural rearrangements occur which lead to major changes in the light scattering but are more difficult to characterize.

Dynamic Light Scattering

The changes in light scattering for a sample undergoing small strain may be studied readily by the dynamic light-scattering technique in which the sample is subjected to a small sinusoidal tensile strain, and the variation of light-scattered intensity at particular scattering angles is followed.[8,23] The scattering is characterized by the angle θ between the incident and scattered ray (Figure 5), the polarization directions of the incident light ψ_1 and that passed by the analyzing polarizer ψ_2, and the angle Ω between the normal to the plane of measurement of θ and the stretching direction. Measurements are made as a function of the frequency of straining and temperature.

(23) T. Hashimoto, Ph.D. Thesis, University of Massachusetts, Amherst, 1970.
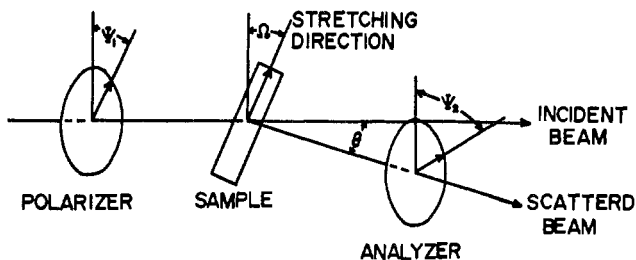(24) T. Hashimoto, P. J. Phillips, and R. S. Stein, in preparation.

Figure 5. The scattering angles θ, Ω, ψ_1, and ψ_2 (from R. S. Stein and T. Hashimoto, *J. Polym. Sci., Part A-2*, **8**, 1503 (1970)).
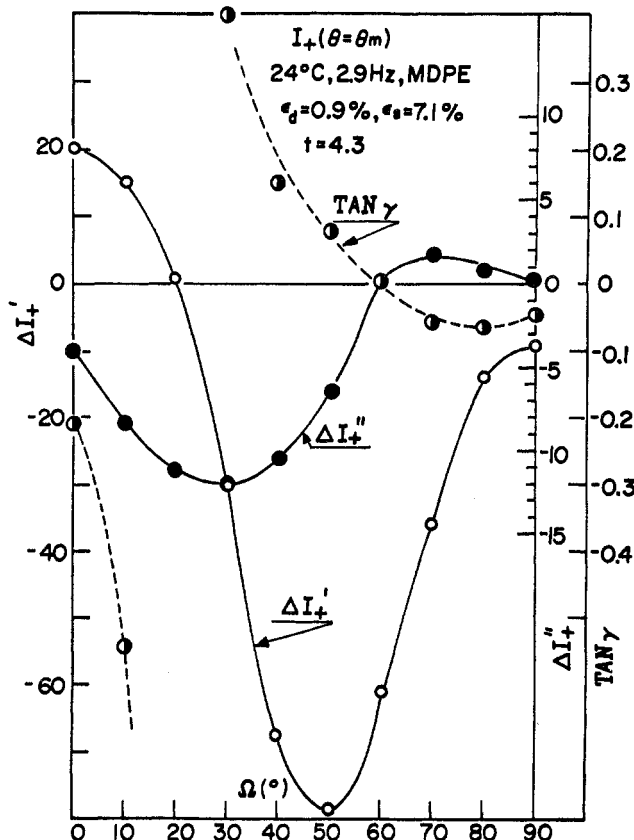

Figure 6. The experimentally measured variation in the real part $\Delta I_{+}'$ and the imaginary part $\Delta I_{+}''$ of the intensity change with light scattering during the sinusoidal variation of strain on a medium density polyethylene sample at a static strain $\epsilon_0 = 7.1\%$, a strain amplitude $\Delta \epsilon = 0.9\%$, and a frequency of 2.9 Hz. The polarization directions are kept crossed such that $\psi_1 = \Omega$ and $\psi_2 = \Omega + 90°$. (From *J. Polym. Sci., Part C*, **No. 32**, 45 (1971).)

When the sample is subjected to a dynamic strain, the scattered intensity change differs in phase from the strain so that it is a complex number consisting of a real part, $\Delta I'$, in-phase with the strain and an imaginary part, $\Delta I''$, out-of-phase. The phase angle γ between the intensity change and the strain is given by tan $\gamma = \Delta I'' / \Delta I'$.

Typical values for the variation of $\Delta I'$ and $\Delta I''$ with the aximuthal angle Ω under conditions of crossed polarization such that $\psi_1 = \Omega$ and $\psi_2 = \Omega + 90°$ are shown in Figure 6 for a medium-density polyethylene film.[23] Measurements are made at $\theta = \theta_m$ corresponding to the distance out from the center of the light-scattering
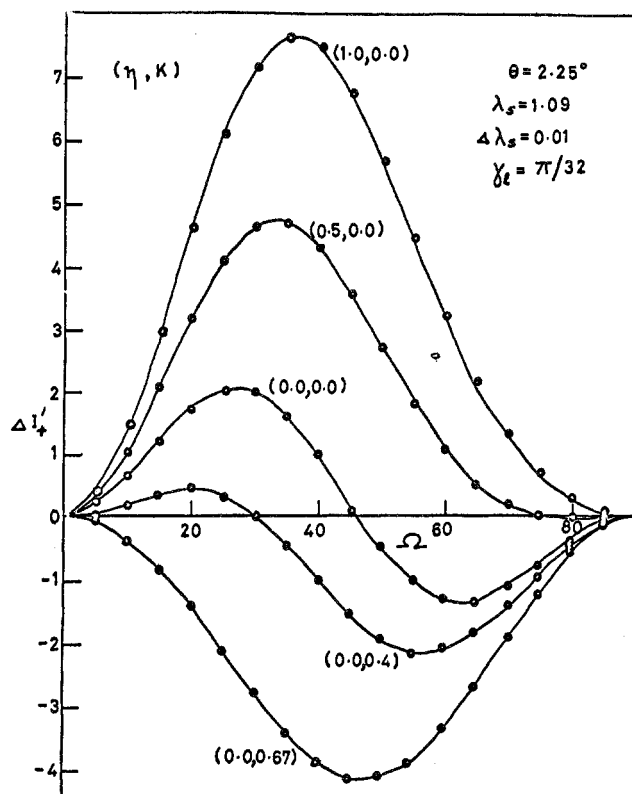

Figure 7. The theoretically calculated variation in $\Delta I_{+}'$ during the uniform straining of a spherulite for various values of the parameters η and K (from *J. Polym. Sci., Part C*, **No. 32**, 45 (1971)).

photograph of Figure 3 at which maxima of the four-leaf-clover pattern occur. Such a plot is equivalent to measuring the intensity change around a circle at a constant distance from the center of Figure 3 which passes through the intensity maxima.

It is noted that the intensity change, $\Delta I'$, is positive at small Ω, passes through zero, and changes to negative values at larger Ω. This sign reversal might be predicted from the photographic observations of Figure 6 and corresponds to the intensity change resulting from scattering lobes moving downward from their 45° positions toward the equator of the pattern.

This intensity variation may be theoretically calculated by use of the theory for the scattering from deformed spherulites.[20,24] The results of such a calculation are plotted in Figure 7 for the case of uniform deformation of a spherulite for various values of the parameters K and η. It is noted that the plot for the completely affine deformation where $K = \eta = 0$ cannot account for the experimental data. It is necessary to assume values of K and η of about 0.6 and 0.4 to produce a curve most resembling the experimental observation, so that the optic axis twists and tilts as the spherulite deforms.

The theoretical curve differs from the experimental one in four important aspects. (a) The theory predicts $\Delta I'$ should be 0 at $\Omega = 0$ and 90°, whereas a finite value is found. This is a consequence of the assumption of an ideal spherulite with no randomness in optic axis orientation. If local deviations from the ideal orienta-

tion directions of the optic axes are permitted, then this excess scattering may be accounted for.[25] (b) This same randomness accounts for the observation that larger intensity changes are found for values of θ appreciably larger than those corresponding to this θ_m which may be interpreted in terms of changes in the orientational correlations among lamellae. (c) The theory predicts that $\Delta I'' = 0$, whereas an appreciable value is seen in Figure 6. The theory may be modified to account for this by allowing the crystal reorientation processes to differ in phase from the applied strain. In fact, a phase angle of $\gamma = \pi/32$ was used for the calculations of Figure 7. (d) The theory cannot account for the excess scattering in experiments carried out with parallel polarization. As previously discussed, this excess scattering arises from density changes accompanying nonuniform spherulite deformation. A modified theory has been proposed[24] which allows greater deformation to occur in the equatorial part of the spherulite which does account for this excess scattering. It also changes somewhat the parameters required to fit the data of Figure 6, and indicates a somewhat smaller value of K, a larger η, and a reversal of sign of γ.

The above theory attempts to account for the scattering in terms of only the crystalline contributions. The scattering actually depends upon the distribution of total spherulite birefringence including the component arising from amorphous orientation. Present efforts are concerned with including this amorphous contribution in the theory.[26]

It is evident that the technique affords a useful tool for the study of the deformation process. Studies[23] that have been carried out on the effect of frequency, temperature, and sample type are too lengthy to report here, but they further confirm the proposed model. While these studies are for a polymer in which the crystals are present in well-ordered spherulitic aggregates, the technique may be applied to cases where a lower degree of order prevails.

Dynamic X-Ray Diffraction

The light-scattering studies show that the deformation of a spherulitic polymer involves a changing orientation of optic axes within the spherulites. The spherulites are composed of both crystalline and amorphous material (being about 50% crystalline for low density polyethylene). It is evident that a direct study of the changing crystalline orientation during a vibration experiment similar to the dynamic light-scattering experiment should complement these studies.

A description and preliminary results from the dynamic X-ray diffraction technique, where the sample is vibrated as in the dynamic light-scattering apparatus, have been reported.[9,11,27,28] An X-ray beam is passed
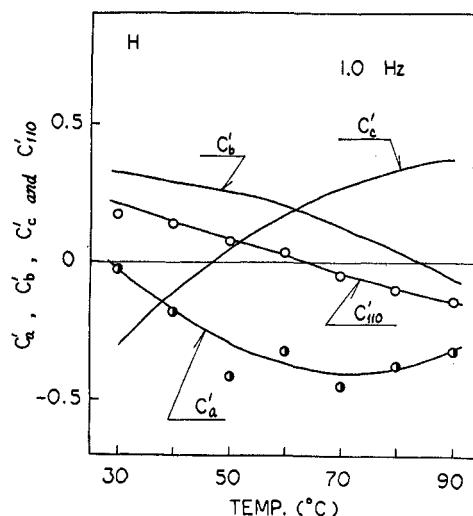
(25) W. Chu and R. S. Stein, *J. Polym. Sci., Part A-2*, **8**, 489 (1970).

(26) T. Hashimoto, R. Prud'homme, and R. S. Stein, in preparation.

(27) T. Oda, K. Kawai, T. Kawaguchi, and D. Keedy, *Rev. Sci. Instr.*, **39**, 1847 (1968).

(28) T. Kawaguchi, T. Ito, H. Kawai, D. Keedy, and R. S. Stein, *Macromolecules*, **1**, 126 (1968).

Figure 8. The variation of C'_a, C'_b, and C'_c, with temperature for a heat treated low-density polyethylene at a frequency of 1 Hz.

through the sample and the real and imaginary variations in diffracted X-ray intensities, $\Delta I'$ and $\Delta I''$, are measured just as with light scattering. A scintillation counter with signal averaging is used.

The degree of orientation of the ith crystal plane may be described by an orientation function[29] $f_i = [3\langle \cos^2 \alpha_i \rangle_{av} - 1]/2$, which may be determined from a measure of the azimuthal variation of the diffracted X-ray intensity. The angle α_i is that between the normal to the diffracting plane and the stretching direction. The function f_i has the property that it is zero for random orientation of a crystal plane, unity if the plane normal is parallel to the stretching direction, and $-1/2$ if it is perpendicular to this direction. From the results of the dynamic experiment, the change in orientation function may be determined; this when divided by the change in strain is called the dynamic compliance, $C_i^* = \Delta f_i/\Delta \epsilon$, which may differ in phase from the strain change and generally be a complex number with real and imaginary parts, C_i' and C_i''.

By measuring diffraction at selected Bragg angles, orientation changes of particular crystal planes may be studied. A plot of C'_a, C'_b, and C'_c against temperature is given in Figure 8 for the a, b, and c crystal axes of a low-density polyethylene which had been quenched from the melt and then heat treated.[30] The c axis is the chain axis while the b axis lies in the radial direction of the undeformed spherulite. It is noted that at low temperatures, C'_c becomes negative, indicating that the c axis orients perpendicularly to the stretching direction, whereas the positive C'_b indicates parallel orientation of the b axis. This is just what would be expected on the basis of a purely affine deformation of the spherulite. With increasing temperature there is an increasing tendency for C'_c to become parallel with a consequent decrease in C'_b, as might be expected with an in-

(29) P. H. Hermans, "Physics and Chemistry of Cellulose Fibers," Elsevier, New York, N. Y., 1949.

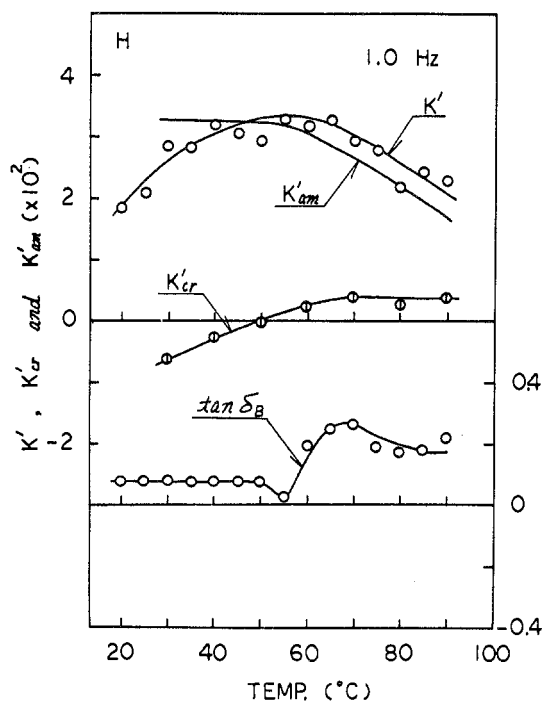(30) A. Tanaka, Ph.D. Thesis, University of Massachusetts, Amherst, 1970.

Figure 9. The variation of the measured strain-optical coefficient K', the calculated crystalline and amorphous contributions, K'_{cr} and K'_{am}, and the tangent of the birefringence-strain phase angle with temperature at a frequency of 1 Hz for heat-treated low-density polyethylene.

Figure 10. The variation of the measured strain-optical coefficient, K', the calculated crystalline and amorphous contributions, K'_{cr} and K'_{am}, and the tangent of the birefringence-strain phase angle with temperature at a frequency of 1 Hz for quenched low-density polyethylene.

crease in crystal tilt and twist processes within the spherulite.

The above behavior is very different from that of the same polyethylene which has been quenched but not heat treated where the crystals behave as individual entities—not as participants of spherulites. In this case the orientational compliances decrease with increasing temperature since there is an increasing tendency for chains to slip past each other within the crystal when the polymer is stretched. This is a consequence of the onset of chain mobility within the crystal so that it becomes easier to pull a chain through the crystal than to change the orientation of the crystal. With increasing frequency of straining, an increase in crystal orientation change is seen since less relaxation of crystal orientation can occur in the shorter time period of the strain cycle.

It should be noted that these rather appreciable differences between the orientation behavior of the two samples occur despite the relatively small difference in degrees of crystallinities (50 and 46%). Also, microscopic examination and low-angle light-scattering patterns indicate that both samples are composed of spherulites of about the same size with a somewhat greater degree of disorder within the spherulites of the quenched sample. None of the simple theories of mechanical behavior of crystalline polymers could account for these large differences. We believe that heat treatment of the quenched sample decreases crystal mobility through its effect on increasing lamellar thickness and perfection and increasing the tautness of tie chains.
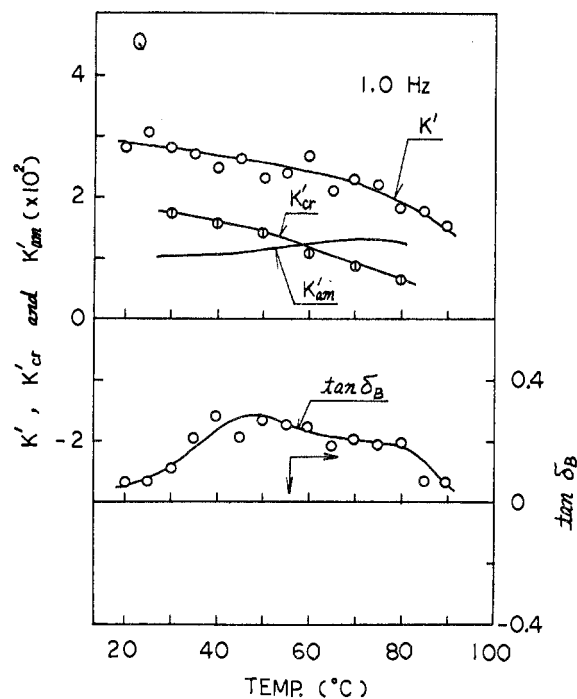
An even more striking difference may be seen by observing the orientation of amorphous chains as may be deduced from measurements of birefringence along with X-ray diffraction.

Dynamic Birefringence

The birefringence or double refraction of a sample is a consequence of the total molecular orientation, and may be expressed as a sum of the crystalline and amorphous contributions as[29,31,32]

$$\Delta = \phi_{cr}\Delta_{cr} + (1 - \phi_{cr})\Delta_{am} + \Delta_{Form}$$

where ϕ_{cr} is the volume fraction crystallinity and Δ_{cr} Δ_{am} are the specified birefringence contributions from crystalline and amorphous regions. The form birefringence, Δ_{Form}, is a small contribution arising from the distortion of the electrical field of the light wave at the phase boundary. The crystalline birefringence depends upon the principal refractive indexes of the crystals for light polarized parallel to the a, b, and c axes, n_a, n_b, and n_c, and the orientation function for two of the axes according to[31]

$$\Delta_{cr} = (n_a - n_c)f_a + (n_b - n_c)f_b$$

For polyethylene, the crystal refractive indexes may be related to the measureable refractive indexes of n-paraffin crystals.

By measuring the total birefringence and subtracting the crystalline contribution calculated by using orientation functions measured by X-ray diffraction,

(31) R. S. Stein, J. Polym. Sci., 31, 1137 (1958).
(32) R. S. Stein and F. H. Norris, ibid., 21, 381 (1958).

the total birefringence has been resolved into components coming from crystalline and amorphous orientation.[32] It was found, for example, that about two-thirds of the birefringence of low-density polyethylene comes from the crystalline contribution. For static deformation, this fraction is not affected very much by thermal treatment.

The dynamic birefringence, measured on a vibrating sample as with the previous measurements, is much more revealing.[9,10,12,33] The birefringence response is conveniently expressed in terms of the strain-optical coefficient, K, the derivative of birefringence with respect to strain. Since the birefringence differs in phase from the applied strain, K is also a complex quantity with a real and imaginary part.

The variation of the real part of the strain-optical coefficient, K', with temperature at a frequency of 1 Hz is shown in Figures 9 and 10 for heat-treated and quenched low-density polyethylene. While the value of K'' for the heat-treated sample passes through a maximum at about 60°, a maximum for the quenched sample occurs below 20°.

The crystalline and amorphous contributions to K' may be obtained by differentiating the preceding equations for birefringence with respect to strain. The only terms which vary with strain are the orientation functions. This gives the orientational compliances which may be evaluated from the dynamic X-ray studies.

The values of K'_{cr} and K'_{am} calculated in this way

(33) S. Onogi, D. A. Keedy, and R. S. Stein, *J. Polym. Sci., Part A-2,* **5,** 1079 (1961).

are included in Figures 9 and 10.[30] It is seen that the most of the birefringence of the heat-treated sample comes from the amorphous contribution. In fact, the crystalline contribution is negative at low temperatures. For the quenched sample, however, the crystalline and amorphous regions contribute about equally to K'.

Further Studies

These studies have been carried out for a particular polyethylene sample and are now being extended to the study of other samples of polyethylene as well as other polymers. Attempts are being made to directly measure amorphous orientational changes from the observation of infrared dichroism of bands arising from amorphous regions.[34,35] Also attempts are being made to observe crystalline orientational changes during relaxation at constant length.[36,37] It is hoped that the interpretation of such experiments will help with the understanding of the physical properties of these important materials.

(34) Y. Fukui, T. Asuda, and S. Onoyi, *Polym. J.,* **3,** 100 (1972).

(35) Y. Uemura and R. S. Stein, *J. Polym. Sci.,* in press.

(36) T. Oda and R. S. Stein, *J. Polym. Sci., B,* **9,** 543 (1971); *J. Polym. Sci, A2,* in press.

(37) R. S. Stein, T. Oda, R. Finkelstein, and Y. Vemura, *Bull. Amer. Phys. Soc., Ser. II,* **17,** 361 (1972).

The Olefin Metathesis Reaction

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Olefin metathesis is a catalytically induced reaction wherein olefins undergo bond reorganization, resulting in a redistribution of alkylidene moieties (eq 1).[1]

All metathesis catalysts are derived from transition metal compounds. It is convenient to classify these catalysts into two main groups: (a) heterogeneous catalysts—transition metal oxides or carbonyls de-

After completing his undergraduate education and earning the M.Sc. degree at the Hebrew University of Jerusalem, Israel, Nissim Calderon came to the United States and enrolled in the then newly created Ph.D. program in Polymer Science at the University of Akron. His research in Jerusalem and Akron involved synthesis of organometallics and their application as polymerization catalysts. After earning his Ph.D. in 1962, he joined the Synthetic Rubbers department of the Goodyear Tire & Rubber Comyany, where his main activity has been research in the area of transition metal-olefin chemistry. In 1967 he was appointed Section Head in the Basic Polymer Research Department in charge of new elastomers.

posited on high-surface-area supports,[3] (b) homoge-

† Contribution No. 469.

(1) "Olefin disproportionation" is the name first selected by the authors of ref 2 to describe the *overall* process of the [metathesis + isomerization] of acyclic olefins using heterogeneous metal oxide catalysts. At the outset of the discovery of homogeneous catalysts capable of inducing a "clean" metathesis reaction, it became evident that the term "olefin disproportionation" was inadequate to properly describe the nature and scope of the reaction, and was even misleading in certain cases. Since the basic process on hand is an alkylidene interchange, it was decided to adopt the name "olefin metathesis," as this name properly conveys the nature and scope of the reaction. In its specific applications (as shown throughout the present Account) it can be utilized to: (a) disproportionate olefins; (b) polymerize cycloolefins; (c) prepare catenanes and other macrocyclics; (d) synthesize dienes and trienes. Hence, olefin disproportionation is to be considered a special case of the more general olefin metathesis reaction.

(2) R. L. Banks and G. C. Bailey, *Ind. Eng. Chem., Prod. Res. Develop.,* **3,** 170 (1964).

(3) For a detailed review see G. C. Bailey, *Catal. Rev.,* **3,** 37 (1969).