THE INVESTIGATION OF SYNTHETIC LINEAR POLYMERS BY X-RAYS[1]

C. S. FULLER

Bell Telephone Laboratories, New York, New York

Received October 3, 1939

CONTENTS

I. INTRODUCTION

The purpose of this paper is to review the results which have been obtained to date by the x-ray and electron diffraction study of synthetic organic linear polymers[2]. The subject matter will be confined to the truly synthetic compounds, and work relating to the derivatives of the natural linear polymers will be omitted. The latter studies for the most part relate to derivatives of cellulose, and these have already been reviewed by Sisson (68). Discussion of the techniques employed will likewise be

---

[1] Presented at the Symposium on X-ray Studies of Substances of High Molecular Weight, held at the Ninety-eighth Meeting of the American Chemical Society in Boston, Massachusetts, September, 1939, under the auspices of the Divisions of Physical and Inorganic Chemistry, Colloid Chemistry, Organic Chemistry, Paint and Varnish Chemistry, and Rubber Chemistry of the American Chemical Society.

[2] This report is written more from the x-ray standpoint. In general, x-rays are better adapted to the study of thick specimens, whereas electrons are more useful for the examination of thin films and surfaces.

omitted, since it will be necessary to conserve space in order to give a unified picture of the results on synthetic polymers in the allotted space. Readers interested in this part of the subject are referred to the literature and to standard works on the subject (1, 15, 30, 48, 42). In order to secure a better appreciation of the meaning of the investigations that have been made, it will be helpful to consider certain related topics before undertaking a study of the results themselves. We shall consider first the various ways in which x-rays can be employed in the examination of high polymeric substances.

II. CLASSIFICATION OF X-RAY METHODS

As in the case of the low molecular compounds there are a number of ways in which x-rays can be applied to the study of high polymeric substances. The various methods may be divided conveniently into three categories, depending on the object of the investigation. It may be desired (*1*) to identify a given substance, (*2*) to study the effect of certain variables on it, or, finally, (*3*) to unravel its inner molecular structure. In the first case, the procedure is the usual one of comparing the diffraction pattern of the unknown with patterns furnished by compounds of known constitution. Although this use of x-rays is of particular value in the case of high molecular substances because of the simple technique involved and because conventional methods are often difficult to apply to these substances, this use of x-rays will not concern us here.

The second category mentioned above is that in which the effect of a given variable on the system is the object of study. According to this method the investigator studies the effect of temperature, pressure, or a second substance on the material in question. The effect of elongation on the x-ray pattern of rubber or the effect of sodium hydroxide on the x-ray pattern of cellulose are typical examples. Such studies are valuable in explaining the influence of external agents on the inner molecular or crystalline nature of the substance under consideration, and much of the work on the natural polymers falls in this classification.

In most of the studies reported here we shall be concerned with the last of the methods mentioned above, that is, with work designed to give information on the structural features of the substances under study. The specific utility of x-rays in this direction has been amply demonstrated by innumerable investigations on inorganic and organic compounds of low molecular weight. In applying this method to substances of high molecular weight the same rules and precautions hold as with these low molecular compounds, but it is perhaps even more essential for the investigator to be aware of its limitations and pitfalls.

In investigations with low molecular compounds single crystals are generally available, but in the case of the high polymers we are limited to the investigation of polycrystalline, mesomorphic, or amorphous masses. Accordingly, the results are less definite and more difficult of interpretation than in the case of the simpler substances. For this reason it is necessary to consider chemical evidence along with x-ray data. In structural studies on high polymers in the past one major difficulty has been the lack of definite knowledge regarding the chemical structure of these compounds. In the last decade considerable progress has been made in the synthesis of polymeric substances of known structure. There can be little doubt that, aided by these new data, the x-ray method will continue to contribute important information regarding the constitution of high polymeric substances.

In addition to the purely structural studies, x-rays also furnish considerable information on the colloidal nature of high polymers. Thus suitable techniques allow estimates to be made of the crystal particle size, the proportion of crystalline to amorphous material present, and finally the orientation of the crystalline components relative to the surfaces of the specimen. The importance of these results in correlating the physical properties of these systems with their colloidal structure will be considered later.

III. LOW MOLECULAR CHAIN COMPOUNDS

No consideration of the x-ray work on linear high polymers can neglect the extensive results which have been accumulated on the lower molecular chain compounds. Without going into detail, some of the important conclusions from these studies may now be reviewed. The first significant result is the proof that the long aliphatic chains in these compounds assume an extended tetrahedral zigzag form. Such a configuration (figure 4a) had been suggested in 1917 by Langmuir (40) from surface studies. Later Piper and Grindley (59), Müller (50), Shearer (66), and Müller and Shearer (52), working with soaps and fatty acids, found that a parallel arrangement of chains in which the atoms were arranged in zigzag fashion accounted well for the x-ray results on these compounds. Subsequent work by Müller (51), Hengstenberg (28), and others has established beyond all doubt the essential correctness of this configuration of the hydrocarbon chains in the crystalline aliphatic compounds.

A second significant conclusion from the work on the chain compounds of lower molecular weight is that in all of these compounds the chains are packed together in the crystals as parallel rods of approximately the same effective cross section (18.5 Å.^{2}). These chains may be perpendicular or at a definite angle to the planes containing the ends of the molecules. Figure 1 illustrates the angles which have been reported for various paraffins, aliphatic alcohols, acids, and esters. The same substance under the proper conditions may show several different angles. It is on the basis of this difference in angle or "tilt" of the molecular chains that various polymorphic forms of certain of these compounds have been differentiated[3].

Recently Kohlhaas and Soremba (33) have investigated carefully prepared single crystals of *n*-triacontane ($C_{30}H_{62}$) and Kohlhaas (32) has examined a single crystal of cetyl palmitate; they have thus verified again the main conclusions in regard to the structures of these compounds. In an important paper T. Schoon (65) has presented a general theory of crystal formation of these aliphatic chain compounds. A brief description of his conception will be of interest, since it has a definite bearing on the results on synthetic polymers to be considered later. Schoon points out that simple geometrical relationships exist between lattices of the various polymorphic crystal forms found in the case of most of these chain substances. The various forms are pictured as originating through a molecular gliding process, as illustrated in figure 2. Thus, an orthorhombic form of crystal lattice such as that pictured in figure 2a may transform into other stable crystalline forms simply by a uniform gliding of rows of chains, as shown in figure 2, b, c, and d. A type of glide such as in b or c gives rise to a monoclinic cell, whereas the type shown in figure 2d results in a triclinic cell[4]. In this manner Schoon has been able to correlate a large

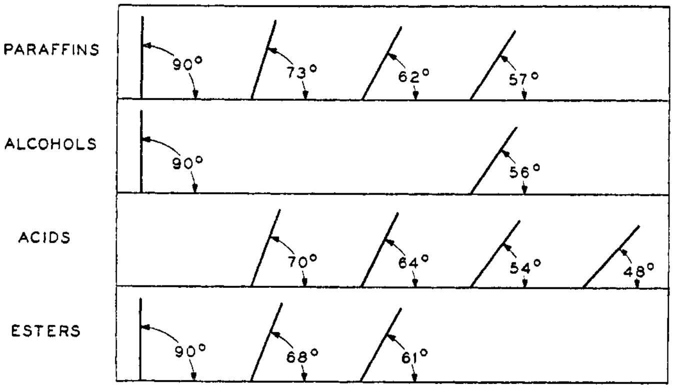


FIG. 1. Inclination of hydrocarbon chains in various aliphatic compounds

---

[3] It should be pointed out that two types of modifications are distinguished in long-chain aliphatic compounds;—the rotating (5) and the non-rotating. The rotating forms always show the perpendicular chain arrangement; the non-rotating forms may be perpendicular or tilted.

[4] So far this type has not been observed.

amount of x-ray data on these compounds in a fairly quantitative way. For example, stearic acid has been found in a form having a unit cell a = 5.62 Å., b = 7.54 Å., and β = 61.2° and in a form having a = 9.46 Å., b = 4.96 Å., and β = 54.2° (65). Schoon's conception accounts for the first form as a glide of successive (100) planes a distance of two chain atoms, as shown in figure 2b. The second form corresponds to a glide of successive (010) planes a distance of four chain atoms, as shown in figure 2c. Further reference to Schoon's theory will be made below.

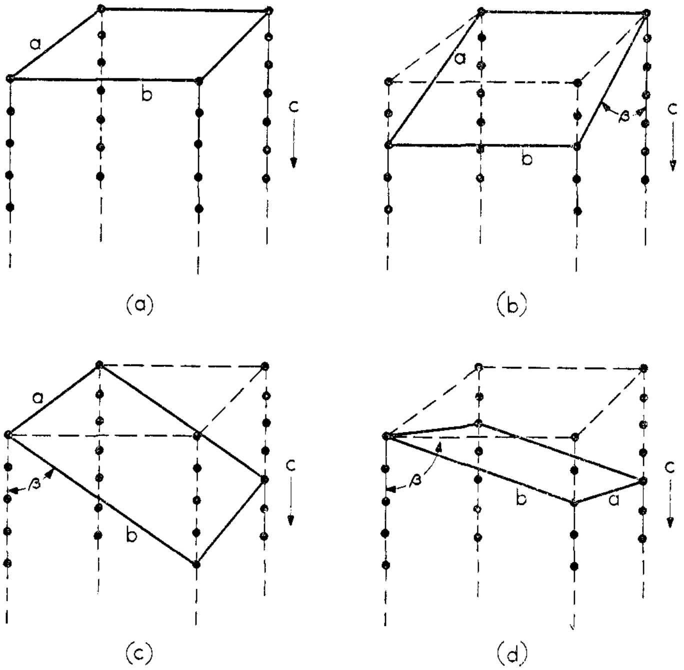
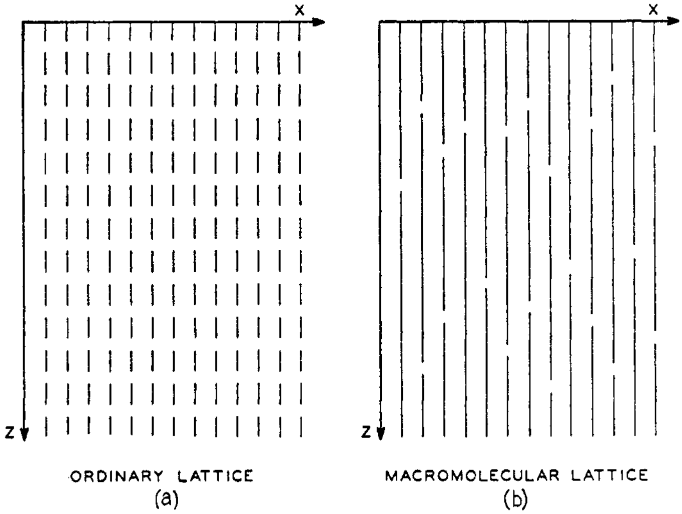


FIG. 2. Origin of polymorphic forms of aliphatic chain compounds (Schoon)

IV. GENERAL CHARACTER OF HIGH MOLECULAR CHAIN STRUCTURES

In the case of the low molecular chain compounds already considered, the crystals are built up of molecules which are identical in structure, size, and shape. These crystals, by virtue of this fact, show well-formed faces and cleavage planes. As the length of the molecules increases, however, the forces arising from the end groups on the molecules become less important in determining the crystal structure than the lateral forces acting between the chains. Under these conditions the simple molecular lattice gives way to what has been called a macromolecular (71) or chain lattice

(*Kettengitter*), in which the ends of the molecules occur at no regular positions in the structure (figure 3), and hence do not give rise to reflections in the x-ray patterns. For convenience, therefore, we may define a high molecular chain system as one which is composed of chain molecules of such length that the effects of the ends of the molecules in determining the structure are negligible in comparison with the rest of the molecule. It follows that x-rays can furnish no direct information regarding the chain length present in these systems.[5] In the ideal case the molecules in such a system are all of the same length. In the case of real systems, however, a distribution of molecule sizes is always present. In this case the definition above refers to the average chain length. In general, the chain molecules comprising real high molecular chain systems are produced by the primary valence repetition of a repeating unit or group. It is evident, therefore, from the above definition that the crystal structure in such systems will depend on the nature of this repeating unit and may be described conveniently in terms of it.



ORDINARY LATTICE
(a)

MACROMOLECULAR LATTICE
(b)

FIG. 3. Plane through (a) an ordinary and (b) a macromolecular type of molecular lattice.

Numerous theories regarding the constitution of high molecular substances have been advanced. We will distinguish here only between the theories which view these substances as composed of "micelles" or "crystallites" of more or less definite size and shape (29, 35, 36) and the theories

---

[5] The proteins are an exception, in that definite units related to the molecule appear to be present (6).

which regard these substances as having a continuous structure containing less well-defined crystalline portions (58, 17, 30, 24).[6] According to the first group of theories the crystalline particles are composed of long chain molecules and are supposed to be held together by micellar forces or by another substance (*Kittsubstanz*). According to the second group the structure is integral in that the chain molecules may traverse both crystalline and amorphous areas. The latter view is taken in this discussion as explaining more satisfactorily the behavior of synthetic high molecular compounds. These compounds may be regarded as consisting of chain molecules of different lengths which, over certain portions of their lengths at least, fit into a lattice-like arrangement (macromolecular lattice). These portions may be termed "crystalline regions" in order to avoid attributing to them any definite form. Over adjacent volumes of the material, however, the chains are to be regarded as in imperfect arrangement and to behave as amorphous or psuedo-crystalline matter. These imperfections in the structure may result from a grouping of molecule ends or from the geometrical inability to fit portions or ends of the long chain molecules into the lattice work. In the case of impure compounds where similar but non-identical chains exist together or where the chain molecule itself possesses an irregular structure, the occurrence of such imperfection areas is obvious (19). The relative proportion of these crystalline and amorphous regions may vary widely. In some cases the amorphous regions may be continuous and in others the crystalline.

On the basis of the above picture we are justified in regarding these compounds as colloidal. It is not correct, however, to regard the system as a crystalline component dispersed in an amorphous one or *vice versa*, since the two regions show no true interfaces but rather a blending of one structure into the other. Regardless of what picture represents the true situation, however, it is only by a consideration of both the amorphous and the crystalline nature of high polymeric substances that a complete explanation of their properties will be obtained. This view has been emphasized by Halle (25) and recently again by Mark (43).

An important characteristic of high molecular chain systems is their property of crystalline orientation. If the crystal regions are not already oriented with respect to one or more directions in the specimen, they are generally susceptible of such orientation by application of the proper stresses. In the case of natural or synthetic fibers the crystalline regions

---

[6] The distinction made here is for purposes of discussion. Except for differences in detail, the continuous structure point of view is now quite widely held (see Kratky and Mark (37)). Kratky (38), however, has recently presented evidence in favor of discrete crystalline units. Evidence of a continuous net structure for hydrate cellulose has been given by Kratky and Platzek (Kolloid-Z. **88**, 79 (1939)).

generally assume an orientation such that an axis of the crystal lattice lies along the fiber axis but the regions are otherwise random (uniaxial orientation). In all cases of fibers encountered in practice in which uniaxial orientation is present, it has been found that the chain molecules are aligned in the direction of the fiber axis. In films it is sometimes possible to cause the crystal regions to assume a fixed orientation with respect to two directions in the specimen (44, 67). In this case, in effect, we have produced an imperfect single crystal (selective uniaxial orientation) (67). Such foil structures are the most suitable specimens for the determination of the crystal structure of the crystalline regions in the system under investigation.

V. X-RAY RESULTS ON SYNTHETIC POLYMERS

In considering the published data on synthetic polymeric compounds it will be evident that the majority of the investigations is concerned with the structure of the crystalline regions as defined above. Since in many cases this portion represents essentially the whole of the system, this restricted view is generally justified and offers the best approach to the more complex cases where the system contains considerable amorphous matter in addition to the crystalline.

A. Polymethylene oxides

Staudinger (69) was one of the first to appreciate the value of studying synthetic polymers in order to throw light on the nature of high polymeric substance. One of the first series of synthetic compounds to receive attention from both the viscosity and the x-ray standpoints was the polyoxymethylene. Employing carefully fractionated samples of polyoxymethylene diacetates containing from nine to nineteen (CH_2O) repeating units in the molecule, Staudinger, Johner, Signer, Mie, and Hengstenberg (70) showed that each of the lower fractions formed true crystals from which the length of the molecule could be determined. From the uniform increase in this length for the various fractions the length of the CH_2O unit was found to be 1.93 Å. In the case of the higher diacetates, however, the reflections corresponding to the length of the molecule disappeared and a macromolecular lattice (figure 3) was considered to form. Hengstenberg (27) pictured the polyoxymethylene chain as consisting of nine CH_2O units arranged in a threefold screw axis. The fiber period was therefore 17.4 Å. From a high polymer he succeeded in drawing oriented threads which gave a typical x-ray fiber pattern. Ott (55), although agreeing with the Staudinger chain molecule concept, disagreed with the results of Hengstenberg on the formation of a macromolecular lattice. Ott found spacings of 45.1 Å. and 113.4 Å., which he identified with the molecule lengths in δ- and γ-polyoxymethylene, respectively. Sauter (61) again undertook the study of these compounds but was unable to find the long spacings observed by Ott. From rotation photographs on a minute single crystal of β-polyoxymethylene Sauter determined an identity period of 17.25 Å. along the *c*-axis (fiber axis) of the crystal. The identity periods in the other two directions were 4.43 Å. and 7.69 Å., in good agreement with the previous work of Hengstenberg. The crystal was believed to belong to the hexagonal space group C_3^2 or C_3^3. In a later paper Sauter (62) considered in detail the chain configuration of the polyoxymethylenes and concluded that the polyoxymethylene chain consists of a nearly planar "tub" form (figure 4b) of chain rather than a zigzag type such as in the paraffins (figure 4a). The presence of the threefold rhythm, however, necessitates a non-planar arrangement.

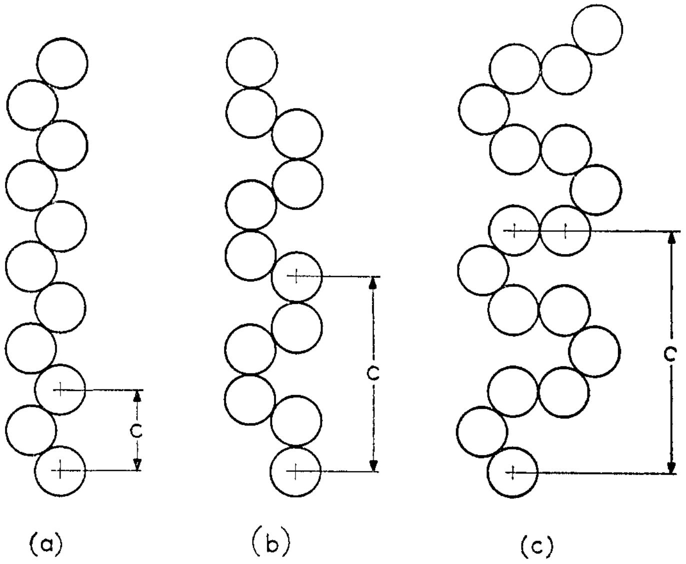


FIG. 4. Planar configurations of single-bonded carbon chains. a, zigzag or *trans* configuration; b, "tub" or *cis* configuration; c, "meander" configuration.

In an interesting paper Kohlschütter and Sprenger (34) showed that cyclic trioxymethylene is transformed under the proper conditions into linear polyoxymethylenes. They found that individual fibers gave a highly oriented fiber pattern apparently identical with that previously observed by Hengstenberg.

B. Polyethylene oxides

From a study of polymers obtained by the polymerization of ethylene oxide, Staudinger (69, page 293) concluded that the chain molecules in solution were much shorter than one would expect from the number of atoms in the molecule. He therefore assumed a "meander form" of chain such as shown in figure 4c. Sauter (63) studied the polyethylene oxides in the solid state and found evidence of a strongly shortened "meander-like" chain as the viscosity measurements indicated for molecules in solution. Sauter found no change in the x-ray patterns (powder) with increase in average molecular weight. From an elongated sample of high polymeric polyethylene oxide he obtained a fiber pattern from which a fiber period of 19.5 Å. was calculated. The unit cell is bounded by four chain molecules aligned in the fiber direction and perpendicular to a simple monoclinic base having $a = 9.5$ Å., $c = 12.0$ Å., and $\beta = 101°$. Thirty-six ethylene oxide units are present in the cell. From symmetry and bond considerations Sauter deduced that nine ethylene oxide units were present in each chain over the distance corresponding to the fiber period. This requires a highly folded configuration and Sauter was led to regard it as a meander-like chain, although he did not picture it as being necessarily planar. H. Staudinger, M. Staudinger, and E. Sauter (72) recently have summarized their findings on the crystalline nature of the polyethylene oxides and polymethylene oxides. They obtained microscopic evidence showing that the crystal size in these polymers varies inversely as the degree of polymerization. For degrees of polymerization above 500 they found that the polyethylene oxides could be "cold-formed" into fibrillar regions of definite cross section. Fibrils of 0.15 μ (1500 Å.) diameter were reported in the case of the polyoxymethylenes from examinations under the ultraviolet microscope. By way of comparison they suggest that fibrillar aggregates as low as 100 Å. in diameter are probably present in cellulose because of fibrillar shattering. The examination of single crystals of β-polyoxymethylene showed no basal cleavage but a rough surface fracture. Bending of these crystals caused fibrillar shattering, indicating them to be intrinsically brittle.

The main findings of Staudinger and his associates on the polymethylene and polyethylene oxides may be summarized as follows: (*1*) As in the case of the low molecular chain compounds, the molecules in the synthetic polymers crystallize with the chains parallel. Oriented fibers of the polymers, like oriented natural fibers, contain the long axis of the chain molecules parallel to the fiber axis[7]. The configuration of the long chain molecules, however, is variable and dependent on the nature of the chemical repeating unit. (*2*) It is unnecessary for the molecules of a polymeric series to be of equal length (molecular weight) in order to form crystals. In such macromolecular crystals the end groups represent imperfections

---

[7] Generally the molecules are included in a narrow cone, the fiber axis forming the axis of the cone.

in the lattice (figure 3), and the chemical repeating unit in the polymer may be considered as the unit of packing. A macromolecular lattice is also supposed to form in the case of equally long molecules of sufficiently great length. There may be, however, in view of Ott's findings, some question as to whether this latter point has been sufficiently proven, since it is extremely difficult to prepare high polymers of strictly uniform length.

Barnes and Ross (3) also studied the polyethylene oxides and compared their x-ray patterns with the higher polyethylene glycols. They were able to detect no difference in the Debye–Scherrer patterns of the polymers prepared by the different methods.

C. Linear polyesters

As a result of previous work by Carothers (9, 10), Carothers and Hill (11) in 1932 prepared linear polymers by the intermolecular polycondensation of dibasic acids and glycols which exhibited the remarkable property of orienting or "cold drawing" when stress was applied to unoriented rods of the material. A. W. Kenney (11) showed that cold-drawn fibers of polyethylene sebacate gave well-oriented fiber patterns from which identity periods could be calculated corresponding roughly to the length of the repeating unit in the chain molecules.

Fuller and Erickson (20) later undertook an x-ray study of various linear polyesters. They found that, analogous to the polymethylene and polyethylene oxides, the polyesters showed identical Debye–Scherrer patterns with increasing average molecular weight. Oriented (uniaxial) specimens of high polymeric ethylene succinate, ethylene adipate, ethylene azelate, ethylene sebacate, trimethylene sebacate, and diethylene sebacate were examined. The identity periods along the fiber axis were obtained from the fiber patterns of the various compounds. It was concluded from this work that in all cases the chain molecules are aligned along the fiber direction. Comparison of calculated lengths for various chain configurations shows that the chain molecules in the adipic, azelaic, and sebacic esters of ethylene glycol agree well with a planar zigzag paraffin type of chain. The succinate ester requires an entirely different chain configuration from the other compounds of the series. A helical type of chain somewhat analogous to that observed by Sauter (62) for polyoxymethylene was found to agree best with the results. The chains in the trimethylene and diethylene polyesters of sebacic acid also deviated from the zigzag form and probably represent helical or folded structures. Storks (73) applied the electron diffraction method successfully to thin films of polyethylene succinate, adipate, and sebacate. His results on oriented specimens agree well with those of Fuller and Erickson (20). Storks concluded that the crystals present in these films are of very small cross section, since they are randomly rotated in the cross section of films less than 400 to 1000 Å. thick. The fiber patterns also clearly showed the presence of meridian reflections which (because of the diffraction angle) were not observed in the case of the x-ray patterns. These reflections in the case of the succinate indicate intermediate planes at 2.1 Å. along the fiber axis and in the case of the other two esters confirm the correctness of the zigzag type of chain configuration. Finally, Storks observed selective uniplanar orientation (67) in unstretched films of polyethylene sebacate. In this case the crystals, although random in the film plane, show an approximately fixed orientation about the chain axis. The work of Storks illustrates clearly the utility of electron methods in the study of thin films of organic polymers.

Subsequently, Fuller and Frosch (21) summarized the work on the ethylene series of polyesters and in a later paper (22) treated the decamethylene series of polyesters. The polymeric self-ester of hydroxydecanoic acid was also considered in the former paper. Without going into detail, the results of these studies may be summarized as follows:

The ethylene series of polyesters above the glutarate and the decamethylene series above the carbonate are found to possess chains which are essentially planar zigzag in configuration. Figure 5 shows the regular increase in the length of the repeating unit with the number of chain atoms for each series. The slope is the same in both cases and corresponds to 1.26 Å. per CH_2 group. This is precisely the slope calculated on the basis of a tetrahedral arrangement of carbon atoms at a distance of 1.54 Å. from each other (51). The slight displacement of the curves for the two series from one another may be real (20). It is, however, close to the experimental error. The deviation from the calculated curve may be due to an error in the assumed oxygen valence angle or in the C—O bond distance (74). The chain molecules pack in the crystal in the same manner as has been found to hold for the paraffins (51, 60)[8]. There is some evidence that a non-base-centered arrangement, such as Kohlhaas (32) has proposed for cetyl palmitate, is the correct one. We may picture the structure of these compounds as shown in figure 6a, which shows the type of chain arrangement assumed in the case of ethylene azelate and in general by the polyesters which contain an odd number of chain atoms. In this case the carbonyl groups in adjacent chains align themselves in horizontal planes. The chains in these esters (as can be seen from their structural formula) possess a twofold screw axis. Figure 6b shows the situation which holds for most of the even esters of both series. In this case, although the chains pack in cross section as in figure 6a, they are no longer arranged with the

---

[8] Decamethylene oxalate is an exception. In this case, the cross section of the unit cell is broader one way and narrower the other than in the case of the paraffins.

carbonyl groups opposite but are apparently displaced various amounts parallel to the chains for different even esters. For comparison the fiber patterns observed for polyethylene azelate (odd) and polyethylene sebacate (even) are given in figures 7a and 7b, respectively. The ethylene esters from the adipate on all appear to conform to the same pattern:—the chains are displaced parallel to their length a distance of two chain atoms in successive (100) planes. This arrangement is analogous to that shown in figure 2b. In the case of the decamethylene esters, with the exception of the oxalate which packs in cross section somewhat differently from the others, the situation is similar. However, instead of a constant displacement of successive planes a distance of two chain atoms, as in the case of the even members of the ethylene series, we find evidence of glides of other magnitudes. Thus, decamethylene sebacate appears to be analogous to

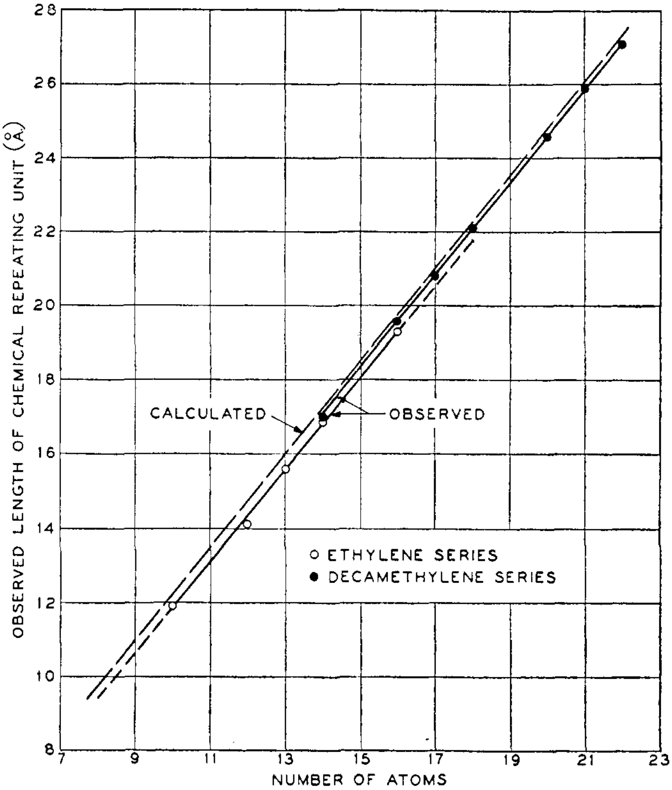
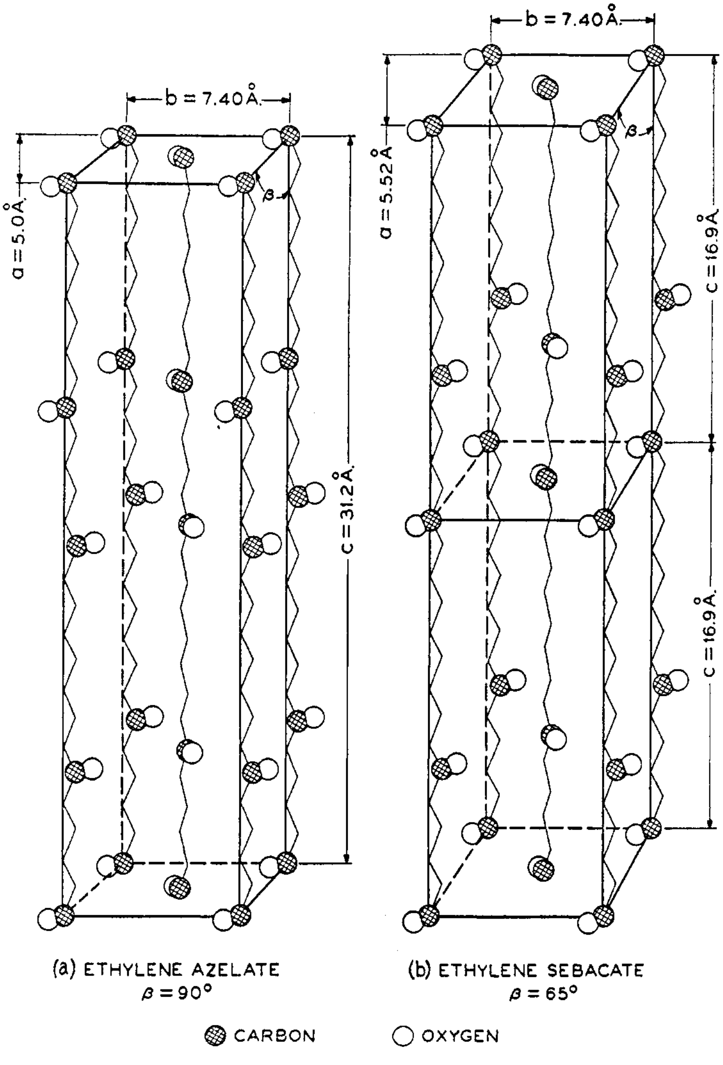


Fig. 5. Length of chemical repeating unit as a function of number of chain atoms for the ethylene and decamethylene series of polyesters.

the ethylene case, whereas decamethylene succinate agrees best with a displacement of four chain atoms in (100) or five chain atoms in (010). In decamethylene suberate half of the chain molecules appear to have been



(a) ETHYLENE AZELATE
$\beta = 90°$

(b) ETHYLENE SEBACATE
$\beta = 65°$

FIG. 6. a, orthorhombic unit cell of polyethylene azelate; b, monoclinic unit cell of polyethylene sebacate, $\beta = 65°$. Only the carbonyl groups are represented.

displaced one-half a repeating distance relative to the other half. In the case of the odd decamethylene esters, as in the odd ethylene esters, second-order meridian reflections are observed, indicating a chain alignment in the crystal as shown in figure 6a. The situation, however, is complicated by the presence of "even" type reflections as well. Likewise, the even adipate ester is complicated by the presence of "odd" type reflections.

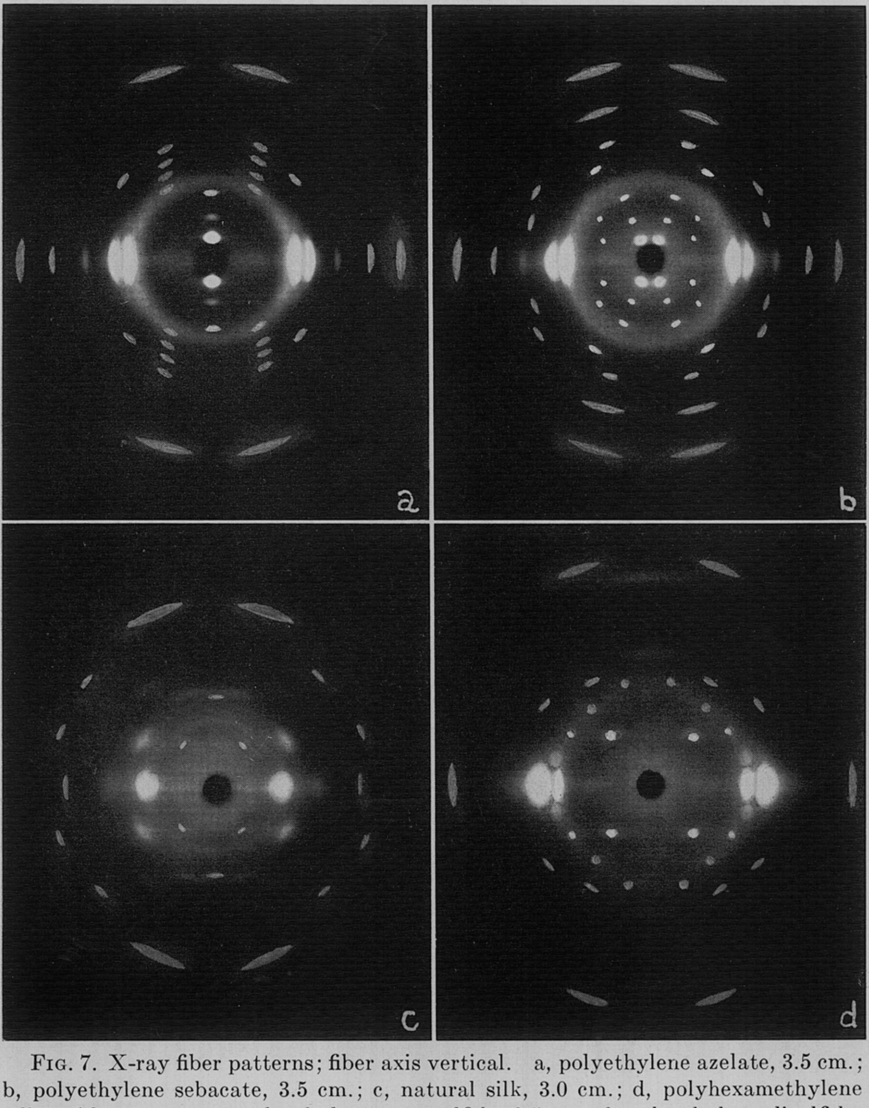


FIG. 7. X-ray fiber patterns; fiber axis vertical. a, polyethylene azelate, 3.5 cm.; b, polyethylene sebacate, 3.5 cm.; c, natural silk, 3.0 cm.; d, polyhexamethylene adipamide, 4.0 cm.; e, polyethylene tetrasulfide, 2.5 cm.; f, polyethylene disulfide, 3.5 cm.; g, gutta-percha, β-form, 4.0 cm.; h, polychloroprene, 4.0 cm.; i, polyvinyl alcohol, 4.0 cm.; j. polyvinyl chloride, 4.0 cm.; k, polyvinylidene chloride, 4.0 cm.; m, polyisobutylene, 4.0 cm.

The best explanation of the simultaneous occurrence of these reflections at the present time is that in these members of the decamethylene series, crystals of both the "odd" (figure 6a) and "even" (figure 6b) types are present.

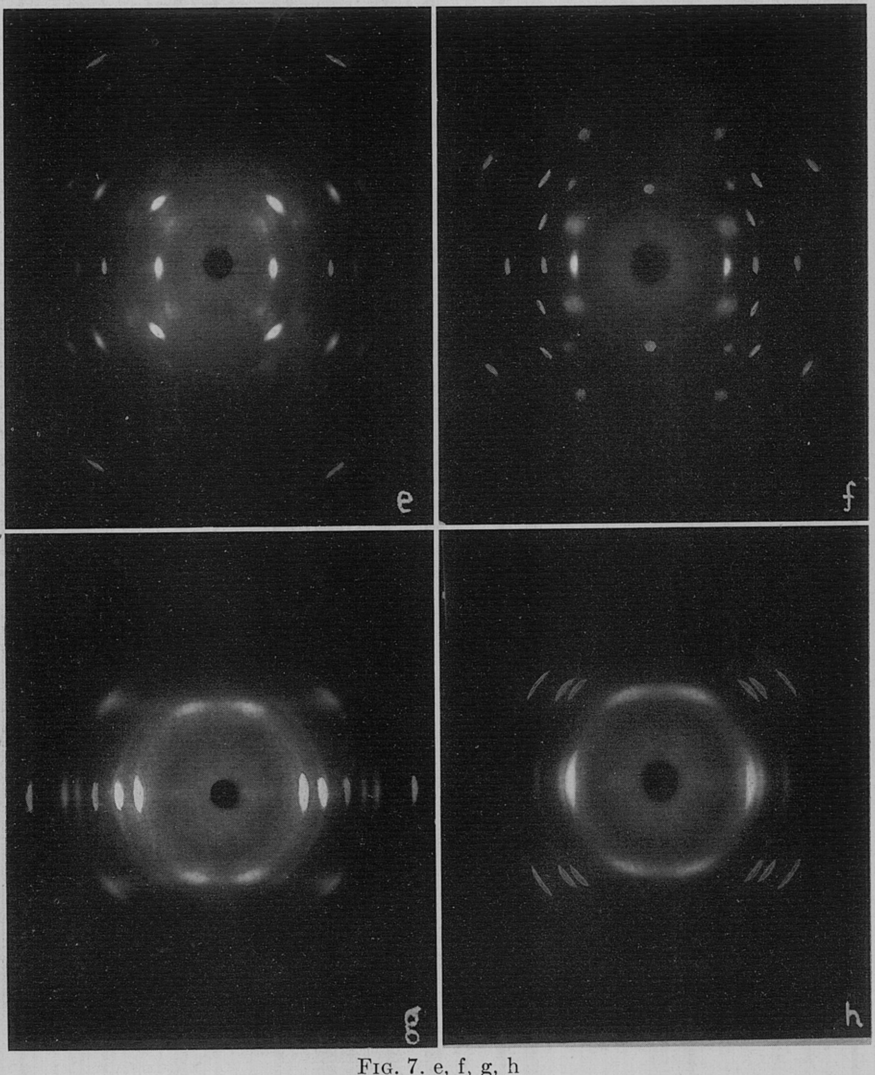


FIG. 7. e, f, g, h

The analogy of the above results to those reported for the low molecular chain compounds is immediately evident. The orthorhombic and monoclinic forms reported for the paraffins and fatty acids (figures 2a, 2b, and

2c) correspond to the forms of the esters shown in figures 6a and 6b, respectively. Thus the structure of the even ethylene esters corresponds closely to the monoclinic form for stearic acid (a = 5.546 Å., b = 7.38 Å,

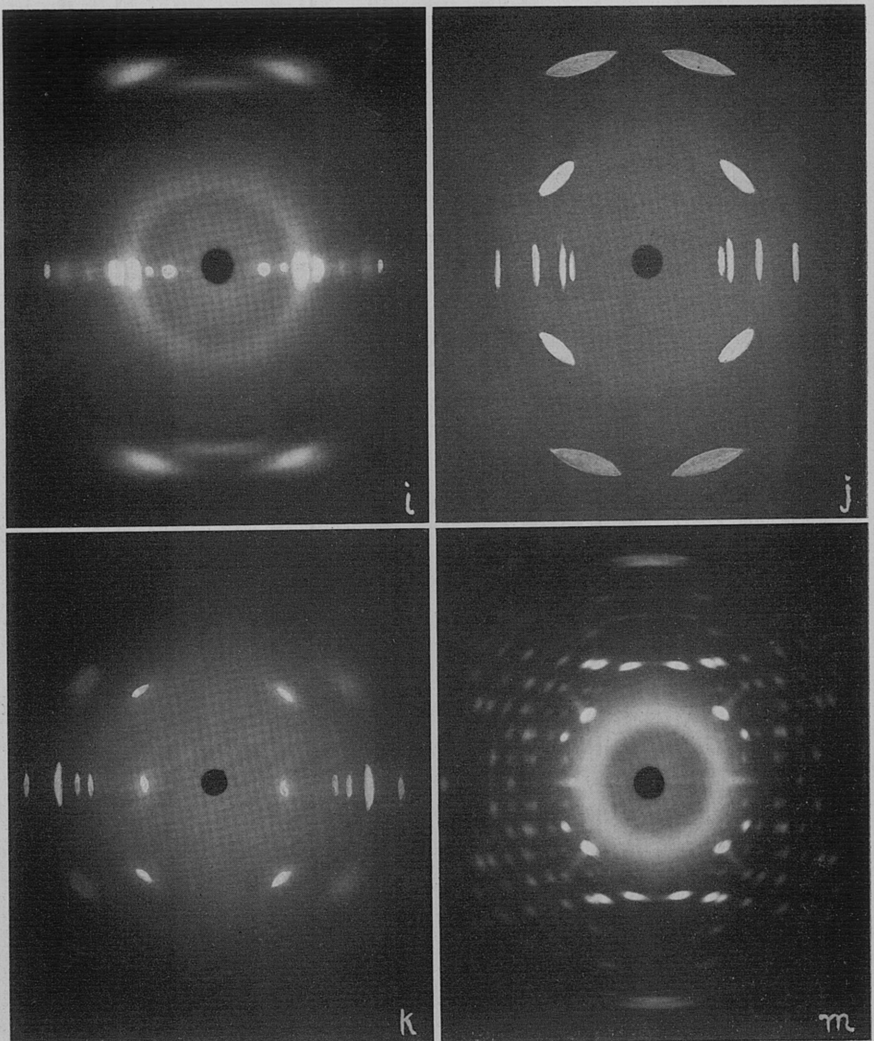


FIG. 7. i, j, k, m

and β = 63° 38′ reported by Müller (51)) except for the c-edge of the cell[9]. The applicability of the theory of Schoon (65) to these polymeric com-

---

[9] A triclinic cell for these esters is not excluded by the present data, but in view of the results on the aliphatic compounds this cell appears unlikely.

pounds is therefore evident. Just as in the case of the low molecular compounds, we may assume a molecule gliding, resulting in a variety of stable crystal forms. The "tilt" of the chains in the low molecular compounds corresponds to a uniform gliding of the molecules along the fiber axis in the case of the high molecular compounds. So far, however, it has not been possible to bring about changes in these forms by heating at definite temperatures, as has been done in the low molecular crystals.

D. Linear polyamides

No work relating to the crystalline nature of the polyamides (12) has yet appeared. Unpublished data of the author, however, show a close analogy to exist between these chain compounds and the linear polyesters. Thus, figure 7c shows a fiber pattern of polyhexamethylene adipamide[10]. The observed fiber period of 17.0 Å. agrees well with that calculated (17.3 Å.) on the basis of a planar zigzag chain[11]. A fiber pattern of natural silk is given in figure 7c for comparison. The pattern (figure 7d) shows that essentially planar zigzag chains are present in somewhat different arrangement in cross section from that in the paraffins. The number of possible polyamide structures is very great, and this class of linear polymers will in the future undoubtedly furnish most valuable information on the structure of both synthetic and natural high polymers.

E. Linear polysulfides

Another interesting class of synthetic compounds on which little has been published is the polymeric organic polysulfides (41). Katz became interested in these compounds in 1934. Katz and Fuller (31) showed certain of them to be crystalline in the unstretched condition and to be capable of a high degree of orientation on elongation. Figure 7e shows the fiber pattern produced by the compound formed by the reaction of ethylene dichloride and sodium tetrasulfide.

The pattern appears to be a composite one, consisting of a strong fiber diagram superimposed on a weaker one. Whether the weaker pattern is due to an impurity (57) or to another crystal modification of the tetrasulfide is not known. Neglecting the reflections which do not rationalize with the main layer-line system, we obtain a fiber period of 4.32 ± 0.03 A. (31). This value agrees with a type of chain (not necessarily planar) shown in figure 8d, in which two sulfur atoms are joined to the ethylene residue and two are joined to these sulfurs to form a ring[12]. This picture

---

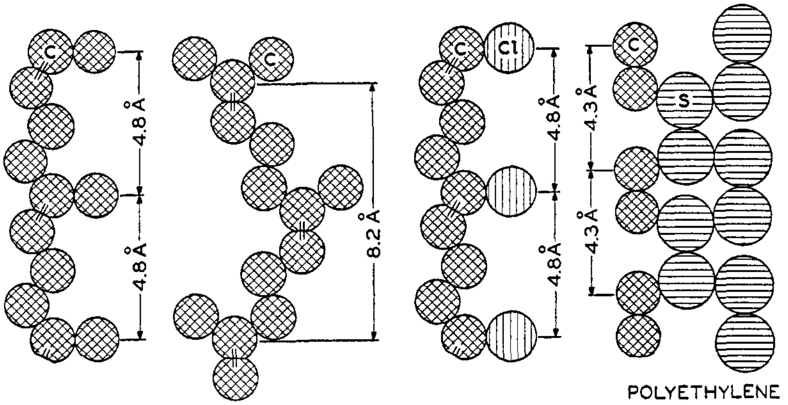
[10] This material was supplied by the du Pont Company.

[11] Brockway's value of 1.46 Å. for C—N (Rev. Modern Phys. **8**, 231 (1936)) is taken. The angles are assumed tetrahedral.

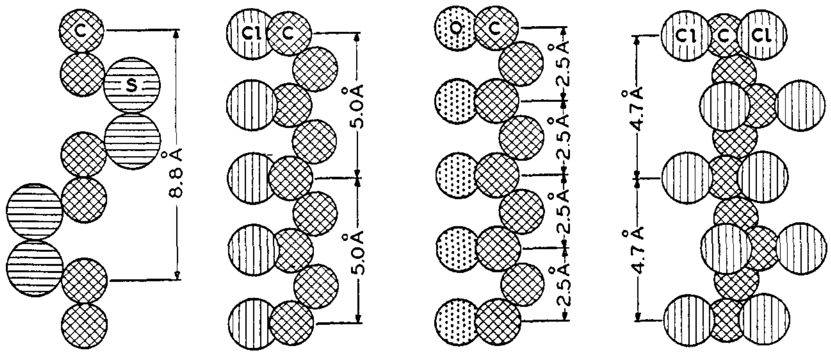
[12] Figure 8 is schematic. It is intended to represent structures which are possible and which agree with the present x-ray data.

appears more likely than the one previously given (31), in which two sulfurs were attached latterly to two sulfurs in the chain. As Patrick (57) has shown, there is good chemical evidence for the fact that two of the sulfur atoms are bonded differently than the other two.

Unlike polyethylene tetrasulfide, polyethylene disulfide[13] prepared from ethylene dichloride and sodium sulfide gives a fiber pattern (figure 7f) which is indicative of a pure compound. The observed fiber period is 8.8 ± 0.05 Å. The appearance of a strong second-order meridian reflection, together with a fiber period which is almost exactly two times that observed for the tetrasulfide, strongly suggests that the disulfide possesses a chain configuration like that shown in figure 8e, in which every alternate



GUTTA-PERCHA NATURAL RUBBER POLYCHLOROPRENE POLYETHYLENE TETRASULFIDE



POLYETHYLENE DISULFIDE POLYVINYL CHLORIDE POLYVINYL ALCOHOL POLYVINYLIDENE CHLORIDE

FIG. 8. Chain configurations of various linear polymers

---

[13] These results are from unpublished work which the author did in collaboration with J. R. Katz. Thanks are due Dr. J. C. Patrick for supplying this sample.

repeating $C_2H_4S_2$ group is rotated through 180°. The length of this unit of between 4.3 and 4.4 Å. is in good agreement with the value 4.34 Å., calculated from the planar form shown in figure 8d assuming C—C = 1.52 Å., C—S = 1.75 Å., and angles of 109.5° and 103° (56) at carbon and sulfur, respectively.

F. Vinyl derivatives

The synthetic polymers produced by the polymerization of compounds possessing the vinyl group, although of great industrial importance, have not been the subject of much careful x-ray investigation. These compounds are now generally conceded to be formed as a result of an activated chain reaction, which results in a distribution of polymers of various chain lengths. Evidence has been presented by Marvel (45, 46, 47) for a "head-to-tail" arrangement of repeating units in most of these compounds. Because of the nature of the polymerization reaction, however, the chain molecules do not appear to possess as high a degree of linearity and regularity as those produced by polycondensation. Nevertheless, in many cases a considerable degree of crystallinity is present and useful information can be obtained by x-ray study.

(*1*) *Polyethylene.* By the polymerization of ethylene it has been possible (16) to build extremely long hydrocarbon chains. Because of the twofold symmetry of the repeating unit, regular molecules arise in this case which crystallize in a macromolecular type of lattice. In a recent work Bunn (8) has determined that the repeating units, as might be anticipated, are arranged in an orthorhombic cell (*Pnam*) having a = 7.4 Å., b = 4.93 Å., and c = 2.534 Å. The chains are paraffinic in configuration (figure 4a) and in a rolled sheet are aligned in the rolling direction with the (110) plane in the sheet plane. From a comparison of the observed and calculated intensities Bunn concludes that the spherical carbon atom in the present conception of the hydrocarbon chain must be replaced by a carbon atom with an electron cloud flattened in the direction of the chain. Presumably this finding applies to all primary valence chains.

(*2*) *Polyhaloprenes.* Carothers and Kenney (13, 14) showed that chloroprene and bromoprene are amorphous in the unstretched condition but crystallize on elongation, giving a fiber diagram as in the case of natural rubber. The observed fiber period is 4.8 Å. in the case of chloroprene.[14] The authors point out that the chain molecules approximate the gutta-percha type of configuration rather than the more folded rubber type. The close analogy to gutta-percha is shown by their respective fiber patterns in figures 7g and 7h. Garbsch and v. Susich (23) obtained a fiber

---

[14] Unpublished work of the author shows polybromoprene to have a fiber period practically identical with that of polychloroprene.

period of 4.8 ± 0.1 Å. at 600 per cent elongation on chloroprene rubber. Krylov (39) studied chloroprene with electron rays and reported an orthorhombic cell with $a = 9.0$ Å., $b = 8.23$ Å., and $c = 4.79$ Å. (fiber axis). Both chloroprene and bromoprene give broad fuzzy reflections in the fiber pattern. This is indicative of an imperfect arrangement of repeating units in the lattice (perhaps because of irregular chain structure) or of extremely thin crystals (64). A comparison of the chain structure for chloroprene with that for gutta-percha is shown in figures 8a and 8c. Since the calculated fiber period for these configurations is approximately 0.2 Å larger than the observed, it is probable that the chain deviates from planar. The Meyer and Mark (48) structure for natural rubber is given in figure 8b.

(*3*) *Polyvinyl alcohol.* Halle and Hofmann (26) have obtained a sharp fiber diagram from polyvinyl alcohol by stretching under the proper conditions. They find a fiber period of 2.57 Å. This is slightly more than the value expected from a planar zigzag chain, and the authors suggest that this may be due to an increase in the tetrahedral valence angle.

The author[15] has repeated this work recently and has found from a sharp fiber pattern (figure 7i) an identity period of 2.52 ± 0.02 Å., in very good agreement with the accepted value for the alternate carbon-to-carbon distance along a planar zigzag chain. The configuration of the polyvinyl alcohol chain is shown in figure 8g and conforms to the finding of the "head-to-tail" structure in this compound by Marvel and Denoon (46).

(*4*) *Polyisobutylene.* Brill and Halle (7) examined polyisobutylene by means of x-rays. They found it to give on stretching a fiber pattern similar to that of natural rubber. The fiber period observed was 18.5 Å. They concluded that helical rather than zigzag chains are present. A fiber pattern obtained on this material[16] by the author is shown in figure 7m. An extremely high degree of orientation and crystallinity is indicated. The meridian reflection observed on the eighth layer-line arises from intermediate planes perpendicular to the fiber axis and 2.3 Å. apart. A "head-to-tail" structure is therefore indicated, the shortening arising from a helical arrangement of the pairs of methyl groups such as Brill and Halle have suggested.

(*5*) *Miscellaneous vinyl derivatives.* Natta and Rigamonti (54) examined a number of vinyl polymers by means of electron rays. They found polyvinyl acetate to be amorphous, polyvinyl chloride and polyvinyl bromide to be partly crystalline, and polyvinylidene chloride to be quite highly crystalline. Misch and Picken (49), however, found a thick-

---

[15] Unpublished work.

[16] The author is indebted to Mr. F. J. Malm for this sample.

ening of the amorphous ring of polyvinyl acetate on stretching at 60°C., in agreement with Katz (31), and concluded that irregular chains are probably present.

The author has found a fiber period[17] of 5.0 ± 0.05 Å. for polyvinyl chloride (figure 7j). This value indicates the presence of a planar zigzag chain and in view of the proof of the 1:3 structure of vinyl chloride (45) necessitates that every other chlorine atom be differently disposed along the chain. A suggested arrangement is that shown in figure 8f, in which the chlorines take up alternate positions on opposite sides of the chain. Such a configuration is in agreement with the repulsion of chlorine atoms at this distance, as found by Beach and Palmer (4) in the case of ethylene dichloride.

The repulsion between chlorine atoms apparently also plays a part in determining the structure of polyvinylidene chloride, $(\text{—CH}_2\text{—CCl}_2\text{—})_n$. Oriented samples of this substance give sharp fiber diagrams (figure 7k). The observed fiber period[18] is 4.7 ± 0.05 Å. A strong second-order meridian reflection is also present, which indicates a 1:3 disposition of the pairs of chlorine atoms. The fiber period shows a definite shortening compared to the planar zigzag arrangement of carbon atoms which requires a period of 5.0 Å. Such a shortening can be obtained by a partial rotation of alternate pairs of chlorine atoms, as illustrated in figure 8h. It is evident that this arrangement, with the individual chlorine atom the maximum distance from its neighbors, is in agreement with the repulsion of these atoms mentioned above.[19]

There can be little doubt that in the case of many of the vinyl polymers we have to do with systems containing much amorphous material. Katz (31) has pointed out that in many cases the "amorphous" rings in these substances correspond closely to rings given by the liquid monomers themselves, and that they often give in addition another ring which he calls the "polymerization ring." Thus, in the case of polystyrene a ring (d = 4.8 Å.) corresponding to liquid styrene and an inner ring (d = 10 Å.) corresponding to an interchain spacing are observed. Likewise in polyvinyl acetate an inner or polymerization ring (d = 7.0 Å.) is observed, which Katz identifies with the interchain distance. In both polystyrene and polyvinyl acetate (as mentioned above) it has been possible to cause

---

[17] The pattern was not sufficiently well formed to exclude the fiber period being a multiple of 5.0 Å. The pattern shown in figure 7j has been reconstructed from the original and shows the positions of the main reflections.

[18] Unpublished work of the author.

[19] An alternative configuration for polyvinylidene chloride which is not excluded by the present evidence is a helical arrangement such as has been suggested for polyisobutylene. The fiber period would then be a multiple of 4.7 Å.

a splitting of these inner rings corresponding to a parallel ordering of the chains. There is therefore good evidence that the long chains in many of these polymers exist in a sort of mesomorphic arrangement, in which portions of the chains are arranged parallel and at a given distance apart but are otherwise unordered.

VI. CONCLUSION

The ultimate aim of research on high polymeric substances is to explain the properties of these substances in terms of their inner colloidal and molecular nature. X-ray and electron diffraction investigations, as we have seen, have furnished considerable data on this inner structure. Nevertheless, it is of the utmost importance that the investigator in this field does not obtain a one-sided view from the past work. Nearly always a given study relates to only one phase of the general problem. For example, it is wrong to assume that, since the "unit cell" for cellulose has been well established, we therefore know its entire structure. In reality we have determined simply that parts of the cellulose have this structure. How these parts fit into the other parts that make up the entire system is still not clear. Here again the synthetic high polymers can be of great help. By employing simple polymeric molecules of known chemical constitution and structure and by determining how these molecules behave in the aggregate, we may expect to make progress in understanding these complex systems. In this endeavor a closer control of both the specimens under examination and the technique itself will serve to make the diffraction method an even more valuable tool for the study of high molecular compounds.

The author is indebted to Mr. C. J. Frosch and Dr. W. O. Baker for many helpful suggestions. Thanks are also due to Mr. N. R. Pape for aid in obtaining certain of the x-ray results.

REFERENCES

(1) Astbury, W. T.: *Fundamentals of Fibre Structure.* Oxford University Press, London (1933).
(2) Astbury, W. T.: Proc. Roy. Soc. (London) **A150,** 533 (1935).
(3) Barnes, W. H., and Ross, S.: J. Am. Chem. Soc. **58,** 1129 (1936).
(4) Beach, J. Y., and Palmer, K. J.: J. Chem. Phys. **6,** 639 (1938).
(5) Bernal, J. D.: Z. Krist. **83,** 153 (1932).
(6) Bernal, J. D.: Nature **143,** 663 (1939).
(7) Brill, R., and Halle, F.: Naturwissenschaften **26,** 12 (1938).
(8) Bunn, C. W.: Trans. Faraday Soc. **35,** 483 (1939).
(9) Carothers, W. H.: J. Am. Chem. Soc. **51,** 2548 (1929), *et seq.*
(10) Carothers, W. H.: Chem. Rev. **8,** 353 (1931).
(11) Carothers, W. H., and Hill, J. W.: J. Am. Chem. Soc. **54,** 1579 (1932).

(12) Carothers, W. H., and Hill, J. W.: J. Am. Chem. Soc. **54,** 1568 (1932). Carothers, W. H.: U. S. patent 2,130,948.
(13) Carothers, W. H., Kirby, J. E., and Collins, A. M.: J. Am. Chem. Soc. **55,** 789 (1933).
(14) Carothers, W. H., Williams, I., Collins, A. M., and Kirby, J. E.: J. Am. Chem. Soc. **53,** 4203 (1931).
(15) Clark, G. L.: *Applied X-Rays,* 2nd edition. McGraw-Hill Book Company, Inc., New York (1933).
(16) Fawcett, E. W., *et al.*: British patent 471,590.
(17) Frey-Wyssling, A.: Protoplasma **25,** 261 (1936); **27,** 372 (1937).
(18) Frumkin, L. S., and Goncharov, I. D.: Zarodskoya Lab. **3,** 1112 (1934).
(19) Fuller, C. S.: Ind. Eng. Chem. **30,** 472 (1938).
(20) Fuller, C. S., and Erickson, C. L.: J. Am. Chem. Soc. **59,** 344 (1937).
(21) Fuller, C. S., and Frosch, C. J.: J. Phys. Chem. **43,** 323 (1939).
(22) Fuller, C. S., and Frosch, C. J.: J. Am. Chem. Soc. **61,** 2575 (1939).
(23) Garbsch, P., and v. Susich, G.: Kautschuk **8,** 122 (1932); Rubber Chem. Tech. **6,** 113 (1933).
(24) Gerngross, O., and Herrmann, K.: Z. physik. Chem. **B10,** 371 (1930); Kolloid-Z. **60,** 276 (1936).
(25) Halle, F.: Kolloid-Z. **69,** 324 (1934).
(26) Halle, F., and Hofmann, W.: Naturwissenschaften **23,** 770 (1935).
(27) Hengstenberg, J.: Ann. Physik **84,** 245 (1927).
(28) Hengstenberg, J.: Z. Krist. **67,** 583 (1928).
(29) Herzog, R. O.: Kolloid-Z. **39,** 98 (1926).
(30) Katz, J. R.: *Die Röntgenspektrographie als Untersuchungsmethode.* Urban & Schwarzenberg, Berlin (1934).
(31) Katz, J. R.: Trans. Faraday Soc. **32,** 77 (1936).
(32) Kohlhaas, R.: Z. Krist. **98,** 418 (1938).
(33) Kohlhaas, R., and Soremba, K. H.: Z. Krist. **100,** 47 (1938).
(34) Kohlschütter, H. W., and Sprenger, L.: Z. physik. Chem. **B16,** 284 (1932).
(35) Kratky, O.: Kolloid-Z. **70,** 14 (1935).
(36) Kratky, O.: Naturwissenschaften **26,** 94 (1938).
(37) Kratky, O., and Mark, H.: Z. physik. Chem. **B36,** 129 (1937).
(38) Kratky, O., and Schossberger, F.: Z. physik. Chem. **B39,** 145 (1938).
(39) Krylov, K. I.: Caoutchouc and Rubber (U. S. S. R.), No. 1, 24 (1938); No. 2, 26 (1938); J. Exptl. Theoret. Phys. (U. S. S. R.) **5,** 524 (1935); Rubber Chem. Tech. **9,** 409 (1936).
(40) Langmuir, I.: J. Am. Chem. Soc. **39,** 1848 (1917).
(41) Martin, S. M., Jr., and Patrick, J. C.: Ind. Eng. Chem. **28,** 1145 (1936).
(42) Mark, H.: *Physik und Chemie der Cellulose.* J. Springer, Berlin (1932).
(43) Mark, H.: Paper presented at the Ninety-seventh Meeting of the American Chemical Society, held in Baltimore, Maryland, March, 1939.
(44) Mark, H., and v. Susich, G.: Kolloid-Z. **46,** 11 (1928).
(45) Marvel, C. S.: J. Am. Chem. Soc. **61,** 3241 (1939).
(46) Marvel, C. S., and Denoon, C. E., Jr.: J. Am. Chem. Soc. **60,** 1045 (1938).
(47) Marvel, C. S., and Levesque, C. L.: J. Am. Chem. Soc. **60,** 280 (1938); **61,** 1682 (1939).
(48) Meyer, and Mark, H.: *Der Aufbau der hochpolymeren organischen Naturstoffe.* Akademische Verlagsgesellschaft, Leipzig (1930).
(49) Misch, L., and Picken, L.: Z. physik. Chem. **B36,** 398 (1937).
(50) Müller, A.: J. Chem. Soc. **123,** 2043 (1923).

(51) Müller, A.: Proc. Roy. Soc. (London) **A120,** 437 (1928).
(52) Müller, A., and Shearer, G.: J. Chem. Soc. **123,** 3156 (1923).
(53) Natta, G.: IX Congr. intern. quím. pura aplicada **4,** 208 (1934).
(54) Natta, G., and Rigamonti, R.: Atti. accad. Lincei **24,** 381 (1936).
(55) Ott, E.: Science **71,** 465 (1930).
(56) Palmer, K. J.: J. Am. Chem. Soc. **60,** 2360 (1938).
(57) Patrick, J. C.: Trans. Faraday Soc. **32,** 347 (1936).
(58) Pierce, F. T.: Trans. Faraday Soc. **26,** 809 (1930).
(59) Piper, S. H., and Grindley, E.: Proc. Phys. Soc. (London) **35,** 269 (1923); **36,** 31 (1923).
(60) Rigamonti, R.: Gazz. chim. ital. **66,** 174 (1936).
(61) Sauter, E.: Z. physik. Chem. **B18,** 417 (1932).
(62) Sauter, E.: Z. physik. Chem. **B21,** 186 (1933).
(63) Sauter, E.: Z. physik. Chem. **B21,** 161 (1933).
(64) Schiebold, E.: Kolloid-Z. **69,** 266 (1934).
(65) Schoon, T.: Z. physik. Chem. **B39,** 385 (1938).
(66) Shearer, G.: J. Chem. Soc. **123,** 3152 (1923).
(67) Sisson, W. A.: J. Phys. Chem. **40,** 343 (1936).
(68) Sisson, W. A.: Ind. Eng. Chem. **30,** 530 (1938).
(69) Staudinger, H.: *Der Aufbau der hochmolekularen organischen Verbindungen.* Hirschwaldsche Buchhandlung, Berlin (1932).
(70) Staudinger, H., Johner, H., Signer, R., Mie, G., and Hengstenberg, J.: Z. physik. Chem. **A126,** 425 (1927).
(71) Staudinger, H., and Signer, R.: Z. Krist. **70,** 193, 202 (1929).
(72) Staudinger, H., Staudinger, M., and Sauter, E.: Z. physik. Chem. **B37,** 403 (1937).
(73) Storks, K. H.: J. Am. Chem. Soc. **60,** 1753 (1938).
(74) Sutton, L. E., and Brockway, L. O.: J. Am. Chem. Soc. **57,** 473 (1935).
(75) Thiessen, P. A., and Schoon, T.: Z. physik. Chem. **B36,** 195, 216 (1937).
(76) Thiessen, P. A., and Spychalski: Z. physik. Chem. **A156,** 309, 435 (1931).