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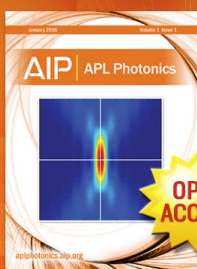J. Rheol. 43, 1195 (1999); 10.1122/1.551034

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Comparison of the Structures of Stretched Linear Polymers*

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Published x-ray data from crystalline selenium and tellurium and from stretched sulfur (amorphous), polyethylene, polyisobutylene, polyvinyl alcohol, polyvinyl chloride, polyvinylidine chloride, polyoxymethylene, polyoxyethylene, polyethylene disulfide, polyethylene tetrasulfide, and polyphosphonitrile chloride are compared. In most cases the experimental identity distance in the direction of the chain axes and the expected interatomic distances and interbond angles are found to be in agreement with the assumption that the chain atoms form a regular spiral, unidirectional in each chain and of uniform pitch. Apparent exceptions are briefly discussed.

X-RAY diffraction data show that substances composed of long chain molecules, when stretched, if not otherwise, tend to form crystalline arrangements in which the chain axes lie parallel to each other. In some cases, as in polyethylene,[1] polyvinyl alcohol,[2-4] and polyvinyl chloride,[3] the data indicate a planar zigzag arrangement of the chain atoms in each chain (Figs. 1 and 2). Each chain is extended as far as possible, consistent with the maintenance of the expected bond distances ($\sim$1.53A for C—C) and bond angles ($\sim$110° for $\angle$C—C—C). In most instances, however, the data are not in agreement with such a structure. The number of chain atoms between like points in a chain is greater than two and the "identity distance"—the distance between consecutive like points—differs

from what would be expected for a plane zigzag arrangement. In this paper, the structures of these substances are discussed.

In accordance with well-established principles of structural chemistry, we should expect a chain composed of chain atoms which are equivalent as regards the atoms to which they are bonded to assume a structure (on crystallization) in which these chain atoms are in crystallographically equivalent positions. This requirement is satisfied by a planar zigzag structure or by a unidirectional spiral structure of uniform pitch. Which type is assumed in a given case (and the constants of the spiral, if the latter) will depend upon intra- and interchain forces, as discussed below.

Polyethylene,[1] (—CH_2—)$_n$, and crystalline "metallic" selenium[5, 6] and tellurium[5, 6] are composed of chain molecules in which the chain atoms (C, Se, Te) are all equivalent. In polyethylene, the chains have the planar zigzag structure; in selenium and tellurium, the chains are

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[1] C. W. Bunn, Trans. Faraday Soc. **35**, 482 (1939).
[2] F. Halle and W. Hofmann, Naturwiss. **23**, 770 (1935).
[3] C. S. Fuller, Chem. Rev. **26**, 143 (1940).
[4] R. C. L. Mooney, J. Am. Chem. Soc. **63**, 2828 (1941).
[5] M. K. Slattery, Phys. Rev. **21**, 378 (1923); **25**, 333 (1925).
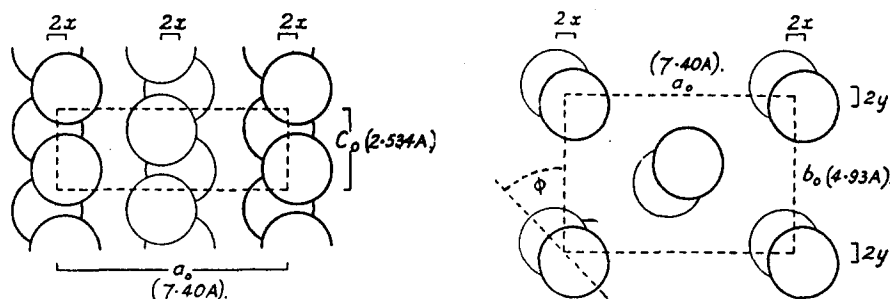[6] A. J. Bradley, Phil. Mag. **48**, 477 (1924).

FIG. 1. Distribution of zigzag carbon chains in polyethylene, (—CH_2—)$_n$, according to Bunn (reference 1).

TABLE I. Data for various polymer structures.

Polymer	Repeating unit	Identity distance (t)	Bond distance (assumed)	Bond angle (calc.)	No. of chain atoms per identity distance (m)	No. of revolutions per identity distance (p)	Rotation per chain bond (α)	
Polyethylene	—CH$_2$—	2.534A	1.53A	112°	2	1	180°	
Selenium	—Se—	4.95	2.32	105°	3	1	120°	
Tellurium	—Te—	5.91	2.86	102°	3	1	120°	
Sulfur	—S—	9.26	2.12	{107° / 107°}	8 / 6	2 / 2	90° / 120°	Reverse ? / Reverse ?
Polyvinyl chloride	—C(H)(Cl)—C(H)(H)—	5.0	1.53	110°	4	2	180°	
Polyvinyl alcohol	—C(H)(OH)—C(H)(H)—	2.52	1.53	110°	2	1	180°	
Polyisobutylene	—C(H)(CH$_3$)—C(H)(CH$_3$)—	18.63	1.53	111°	16	7	157.5°	
Polyvinylidene chloride	—C(H)(Cl)—C(H)(Cl)—	4.67	1.53	122°	4	Not a uniform spiral		
Polyoxymethylene	—C(H)(H)—O—	17.3	1.43	111°	18	5	100°	
Polyoxyethylene	—C(H)(H)—C(H)(H)—O—	19.5	C—C 1.53 / C—O 1.43	{108° / 110° (assumed)}	24 / 27	6 / 5	90° / non-uniform spiral	Reverse ? / ?
Polyphosphonitrile chloride	—N=P(Cl)(Cl)—	4.92	1.65	124°	4	1	90°	
Polyethylene disulfide	—C(H)(H)—C(H)(H)—S—S—	8.8	1.825 (Av.)	111°	8	2	90° (Av.)	Reverse ?
Polyethylene tetrasulfide	—C(H)(H)—C(H)(H)—S$^+$—S$^+$— (S$^-$ S$^-$)	4.32	1.825 (Av.)	110°	4	1	90° (Av.)	

uniform spirals with three chain atoms per identity distance (Figs. 3[7] and 4). The bond distances and bond angles (Table I) agree with what would be expected from structure theory and from our knowledge of corresponding distances and angles in the substances.

A planar zigzag structure can be considered as a special case of a uniform spiral, in which for each bond in the chain there is an angular rotation (α) of 360°/2 and a translation of $t/2$, where t is the identity distance. In selenium or tellurium, the angular rotation and translation per chain bond are 360°/3 and $t/3$, respectively. In general, for a uniform spiral, there is, per chain bond, an angular and translational shift of magnitudes $p360°/m$ and t/m, respectively, where p and m are integers. From x-ray data, t and m may be deduced. Knowing these, one can compute a value of α corresponding to any pair of assumed values of bond distance and angle. If p, computed

[7] Strukturbericht 1, 27 (1931).

from the equation

$$p = \alpha m / 360°,$$

is found to be approximately integral, values of bond distance and angle close to those assumed are consistent with the assumption of a uniform spiral and with the experimental t and m values. By assuming p to be *exactly* integral, one may then compute the exact value of bond angle consistent with the observed t and m values and an assumed bond distance. This procedure was followed in deducing the bond angles in Table I. (Alternatively, one might assume bond angles and deduce bond distances.)

The data on fibrous sulfur should be mentioned. Meyer and Go[8,9] have deduced unit cell dimensions, including a fiber period of 9.26A, and suggested (on the basis of very meager evidence) that there are 14 chains of 8 S atoms, each passing through this cell. Meyer later proposed, as an alternative, 16 chains of 8 atoms each. The published data seem to be in as good or better agreement with 18 chains of 6 atoms each. Either 8 or 6 atoms per 9.26A in the fiber direction would be consistent with the assumption of uniform spirals if one permits *two* complete rotations per identity distance (see Table I). The doubled identity distance could be accounted for by assuming a reversal of direction of the helix after each complete rotation (Fig. 5). Obviously, a more detailed structure analysis is required.
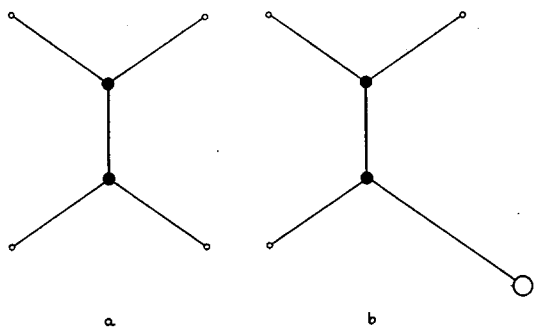

FIG. 2. Projections of proposed structures for polyethylene (a) and polyvinyl alcohol (b). The hydroxyl hydrogen atoms of the latter are not shown. Polyvinyl chloride is presumed to have a structure like (b), but with the Cl atoms of the CHCl groups alternating from one side to the other of the plane of the C—C zigzag.

[8] K. H. Meyer and Y. Go, Helv. Chem. Acta **17**, 1081 (1934).
[9] K. H. Meyer, *Natural and Synthetic High Polymers* (Interscience Publishers, Inc., New York, 1942), p. 51.
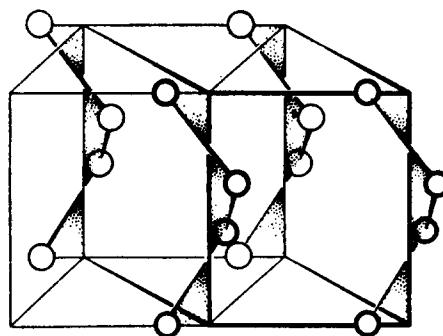

FIG. 3. The structure of Se and Te crystals. From the *Strukturbericht* (reference 7).

Plane zigzags or uniform spirals are also necessary when alternate chain atoms are different with respect to their attachment to other atoms, as in vinyl polymers, if all the bonds in a chain are equivalent. Interaction between the groups attached to the chain atoms within each chain or between neighboring chains may, however, make another arrangement more stable. (See the discussion of polyvinylidene chloride below.)

Polyvinyl chloride[3] and polyvinyl alcohol[2–4] give x-ray data agreeing with a plane zigzag structure having the customary C—C distances and $\angle$C—C—C bond angles. The identity distance in polyvinyl chloride is approximately twice that in polyvinyl alcohol. As pointed out by Fuller, the larger value would be expected if the chloride atoms are alternately placed, first on one side and then on the other, with respect to the plane of the zigzag (Fig. 2).

X-ray data from polyisobutylene have been interpreted by Fuller, Frosch, and Pape[10] as showing 16 chain atoms per fiber period, 18.63±0.05A. These figures are in agreement with the assumption of a uniform spiral with tetrahedral bond angles and the usual C—C distance. The angular shift α is 157.5°. The departure from a plane zigzag structure, for which $\alpha = 180°$, is thus not very great (Figs. 4 and 6).

Reinhardt[11] has reported a fiber period of 4.67A for polyvinylidene chloride with 4 chain atoms (two residues) per unit in each chain. These data are not in accord with a uniform spiral structure. The arrangement (Fig. 7) he proposes is a reasonable one, although it is neces-

[10] C. S. Fuller, C. J. Frosch, and N. R. Pape, J. Am. Chem. Soc. **62**, 1905 (1940).
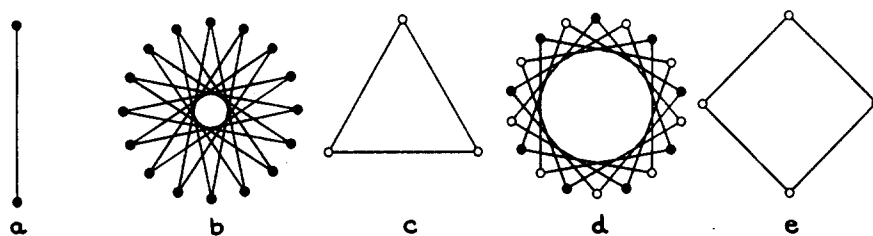[11] R. C. Reinhardt, Ind. Anal. Chem. **35**, 422 (1943).

FIG. 4. Projections of the chain atoms and bonds in certain structures, assuming uniform spirals. (a) Polyethylene, polyvinyl alcohol, polyvinyl chloride. (b) Polyisobutylene. (c) Selenium, tellurium. (d) Polyoxymethylene. (e) Polyphosphonitrilechloride, polyethylene tetrasulfide.

sary to assume a C—C—C bond angle greater than 120°. The type of arrangement can be attributed to strong interaction between the side atoms, H and Cl, of opposite polarity.

In polyoxymethylene, $(—CH_2—O—)_n$, as in the vinyl polymers, the chain atoms are alternately of two types: Both OCO and COC bond angles would be expected to be in the neighborhood of "the tetrahedral angle." The C—O distance should be about 1.43A. These expectations and the experimental value[12, 13] of the fiber period, 17.3A for 9 —CH$_2$O— groups (18 chain atoms), agree with the assumption of a uniform spiral (Table I and Fig. 4).

In polyoxyethylene or polyethylene oxide $(—CH_2—CH_2—O—)_n$, the chain bonds are not all alike. The assumption of a uniform spiral, with the expected bond distances and with all bond angles in the neighborhood of 110°, leads to an identity distance just one-third of the experimental value.[14] There is no obvious reason for this discrepancy. It is likely that in this case the assumption of a spiral of uniform slope is in error. There is no symmetry argument for it, and it is certainly reasonable to expect better packing and greater stability for a structure in which the slope of the C—C bonds differs from that of the C—O and O—C bonds. Assuming a unidirectional spiral with slopes of C—O and O—C bonds the same and with 110° bond angles throughout, the observed identity distance[12] is found to correspond to 5 revolutions of the chain, with the C—C bonds nearly parallel to the spiral axis (the projection of the 1.53A bond distance on the axis is 1.48A) (see Fig. 8). This differs

considerably from the meandering structure assumed by Sauter,[13] in which the C—C bonds are roughly perpendicular to the chain axis.

Sauter's conclusion that there are 9 —CH$_2$—CH$_2$—O— residues per identity distance, in the polyoxyethylene structure, is questionable.[15] If there should really be only 8 such residues per identity distance, a reverse spiral of uniform slope would be possible. [See Table I and Fig. 6(b).] Further structure work is obviously necessary.

Polyphosphonitrile chloride is another substance which consists of chain molecules in which the chain atoms are alternately of two types. The structure can be considered as resonating, according to the scheme

$$\left(—N=\underset{Cl}{\overset{Cl}{P}}—\right)_n \leftrightarrow \left(=N—\underset{Cl}{\overset{Cl}{P}}=\right)_n.$$
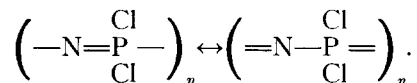
The distance between adjacent N and P atoms can be taken as 1.65A, the value found by Brockway and Bright[16] for the trimer, a ring compound, by electron diffraction methods.

[12] J. Hengstenberg, Ann. d. Physik [4] **84**, 245 (1927).
[13] E. Sauter, Zeits. f. physik. Chemie **B18**, 417 (1932); **B21**, 186 (1933).
[14] E. Sauter, Zeits. f. physik. Chemie **B21**, 161 (1933).

[15] Cf. Meyer, reference 9, p. 196.
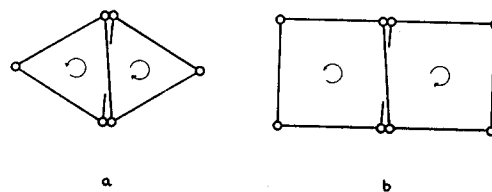[16] L. O. Brockway and W. M. Bright, J. Am. Chem. Soc. **65**, 1551 (1943).

FIG. 5. Projections of two possible reverse spiral structures for fibrous sulfur. So as to show better the spiral arrangements, the projections of the middle atoms, in both structures, have been shifted slightly from their true positions. A structure of the type of (b) may also be correct for polyoxyethylene and polyethylene disulfide.
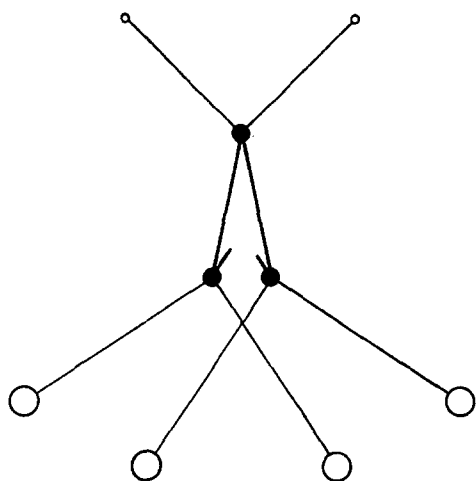
FIG. 6. Projection of a small section of a polyisobutylene spiral. Large circles denote carbon atoms of methyl (CH_3) groups.

Meyer, Lotmer, and Pankow,[17] in their x-ray study of the polymer, deduced 4.92 ± 0.05A for the fiber period and concluded that there are 4 chain atoms in this distance. From these results,

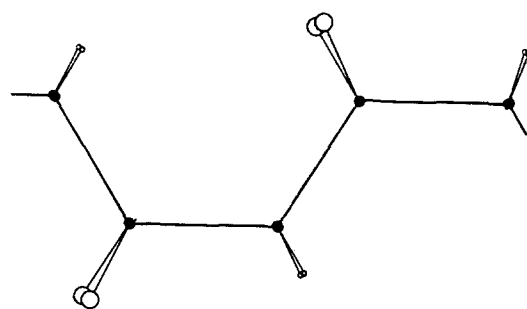[17] K. H. Meyer, W. Lotmar, and G. W. Pankow, Helv. Chem. Acta **18**, 930 (1936).

FIG. 7. Projection of the polyvinylidene chloride structure onto the plane of the —C—C— chain, according to Reinhardt. The positions of the H and Cl projections have been displaced slightly.

the assumption of a uniform spiral leads to an average bond angle, $\angle$ PNP or $\angle$ NPN, of 124° (Table I and Fig. 4). This is reasonable, being close to 125° 16', the calculated angle between a single and a double bond for regular tetrahedra. In the trimer ring, the average angle is about 120°.

In polyethylene disulfide, $(-CH_2-CH_2-S-S-)_n$, and polyethylene tetrasulfide,

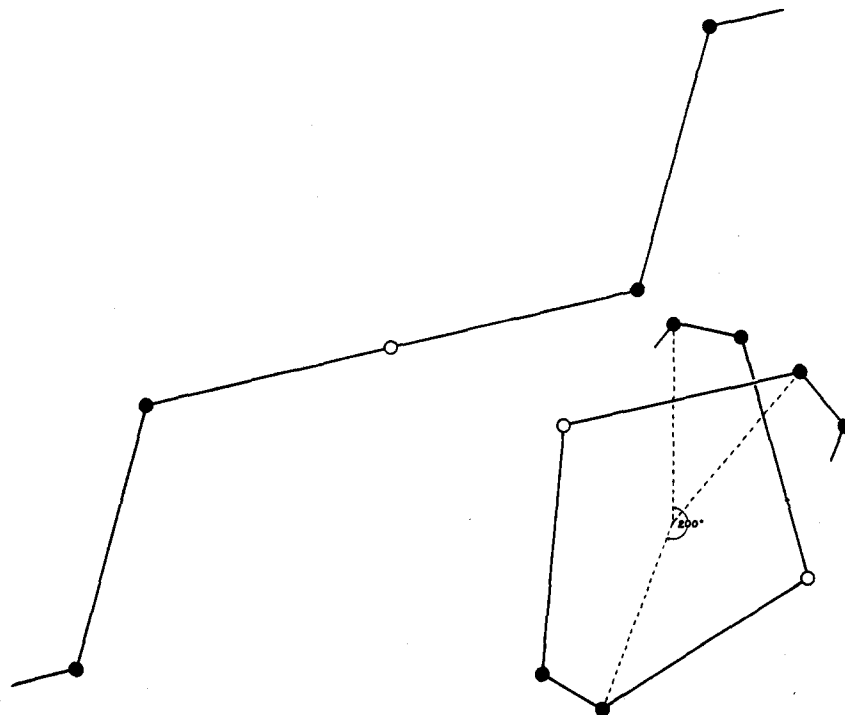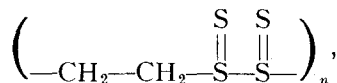$$\left(-CH_2-CH_2-\overset{\overset{\displaystyle S}{\|}}{S}-\overset{\overset{\displaystyle S}{\|}}{S}- \right)_n ,$$

FIG. 8. Illustrating a possible structure for polyoxyethylene (polyethylene oxide), $(-CH_2-CH_2-O-)_n$. A projection of a portion of the helical chain is shown at the lower right. Above and to the left is the arrangement obtained by unrolling the helix onto a plane; this shows the different pitch of the C—C and C—O—C portions of the chain.

as in polyoxyethylene, symmetry and similar arguments do not require uniform slopes for the chain bonds. Nevertheless, the observed fiber distances[3,18] are in agreement with the assumption of spirals of uniform pitch with approximately tetrahedral bond angles (see Table I and Figs. 4 and 5)—a reverse spiral in the case of the disulfide.

With regard to rubber, guttapercha, polychloroprene, polyamides, polyesters, and other substances composed of chains more complex than those already considered, we might expect uniform, or nearly uniform, spirals except when prevented by strong atomic interactions (other than those determining the bond distances and angles), either within the same chain or between chains. Detailed consideration of these structures will not be attempted at this time.

The angular shift per chain atom in a molecular spiral may be determined primarily by the requirements for most stable (lowest energy) packing of the chain molecules in the mass or by forces between atoms in the same chain. In addition, if the substance is held under tension, there is the stretching force tending to extend

the chain in the direction of its axis as much as possible. If not prevented by other forces, this stretching force produces a plane zigzag arrangement—the most extended one possible for given bond angles and distances. Intrachain forces may make this structure impossible, as, for instance, in the case of polyisobutylene, in which repulsion between the methyl groups on alternate carbon atoms forces a small angular shift of these atoms around the chain axis (Fig. 6). In a case such as selenium or tellurium, the form of spiral is probably largely determined by forces between atoms in different chains, tending to produce an arrangement of atoms as closely packed as possible consistent with the maintenance of stable bond distances and angles.

In conclusion, it must be emphasized that most of the structural arrangements which have been discussed require further experimental confirmation. Work along this line is planned by the writer when war conditions permit. In the meantime, it must be considered interesting and probably significant that, of the variety of simple polymer structures for which identity distance data are available, nearly all are in accord with the simple reasonable hypothesis of uniform spiraling.

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[18] J. R. Katz, Trans. Faraday Soc. **32**, 77 (1936).