[CONTRIBUTION FROM THE POLYMER STRUCTURE SECTION, NATIONAL BUREAU OF STANDARDS]

# Dimensional Changes in Systems of Fibrous Macromolecules: Polyethylene[1]

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Fibrous polyethylene of extremely high axial orientation was crosslinked by means of ionizing radiation, and the anisotropic changes in length that occur as a consequence of this process were investigated. In accord with theoretical expectations and with previous results obtained in a study of fibrous natural rubber, the length in the isotropic state subsequent to the crosslinking process increases as the crosslinking level increases. However, because of the initially higher axial orientation possessed by the polyethylene fibers much greater elongations are observed in the liquid state in this instance. As a consequence of this fact, on subsequent recrystallization a preferential axial crystalline orientation develops without the application of any external force. The melting and recrystallization of these fibers results in a reversible contractile system without the necessity of maintaining any external force. Anisotropic reversible dimensional changes of about 25% are observed, and these results are explicable on the basis of well established physical-chemical principles appropriate to macromolecular systems. These principles are then invoked to explain many of the observed anisotropic dimensional changes that occur in systems of naturally occurring fibrous proteins.

## Introduction

Fibrous macromolecules possess, as a characteristic property, the ability to alter their dimensions when subject to appropriate changes in their chemical or thermal environment. This phenomenon is observed in all synthetic fibers and manifests itself in naturally occurring systems of fibrous macromolecules by the well known dimensional changes that occur in keratin, by the process of muscular contraction and by cell motility and mitosis, to cite but a few examples. Though in many instances the dimensional changes that are incurred are not recoverable, reversible dimensional changes lead to processes wherein thermal or chemical energy can be converted to mechanical work. Until recently, studies of the properties inherent in such a collection of macromolecules that could lead to an understanding of the underlying general principles governing dimensional changes have not received attention commensurate with the prime importance of the phenomena.

Flory[2-4] repeatedly has stressed that the now well established crystal-to-liquid phase transformation in macromolecular substances[5] should play an important role in the mechanism of dimensional change. It is known experimentally that a substantial contraction does occur when an axially oriented crystalline polymer melts and conversely the crystallization of an axially oriented system results in an increase in the length.[6] For example, both for natural rubber which had been rendered fibrous[7] and for collagen,[8,9] large irreversible contractions occur on complete melting. In order for such fibrous polymers to undergo their anisotropic dimensional changes in a thermodynamically reversible manner, complete melting must be avoided. However, dimensional changes which are reversible can be obtained by partial melting and recrystallization if a two-phase equilibrium is maintained by the application of an appropriate stress.[10]

Recently, a different mechanism by which a polymeric system can undergo dimensional change has been pointed out.[3] When a collection of highly oriented chain molecules are intermolecularly crosslinked it is expected that the axial shrinkage that occurs upon disorientation should decrease as the fraction of the units crosslinked is increased. This expectation has been verified in the case of natural rubber[11,12] wherein a threefold increase in the isotropic length is observed when about 3% of the chain units are crosslinked in the fibrous state. This observation should be applicable to all polymeric systems fulfilling the initial requirements, and the changes in length that are incurred in the isotropic state should be maintained during any subsequent transformation of the system.

In the present paper we consider in greater detail these two mechanisms by which anisotropic dimensional changes can be induced in polymers by selecting for study a linear polyethylene specimen of high axial orientation. It already has been reported[13] in a preliminary communication from this Laboratory that by introducing an appropriate number of crosslinks into this fibrous polymer, a contractile system results which is thermodynamically reversible without the application of any external force.

## Experimental

Materials.—The polymer studied was a linear polyethylene manufactured by the Phillips Petroleum Company under the name Marlex-50. Various physical properties of this polymer already have been reported,[14] and a detailed investigation of the thermodynamics of the fusion process[15] and the kinetics of crystallization[16,17] have been made. The

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[1] Supported in part by Research Grant D-572, U. S. Public Health Service.

[2] P. J. Flory, *Science*, **124**, 53 (1956).

[3] P. J. Flory, THIS JOURNAL, **78**, 5222 (1956).

[4] P. J. Flory, *J. Cell. Comp. Physiol.*, **49**, Supplement 1, 175 (1957).

[5] L. Mandelkern, *Chem. Revs.*, **56**, 903 (1956).

[6] W. H. Smith and C. P. Saylor, *J. Research Natl. Bur. Standards*, **21**, 257 (1938).

[7] J. F. M. Oth and P. J. Flory, THIS JOURNAL, **80**, 1297 (1958).

[8] K. H. Gustavson, "The Chemistry and Reactivity of Collagen," Academic Press, Inc., New York, N. Y., 1956, p. 211.

[9] P. J. Flory and R. R. Garrett, THIS JOURNAL, **80**, 4836 (1958).

[10] J. F. M. Oth, E. T. Dumitru, O. K. Spurr, Jr., and P. J. Flory, *ibid.*, **79**, 3288 (1957).

[11] D. E. Roberts, L. Mandelkern and P. J. Flory, *ibid.*, **79**, 1515 (1957).

[12] D. E. Roberts and L. Mandelkern, *ibid.*, **80**, 1289 (1958).

[13] L. Mandelkern, D. E. Roberts and A. F. Diorio, *ibid.*, **80**, 500 (1958).

[14] D. C. Smith, *Ind. Eng. Chem.*, **48**, 1161 (1956).

[15] F. A. Quinn, Jr., and L. Mandelkern, THIS JOURNAL, **80**, 3178 (1958).

[16] S. Buckser and L. H. Tung, paper presented at the 133rd Meeting of the American Chemical Society, San Francisco, Calif., April 12-18, 1958.

[17] L. Mandelkern, in "Growth and Perfection of Crystals," edited by R. H. Doremus, B. W. Roberts and D. Turnbull, John Wiley and Sons, Inc., New York, N. Y., 1958, p. 467.

polymer was rendered fibrous by the Research Department of the American Viscose Company,[18] using melt spinning and drawing techniques. The state of extremely high axial orientation that is obtained is evidenced by several factors. The wide-angle X-ray diffraction pattern is similar to that of a well-developed single crystal with rotational symmetry about an axis perpendicular to the incident X-ray beam. The amorphous scatter is weak in this material, and the unit cell was verified to be orthorhombic with dimensions identical to those given by Bunn.[19,20] It is also verified that in this specimen the *c*-axis, which is the chain direction in the crystal, is coincident with the macroscopic fiber axis. This fiber also displays well-defined meridional diffraction maxima at smaller angles. Thus, long-period spacings corresponding to values of $d$ = 408, 196 and 96 Å. have been reported for this material.[21] These observations can also be interpreted as evidence of high axial orientation.

When this fiber is heated above its melting point and then allowed to cool to room temperature an irreversible axial contraction of about sixty-fold occurs. This observation gives further strong indication of the high orientation of the crystallites in the sample. It is doubtful whether the properties of a synthetic macromolecule possessing this degree of axial orientation has been studied heretofore. The density of the fiber was 0.95 to 0.96 g./cc. at 25° which is in good agreement with the values reported for the unoriented but highly crystalline polymer. This indicates that no significant mechanical defects were introduced during the orientation process.

Crosslinks were introduced into this fiber by subjecting samples to the action of high-energy ionizing radiation. It has been established[22-24] that the major consequence of this process is intermolecular crosslinking since reactions involving chain scission processes occur only to a limited extent. For the major portion of this study $\gamma$-radiation was utilized from a 2500-curie $Co^{60}$ source located at the National Bureau of Standards and operating at a dose rate of $5.7 \times 10^5$ roentgen/hr. For the $\gamma$-irradiation the specimens were sealed in an evacuated Pyrex tube and maintained at 17° for the necessary time interval. In a few experiments the crosslinking was accomplished by electron irradiation from a GE resonant transformer beam unit operating at 1000 kvp. and 0.450 milliamp. outbeam current.[25] The dose rate was 10 megareps per pass, each pass being of two minutes duration, and the time interval of the radiation was so controlled that the temperature rise did not exceed 20°.

**Methods.**—The wide-angle X-ray diffraction patterns of the fibers were obtained using a North American Phillips flat-plate camera equipped with a pinhole collimating system. Nickel-filtered Cu radiation was employed, and the X-ray generating tube was operated at 40 kv. and 20 milliamp. In the work reported here the incident X-ray beam was always normal to the macroscopic fiber axis of the specimen. The film-to-sample distance was 4 cm. and the exposure time was approximately 4 hr.

The ratio of the length of a specimen that had been crosslinked, melted and recrystallized to that of a corresponding non-crosslinked specimen was determined by utilizing the following procedures. The initial irreversible shrinkage ratio of each fiber was determined by measuring the length of a specimen at 25°, both prior to melting and after immersion in a silicone oil-bath maintained at 160° for 0.5 hr. A ruled scale which could be read to 0.1 mm. was used for this purpose. After the initial shrinkage each specimen was placed on a calibrated heated stage, which was coated with silicone grease, and the change in length as a function of temperature was determined by means of a measuring microscope. The initial temperature of measurements was 25°, and in all cases the maximum temperature of measurement always exceeded 140°, which is above the melting temperature of all the fibers. These procedures enabled a calculation to be made of the length of a crosslinked fiber at any temperature, relative to the length that would be obtained in the fiber of the same initial dimensions if no crosslinks were introduced. Thus both the relative change in length in the amorphous state caused by the introduction of the crosslinks and the change in length with temperature through the melting–crystallization cycle for each individual specimen were determined.

## Results

**Isotropic Length.**—Subjecting the highly oriented polyethylene fiber to the radiation doses employed in this study causes only minor changes in the dimensions of the specimen prior to their melting. However, upon the initial melting of the crosslinked fibers marked irreversible axial contractions result, which range in magnitude from about sixty-fold for the original unirradiated material to about two-fold for the specimens subjected to the higher levels of irradiation. From a theoretical point of view an important property to consider[8,12] is the isotropic length of the specimen $L_i$, defined as the length of the material in the amorphous state. This quantity characterizes the length of the retracted material in the non-crystalline state when it had been crosslinked in the highly oriented state. For the polyethylene studies the value of $L_i$ is referred to 140° since this temperature is above the melting point of all the specimens. In making the necessary calculations and in interpreting the results it is convenient to consider the ratio $L_i/L_0$, in which $L_0$ is defined as the corresponding length of the specimen in the amorphous state in the absence of crosslinks.

The values obtained for the quantity $L_i/L_0$ are plotted in Fig. 1 as a function of the square root of the radiation dose $R$. The solid triangles designate samples that were subjected to $\gamma$-radiation from the $Co^{60}$ source; the open triangles represent samples irradiated by the electron beam in the manner described. Values of the radiation dose to which the samples were subjected range from 2.7 to 1000 megareps, and good agreement is obtained

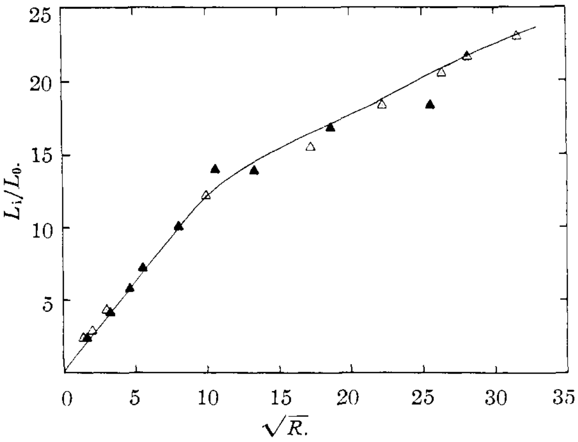

Fig. 1.—Plot of quantity $L_i/L_0$ against the square root of the radiation dose in megareps. $Co^{60}$ $\gamma$-irradiation △; irradiation by means of electron accelerator ▲.

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(18) We wish to thank the Research Department of the American Viscose Company for supplying this material.

(19) C. W. Bunn, *Trans. Faraday Soc.*, **35**, 483 (1939).

(20) An extra reflection, corresponding to one of those reported by P. W. Teare and D. H. Holmes (*J. Polymer Sci.*, **24**, 496 (1957)), was observed at 4.53 Å. This reflection can be most simply interpreted as a beta spot of the {110} reflection since it closely corresponds to this in both position and relatively intensity.

(21) L. Mandelkern, C. R. Worthington and A. S. Posner, *Science*, **127**, 1052 (1958).

(22) E. J. Lawton, J. A. Balwit and R. S. Powell, *J. Polymer Sci.*, **32**, 257 (1958).

(23) A. Charlesby, *Proc. Roy. Soc.* (*London*), **A215**, 187 (1952).

(24) R. W. Pearson, *J. Polymer Sci.*, **25**, 189 (1957).

(25) We wish to thank Dr. A. R. Shultz of the Minnesota Mining and Manufacturing Company for performing the electron beam irradiations for us.

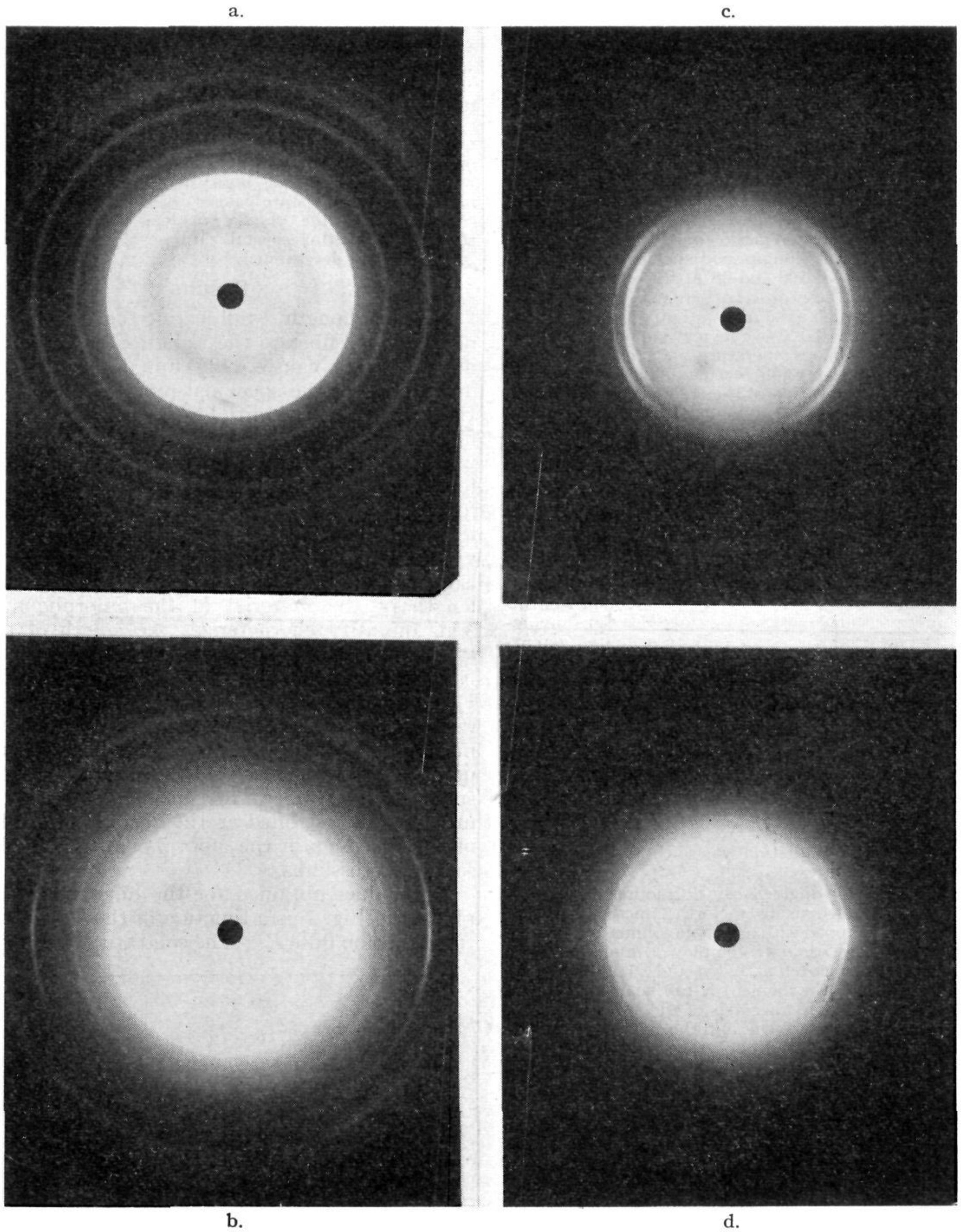

Fig. 2.—Wide-angle X-ray diffraction patterns taken at room temperature of crosslinked recrystallized polyethylene fibers for various radiation doses: (a) $R = 0$; $L_i/L_0 = 1$; (b) $R = 179$ megareps, $L_i/L_0 = 13.7$; (c) $R = 353$ megareps; $L_i/L_0 = 16.8$; (d) $R = 660$ megareps, $L_i/L_0 = 18.3$. Flat-plate camera, Cu K$\alpha$ radiation, specimen-to-film distance 4 cm.

in the quantity $L_i/L_0$ irrespective of the type of ionizing radiation employed. The curve in Fig. 1 is linear for values of the radiation dose up to about 100 megareps, corresponding to $L_i/L_0$ of about twelve, and extrapolates reasonably well to the origin.[26] At the higher levels of irradiation deviations from this proportionality occur and the quantity $L_i/L_0$ increases at a much slower rate. However, despite the deviation from proportionality and the slower rate of increase that develops, a maximum value of 23 for $L_i/L_0$ is obtained. The rather enormous extension that is developed in the amorphous state is achieved without the application of any external stress.

**Crystalline State.**—The irradiation of the highly oriented fibers results in no significant difference in the wide-angle X-ray diffraction pattern as compared to that of the non-irradiated fiber. However, after melting and subsequent recrystalliza-

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[26] Strictly speaking the data are not adequate to rule out the possibility that the lowest values would extrapolate to a value of unity as was observed with natural rubber.[12]

tion significant differences appear in the X-ray diffraction patterns. These results are illustrated in Fig. 2, where patterns for four different samples representative of different irradiation levels are given. Also listed are the appropriate values of the radiation dose and the quantity $L_i/L_0$.

For the sample into which no crosslinks have been introduced, Fig. 2a, the resulting pattern after melting and recrystallization consists of a series of concentric rings with uniform intensity around each circumference. The *d*-spacings correspond to that given for polyethylene[19] and it can be deduced that in this specimen the crystalline state is characterized by a randomly arranged collection of crystallites. As the radiation level is increased the recrystallized samples begin to develop a preferential crystallite orientation, as is indicated in Fig. 2b. This pattern is representative of a sample that has received a radiation dose of 179 megareps. In the amorphous state $L_i/L_0$ is equal to 13.7, and the preferential crystallite orientation is evidenced by the fact that the intensity of the diffraction maxima is no longer uniform in the azimuthal direction. The orientation that is beginning to develop is such that the *c*-axis of the crystallites, which represents the direction of the polymer chains in the crystal, is tilted relative to the macroscopic fiber axis. A similar orientation phenomenon has been reported by Brown[27] and by Narcarrow and Horsely[28] when branched polyethylene in the crystalline state is mechanically oriented. In the work reported here, of course, this orientation is developed without the application of any external force subsequent to the production of the initial fiber. In Fig. 2c this type of orientation, wherein the *c*-axis of the crystallites is tilted relative to the fiber axis while the *b*-axis remains perpendicular to the fiber axis, is further enhanced, for a sample that received a dose of 353 megareps. The angle of inclination between the fiber axis and the *c*-axis in this specimen was calculated by using the reciprocal lattice method and utilizing the intensity maxima of the arcs, and the splitting of the {110}, {200}, {210} and {310} reflections. An angle of inclination of about 30° was calculated by this method, which is in good agreement with that previously reported.[27,28] Figure 2d represents the X-ray pattern for a fiber which received a radiation dose of 660 megareps, corresponding to a maximum value of $\rho$ of $2.65 \times 10^{-2}$, and that had also been completely melted and recrystallized. In this instance the intensity maxima are located on the equator of the diagram and indicate that the *c*-axes of the crystallites are now preferentially oriented parallel to the fiber axis. Thus preferential crystallite orientation, representing the equilibrium state of the system, can be developed by these procedures without maintaining an equilibrium stress.

**Crystal–Liquid Transformation.**—The length–temperature relations of some typical fibers are illustrated in Fig. 3. Prior to initiation of these measurements the specimens were melted and allowed to recrystallize so that they are representative of the equilibrium crystalline state. For all three samples there is noted, at the lower temperatures of measurement, a slight positive thermal expansion coefficient, typical of a crystalline material.[2] The data in the upper curve of this plot, which represents the recrystallized fiber that had not been crosslinked, show an increase of length starting at 125° and terminating rather abruptly at 138°. This temperature interval corresponds to the melting range of non-irradiated linear polyethylene[15] and the increase in length that is observed is merely a reflection of the latent volume increase that occurs on fusion. The middle curve represents the data for a sample that received a radiation dose of 179 megareps (corresponding to the same sample illustrated in Fig. 2b) and in which a preferential axial orientation of the crystallites has begun to develop. During the melting process this fiber first displays a slight increase in its length and then a decrease occurs. The lower curve represents length–temperature data for a specimen that received a radiation dose of 353 megareps and in which the crystallite orientation is more pronounced. The melting process in this instance results in a 20% axial contraction, which occurs over a very narrow temperature interval and again terminates rather abruptly. Above the melting temperature, the length–temperature coefficient is slightly positive, and in this region it is characteristic of the expected thermal expansion in the liquid state when no external force is applied.

On cooling, recrystallization of the specimens occurs, and concomitantly the samples regain their original dimensions. The reversibility of the dimensional change that accompanies the crystal–liquid transformation is illustrated in more detail in Fig. 4. The relative length is plotted against temperature for a fiber corresponding to the one illustrated in Fig. 2d. In the crystalline state this sample possesses pronounced *c*-axis orientation, and consequently a 25% contraction is observed on melting. When the sample is cooled slowly after the completion of fusion at the rate of about 1°/5 min., supercooling occurs, as is indicated in the figure. Despite the supercooling, the original dimensions of the sample are eventually regained. The time required for the return to the original state can be reduced substantially by bringing the sample immediately to a large value of undercooling rather than adopting a slow cooling process. Thus, this melting–crystallization process is completely cyclic, and there is obtained a reversible contractile system, without the necessity of maintaining any external stress.

In Fig. 5 there is plotted the fractional change in length that occurs on melting against the radiation dose received by the sample. No significant contraction is observed on melting until a sample has received a radiation dose of about 100 megareps, which corresponds to a value of $\rho$ equal to $3.90 \times 10^{-3}$. From about 100 to 350 megareps of irradiation a continuous increase occurs in the amount of reversible contraction and a maximum change in length of 25% is achieved at a value of $\rho$ equal to $1.35 \times 10^{-2}$. This value of the contraction remains invariant upon further irradiation.

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(27) A. Brown, *J. Applied Phys.*, **20**, 552 (1949).

(28) H. A. Narcarrow and R. A. Horsley, *British J. Appl. Phys.*, **2**, 345 (1951).

## Discussion

**Isotropic Length.**—When amorphous crosslinked polymers are mechanically deformed the extension ratios that can be developed are severely restricted. Crystallization will intervene usually to limit the amount of extension or the rupture of the constituent polymer chains will occur. In either case, mechanical deformation does not usually result in extension ratios in the amorphous state that are comparable to those reported here. In the case of the polyethylene fibers the large extension ratios that are observed result solely as a consequence of the introduction of a sufficient number of crosslinks into the system when the constituent chains are highly ordered relative to one another. In a similar study of natural rubber, a maximum value of $L_i/L_0$ of only three was obtained. The phenomenal increases in isotropic length that are achieved in the liquid state in polyethylene without the application of any external stress, afford the opportunity of studying some unusual properties of the liquid state as well as studying effects that occur during a subsequent transformation to another state.

The physical basis for the observed increase in the isotropic length subsequent to the crosslinking of polymer chains that are oriented along the fiber axis has been discussed previously in detail.[12] Theoretical expectations are that the quantity $L_i/L_0$ will increase in direct proportion with the square root of the fraction of the units crosslinked.[3,12] The following expression has been derived relating the isotropic length to the crosslinking density when perfectly axially ordered chains are crosslinked

$$L_i/L_0 = (L_r/L_0)\{[N_a a/(\sqrt{3}\,M_0^{1/2}\bar{v})](\bar{r}_0^2/M)^{1/2}\}\,\rho^{1/2}\langle\alpha\rangle_0 \tag{1}$$

where $L_r/L_0$ is the ratio of initial length to the shrunken length of the original fiber into which no crosslinks have been introduced. $N_a$ is Avogadro's number, $a$ is the cross-sectional area of a single chain, $\overline{r_0^2}$ is the unperturbed mean square end-to-end distance of an unconstrained chain of molecular weight $M$, $M_0$ is the molecular weight of a chain repeating unit, $\bar{v}$ is the specific volume, and $\langle\alpha\rangle_0$ represents the linear dilation of a network relative to its reference state.[3] If the fraction of the units crosslinked, $\rho$, is directly proportional to the radiation dose, as has been assumed to be the case for many polymer systems,[29-31] a straight line would be expected in Fig. 1. The deviation from proportionality that occurs in this plot at the higher radiation dose can result from failure of the assumed proportionality between $\rho$ and radiation dose or from the failure of the theory, as embodied in equation 1, when such relatively large extensions are involved.

Although it is well established that when linear polyethylene in the crystalline state is subjected to ionizing radiation *in vacuo*, the predominating effect is that of introducing intermolecular crosslinks, a quantitative relationship between $\rho$ and radiation dose is difficult to establish at present. The problems that are involved in determining the value of $\rho$ for a polymeric network when the crosslinks are introduced into systems of ordered polymer have been discussed previously, and the conventional procedures of measuring either the equilibrium swelling ratio or the elastic modulus in the amorphous state does not suffice. The method that was employed to quantitatively determine $\rho$ for networks formed from fibrous natural rubber is not applicable to the polymer studied in the present work. This situation arises because of the fact that the mode of partitioning of the polyethylene into sol and gel components when irradiated in the amorphous state or when irradiated in the crystalline state is drastically different in the two cases.[32] An analysis of the partitioning of the crystalline polymer between sol and gel indicates, however, that the value of $\rho$, calculated by assuming it to be proportional to radiation dose, would place an upper limit on this quantity. The adoption of this procedure will allow a reasonable estimate to be made of the fraction of the units crosslinked in a given fiber. This, of course, does not account for the deviations of the data in Fig. 1. This latter problem remains as yet unsolved.

It is found experimentally for the polymer studied, whose weight-average molecular weight is 130,000,[33] that the gel point occurs at a dosage of 2.74 megareps. By using the well known relation[34,35] between weight-average molecular weight and the critical number of crosslinks required for gelation and assuming proportionality between $\rho$ and radiation dose, the maximum value of the fraction of ethylene units that are crosslinked at 1000 megareps is found to be $3.90 \times 10^{-2}$.

If the data of Fig. 1 are replotted with the $\sqrt{\rho}$ as abscissa instead of the $\sqrt{R}$, using the maximum values of $\rho$ determined in the manner just described, the first portion of the curve yields a slope of 200. This value is about thirteen times as great as the corresponding quantity found in the case of rubber.[12] According to equation 1 the quantities that determine the magnitude of the slope are either known or can be reliably estimated for polyethylene, with the exception of $\langle\alpha\rangle_0$ which should have a value close to unity.[3] Thus a comparison can be made between the slope obtained for polyethylene and that previously deduced for natural rubber. The ratio of the quantity containing the molecular constants $(a/M_0^{1/2}\bar{v})(\overline{r_0^2}/M)^{1/2}$ is 2.10 times greater for polyethylene than for natural rubber.[36] Since the quantity $L_r/L_0$ for the polyethylene fiber studied is 5.45 times that for fibrous natural rubber, an eleven to twelve-fold greater slope is expected for the polyethylene on the basis of equation 1. This calculation is thus in good accord with that which is actually observed and gives

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(29) A. Charlesby and M. Ross, *Proc. Roy. Soc.* (*London*), **A217**, 122 (1953).

(30) A. R. Shultz and F. A. Bovey, *J. Polymer Sci.*, **22**, 485 (1956).

(31) A. Charlesby, *ibid.*, **11**, 521 (1953).

(32) L. Mandelkern, D. E. Roberts and J. C. Halpin, unpublished results.

(33) L. Mandelkern, D. E. Roberts, J. C. Halpin and F. P. Price, THIS JOURNAL, **81**, in press (1959).

(34) P. J. Flory, *ibid.*, **63**, 3097 (1941).

(35) W. H. Stockmayer, *J. Chem. Phys.*, **12**, 125 (1944).

(36) In making this estimate for polyethylene the value of $a$ was determined from Bunn's crystallographic data, the ratio of $(\overline{r_0^2}/M)^{1/2}$ to the corresponding quantity for the freely rotating polyethylene chain was taken to be 2.3 (W. R. Krigbaum, *J. Polymer Sci.*, **28**, 213 (1958))

strong support to the theoretical considerations which led to equation 1. It thus can be concluded that all macromolecular systems possess the inherent property that if intermolecular crosslinks are introduced when the chains are in a highly axially oriented state a substantial increase in the isotropic length will occur.

Despite the fact that the curve in Fig. 1 does not completely follow theoretical expectations the significant experimental observations are the very large extensions that can be obtained in the amorphous state of a crystallizable polymer without the application of any external stress. This and the previous observations demonstrate a fundamental mechanism whereby the dimensions of a polymer can be altered in a systematic and understandable manner. Thus, if for any given specimen in the amorphous state, the crosslinks were systematically severed, an axial contraction would occur which would follow the curve of Fig. 1. The original dimensions can only be recovered, however, by stretching the polymer to its original extended length and reintroducing the requisite number of crosslinks.

**Crystalline State.**—When the environmental temperature of an amorphous polyethylene sample is lowered below that of the melting temperature, spontaneous crystallization will occur. The transformation between the crystalline and liquid states in polymeric systems has been demonstrated to be a phase transition of the first order and is governed by the appropriate thermodynamic laws.[5,37] Though the complete initial melting of the crosslinked fibers is an irreversible phenomenon akin to the shrinking of collagen[3] and of fibrous rubber,[7] the subsequent recrystallization and melting are completely reversible processes.

From the analyses of the X-ray diffraction patterns illustrated in Fig. 2 for the crosslinked fibers that had been melted and recrystallized, we can conclude that a preferential axial orientation of the crystallites has been developed without the application of any external force. Heretofore, orientation in the crystalline state has only been observed in systems where a deformation by mechanical means has been imposed. The occurrence of this unique situation must be intimately related to the extremely large values of $L_i/L_0$ that are achieved in the amorphous state by the initial introduction of the crosslinks. The large extension ratios that are developed in the axial direction must result in the establishment of a preferential axis for the subsequent transformation. Therefore, nuclei of the crystalline phase, which must be formed in order for the transformation to occur, are also preferentially directed, and axially oriented crystallization results. Evidence for the preferential axial recrystallization of networks formed from fibrous natural rubber has been offered recently by Oth and Flory.[7] The preferred axial orientation of the crystallites in these polyethylene fibers is an inherent part of the system and will be present after any subsequent melting and recrystallization cycles, as long as the crosslinkages are maintained. This situation occurs, despite the lack of any external force, as a result of the fact that this condition represents the equilibrium state of the system.

**Crystal-to-Liquid Transformation.**—Three states of the fibrous polyethylene can be distinguished at any level of crosslinking. There is the initial state (state I) which irreversibly transforms to the liquid state (state II) at an appropriate temperature above the melting temperature This transformation is accompanied by the large axial contraction previously noted. Recrystallization from the liquid state to the new crystalline state (state III) is accomplished easily merely by appropriately reducing the temperature, and it is the X-ray diffraction pattern of specimens in this latter state that is depicted in Fig. 2. Though state I is irrevocably lost on melting, states II and III are interconvertible by subjecting the specimens to conditions that are conducive to either melting or crystallization. Thus the plots in Figs. 3 and 4 represent the change in length that occurs

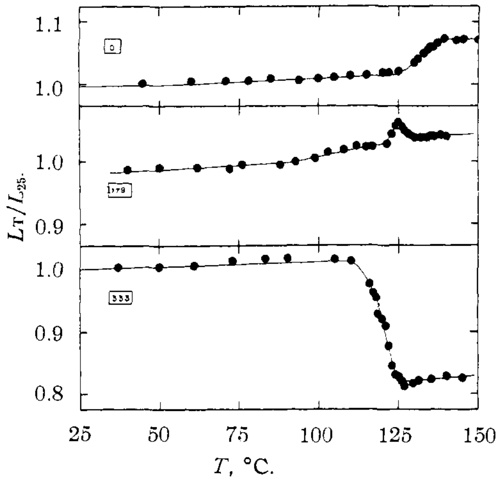

Fig. 3.—Plot of the relative length as a function of temperature of some typical crosslinked polyethylene fibers. State of the system at the lowest temperatures of measurement represents the equilibrium crystalline state. Radiation dose of each specimen is indicated by number in rectangle.

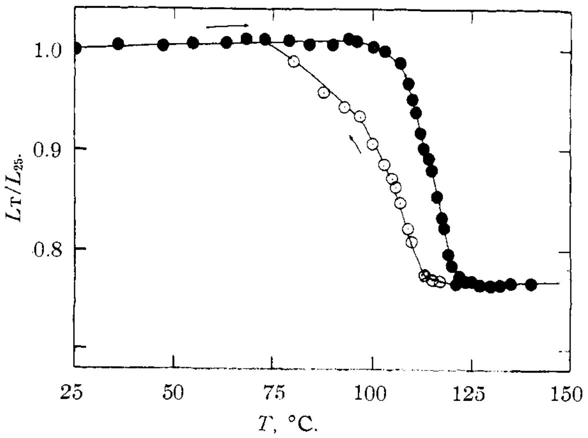

Fig. 4.—Plot of relative length as a function of temperature for polyethylene fiber which has received a radiation dose of 660 megareps: heating cycle ●; cooling cycle ○.

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(37) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 563ff.

during the transformation between states III and II.

On melting, polymeric systems display marked changes in their physical and mechanical properties, and latent changes in the volume and the enthalpy also are observed.[5] When the crystallites are randomly arranged relative to one another in specimens of fibrous form, the latent volume change manifests itself as an increase in length. This is illustrated by the upper curve of Fig. 3 for a sample which had not been crosslinked and in which, therefore, the crystallites are randomly arranged. On the other hand, the melting of an axially oriented crystalline polymer is accompanied by a latent decrease in length. This latter property, which is demonstrated by the lower curve of Fig. 3 and by Fig. 4, is unique to polymer systems. It arises from the fact that for most cases of interest the distance traversed by a collection of connected chain elements in the crystalline state greatly exceeds the distance traversed by the same number of elements in the amorphous state. As already has been pointed out,[7] the shrinkages that are observed in many initially axially oriented macromolecular systems are a consequence of melting. Thus, the sixty-fold contraction observed on the initial melting of the polyethylene fiber studied here, the retraction of fibrous natural rubber,[7] the thermal shrinkage of collagen[8] and the contraction or supercontraction of oriented specimens of keratin, epidermis, myosin and fibrin[38] all occur for the same basic reason. However, in the examples cited, if the melting process is carried to completion, the initial length is not regenerated merely by subjecting the system to crystallization conditions, since some mechanism to ensure the preferential axial recrystallization must be present.

In the polyethylene fibers studied here the X-ray diffraction patterns indicate that as a consequence of the state of the material at the time at which the crosslinks were introduced, an oriented crystalline state (formed after melting and subsequent recrystallization) and representing the equilibrium condition is achieved. Thus, since the crystallites formed from the melt are axially oriented, re-elongation should occur on crystallization. As is indicated by the data of Fig. 4, this expectation is fulfilled and a reversible contractile system, governed by the melting–crystallization cycle, has been achieved.

The narrow temperature range over which the transformations occur is characteristic of a cooperative process as is the abruptness at which the process terminates. The sharpness of the melting is further enhanced by the fact that the polymer undergoing the transformation is a homopolymer. For a copolymeric substance, one in which not all the chain repeating units participate in the crystallization process, the melting range will become much broader, even though the fusion is still describable as a first-order phase transition.[5,39]

The reversible dimensional changes that are observed are representative of the results obtained on completely melting the sample. The return to the original length, from the completely molten polymer must inevitably be accompanied by some supercooling. Supercooling is characteristic of the crystallization from the melt of all polymeric systems and is a consequence of the fact that the crystallization process is governed by a nucleation mechanism.[17] If, however, the transformation is not carried to completion so that only partial melting occurs, then the amount of supercooling that is required for the subsequent recrystallization is severely restricted. Consequently, the accompanying dimensional changes which are, of course, smaller in magnitude in this case, do not display the temperature hysteresis typical of the system in which complete melting occurs. For the partial melting process just described only small changes in the degree of crystallinity need be incurred, which will be difficult to detect by many of the experimental techniques used to determine changes in the degree of crystallinity.

The magnitude of the reversible anisotropic dimensional change that occurs on melting depends on the orientation of the fiber in state III and the number of crosslinkages that were initially introduced. The latter factor governs both the orientation and the isotropic length. For the lower values of crosslinking where crystallite orientation is just beginning to develop in state III only small contractions are observed as is indicated in Fig. 5. In the dose range between 100 and 350 megareps the orientation becomes more perfectly developed, so that continuously larger contractions are observed despite the fact that the equilibrium length in the amorphous state is concurrently also increasing. A point is eventually reached, however, where a compensation develops between the orientation in the crystalline state and the increased length in the amorphous state so that the amount of contraction remains essentially invariant with further crosslinking.

The anisotropic reversible change in dimensions that has been demonstrated for the fibrous polyethylene occurs as a result of a phase transition. As has been pointed out by Flory[2,4] and Pryor,[40] fibers such as are described here can serve as the working substance of an engine that converts thermal energy to mechanical energy.[41] It should be emphasized that this cyclic process does not require the application of a specified external force but will operate with any applied load consistent with the tensile properties of the fiber. The two primary principles that govern the dimensional change are the facts that an axial contraction will result on the melting of an oriented polymer system, and the crosslinking of an oriented fiber results in a preferential axis for recrystallization which is maintained during subsequent melting–crystallization cycles.

In the system described here thermal energy is utilized to initiate the transformation between the crystalline and amorphous state. This phenomenon is, of course, more general, and in principle the

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[38] K. M. Rudall, "Symposium on Fibrous Proteins," Society of Dyers and Colourists, 1946, p. 15.

[39] P. J. Flory, *Trans. Faraday Soc.*, **51**, 848 (1955).

[40] M. G. M. Pryor in "Progress in Biophysics," edited by J. A. V. Butler and J. T. Randall, Butterworths–Springer, 1950, p. 216.

[41] In fact, such an engine, utilizing a polyethylene fiber described here as the working substances has been constructed by Dr. S. G. Weissberg of this Bureau.

phase transition also can be initiated by an appropriate chemical reaction. Thus for a macromolecular system that is chemically more reactive and which is rendered fibrous and crosslinked in this state, in a manner similar to that by which the polyethylene fibers were prepared, contraction will still occur on fusion and spontaneous elongation on recrystallization. For such a system the fusion process could be carried out isothermally by a variety of chemical means, and an engine capable of converting chemical energy to mechanical energy would result. For example, Flory has pointed out[2,4] that melting and the accompanying contraction could be caused by offering to the polymer units originally in the crystalline state the thermodynamically more favorable situation of forming complexes with appropriate reagents in the amorphous state. Crystallization of the amorphous network then could be induced by removal of the complexing reagent. In a similar manner, if certain functional groups on the polymer chain were allowed to ionize, melting should result, as would be the case for other more direct chemical reactions. With these generalizations, it is thus important that a distinction be made between the actual reversible contractile mechanism caused by melting and recrystallization and that process or chemical reaction which actually induces the phase transition. When this distinction is made it is then possible to investigate many of the observed contractile processes from a unified point of view in terms of the principles discussed above. This approach is particularly useful in systematizing and investigating the cause of the anisotropic dimensional changes that have been reported for various fibrous proteins.

**Dimensional Changes in Fibrous Proteins.**—The pioneering wide-angle X-ray diffraction studies of Astbury[42-44] and co-workers has shown that a wide variety of protein systems occur naturally in the crystalline state. Besides being crystalline these protein systems also occur with a high degree of axial orientation and can thus be termed fibrous. This situation arises from the fact that the chain elements of each polypeptide molecule are arranged in a helical conformation[45] (beta conformations being excepted) which is stabilized by intramolecular hydrogen bonds. Thus each individual chain assumes a rod-like form and is highly asymmetric, having a length which is many times greater than its diameter. It has been pointed out[2,3] that the grouping together or aggregation of a collection of such highly asymmetric molecules must inevitably result in a system that assumes fibrillar form. This arises solely as a consequence of geometrical considerations and requirements.[46] Thus a fibrous protein can be considered to be composed of rod-like highly asymmetric molecules arranged in regular array in the transverse direction. In certain of the fibrous proteins, notably those in the keratin class, intermolecular covalent crosslinks are also present. It can be presumed in this instance that the cross linkages are made after fiber formation and are therefore imposed on a previously ordered structure. For these and similar proteins the chain arrangement, the state of the system and the mode of crosslink introduction are strikingly similar to those of the polyethylene fibers prepared in the present work. With this similarity in fundamental structure it could be expected that the dimensional changes observed in the protein systems might parallel and arise from the same cause as those of the reversibly contractile polyethylene fibers.

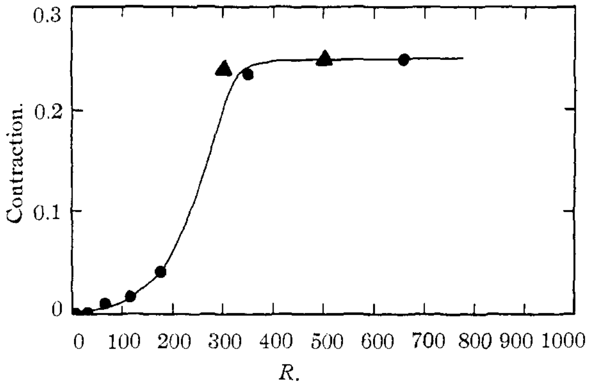

Fig. 5.—Plot of the fractional decrease in length that occurs on melting as a function of the radiation dose of the specimen. Radiation dose in megareps.

For the fibrous proteins that are not intermolecularly crosslinked, or in which the crosslinkages are not maintained during the melting process, a decrease in length should be observed on melting, but if the melting is carried to completion, the dimensional change will not be reversible. As has been previously indicated, this is indeed the case for all of the fibrous proteins which fit this category, and the contractions that occur can always be identified with a simultaneous melting process. Though it has been widely observed[47] that axial contractions can be induced in a number of different proteins by use of a variety of reagents and conditions, the basic mechanisms involved have not been apparent. Once it is recognized that melting is the cause of the contraction and that there are many ways in which the melting process can be induced, *i.e.*, by suitable variation of the thermodynamic environment, the now existing confusion in regard to this matter can be dispelled. Furthermore, for contraction to occur only very simple requirements need be satisfied. Initially, there must be present an oriented crystalline state, and the melting transformation must take place to an amorphous state, or under certain conditions to the disoriented crystalline state. The fundamental basis for this mechanism does not find its origin or explanation in a detailed crystallographic analysis of either the initial or final states, as has been supposed by some investigators.[48,49]

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(42) W. T. Astbury, *Proc. Roy. Soc. (London)*, **B134**, 303 (1947).

(43) K. Bailey, W. T. Astbury and K. M. Rudall, *Nature*, **151**, 716 (1943).

(44) W. T. Astbury, *Trans. Faraday Soc.*, **34**, 378 (1948).

(45) L. Pauling and R. B. Corey, *Proc. Natl. Acad. Sci. U. S.*, **37**, 272 (1951).

(46) P. J. Flory, *Proc. Roy. Soc. (London)*, **A234**, 73 (1956).

(47) J. C. Kendrew, in "The Proteins," Vol. II, Part B, edited by H. Neurath and K. Bailey, Academic Press, Inc., New York, N. Y., 1954, p. 862.

(48) B. Low, in "The Proteins," Vol. I, Part A, edited by H. Neurath and K. Bailey, Academic Press, Inc., New York, N. Y., 1953, p. 236.

(49) L. Pauling and R. B. Corey, *Proc. Natl. Acad. Sci. U. S.*, **37**, 261 (1951).

In those protein systems wherein crosslinks are imposed after fiber formation, an analogy with the polyethylene fibers in either the original crosslinked state (state I) or the recrystallized state (state III) can be made depending on the number of crosslinks that are present. Upon melting the protein fibers, corresponding dimensional changes should result. The fact that in most protein systems melting is usually carried out while the fiber is immersed in a suitable liquid medium does not in any way limit the analogy. The proteins of the keratin class should fulfill the requirements set forth above since they occur in the oriented crystalline state and are intermolecularly crosslinked by means of covalent disulfide bonds.

Alexander and Hudson[50] have recognized that two distinctly different types of contractile processes are observed in fibers of the α-keratins. One process involves the breaking of the disulfide crosslinks by chemical means, and the dimensional changes that are observed in this instance are irreversible. These observations have a close analogy to the results illustrated in Fig. 1 where it is shown that the relative lengths of the polyethylene fibers decrease as the number of intermolecular crosslinks is decreased. Thus when α-keratin is treated with a variety of reagents that are known to break disulfide bonds[51] axial contractions occur without any change in the state of the system since in most cases the α-keratin structure is still maintained.

In contrast to this process, anisotropic dimensional changes are observed without the breaking of the intermolecular crosslinks by subjecting the fibers to conditions conducive to melting. In many instances recrystallization subsequently is induced and the fibers will revert to their original length. An example of this type of reversible contraction is illustrated for keratin, in either the alpha or beta form, by the observations of Whewell and Woods.[52] In these experiments the fibers are immersed in a cuprammonium solution of appropriate concentration, and an approximately 20% decrease in length is observed. The shrinkage is accompanied by loss of the characteristic wide-angle X-ray diffraction pattern and is a clear indication that melting has occurred. The melting process in this instance appears to be caused by a complexing reaction between appropriate amino acid residues and the cuprammonium solution. If the shrunken amorphous fibers are now immersed in dilute acid solution, the initial length and X-ray pattern are both regained. It is important to note that if the keratin fibers are immersed in this alkaline medium for too long a time, although contraction is still observed, the process is no longer reversible. These conditions are known to be conducive to the severance of disulfide crosslinks, and the necessity of maintaining an adequate number of crosslinks during the transformation in order for the dimensional changes to be reversible is again pointed out. Thus from the evidence already existing in the literature it appears that the contractile processes observed in one class of fibrous proteins, the keratins, are explicable by the same principles that govern dimensional changes in synthetic macromolecules.[53]

Elastoidin is another fibrous protein that shows reversible contraction and relaxation under appropriate conditions.[54,55] When the native fiber is heated in water, a large axial contraction is observed at about 65°, and on subsequent cooling to room temperature about half of the initial length is regained without the application of any external force.[54] After this initial shrinkage the process can be carried out cyclically, with contraction occurring on heating above 65° and relaxation occurring on cooling. Champetier and Fauré-Fremet[55] observed that the initial, oriented collagen type, wide-angle X-ray diffraction pattern typical of elastoidin is completely converted to an amorphous pattern on shrinkage and is recovered on the subsequent relaxation. These investigators correctly attributed the observed dimensional changes to a crystal–liquid transformation, a fact that has been ignored in many subsequent studies of similar materials. The reversibility of dimensional changes in this fibrous protein system can be attributed to the known presence of cystine residues and the covalent disulfide crosslinks.[56] This system again bears a striking resemblance to the crosslinked polyethylene fibers, and the dimensional changes are explicable on the same basis. In this instance there is an irreversible initial shrinkage, after which the dimensional changes are reversible.

In contrast, the hydrothermal shrinkage of collagen, which has been demonstrated to be a consequence of melting, is an irreversible process when carried to completion. Though its amino acid composition and wide-angle X-ray pattern are very similar to that of elastoidin there are no cystine groups present. Thus in native collagen the stable types of intermolecular crosslinks that are necessary for preferential axial recrystallization to occur are absent and the dimensional changes are not reversible. However, if collagen in the native state is crosslinked (tanned) with formaldehyde then the well known Ewald process results[57] with hydrothermal shrinkage, wherein the melting–crystallization process is now accompanied by reversible dimensional changes. Thus the significant role played by appropriately introduced crosslinks in maintaining the reversibility of the dimensional

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(50) P. Alexander and R. F. Hudson, "Wool, Its Chemistry and Physics," Reinhold Publ. Corp., New York, N. Y., 1954, p. 378.

(51) See ref. 50, p. 74 ff. for a summary of reactants.

(52) C. S. Whewell and H. J. Woods, "Symposium on Fibrous Proteins," Society of Dyers and Colourists, 1946, p. 50.

(53) The well known phenomena of "permanent set" in keratin which occurs when stretched α-keratin, is converted to oriented β-keratin in the presence of steam (W. T. Astbury and H. J. Woods, *Phil. Trans. Proc. Royal Soc.*, **232A**, 336 (1933)), is also explicable by known polymer principles. The increase in length that is observed is a natural consequence of the differences in the crystal structure of the two forms. The stress–relaxation that is observed invariably occurs during the oriented crystallization of a macromolecular system. Thus, it is not required that crosslinks be severed and then re-formed, as often has been proposed. The melting of α-keratin and the crystallization of the β-form in an axially oriented condition is sufficient to explain the observed dimensional changes and the stress–relaxation. Explanation of the apparently greater stability of the beta form must await a detailed analysis of the thermodynamics of fusion of both crystalline forms.

(54) E. Fauré-Fremet, *J. chim. phys.*, **34**, 126 (1937).

(55) G. Champetier and E. Fauré-Fremet, *ibid.*, **34**, 197 (1937).

(56) K. H. Gustavson, "The Chemistry and Reactivity of Collagen," Academic Press, Inc., New York, N. Y., 1956, p. 217.

(57) A. Ewald, *Z. physiol. Chem.*, **105**, 115, 135 (1919).

changes is again illustrated. It has been indicated recently that when collagen is tanned with an epoxy resin, reversible dimensional changes also are observed.[58]

On the basis of the above discussion, it can be deduced that anisotropic dimensional changes in the fibrous proteins can be attributed to a phase transformation between the crystalline and amorphous states, and in analogy with fibrous polyethylene for oriented recrystallization to occur without the application of any external force, intermolecular cross-links must be imposed on the system when the chains are in an oriented state. It may be expected that with further investigations the contractile processes observed in other naturally occurring fibrous macromolecular systems may receive explanation from similar considerations. In fact, it has been proposed by Pryor[40] and by Flory[2,4] that the contraction of muscle is caused by the melting or the partial melting of the highly ordered polypeptide chains comprising the myofibril. The validity of applying these principles to the muscle system must, of course, await further experimental confirmation.

WASHINGTON, D. C.

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(58) J. G. Fee, R. R. Calhoun and L. P. Witnauer, *J. Amer. Leather Chemists Assoc.*, **56**, 530 (1956).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE PURDUE RESEARCH FOUNDATION, PURDUE UNIVERSITY]

# The Molecular Structure of 1,1-Dichloroethane by Electron Diffraction[1]

BY M. D. DANFORD AND R. L. LIVINGSTON

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The molecular structure of 1,1-dichloroethane has been investigated by electron diffraction using the visual correlation procedure, with qualitative aid by the sector method. The following results were obtained: C–Cl = 1.795 ± 0.02 Å., Cl--Cl = 2.925 ± 0.03 Å., C–C = 1.55 ± 0.07 Å., and ∠C–C–Cl = 110 ± 4°. Results are compared with those obtained for other chloroalkanes.

## Introduction

Structural investigations of most chloroalkanes have yielded C–C distances ranging from 1.54 to 1.56 Å. However, an electron diffraction investigation of the structure of 1,2-dichloroethane by Ainsworth and Karle,[2] using the rotating sector method, yielded an unusually short C–C distance of 1.49 ± 0.03 Å. In addition, an X-ray diffraction investigation of the crystal structure of solid 1,2-dichloroethane by Reed and Lipscomb[3] gave C–C = 1.49 ± 0.04 Å. The present investigation was undertaken to attempt to determine whether any difference exists between the C–C bond distances in 1,1-dichloroethane and in 1,2-dichloroethane and to compare the C–Cl distance in 1,1-dichloroethane with similar distances in other chloroalkanes.

## Experimental

The 1,1-dichloroethane was obtained from a commercial sample and subjected to numerous distillations, with the middle portion of the final fraction, boiling at 57.2° (uncorrected), being used for preparation of photographs. Photographs which extended to $q = 90$ were obtained for visual analysis, and four plates with electron wave lengths ranging from 0.05495 to 0.05933 Å. were selected for analysis. Sector photographs extending from $q = 21$ to $q = 52$ were taken to aid in the determination of feature intensities in this range, and two plates, both with electron wave lengths of 0.05527 Å., were traced with a Leeds and Northrup recording microphotometer. The visual curve is the result of about twenty-five measurements of one author (M.D.) and intensity assignments for each feature by both authors. Both the visual and sector curves are shown in Fig. 1.

The radial distribution[4,5] and visual correlation method[6,7] were used in the analysis of the diffraction pattern. Theoretical intensity curves were calculated by the equation

$$I(q) = \sum_i \sum_j \frac{Z_i Z_j}{r_{ij}} \exp(-b_{ij}q^2) \sin \frac{\pi q r_{ij}}{10} \qquad (1)$$

using punched cards.[5] The constant $b_{ij}$ in the vibration factor was assigned the values 0.00016 for bonded C–H terms, 0.0003 for non-bonded C---H and Cl---H terms, 0.00008 for non-bonded C---Cl terms and zero for the other terms.

TABLE I

QUANTITATIVE ELECTRON DIFFRACTION DATA FOR 1,1-DICHLOROETHANE

| Max. | Min. | $q_{\text{obsd}}$ | $E_3$ $q/q_0$ | $D_3$ $q/q_0$ | $C_5$ $q/q_0$ | $B_4$ $q/q_0$ |
|---|---|---|---|---|---|---|
| 1 | | 16.37 | (0.947) | (0.947) | (0.947) | (0.947) |
| | 2 | 19.80 | (0.979) | (0.980) | (0.981) | (0.981) |
| 2 | | 23.06 | 1.006 | 1.008 | 1.010 | 1.012 |
| | 3 | 26.30 | 1.005 | 1.005 | 1.006 | 1.007 |
| 3 | | 29.01 | 1.002 | 0.999 | 0.996 | 0.993 |
| | 4 | 33.00 | 0.986 | 0.986 | 0.986 | 0.985 |
| 4 | | 36.60 | 0.998 | 0.999 | 1.000 | 0.998 |
| | 5 | 40.56 | (0.999) | (0.999) | (1.000) | (1.002) |
| 5 | | 43.64 | (1.019) | (1.017) | (1.016) | (1.016) |
| | 6 | 46.02 | (1.010) | (1.010) | (1.009) | (1.007) |
| 6 | | 48.25 | (1.009) | (1.013) | (1.018) | (1.021) |
| | 7 | 52.99 | 0.999 | 0.999 | 1.001 | 1.004 |
| 7 | | 56.31 | 1.020 | 1.019 | 1.019 | 1.020 |
| | 8 | 65.92 | 0.993 | 0.992 | 0.993 | 0.994 |
| 8 | | 69.47 | 1.004 | 1.002 | 1.002 | 1.002 |
| | 9 | 73.22 | (1.010) | (1.007) | (1.006) | (1.006) |
| 9 | | 76.28 | (1.015) | (1.016) | (1.016) | (1.015) |
| | 10 | 79.28 | (0.993) | (0.993) | (0.996) | (0.998) |
| 10 | | 82.25 | 1.006 | 1.005 | 1.004 | 1.005 |
| | 11 | 86.70 | 1.002 | 1.001 | 1.000 | 1.000 |
| 11 | | 89.93 | 1.010 | 1.012 | 1.012 | 1.010 |
| | Av. | | 1.003 | 1.002 | 1.002 | 1.003 |
| | Av. dev. | | 0.006 | 0.006 | 0.006 | 0.007 |

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(1) Contains material from the Ph.D. thesis of M. D. Danford, Purdue Research Fellow in Chemistry, 1953–1954.

(2) J. Ainsworth and J. Karle, *J. Chem. Phys.*, **20**, 425 (1952).

(3) T. B. Reed and W. N. Lipscomb, *Acta Cryst.*, **6**, 45 (1953).

(4) P. A. Shaffer, V. Schomaker and L. Pauling, *J. Chem. Phys.*, **14**, 659 (1946).

(5) L. Pauling and L. O. Brockway, THIS JOURNAL, **57**, 2684 (1935).

(6) L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

(7) L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).