weight, 59.7 mm. long where the ratio of length to diameter was only 1933 instead of 2500. The diameter of the fibers was 0.040 mm., that of the spheres 0.485 mm.; probably they were all still too coarse for the requirements of the formula, but the results are of interest as approximately illustrative of the general formulas.

Vertical fibers fell 17.7 cm. through sucrose solution in 901 and 949 seconds, respectively, whereas the spheres required a minimum of 84 sec. The value calculated for the sphere from Stokes' formula was 68.9 sec. The ratio between the fibers and the theoretical value for the sphere was 13.07 and 13.77, mean 13.4, whereas the theoretical ratio predicted was 13.3, and the actual ratio found was not larger than 11. In water, typical experiments gave a ratio between that observed for a vertical fiber and that calculated for a sphere the same weight equal to 14.3 as compared with the predicted value 15.3.

The effect of elongation is even less under conditions where turbulence is prominent in the observation of rate of fall. For the silica fibers and spheres falling through water the observed effect was only between 4-fold for vertical and 8-fold for horizontal fall. In dropping $^3/_8''$ (9.5 mm.) steel balls through still water and comparing them with the same weight of steel wire (0.0243″ (0.61 mm.) in diameter) whose length was again 5000 times its radius, the relative rates varied only between 1.6 for vertical and 4.5 for horizontal. Hence, in viscosity measurements the effect of elongation is even less when turbulence is not eliminated.

Summary

From observations on the actual effect on resistance to movement when a sphere is elongated to a fiber 2500 longer than its diameter, it is concluded in accordance with the hydrodynamic theory employed by Einstein for colloidal particles and large molecules that although the effect of extreme departure from sphericity is measurable it is of too low a magnitude to explain the high viscosity which 0.1% of certain colloids, such as nitrocotton, impart to solvents in which they are dissolved. It is therefore concluded that the chief factor is structural viscosity due to entanglement and local adherence of molecules and particles, effectively immobilizing a disproportionate amount of the solvent in comparison with the amount of the colloid itself.

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[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES]

An X-Ray Study of Some Linear Polyesters

BY C. S. FULLER AND C. L. ERICKSON

By means of intermolecular polycondensation reactions Carothers and his co-workers[1] have been able to synthesize linear polyesters of high molecular weight from dihydric alcohols and dibasic aliphatic acids. Carothers and Hill[2] have pointed out the surprising fiber-like characteristics which can be obtained in certain of these polyesters when the molecular weights are sufficiently high (superpolyesters). They have also demonstrated that the polyesters in massive form are microcrystalline, furnishing sharp X-ray powder diagrams, while in the oriented state (cold-drawn fibers) they are capable of giving fiber patterns. Up to this time, however, no attempt apparently has been made to verify the chemical structures which have been proposed for these compounds by means of a study of their X-ray fiber patterns.[3] The X-ray structure of synthetic fibers of known chemical constitution is also of considerable interest since it offers a means of confirming present conceptions in regard to high polymeric substances.

In the present investigation a series of polyesters has been prepared and examined by means of X-rays. Six of these have been carried to the superpolyester state so that highly oriented fiber patterns could be obtained from them. It is the purpose of this investigation to present and discuss the results of the measurement of these fiber patterns.

Materials and Method

Since many polyesters do not crystallize, or do so very slowly, the number which is suitable for X-ray study is somewhat limited. Table I lists the materials which have been investigated together with the approximate molecular

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[1] W. H. Carothers, THIS JOURNAL, **51**, 2548 (1929), *et seq.*

[2] W. H. Carothers and J. W. Hill, *ibid.*, **54**, 1579 (1932).

[3] A. W. Kenney (ref. 2) has found that the fiber period of some polyesters approximates the length of the chemical repeating unit.

weights,[4] the melting[5] or softening points, densities and drawing properties of each. The preparation and other properties of these materials are described in the experimental part of this paper.

For the purpose of obtaining the X-ray diagrams the substances were examined in the form of bars (for the Debye–Scherrer photographs) 0.4 mm. thick, 1.0 mm. wide and about 15 mm. long or in the form of cylindrical fiber bundles (for the fiber diagrams) 0.5 to 1.0 mm. in diameter. The fibers were prepared by cooling the molten polyesters into solid rods of suitable sizes and cold drawing these so as to form well oriented fibers. These were then wound under tension on U-shaped holders so as to form bundles of parallel fibers. The fiber bundles were fixed in a perpendicular position to the X-ray beam which was collimated to a diameter approximately equal to that of the sample.

The X-ray cameras employed were similar in construction to those described by J. R. Katz.[6] Except in the case of very weak or diffuse reflections the precision of measurement of the X-ray reflections was approximately 1% on check photographs of the same material.

The source of X-rays was a Philips Metalix X-ray tube which was operated at 13 ma. and approximately 25 kv. A copper target was employed and the resulting K-alpha radiation (1.539 Å.) separated from the K-beta by means of a nickel filter 0.015 mm. thick. The maximum due to the white radiation, which occurred at approximately 0.8 Å., was observed near the primary beam in nearly all cases but it is not believed that the effects due to it have been confused with the monochromatic reflections from the samples. Exposure times varied between four and six hours.

Results

Debye–Scherrer photographs of samples of polyethylene sebacate representing bands of progressively increasing average molecular weight (1–4, Table I) showed the same interplanar spacings within the precision of measurement in all cases. The relative intensity (visual) of corresponding rings was also found to be the same on all photographs. The interplanar distances determined from these photographs agreed with those determined from the fiber pattern of polysebacate.

Highly oriented fiber diagrams were obtained from polyethylene succinate, polyethylene adipate, polyethylene azelate and polyethylene sebacate. The fibers drawn from polytrimethylene sebacate and polydiethyleneoxide sebacate yielded less well defined photographs. In all cases an uniaxial type of crystallite orientation is present. Several attempts to produce a higher degree of orientation[7] (folienstruktur) by rolling the polyethylene sebacate ester into thin films showed that no further orientation of the crystallites occurred, since the same fiber diagram was obtained when the film was exposed parallel and perpendicular to the film plane. Further efforts to secure such samples of higher orientation are being made. In Fig. 1, (a) to (f) are schematic drawings of the fiber patterns obtained from the six polyesters.

TABLE I

PROPERTIES OF THE POLYESTERS

		Average mol. wt.	Softening point, °C.	Density (25°C.)	Cold-drawing properties
	Debye–Scherrer photographs				
1	P-ethylene sebacate	4,000	69	...	Does not draw
2	P-ethylene sebacate	13,000	69–70	...	Does not draw
3	P-ethylene sebacate	15,000	68–71	...	Draws well
4	P-ethylene sebacate	18,000	70–74	1.148	Draws well
	Fiber patterns				
5	P-ethylene succinate	13,000	104–106	1.358	Draws well
6	P-ethylene adipate	12,000	52–54	1.250	Draws well
7	P-ethylene azelate	10,000	44–46	1.172	Draws well
8	P-ethylene sebacate (same as 4)	18,000	70–74	1.148	Draws well
9	P-trimethylene sebacate	13,000	54–55	1.090	Draws well (cold)
10	P-diethylene oxide sebacate	18,000	36.5–39	1.128	Draws well (cold)

In the case of each of the polyesters the identity periods along the fiber axis have been calculated from averaged measurements of the reflections obtained from at least two and generally three independent exposures. The interplanar distances, identity periods along the fiber axes and relative intensities of the reflections for the six polyesters listed in Table I, 5–10 are recorded in Table II. The average values of the fiber periods are collected in the second column of Table IV. In the case of polyethylene azelate, polytrimethylene sebacate and polydiethyleneoxide sebacate several values for the fiber periods are possible because of

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[4] No great significance can be attached to the molecular weight values in Table I since in every case mixtures of polymers are present. The values here given were obtained by the use of Staudinger's viscosity method ("Die hochmolekulären organischen Verbindungen"). The constant ($y = 1.5 \times 10^{-3}$) given by Staudinger and Schwalenstöcker (ref. 20) for aliphatic glycol esters in chloroform solution has been employed.

[5] As W. H. Carothers and J. A. Arvin, THIS JOURNAL, **51**, 2560 (1929), have pointed out the melting points are not sharp.

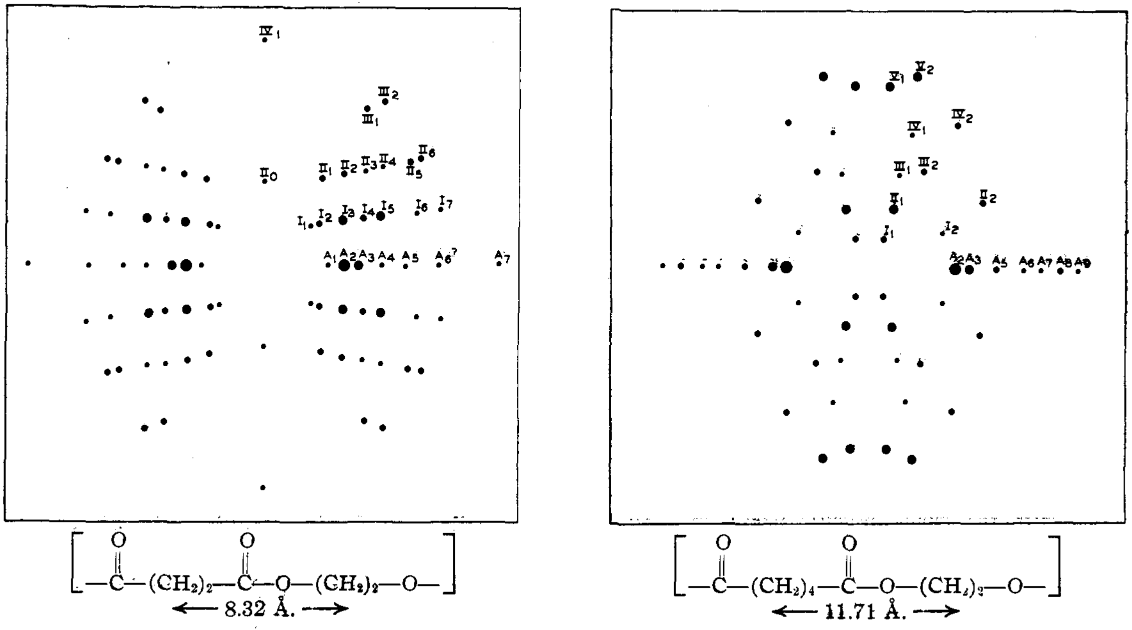
[6] J. R. Katz, "Die Roentgenspektrographie als Untersuchungsmethode," Urban and Schwarzenberg, Berlin, 1934, p. 54.

[7] K. Weissenberg, *Ann. Physik*, **69**, 409 (1922); W. A. Sisson, *J. Phys. Chem.*, **40**, 343 (1936).

missing spectra. A consideration of the chemical structures, however, together with the probable lengths of the radicals involved, leads in each case to a choice of the value given as the true one.

For polyethylene azelate it appears from these considerations that only every third layer-line is present up to the sixth layer-line. In the case of polytrimethylene sebacate the first six layer-lines prove to be missing and in the case of polydiethyleneoxide sebacate the layer-lines 1, 2, 3, 5, 6, 7 are absent or very weak.

Strong diatropic planes occur in the normal fiber diagram for polyethylene azelate (Fig. 1 (c)), indicating the presence of a two-fold screw axis of symmetry parallel to the fiber axis. Polytrimethylene sebacate and polydiethyleneoxide se-



$\left[-\overset{O}{\overset{\|}{C}}-(CH_2)_2-\overset{O}{\overset{\|}{C}}-O-(CH_2)_2-O-\right]$

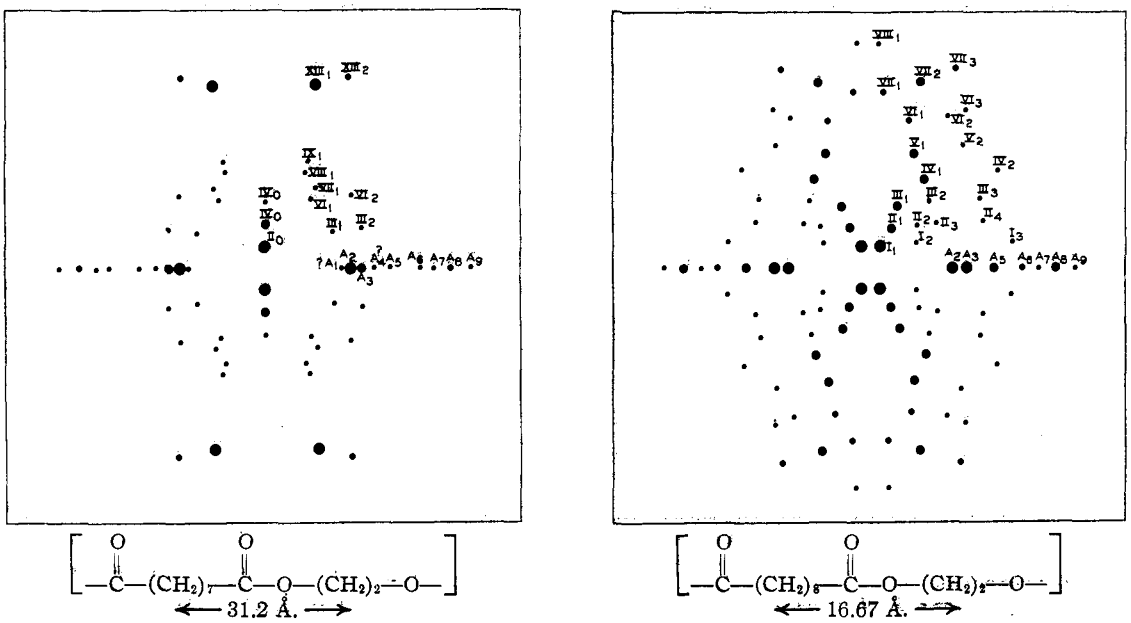
← 8.32 Å. →

(a) Polyethylene succinate.

$\left[-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-O-(CH_2)_2-O-\right]$

← 11.71 Å. →

(b) Polyethylene adipate.



$\left[-\overset{O}{\overset{\|}{C}}-(CH_2)_7-\overset{O}{\overset{\|}{C}}-O-(CH_2)_2-O-\right]$

← 31.2 Å. →

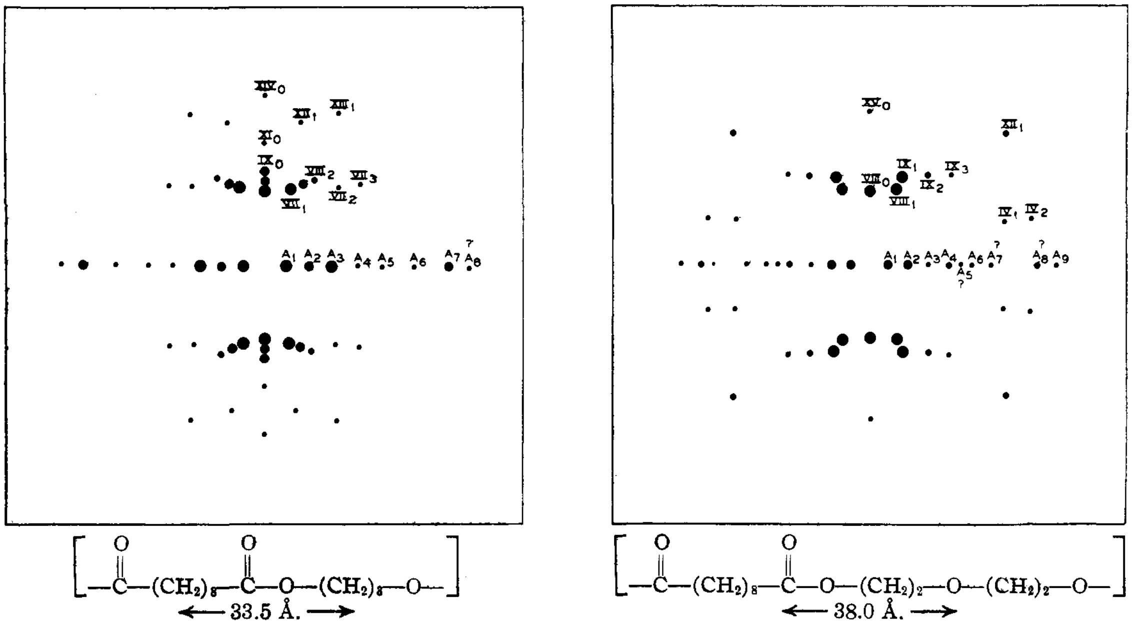
(c) Polyethylene azelate.

$\left[-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-O-(CH_2)_2-O-\right]$

← 16.67 Å. →

(d) Polyethylene sebacate.

Fig. 1.—Schematic drawings of the fiber diagrams of the polyesters.



$$\left[-\overset{\displaystyle O}{\overset{\|}{C}}-(CH_2)_8-\overset{\displaystyle O}{\overset{\|}{C}}-O-(CH_2)_3-O-\right]$$

$\longleftarrow$ 33.5 Å. $\longrightarrow$

(e) Polytrimethylene sebacate.

$$\left[-\overset{\displaystyle O}{\overset{\|}{C}}-(CH_2)_8-\overset{\displaystyle O}{\overset{\|}{C}}-O-(CH_2)_2-O-(CH_2)_2-O-\right]$$

$\longleftarrow$ 38.0 Å. $\longrightarrow$

(f) Polydiethyleneoxide sebacate.

Fig. 1.—Schematic drawings of the fiber diagrams of the polyesters.

bacate also show strong reflections on the meridian line which appear to arise from planes parallel to (001). Diatropic planes for the other esters were sought by exposures in which the primary beam formed various acute angles with the fiber axes (Schiefeaufnahme). In this way a definite diatropic plane was found on the second layer-line of the polyethylene succinate diagram indicating the presence of a two-fold screw axis. No strong diatropic planes were observed for polyethylene sebacate or polyethylene adipate. However, weak reflections appear to exist on the seventh and fifth layer-lines of these esters, respectively. Calculations of the fiber periods from the diatropic planes agree well with those made in the usual manner by the application of the Polanyi equation.[8]

The limitations of the fiber diagram in furnishing further crystallographic information other than the identity period along the fiber axis have often been pointed out.[9] There are, however, certain observations which can be made on these diagrams which are of value, especially when chemically related substances of known constitution are under consideration. In addition, in cases where the diagrams are rich in reflections and in which the reflections are sharp enough to allow accurate measurements of the spacings to be obtained, the method, based on the use of the reciprocal lattice, described by Sauter,[10] offers a means of indexing the reflections and arriving at a plausible determination of the unit cell. These solutions are, of course, not necessarily unique[11] but they serve the purpose of furnishing a basis for further crystallographic study.

This method has been applied to each of the fiber diagrams represented in Fig. 1 (a) - (f) with the results summarized in Table III.

A comparison of the fiber diagrams of the six polyesters (Fig. 1) shows immediately that the crystal structure of polyethylene adipate, azelate and sebacate are very similar to one another and different from the other esters. For example, the equatorial spacings prove to be almost identical within the limit of experimental error and the arrangement and intensity of the layer-line reflections is analogous in all three cases.[12] There can be little doubt therefore that these esters possess

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[8] M. Polanyi, *Z. Physik*, **7**, 149 (1921).

[9] J. R. Katz, *Trans. Faraday Soc.*, **32**, 77 (1936); H. Mark, "Physik und Chemie der Cellulose," Julius Springer, Berlin, 1932, p. 136; Trogus and Hess, "Ergeb. der tech. Roentgenkunde," Vol. IV, Eggert and Schiebolt, Akademische Verlagsgesellschaft, Leipzig, 1934, p. 60.

[10] E. Sauter, *Z. Krist.*, **84**, 453 (1933).

[11] For example the reflections of the ethylene adipate, azelate and sebacate esters in Table II agree almost as well, with orthorhombic units cells of cross-section: a = 21.8 Å., b = 33.3 Å., and c-axes equal to the corresponding fiber periods as with the monoclinic cells proposed in Table III.

[12] Two additional weak equatorial reflections occur in the case of the azelate. These, however, may be due to errors in observation or to planes too weakly reflecting to be observed in the other esters.

TABLE II

INTERPLANAR DISTANCES AND FIBER PERIODS OF POLYESTERS

Reflection	P-ethylene succinate			P-ethylene adipate			P-ethylene azelate			P-ethylene sebacate			P-trimethylene sebacate			P-diethyleneoxide sebacate		
	d, Å.	I	Int.	d, Å.	I	Int.	d, Å.	I	Int.	d, Å.	I	Int.	d, Å.	I	Int.	d, Å.	I	Int.
A_1	5.37		V W	. . ?		. .	4.63?		V W	. . ?		. .	15.6		V S	17.7		V S
A_2	4.41		V S	4.15		V S	4.17		V S	4.17		V S	7.82		S	8.87		S
A_3	3.85		S	3.63		S	3.70		S	3.67		V S	5.22		V S	5.90		W
A_4	3.12		W	. . ?		V W	3.30?		W	3.42?		V W	3.86		V W	4.39		M
A_5	2.70		V W	2.95		M	2.97		M	2.96		S	3.14		W	3.88?[a]		W
A_6	2.29?		V W	2.52		W	2.40		W	2.51		M	2.56		V W	3.50		W
A_7	1.92		W	2.36		V W	2.36		V W	2.36		V W	2.21		S	2.69?[a]		W
A_8				2.17		M	2.21		M	2.18		S	2.10?		W	2.36?[a]		M
A_9				2.08		W	2.08		W	2.08		W				2.19		W
I_1	5.68	8.87	W	10.3	11.22	M				14.7	16.51	V S						
I_2	5.02	8.56	M	5.35	11.34	W				6.64	16.14	W						
I_3	3.91	8.36	S							2.63	(21.69)	V W						
I_4	3.31	8.39	M															
I_5	2.94	8.13	S															
I_6	2.43	7.99	V W															
I_7	2.19	7.90	V W															
II_0	4.17	8.34	W				15.8	31.6	V S									
II_1	3.46	8.36	M	5.46	11.78	S				7.57	16.71	S						
II_2	3.04	8.33	M	2.88	11.77	M				5.35	16.84	W						
II_3	2.73	8.27	W							4.39	16.00	W						
II_4	2.52	8.19	W							3.00	16.71	V W						
II_5	2.26	8.29	M															
II_6	2.18	8.31	M															
III_1	2.20	8.47	M	3.67	11.85	W	4.51	29.8	W	5.14	16.92	S						
III_2	2.09	8.30	M	3.31	11.70	M	3.39	(27.9)	W	3.97	16.39	W						
III_3										2.88	16.89	W						
IV_0							7.78	31.1	S									
IV_1	1.98	. .	W	2.72	11.85	W				3.47	16.83	S				2.69	(36.0)	V W
IV_2				2.37	11.80	M				2.43	16.76	V W				2.36	37.8	V W
V_1				2.23	12.01	S				3.02	16.72	S						
V_2				2.12	11.78	S				2.52	16.84	W						
VI_0							5.18	31.1	W									
VI_1							4.26	31.6	W	2.56	16.76	M						
VI_2							3.24	31.2	W	2.35	16.74	W						
VI_3										2.21	16.71	W						
VII_0													4.77	33.4	V S			
VII_1							3.75	31.7	V W	2.30	. . .	M	4.28	31.9	V S			
VII_2										2.16	16.81	S	3.38	33.3	W			
VII_3										2.01	16.77	M	2.97	32.5	W			
VII_4										1.89	. . .	W						
$VIII_0$													4.19	33.5	S	4.80	38.4	V S
$VIII_1$							3.46	30.9	W	1.97	. . .	M	3.91	34.8	S	4.43	38.0	V S
$VIII_2$													3.63	33.3	M			
IX_0													3.78	34.0	S			
IX_1							3.17	31.5	W							3.83	37.0	V S
IX_2																3.40	37.8	M
IX_3																3.04	37.0	W
XI_0													3.04	33.4	W			
XII_1													2.58	33.7	W	2.17	39.1	M
$XIII_1$							2.18	31.4	V S				2.31	35.6	V W			
$XIII_2$							2.12	31.3	M									
XIV_0													2.36	33.0	W			
XV_0																2.58	38.7	W

[a] These reflections are probably pseudo-equatorial points formed by the overlapping of layer-line arcs.

unit cells of the same dimensions in the plane at right angles to the fiber axis and belong to the same crystal system. That this is the case is confirmed by a calculation of the number of chain molecules (number of X-ray repeating units) passing through the unit cell in each case from the formula

$$Z = Vd/1.65\,M \qquad (1)$$

where V, d and M are the volume of the unit cell, the density (Table I) and the molecular weight of the repeating unit, respectively. The values of Z

TABLE III

MINIMUM VALUES FOR THE UNIT CELLS OF THE POLYESTERS

	a	b	c[1]	β	z
P-ethylene succinate	9.05	11.09	8.32	102.8	4.6
P-ethylene adipate	25.7	30.7	11.71	103.8	39.5
P-ethylene azelate	25.7	30.7	31.2	103.8	39.8
P-ethylene sebacate	25.7	30.7	16.67	103.8	39.0
P-trimethylene sebacate	31.2	31.2	33.5	90	44.5
P-diethylene oxide sebacate	17.6	17.6	38.0	90	14.8

[1] Fiber period.

are given in Table III and for the esters in question are identical within the limit of error.

There is likewise a close similarity between the fiber diagrams obtained for polytrimethylene sebacate and polydiethyleneoxide sebacate. In these cases, although the equatorial spacings are not identical, the fact that one side spacing, different in each case, occurs in several orders makes a tetragonal form of unit cell probable.

Discussion

Crystal Lattice of the Polyesters.—Carothers[13] has suggested that the linear polyesters may have a macromolecular type of crystal lattice[14] in which molecules of various lengths crystallize together. Since the reflections corresponding to the lengths of even the smallest polymers of these compounds would fall very close to the central beam, the identity of the Debye–Scherrer photographs (1–4, Table I) does not constitute proof that such a lattice does or does not exist.[15] In whatever manner in which the individual molecules are grouped in the crystal lattice, however, the existence of well-defined fiber diagrams shows that the microcrystals are arranged with an important crystallographic axis parallel to the direction of the fiber axis and that all degrees of rotation around this axis exist. Furthermore, the observation of meridian reflections (from planes perpendicular to the fiber axis) requires the presence of crystal systems of symmetry higher than the triclinic and also that the orthogonal monoclinic axis is parallel to the fiber axis. The molecules in the polyesters therefore should be arranged in the crystals with their long axes parallel to the fiber direction.

The determination of the exact arrangement of the long chain molecules in the unit cells with regard to axial orientation and displacement lengthwise relative to one another is much too complex a problem to be solved on the basis of the existing data. The relatively large number of chains involved in the unit cells suggests that the positions with respect to one another are determined by the interaction of the polar carbonyl groups along the chains in such a way that identity is established only after the association of a considerable number of chains. It should be emphasized again that the unit cells which have been given above as a result of the application of the reciprocal lattice method are not necessarily the true ones since they are based on the data provided by fiber patterns alone. It is believed, however, that the lengths of the axes found for these cells as given in Table III at least set a lower limit to the size since it is not possible to secure satisfactory agreement with the observed reflections if smaller values are assumed.

Chain Configurations of the Polyesters.—Lycan and Adams[16] and Carothers and Arvin[5] have postulated a long chain structure for the polyesters. As in the case of most reactions leading to high polymers, chain molecules of various lengths are formed.[17] The X-ray studies of Müller[18] and others on the paraffins and aliphatic acids have established the fact that planar zig-zag chains of carbon atoms joined at the tetrahedral angle are present. The recent work of Sutton and Brockway[19] has shown that the tetrahedral angle is observed (within a few degrees) for oxygen in ethereal linkage. These authors have also determined accurately the length of the C–O bond as 1.43 Å. These data, together with the known C–C bond distance of 1.54 Å., enable the calculation of the lengths of the chemical repeating units of the polyesters on the assumption that planar zig-zag chains are present.

The results of these calculations are given in the third column of Table IV. The fourth column of this table records the difference between the observed and calculated periods referred to the chemical repeating unit. It is noted immediately that in the case of the esters having an odd number of chain atoms (3, 5 and 6, Table IV) the length of the chemical repeating unit is approximately one-half the observed fiber period. Since this occurs for the polyethylene azelate in which the acid is odd and in the polytrimethylene sebacate and polydiethyleneoxide sebacate in which the glycols are odd and does not occur for the even esters, the presence of a zig-zag chain is indicated. However, the difference between the observed and calculated lengths of the chemical repeating units (column 4, Table IV) is in all cases too large to be accounted for by experimental error. We must conclude, therefore, that the chains are

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[13] W. H. Carothers, *Chem. Rev.*, **8**, 416 (1931).

[14] H. Staudinger and R. Signer, *Z. Krist.*, **70**, 193, 202 (1929).

[15] *Cf.* J. Hengstenberg, *Ann. Physik*, **84**, 245 (1927); E. Sauter, *Z. physik. Chem.*, **18B**, 417 (1932); **21B**, 161, 186 (1933).

[16] W. Lycan and R. Adams, THIS JOURNAL, **51**, 625, 3450 (1929).

[17] W. H. Carothers, *Trans. Faraday Soc.*, **32**, 48 (1936); P. J. Flory, THIS JOURNAL, **58**, 1877 (1936).

[18] A. Müller, *J. Chem. Soc.*, **123**, 2043 (1923), *et seq.*

[19] L. E. Sutton and L. O. Brockway, THIS JOURNAL, **57**, 473 (1935).

either planar but not zig-zag or that they are non-planar. Since it has not been possible to obtain satisfactory agreement with the observed fiber periods on the basis of any planar arrangement of atoms, it is believed that the polyesters have non-planar chain configurations.

TABLE IV

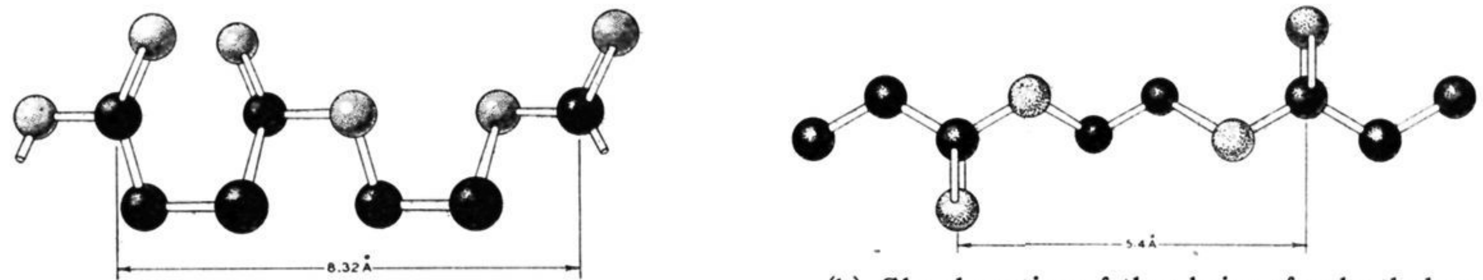
COMPARISON OF OBSERVED AND CALCULATED FIBER PERIODS (ÅNGSTRÖM UNITS)

	Polyester	Obsd. fiber period	Calcd. chem. rep. unit	Difference based on chem. rep. unit
1	P-ethylene succinate	8.32 ± 0.06	9.70	1.4
2	P-ethylene adipate	11.71 ± .07	12.21	0.5
3	P-ethylene azelate	31.2 ± .2	16.0	.4
4	P-ethylene sebacate	16.67 ± .06	17.24	.5
5	P-trimethylene sebacate	33.5 ± .3	18.5	1.7
6	P-diethyleneoxide sebacate	38.0 ± .3	20.8	1.8

This is particularly the case with polyethylene succinate, in which the observed fiber period of 8.32 Å. can be produced only by a helical arrangement of the chain atoms. The close analogy to the polymethyleneoxides and polyethyleneoxides described by Sauter[16] is particularly striking, and suggests that the spiral structure is derived from the cis or "tub" form of chain rather than from the zig-zag form. Figure 2 (a) illustrates this type of chain.

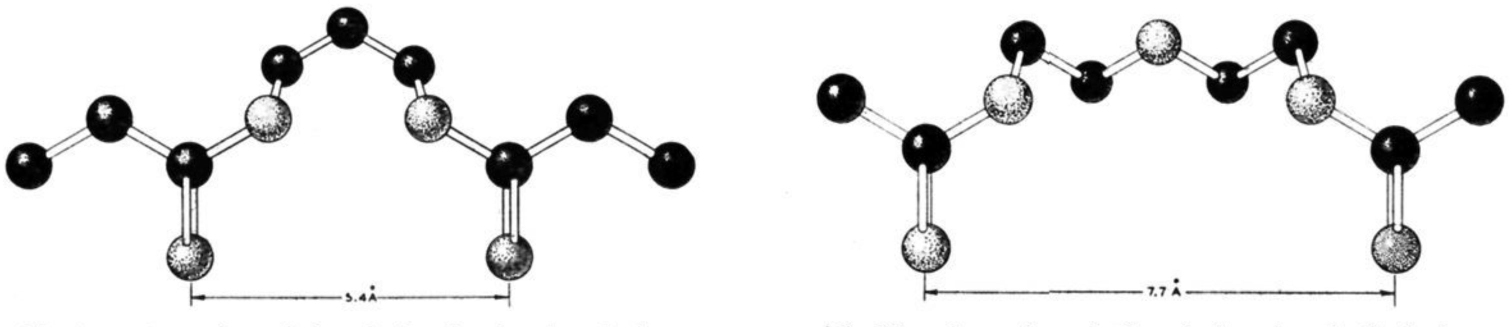
The equality of the differences observed in Table IV for the ethylene glycol esters of adipic, azelaic and sebacic acids is again in agreement with the identities in the dimensions of the unit cells mentioned above, and suggests that these esters have the same chain configuration and depart only slightly from the plane zig-zag arrangement of chain atoms. The constancy of the deviation (*ca.* 0.5 Å.) indicates that any shortening of the chains occurs in the ethylene glycol portion since the acid portions of the chains are of varying lengths. Figure 2 (b) shows how a shortening of the planar zig-zag chain may arise through a displacement of the chain oxygen atoms toward one another. This motion of the oxygen atoms results in forcing the carbon atoms between them out of the plane of the chain.

The last two esters, polytrimethylene sebacate and polydiethyleneoxide sebacate, in Table IV likewise show deviations from the planar zig-zag form. A number of configurations which agree with the observations is possible in these cases. It might be assumed that since the sebacic acid radical in polyethylene sebacate appears planar, this structure would be retained in its other esters. If this assumption is made the shortening can be accounted for in the glycol radical. Figure 2 (c) and (d) indicate (schematically) glycol configurations for these esters which produce the desired agreement.



(a) Chain atoms of polyethylene succinate.

(b) Glycol portion of the chains of polyethylene adipate, polyethylene azelate and polyethylene sebacate.



(c) Glycol portion of the chain of polytrimethylene sebacate.

(d) Glycol portion of the chain of polydiethyleneoxide sebacate.

Fig. 2.—Chain configurations of the polyesters which reproduce the observed spacings. Dark balls represent carbon and light balls represent oxygen atoms.

Staudinger and Schwalenstöcker[20] on the basis of viscosity studies report that ethylene glycol esters in solution have an extended form of chain which is shortened because of the attraction of the "secondary valences" of the oxygen atoms. Since these authors believe their conclusions apply equally well to the solid state, it might be expected that the polyesters would behave in a similar manner with regard to the glycol configuration. The chain forms given above are in qualitative agreement with the conclusions of Staudinger and Schwalenstöcker. It therefore seems reasonable to conclude that the chain configurations assumed by the polyesters can be regarded as resulting from the attractions of atoms or dipoles attached at intervals to the chains.

Experimental Part

The polyesters were prepared by heating together dibasic acids and glycols according to a modification of the method employed by Carothers and Arvin.[5] The acid and the glycol (in the ratio of 1 to 1.05 moles) corresponding to the ester desired were placed in a distilling flask deeply immersed in a sand-bath. A slow stream of pure, dry nitrogen was bubbled through the heated mixture during the reaction. The nitrogen served the purpose of providing an inert atmosphere and of removing the water formed in the reaction. For the first few hours of reaction a condenser and receiver were attached to the flask. During this time the temperature rose from about 160 to 180° and about 75 to 90% of the theoretical amount of water distilled over. The temperature was then raised to 200 ± 10° and maintained at this point until the molecular weight required for cold drawing was obtained (forty-eight to one hundred and twenty hours). The samples of polyethylene sebacate of lower average molecular weight than that required for cold drawing were obtained by taking out samples periodically during the reaction.

The succinic (m. p. 184–186°), adipic (m. p. 151–153°) and sebacic (m. p. 129–129.5°) acids were obtained from the Eastman Kodak Company. The azelaic acid (m. p. 106°) was prepared from castor oil by oxidation of the ricinoleic acid by means of potassium permanganate.[21] The glycols employed for the preparation of the esters were obtained by distilling the purest compounds that could be obtained commercially. In each case the middle portion was selected. The ethylene glycol was distilled at atmospheric pressure (b. p. 195–195.5°), the trimethylene glycol and diethyleneoxide glycol were distilled under reduced pressure.

The polyesters prepared as above showed the following values of carbon and hydrogen on ultimate analysis as compared with theoretical. Polyethylene succinate—found, 50.03% C, 5.93% H; calcd., 49.98% C, 5.59% H. Polyethylene adipate—found, 55.85% C, 6.67% H; calcd., 55.78% C, 7.03% H. Polyethylene azelate—found, 61.75% C, 8.41% H; calcd., 61.64% C, 8.47% H. Polyethylene sebacate—found, 63.71% C, 8.41% H; calcd., 63.11% C, 8.84% H. Polytrimethylene sebacate—found, 64.97% C, 8.93% H; calcd., 64.41% C, 9.16% H. Polydiethyleneoxide sebacate—found, 62.31% C, 8.83% H; calcd., 61.72% C, 8.89% H. These were considered sufficiently pure for the X-ray work. Small portions of the polyesters were purified by solution in chloroform and precipitation with petroleum ether for the determination of the densities and the softening points.

Summary

1. Debye-Scherrer photographs of polyethylene sebacates of increasing average molecular weight are identical and show the same interplanar spacings as the fiber diagrams of the oriented materials.

2. Fiber diagrams of six highly oriented polyesters show that in the oriented state the chain molecules are parallel to the axes of the fibers. A comparison of the observed fiber periods with the lengths of the chemical repeating units calculated on the basis of a planar zig-zag chain shows that polyethylene succinate possesses a helical arrangement of the chain atoms whereas polyethylene adipate, polyethylene azelate and polyethylene sebacate have similar configurations which deviate only slightly from the planar zig-zag form. The sebacate polyesters of trimethylene glycol and diethyleneoxide glycol also conform best to a configuration in which the chain atoms are nonplanar. The deviations of the configurations from the planar zig-zag type of chain are attributed to attractive forces residing in the ester groups.

3. The data obtained from the fiber patterns have been treated graphically and solutions for the unit cells found which agree in all cases with the observed interplanar spacings.

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[20] H. Staudinger and H. Schwalenstöcker, *Ber.*, **68**, 727 (1935).

[21] *Organic Syntheses*, **13**, 3 (1933).