with dry pyridine exactly as was A, no definitely crystalline product was obtained. Nor was a definitely pure crystalline product obtained when 650 mg. of compound C was refluxed with 60 cc. of butyl alcohol containing 3 g. of potassium acetate. The impure products, in each case, did not give a typical positive diosphenol reaction with ferric chloride. It did give a dirty brownish-red color, which, possibly, could be called positive.[26]

The Action of *o*-Phenylenediamine upon Compound C (m. p. 194°).—A solution of 0.5 g. of C and 0.2 g. of *o*-phenylenediamine in 170 cc. absolute alcohol was refluxed for five hours. The alcohol was then carefully distilled at low temperature *in vacuo*. The residue was dissolved in ether and the excess phenylenediamine was extracted with dilute hydrochloric acid. The ether, after being washed thoroughly, was dried and distilled *in vacuo*. The residue, dissolved in alcohol, yielded crystals which melted at 184°. This was the same as the melting point given for the compound said to be the quinoxaline derived from the purported 2,2-dibromocholestanone.[14] But our derivative still contained halogen.

Anal. Calcd. for $C_{33}H_{50}N_2Br_2$: N, 4.41; Br, 25.2. Found: N, 4.34; Br, 25.6.

Summary

1. The reactions of cholestenone and of cholestanone with iodine monobromide possess autocatalytic characteristics.

2. The reaction of iodine monobromide with cholestenone, with cholestanone, and with 2-monobromocholestanone is first order.

3. The oximes of cholestenone and cholestanone do not react readily with iodine monobromide in glacial acetic acid.

4. As in the case of the action of bromine upon cholestenone, evidence indicates that enolization is the first step in the reaction of cholestenone with iodine monobromide.

5. Hydrogen bromide speeds the action of iodine monobromide upon cholestenone, cholestanone, and 2-monobromocholestanone, but it has no detectable influence on the reaction with the oxime of either cholestenone or cholestanone.

6. The double bond in cholestenoxime is resistant to halogenation in a glacial acetic acid containing medium.

7. There is some evidence that cholestenoxime undergoes a rearrangement in glacial acetic acid.

8. In concentrations of hydrogen bromide greater than a small amount, the total halogen consumed by cholestenone, by cholestanone, and by 2-monobromocholestanone is decreased, but the proportion of organically bound halogen is increased.

9. The inhibiting influence of the larger concentrations of hydrogen bromide may be due to its effect on intermediate steps in the reactions, or to its formation of complexes with bromine or with iodine monobromide.

10. Bromine is the active ingredient of iodine monobromide.

11. 2-Monobromocholestanone, m. p. 171.5°, is a product of the reaction of cholestanone with iodine momobromide.

12. An unidentified dibromo derivative of cholestanone was isolated (m. p. 147°).

13. Further evidence that the dibromocholestanone, melting at 194°, is 2,4-dibromocholestanone, and not 2,2-dibromocholestanone, is given.

BUFFALO, N. Y. RECEIVED MARCH 30, 1938

[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES]

An Electron Diffraction Examination of Some Linear High Polymers

BY K. H. STORKS

Because of the general structural similarities between synthetic linear polyesters and many natural fibers, fundamental studies of the simpler compounds are of obvious importance. Several members of a series of these esters have been made the subject of X-ray study by Fuller and Erickson.[1] It is possible to prepare many of these in the form of films suitable for examination by electron diffraction. The experiments to be described here have two purposes: to demonstrate the utility of the electron diffraction method for studies of the structure of highly polymerized materials, and to discover the behavior of macromolecules in extremely thin layers. The methods are shown to be equally applicable to the natural polymer gutta-percha.

The fact that these materials can be cold drawn to a considerable extension without breakage is well known,[2] a high degree of orientation

---

[1] C. S. Fuller and C. L. Erickson, THIS JOURNAL, **59**, 344 (1937).

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

being produced in the samples by this "stretching." Electron diffraction data for stretched polymers are directly comparable with many of the available X-ray data, and such a comparison will serve to demonstrate the utility of the method. In order to make this comparison polyethylene succinate, polyethylene adipate, polyethylene sebacate and two specimens of unvulcanized gutta-percha[3] (containing a small amount of antioxidant) have been examined in the stretched condition.

The second aim of this paper is accomplished by examinations of the conditions existing in unstretched films. Unstretched films of polyethylene sebacate and the two grades of gutta-percha have been studied.

Experimental

The transmission method is used exclusively in the experiments to be described here, the materials to be examined being prepared in the form of films 10^{-5} cm. or less in thickness. A film to be examined is placed in the path of a well-defined beam of electrons of homogeneous velocity and the resulting diffraction pattern recorded on a photographic plate. The camera employed has been described by Germer.[4]

Preparation of Stretched Films.—Specimens for examination in the stretched condition are prepared from relatively thick preliminary films. Such a preliminary film, approximately 10^{-4} cm. thick, is deposited on a conditioned microscope slide[5] by evaporation of a solution (approximately 2%) of the polymer in chloroform. If the slide is held at an angle of approximately 30° to the horizontal a long narrow strip of film with one end relatively thick is deposited when a drop of this solution is allowed to flow freely along the length of the slide.

The preliminary film prepared in this way on a glass slide may be stretched by one or both of two different methods, the choice of method being determined by ability of the film to resist change on contact with water. Films of polyethylene adipate and polyethylene sebacate are transferred from the slide to a water surface[6] and thence to a pair of jaws that can be separated by a screw. When all trapped water has evaporated the film is stretched by turning the screw. The stretched film is refloated and transferred to a slit type foil holder.[7] The orientation of the stretching direction is carefully noted. After all water has evaporated the film is found to be mounted firmly but without tension.

Films of stretched polymers also can be prepared and mounted without contact with liquid water. After the preliminary film is deposited, the thick end is loosened from the glass with a razor blade and the free end wound up on a round jeweler's file. The film can now be separated from the glass and stretched in the same operation. Best results are accomplished if the film leaves the slide at an angle of approximately 30° and if the stretching is continuous and rather rapid. If the stretched film is held under tension and laid across the foil holder the natural tackiness of the material will hold it in place and maintain the tension. This technique is found to be necessary when preparing polyethylene succinate films, and to be the simplest method of preparing stretched specimens of gutta-percha.

A double purpose is accomplished by each method of stretching; the films are thinned sufficiently for examination, and a high degree of fibrous orientation is produced.

Preparation of Unstretched Films.—If the pattern of an unstretched specimen is to be obtained, the proper thickness for examination must be deposited upon the glass slide. The thinner film is deposited from a more dilute solution (approximately 0.4%). These chloroform solutions do not spread well on monolayers of grease and mechanical spreading is found to be necessary. An efficient mechanical spreader has been made by clamping a new and freshly cleaned razor blade, edge down, above and parallel to a smooth level surface. A microscope slide, beneath which lies a thin sheet of paper, is placed under the blade which is lowered to a position of uniform and light contact. After removal of the paper spacer and after conditioning the slide, the latter is replaced and a drop of solution, in position near one end, is uniformly distributed over the conditioned surface by a single translation of the slide under the blade. After evaporation of the solvent the film is transferred to a water surface and finally to a foil holder. No indications have been found that a film is stretched by this manipulation.

Film Thickness Measurements.—Since knowledge of film thickness is of importance in interpretation of some of the following results, the method of obtaining this value will be indicated. A film of the polymer is prepared and mounted, from water, on a clean polished chromium surface. A known number of layers of barium stearate are now added to the polymer film by the Blodgett technique.[8] The interference color of the composite film is compared with colors of known numbers of barium stearate layers on a reference slide, and the barium stearate equivalent thickness is easily and accurately determined.

Extra Precautions.—All films are prepared at room temperature and, in most cases, under normal illumination from tungsten filament lamps. The early experiments upon the "Br-4" grade of gutta-percha have been repeated with the "Pure White" product[9] under low intensity

---

(3) These specimens were the "Br-4" and the "Pure White" grades of gutta-percha from "The Netherlands East Indies Government Rubber and Gutta-Percha Plantations, Buitenzorg, Java."

(4) L. H. Germer, *Rev. Sci. Instruments*, **6**, 138 (1935).

(5) A conditioned microscope slide is a slide coated with a monomolecular layer of grease. This layer is of considerable importance if thin films are to be easily separated from glass. The monolayer can be deposited from clean dry cheesecloth if a freshly cleaned slide is vigorously rubbed with this material.

(6) The transfer, microscope slide to water surface, is easily accomplished if the slide is held, film side up, at an angle of approximately 15° to the horizontal and lowered slowly through a clean water surface. The film is separated from the glass by this procedure and is left floating. The floating film is transferred to a holder by raising the holder under the film. The film is mounted more smoothly if the holder is uniformly wet by water.

(7) See Fig. 4, L. H. Germer and K. H. Storks, *Proc. Nat. Acad. Sci.*, **23**, 390 (1937).

(8) K. B. Blodgett, This Journal, **56**, 495 (1934).

(9) This material had been removed from the sealed shipping container and stored in a refrigerator away from light for about six months. The stock solution was made up from material from the inside of a massive block.

illumination from a 10-watt Mazda red lamp. Rate of oxidation should be decreased considerably by this precaution. In addition, the stretching properties of a preliminary film have always been tested immediately prior to preparation of a film for examination in the unstretched condition; satisfactory stretching characteristics are taken as sufficient evidence that oxidation in solution has not been serious.

Experimental Results

Data from Stretched Polymers.—Figures 1–5[10] are electron diffraction patterns from stretched samples of polyethylene succinate, polyethylene adipate, polyethylene sebacate, gutta-percha "Br-4" and gutta-percha "Pure White." The vertical axis of each of these patterns is parallel to the direction along which the material was stretched. In each case the primary beam was normal to the foil surface. No additional reflections are found when a foil is rotated around the stretching direction.

Table I contains representative data from patterns of this sort. Columns headed (*D*) contain the diametral separation of symmetrical spots in mm.; estimated intensities of these reflections are given in the columns headed (Int.), the higher numbers being assigned to the stronger reflections; the small letter (*d*) indicates interplanar spacings, in one column X-ray values, and in the other, values calculated in these experiments from measured separations (*D*) by means of the formula

$$d = 2L\lambda/D \qquad (1)$$

(In Eq. (1) λ is the electron wave length and *L* the plate specimen separation; the constant $L\lambda$ is determined by calibration against a foil of metallic silver.) The X-ray values of (*d*) are those given by Fuller and Erickson[1] and the customary designation of reflections, which they use, are given in the first columns.

TABLE I

Ref.	*D*, mm.	Int.	*d*, Å. (These expts.)	*d*, Å. (X-rays)
Polyethylene succinate $L\lambda = 2.00_{(0)} \times 10^{-6}$ mm.^{2}				
A_1	7.45	0.5	5.37	5.37
A_2	8.95	10	4.47	4.41
A_3	10.5	12	3.81	3.85
A_4	12.9	2	3.10	3.12
A_5	14.9	2	2.68	2.70
A_6	17.2	1	2.33	2.29
A_7	21.0	2	1.90	1.92
A	30.0	0.5	1.33	
I_2	8.0	1	5.00	5.02
I_3	10.4	10	3.85	3.91
I_4	12.1	4	3.31	3.31
I	13.0	3	3.08	
I_5	13.5	3	2.96	2.94
II_2	13.0	4	3.08	3.04
II_4	15.55	1	2.57	2.52
II_5	17.45	2	2.29	2.26
II_6	18.4	1	2.17	2.18
II	20.4	2	1.96	
II	21.4	1	1.87	
II	23.3	1	1.72	
II	24.0	1	1.67	
III?	15.0	3	2.67	
III?	16.0	1	2.50	
III_1	17.9	4	2.23	2.20
III_2	18.9	4	2.12	2.09
IV_0	19.0	20	2.11	
IV_1	20.0	1	2.00	1.98
IV	21.0	1	1.90	
IV	21.7	2	1.84	
V	24.5	1	1.63	
V	25.4	2	1.57	
VI	29.6	1	1.35	
VI	32.3	3	1.24	
VI	33.6	1	1.19	
VII	34.2	1	1.17	
$VIII_0$	38.1	2	1.05	
Polyethylene adipate $L\lambda = 2.01_{(5)} \times 10^{-6}$ mm.^{2}				
A_2	9.6	14	4.20	4.15
A_3	11.3	13	3.57	3.63
A_5	13.8	4	2.92	2.95
A_6	16.0	5	2.52	2.52
A_8	18.4	5	2.19	2.17
A_9	19.5	5	2.07	2.08
A	20.9	1	1.93	
A	22.3	1	1.81	
A	24.6	2	1.64	
II_1	7.4	1	5.45	5.46
II_2	14.1	3	2.86	2.88
IV_1	14.9	3	2.70	2.72
IV_2	17.0	1	2.37	2.37
V_1	18.1	2	2.23	2.23
V_2	19.1	8	2.11	2.12
V	20.4	1	1.98	
V	22.8	1	1.77	
V	24.3	2	1.66	
VI	21.6	1	1.87	
IX_0	30.5	2	$1.32_{(1)}$	
X_0	33.9	5	$1.18_{(9)}$	
XI_0	37.1	1	$1.08_{(6)}$	
Polyethylene sebacate $L\lambda = 2.01_{(8)} \times 10^{-6}$ mm.^{2}				
A_2	9.6	15	4.20	4.17
A_3	11.2	14	3.60	3.67
A_5	13.6	4	2.97	2.96
A_6	16.0	8	2.52	2.51
A_8	18.2	5	2.22	2.18
A_9	19.3	7	2.09	2.08
A	20.7	2	1.95	
A	21.8	2	1.85	
A	23.0	2	1.75	

---

[10] The extra expense for the illustration insert was borne by the Bell Telephone Laboratories.

Table I (*Concluded*)

Ref.	*D*, mm.	Int.	*d*, Å. (These expts.)	*d*, Å. (X-rays)
A	24.5	3	1.65	
A	28.8	1	1.40	
A	31.6	1	1.28	
III$_1$	7.8	1	5.17	5.14
III$_3$	13.95	1	2.89	2.88
V?	13.0	5	3.10	
V$_2$	15.9	2	2.54	2.54
VI$_1$	15.8	5	2.56	2.56
VI$_2$	17.05	3	2.37	2.35
VII$_2$	18.6	12	2.17	2.16
VII$_3$	19.8	3	2.04	2.01
VII$_4$	21.5	4	1.88	1.89
VII	23.6	3	1.71	
VII	25.6	2	1.58	
VII	28.5	2	1.42	
VII	29.5	2	1.37	
VII	31.5	1	1.28	
VII	32.7	1	1.23	
VII	36.6	1	1.10	
VIII$_1$	20.5	4	1.97	1.97
IX	22.6	2	1.79	
X	24.5	1	1.65	
XI	26.4	2	1.53	
XIII$_0$	31.0	5	1.30$_{(2)}$	
XIII	32.0	3	1.26	
XIV$_0$	33.4	6	1.20$_{(8)}$	
XIV	34.5	3	1.17	
XV$_0$	35.8	3	1.12$_{(8)}$	
XV	36.7	2	1.10	
XVI$_0$	38.15	2	1.05$_{(8)}$	
"Pure White" Gutta-percha[a] $L\lambda = 2.70_{(9)} \times 10^{-6}$ mm.^{2}				
A$_4$	9.2	0.5	5.89	5.95
A$_7$	11.5	10	4.71	4.73
A$_8$	14.0	10	3.87	3.91
A$_{11}$	18.4	3	2.94	2.98
A$_{12}$	19.7	4	2.75	2.78
A$_{13}$	23.0	8	2.36	2.37
A$_{16}$	28.0	1	1.94	1.95
A	28.5	3	1.90	
A	31.1	1	1.74	
A	34.5	1	1.57	
II$_1$	12.25	2	4.42	4.45
II$_2$	14.1	1	3.84	3.87
II$_4$	17.9	1	3.03	3.08
II$_5$	18.55	2	2.92	2.93
II$_6$	22.8	1	2.38	2.42
II$_7$	24.2	1	2.24	2.25
II	30.5	1	1.78	
II	43.3	1	1.25	
IV$_0$	22.9	8	2.36$_{(6)}$	2.36
IV$_1$	26.5	4	2.04	2.02
VI	35.8	3	1.51	
VIII$_0$	45.9	5	1.18$_{(0)}$	
XII$_0$	68.8	1	0.788	

[a] The plates for the two grades of gutta-percha are identical and only data from the "Pure White" grade are listed

Values of the fiber periods obtained from the data of Table I are written down in the second column of Table II, together with the X-ray values of Fuller and Erickson in the third column.

Table II

	Fiber periods, Å. (Storks)	Fiber periods, Å. (Fuller and Erickson)
Polyethylene succinate	8.42	8.32
Polyethylene adipate	11.91	11.71
Polyethylene sebacate	16.92	16.67
Gutta-percha (β modification)	9.46	9.54

Data from Unstretched Polyethylene Sebacate.—Electron diffraction patterns from an unstretched specimen of polyethylene sebacate are reproduced in Figs. 6 and 7. The former was obtained with the electron beam incident normally upon the film, and the latter at 45° incidence, the film having been rotated about a horizontal axis as the pattern is reproduced here. The film which produced these patterns had a thickness of 200 ± 25 Å.

In order to describe data obtained from Fig. 7, Cartesian coördinates have been chosen on the photographic plate, with their origin at the primary beam position and the x-axis parallel to the axis about which the film was rotated when Fig. 7 was produced. These coördinates, and other useful quantities, are designated on Fig. 10. In this figure P represents the photographic plate and S the specimen film. O′O is the primary beam direction, O′X′ the axis of rotation in the specimen (parallel to OX), and O′N the normal to the film surface. The angle α defines the rotation of the specimen from the position normal to the beam, and the angles ϕ_1 and ϕ_2 the angular limits measured from the x-axis of a particular diffraction arc AB recorded on the photographic plate.

Numerical data obtained from the patterns of Figs. 6 and 7 are given in Table III. Except for the angles ϕ_1 and ϕ_2 which refer to arcs in Fig. 7, the quantities described in this table are the same as those of Table I. (X-Ray values of d have not been tabulated again.) For those arcs in Fig. 7 which are continuous across the x-axis no values of ϕ_1 can be recorded, and for arcs across the y-axis no values of ϕ_2.

Data from Unstretched Gutta-percha.—Patterns from unstretched gutta-percha, at normal and at 45° incidence, are reproduced in Figs. 8 and 9; data obtained from these patterns are given in Table IV. The angles ϕ referring to the pattern of Fig. 9 are values of $(\phi_1 + \phi_2)/2$.

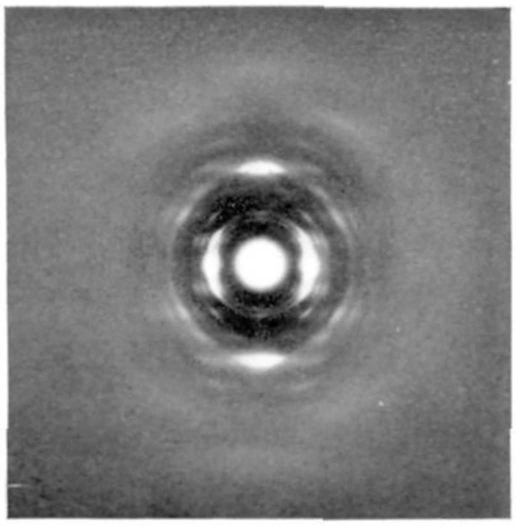

Fig. 1.—Electron diffraction pattern from stretched polyethylene succinate.
($L\lambda = 2.00_{(0)} \times 10^{-6}$ mm.^{2}.)

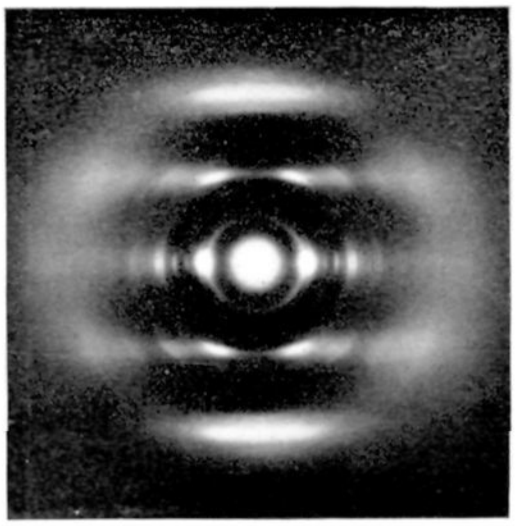

Fig. 2.—Electron diffraction pattern from stretched polyethylene adipate.
($L\lambda = 2.01_{(5)} \times 10^{-6}$ mm.^{2}.)

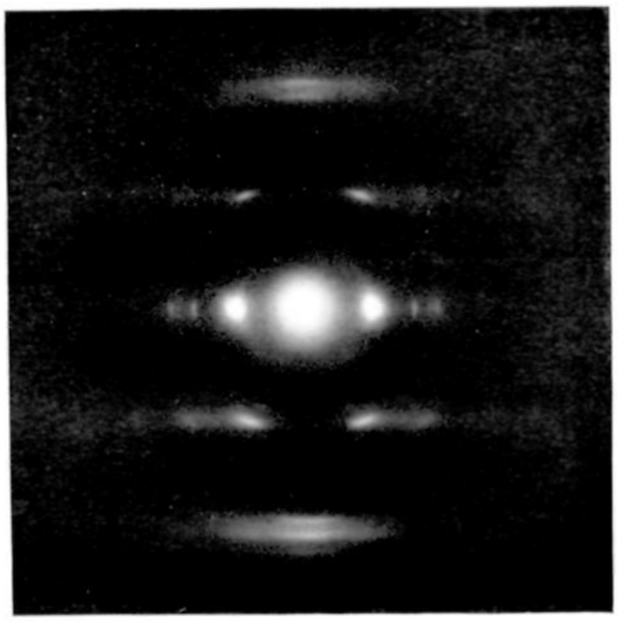

Fig. 3.—Electron diffraction pattern from stretched polyethylene sebacate.
($L\lambda = 2.74_{(4)} \times 10^{-6}$ mm.^{2}.)

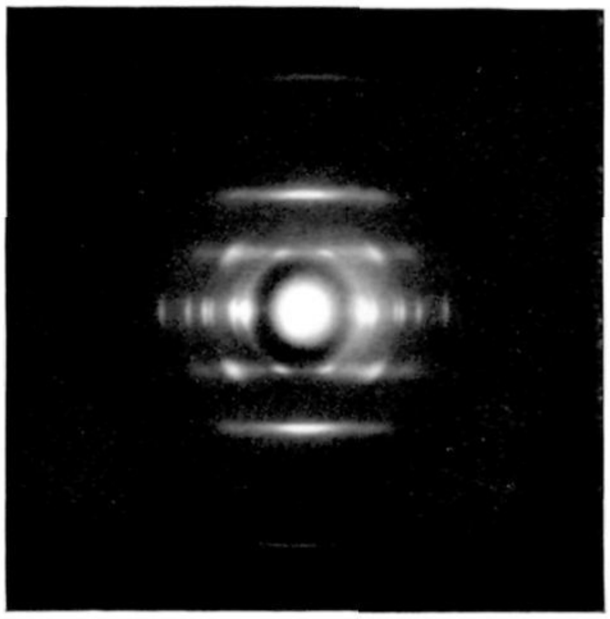

Fig. 4.—Electron diffraction pattern from stretched "Br-4" grade gutta-percha.
($L\lambda = 2.73_{(0)} \times 10^{-6}$ mm.^{2}.)

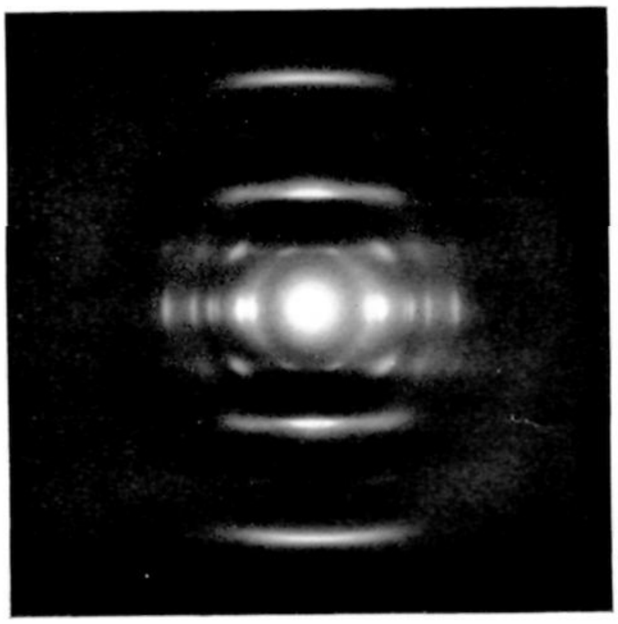

Fig. 5.—Electron diffraction pattern from stretched "white" gutta-percha.
($L\lambda = 2.70_{(9)} \times 10^{-6}$ mm.^{2}.)

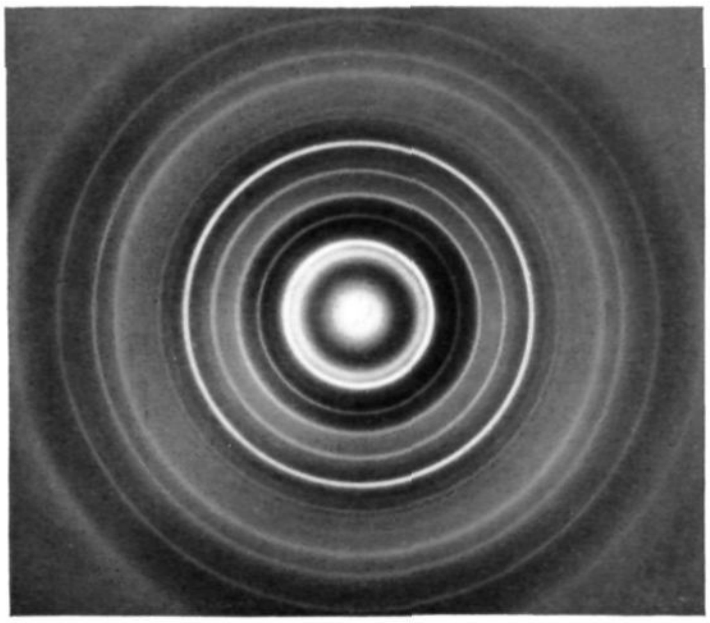

Fig. 6.—Electron diffraction pattern from unstretched polyethylene sebacate at normal incidence. ($L\lambda = 2.74_{(4)} \times 10^{-6}$ mm.^{2}.)

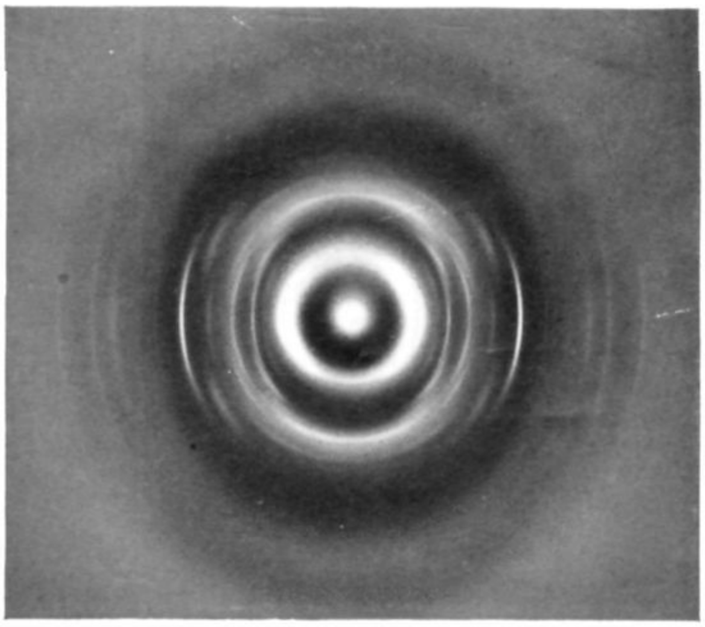

Fig. 7.—Electron diffraction pattern from unstretched polyethylene sebacate at 45° incidence. ($L\lambda = 2.74_{(4)} \times 10^{-6}$ mm.^{2}.)

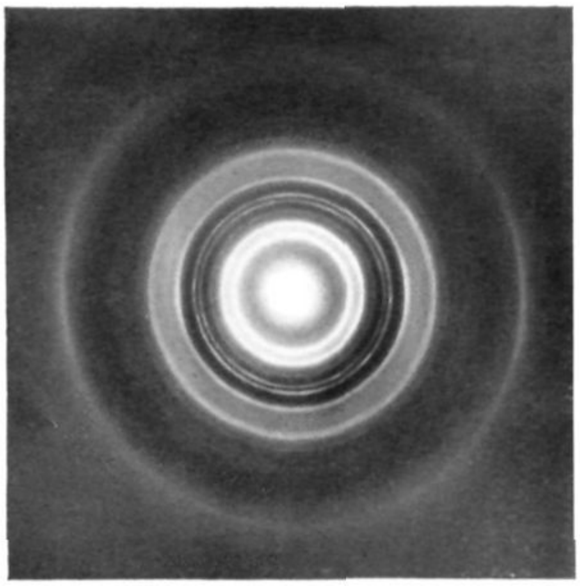

Fig. 8.—Electron diffraction pattern from unstretched "white" gutta-percha at normal incidence. ($L\lambda = 2.70_{(9)} \times 10^{-6}$ mm.^{2}.)

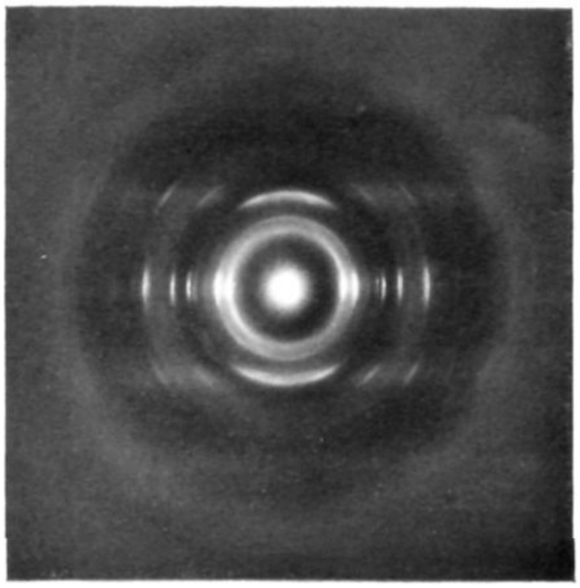

Fig. 9.—Electron diffraction pattern from unstretched "white" gutta-percha at 45° incidence. ($L\lambda = 2.70_{(9)} \times 10^{-6}$ mm.^{2}.)

TABLE III

UNSTRETCHED POLYETHYLENE SEBACATE

$L\lambda = 2.74_{(4)} \times 10^{-6}$ mm.^{2}

Ref.	Fig. 6 Normal incidence D, mm.	Int.	d, Å.
A_2	13.0	5	4.22
A_3	14.9	15	3.68
V_1, A_5	18.05	1	3.04
[a]	20.45	7	2.68
A_8, VII_2	24.7	7	2.22
A_9, VII_3	26.45	0.5	2.07
A, VII_4	29.65	7	1.85
VII, A, IX	31.55	1	1.74
X, A	33.05	0.5	1.66
[a]	35.3	12	1.55
VII, A	38.8	1	1.41
[a]	40.8	3	1.35
$XIII_0$, VII, A	42.45	1	1.29
XIV_0, XIV	46.0	0.5	1.19
XV_0, VII, XV	49.8	4	1.10
[a]	54.0	4	1.02
	61.2	4	0.897
	70.9	2	.774
	73.9	1	.743

Ref.	Fig. 7 45° Incidence D, mm.	Int.	d, Å.	ϕ_1	ϕ_2
A_2	13.0	15	4.22	13°	52°
A_3	15.0	13	3.66		19
V_1	18.0	3	3.05	12	52
[a]	20.4	6	2.69		39
A_6	21.5	6	2.55	18	49
VI_2	23.2	1	2.37	32	58
A_8	24.8	6	2.21	2	38
VII_2	24.8	8	2.21	41	
A_9	26.5	5	2.07	17	46
A	27.5	1	2.00	71	
A	29.2	4	1.88	37	72
A, VII_4	29.8	4	1.84		17
A	31.2	2	1.76	14	38
VII	32.5	3	1.69	18	45
A	33.5	2	1.64	30	52
[a]	35.4	10	1.55		45
?	37.2	0.5	1.48	36	
[a]	40.8	2	1.35		16
$XIII_0$, VII, A	42.4	1	1.29		16
XIV_0, XIV	45.0	0.5	1.22		10
XV_0, VII, XV	49.6	2	1.11		23
[a]	53.6	2	1.02		29
	61.0	2	0.90		30

[a] These reflections arise from an impurity that is occasionally found associated with organic films. Reflections which are designated without subscripts are assigned to layer lines only. Two designations are given to the same reflection if the spacing is too close for resolution.

These diffraction patterns were obtained from a film of "Pure White" gutta-percha about 200° Å. thick. Patterns also have been obtained from the "Br-4" grade of gutta-percha. These are found to be similar to those of Figs. 8 and 9 except for greater "spottiness" of diffraction features, indicating that the crystallites are considerably larger in films made from the "Br-4" grade than in films made from the "Pure White" grade.

TABLE IV

GUTTA-PERCHA UNSTRETCHED

$L\lambda = 2.70_{(9)} \times 10^{-6}$ mm.^{2}

	Fig. 8 Normal incidence			Fig. 9 45° incidence				
Ref.	D, mm.	Int.	d, Å.	D, mm.	Int.	d, Å.	ϕ (obsd.)	ϕ (calcd.)
A_7	11.5	10	4.71	11.3	10	4.79	0	0
A_8	14.0	10	3.87	13.8	9	3.93	0	0
[a]	16.3	3	3 32	16 2	2	3 34	0	0
A_{11}	18 3	4	2.96	18.2	4	2.98	0	0
A_{12}	19.7	5	2.75	19.5	8	2.78	0	0
A_{13}	22.8	8	2.38	22.5	7	2.41	0	0
A_{14}	25.0	0.3	2.17					0
A_{15}	26.5	0.3	2.04					0
A_{16}	27.5	3	1.97	27.5	3	1.97	0	0
A	28.4	4	1.91	28.0	6	1.94	0	0
A	30.8	1	1.76	30.5	1	1.78	0	0
A				34.0	1	1.59	0	0
A				35.5	0.3	1.53	0	0
A	45.5	2	1.18	45.5	1	1.18	0	0
II_4				17.5	2	3.10		
II_5				18.5	7	2.93		
II_6				22.5	2	2.41	51	46
II_7				24.0	4	2.26	47	42
II				30.2	0.3	1.79		
II				34.6	0.3	1.57		
II				36.3	1	1.49	29	26
II				42.9	1	1.26	22	22

[a] Reflection from the alpha modification.

Discussion of Results

Stretched Polymers.—In the introduction it was stated that the experiments to be described in this paper have two purposes, to demonstrate the utility of the electron diffraction method in the field of polymeric compounds, and to obtain new information regarding the structure of macromolecules in extremely thin layers—which cannot be studied by X-rays. The first of these purposes has been accomplished by the direct comparisons of X-ray and electron diffraction results upon stretched polymers. These comparisons are given in Table I and Table II. A few additional remarks regarding these data seem to be necessary, before passing on to the second part of the paper, which is concerned with the data of Table III and Table IV.

It has been pointed out that no additional reflections are found when a stretched foil is rotated around the stretching direction. This fact proves that individual crystallites are oriented with all degrees of rotation around this direction. Crystallites of small cross sectional areas in the planes normal to their fiber directions seem to be required to account for random rotation in foils as thin as those of these experiments, (400–1000 Å.).

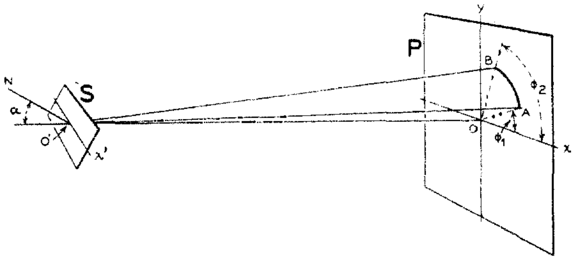

Fig. 10.

Fiber period reflections have not been observed in X-ray experiments upon polyethylene adipate or polyethylene sebacate, values of the fiber period spacings having been determined indirectly.[1] Such reflections are, however, shown clearly in Figs. 2 and 3[11] and are tabulated in Table I. The orders which appear are the 9th, 10th and 11th for the former and the 13th, 14th, 15th and 16th for the latter polymer. The occurrence of these particular high orders only seems rather curious. An approximate calculation of relative intensities has been carried out in order to understand why only these high orders are found. Assuming a macromolecular type of lattice[12,13] and macromolecules that are straight for distances greater than the length of a single chemical repeating unit, it is not difficult to show that, on account of the comparable sizes of the C–C and the C–O spacings, the geometrical structure factor for fiber period reflections has appreciable magnitude at a few orders only. These orders are multiples of the nth, and one or two successive orders above and below, where n represents the number of chain atoms in a chemical repeating unit. To obtain this result one assumes that any lengthwise displacement of neighboring chains is an integral multiple of the fundamental atomic spacing along the axis of the chain. Since there are 10 chain atoms in the repeating unit of polyethylene adipate and 14 in that of polyethylene sebacate, the observation of only the 9th, 10th and 11th orders of the fiber period reflection from the former and only the 13th, 14th, 15th and 16th orders from the latter seems to be adequately accounted for.

Unstretched Gutta-percha.—From the continuous but spotty rings of Fig. 8 one concludes that the individual crystals in a thin unstretched film of gutta-percha are relatively large and randomly oriented about the normal to the film surface. Inspection of Figs. 8 and 9 reveals at once, however, that these crystals are highly oriented. The nature of the orientation is immediately clear from the fact that the first four columns of Table IV (obtained from Fig. 8) contain only equatorial reflections ($hk0$); with the exception of five described by Fuller[13a] as very weak (VW), all equatorial reflections observed by him are obtained in the present studies and written down in the first four columns of Table IV. Thus in the unstretched film of gutta-percha the crystallites are oriented with their fiber axes approximately normal to the film surface. Furthermore, it seems possible to conclude that no appreciable number of crystallites have fiber axis directions that deviate by more than 15° from parallelism with this normal. Greater deviation would allow the occurrence of the layer line reflection for which $d = 1.25$ Å.

Figure 9 and the data of the last five columns of Table IV confirm these conclusions and enable one to calculate the precision of orientation of the fiber axis directions of the crystallites. From the orientation just described it is evident that for $\alpha \neq 0$ the equatorial reflections must occur as arcs across the x-axis of the plate, and some layer line reflections will in general appear as arcs on displaced layer lines. The first twelve reflections indicated on the right-hand side of Table IV, which are equatorial reflections occurring along the horizontal center line in Fig. 9, are in excellent agreement with the reflections observed at normal incidence.

The extreme half angle width of equatorial reflections in Fig. 9 is measured to be about $\Phi_A = 8°$. This is related to the largest angle (δ') between the normal to the specimen surface and an appreciable number of fiber axis directions by the equation

$$\sin \delta' = \sin \alpha \sin \Phi_A \qquad (2)$$

For $\alpha = 45°$ (Fig. 9) this yields $\delta' = 6°$ as a quantitative measure of the precision of orientation in the unstretched "Pure White" gutta-percha foil. Corresponding diffraction patterns and measurements upon an unstretched film of "Br-4"

---

(11) See reflections lying across the vertical axes.

(12) W. H. Carothers, *Chem. Rev.*, **8**, 416 (1931).

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

(13a) C. S. Fuller, *Ind. Eng. Chem.*, **28**, 907 (1936).

grade gutta-percha have yielded $\delta' = 4°$ for this particular foil. It is clear that in general the orientation in thin unstretched films of gutta-percha is nearly perfect.

As a further check it is interesting to compare calculated with observed angular positions of the layer line reflections which appear in Fig. 9; this comparison is given in the last two columns of Table IV. The quantity ϕ represents here the mean value of ϕ_1 and ϕ_2 (see Fig. 10). Measured values of ϕ are taken directly from Fig. 9, and calculated values are obtained from the relation

$$\sin \phi \approx \cos \Theta / \sin \alpha, \tag{3}$$

in which Θ is the inclination of the crystallographic plane giving rise to the particular layer line reflection to the plane normal to the fiber axis. Values of Θ, necessary to calculate ϕ, have been obtained by direct angular measurement upon a diffraction pattern from a stretched film, Fig. 5. It is obvious that only those fiber period reflections can occur for which $(\Theta + \delta') > \alpha$, and that reflections for which α lies between $(\Theta + \delta')$ and $(\Theta - \delta')$ will lie across the vertical axis in Fig. 9.

In Table IV is listed a single reflection attributed to the alpha crystallographic modification, suggesting that the foil is a mixture of two polymorphic forms of gutta-percha. One concludes that the film is a mixture of the beta modification and a very small quantity of the alpha modification. No reflections attributable to the alpha modification have been observed in experiments on stretched specimens.

It is surprising that most of the crystallites are oriented with their fiber axis directions normal to the plane of a film the thickness of which is much less than the total length of a macromolecule. There is considerable evidence that the material has not oxidized sufficiently to cause serious depolymerization for some time after all but possible traces of "absorbed" solvent have evaporated. The possibility of crystallite rearrangement in the solid film after subsequent oxidation has shortened the chains appears to be doubtful. It therefore seems necessary that the macromolecular configuration of gutta-percha is not generally linear in these thin films. The gutta-percha macromolecule may possibly fold by a mechanism of rotation around single bonds. The chemical repeating unit of this polymer is short and relatively few folds per macromolecule are required in a film 200° Å. thick. It is conceivable that such infrequent folding would not affect the crystal structure.

Unstretched Polyethylene Sebacate.—From the continuous rings of Fig. 6 one concludes that the individual crystals in a thin unstretched film of polyethylene sebacate are relatively small and, as in the case of unstretched gutta-percha films, are randomly oriented about the normal to the film surface. The marked difference between Figs. 7 and 9 suggests at once that the type of orientation in the unstretched polyethylene sebacate film is, however, entirely different from that in gutta-percha. The nature of the orientation in thin unstretched films of polyethylene sebacate is not established so readily as is that in gutta-percha films. The difficulty arises from the low intensity of many of the reflections, and from the fact that in many instances layer line and equatorial reflections are found to correspond to nearly equal interplanar spacings.

The absence of the A_6 reflection in the data of Table III rules out the possibility of an orientation like that in gutta-percha. An indication of a possible orientation is found in the weak reflections corresponding to the spacings 1.29 and 1.19 Å. From the polyethylene sebacate data of Table I we find that the first of these could be a weak equatorial reflection, a weak seventh layer line reflection or the strong fiber period reflection (XIII_0); the second must be one or both of the strong reflections (XIV_0) or (XIV). The stronger reflection for which $d = 1.10$ could possibly be a weak seventh layer line reflection or the medium reflections (XV_0) and/or (XV). The occurrence of these reflections can be explained if the fiber axis directions lie approximately in the plane of the foil. If this is the case, the evidence of missing and abnormally weak reflections does not allow the crystallites of the foil to have all degrees of rotation around the fiber axis directions.

It is possible that confirmation of these ideas can be found in the pattern from the same foil with the primary beam incident at 45° from the surface normal. (A pattern at near grazing incidence could be interpreted more easily, but it is not possible to obtain such patterns from foils mounted for study by the transmission method.) The 45° incidence pattern is shown in Fig. 7, and numerical data obtained from it are recorded in the last six columns of Table III. Several facts are immediately apparent. All reflections which are observed with normal intensity in the normal incidence pattern occur as continuous arcs across the x-axis of the plate while those of abnormally low intensity have strengthened, on the average, to normal with extremely low intensity across x. Many reflections not observed in Fig. 6 are found as arcs lying in a single quadrant of the pattern. These observations confirm the existence of crystallite orientation and give assurance that the foil is actually scattering as a three dimensional grating. It is still impossible to identify positively all reflections and hence to establish the orientation unequivocally; but, with the designations assigned in column five of Table III, the results are in good agreement if the fiber axes of the crystallites lie approximately in the plane of the foil with a small degree of rotational freedom around the directions of these axes. Such orientation is probably due in part to the presence of carbonyl groups along the chain. The minimum value for the angle between chain axis directions and foil surface normal is estimated, from the angular positions of the arcs listed in Table III, to be of the order of 79°. The freedom of crystallite rotation around the fiber axis directions is estimated to be ±10°.

The angular limits of the arc positions are given by the equations

$$\sin \phi_1 = \frac{\sin \Theta \cos \delta \cos A - \cos \Theta \sin \delta}{\sin \alpha} \tag{4}$$

$$\sin \phi_2 = \frac{\sin \Theta \cos \delta \cos B + \cos \Theta \sin \delta}{\sin \alpha} \tag{5}$$

In these, $(90 - \delta)$ = the minimum angle between fiber axis directions and the specimen surface normal, $A = (\psi + \gamma_1)$, $B = (\psi - \gamma_1)$ or *vice versa*, while Θ and α have their former significance. The angle δ can be determined from the half angle width (Φ_F) of fiber period reflections and the equation

$$\sin \delta = \sin \alpha \sin \Phi_F \tag{6}$$

The angle ψ is most clearly visualized by consideration of an average crystallite having the average rotation around the fiber axis and lying with this axis in the plane determined by the specimen surface normal and the rotation axis. ψ is the angle between this plane and the plane containing the fiber axis direction and the reciprocal lattice point corresponding to any reflection. γ_1 is the limit of crystallite rotation around the fiber axis directions, and is measured from the mean position.

A value of $\sin \phi_2 > 1$ indicates that the rotation of the foil around the surface normal cannot bring all planes of the particular set under consideration into diffracting positions. This condition produces an arc across the y-axis of the plate. Such an arc shows a relative intensity somewhat below normal.

A weakness of this interpretation lies in the low relative intensity of the several high order reflections previously mentioned as well as in the uncertainty of identification of a number of general reflections. Dr. Fuller has suggested that the perfection of chain arrangement may be greatly increased by the stretching process; if this is the case, a difference in intensity of fiber period reflections in patterns of stretched and unstretched material is understandable.

The electron diffraction method should supply an easy means of studying conditions in films of this and similar materials from the oriented unstretched state through a series of controlled degrees of stretching. Diffraction patterns obtained from the same film after varying amounts of stretching should not only definitely establish the orientation in the unstretched condition, but should supply considerable information concerning the mechanism of stretching. It is proposed to conduct such experiments in the near future.

It seems of further interest to consider briefly an estimate of the angle δ made by assuming thin rod-like crystallites of a length comparable to the average length of the polyester chain. The sample of polyethylene sebacate used in these experiments has an average chain length of approximately 1400 Å. If rod-like crystallites of this length are arranged at random between two surfaces 200 Å. apart, $(90 - \delta)$ is found to be of the order of 82°. The agreement of this value with the value of 79° previously estimated from the experiments suggests that the polyethylene sebacate chain configuration is generally linear.

Additional experiments with films of various thicknesses indicate that both δ and γ_1 increase as the film thickness increases. Combining this observation with the observation of Fuller and Erickson[1] that thick unstretched polyethylene sebacate specimens give complete Debye–Scherrer ring patterns, it seems likely that films of such esters will show a preferred orientation until the film thickness exceeds the average chain length. It is proposed that a systematic study of orientation, film thickness, and molecular weight distribution may provide interesting and useful information concerning the molecular structure and film behavior of various polymeric type compounds.

Acknowledgments.—The author wishes to make the following acknowledgments: to Dr. C. S. Fuller for the samples of synthetic polyesters and for many helpful suggestions and criticisms, to Dr. L. H. Germer for many suggestions concerning the preparation of this paper, to Mr. F. S. Malm for the samples of gutta-percha, and to Mr. A. J. Parsons for valuable assistance with the experimental work.

Summary

1. Electron diffraction experiments have been carried out upon very thin films of several synthetic polyesters and natural gutta-percha.

2. *Stretched films* show diffraction patterns characteristic of sharply oriented crystals. Measurements upon these patterns are in excellent agreement with existing X-ray data upon the same materials. The utility of the electron diffraction method for structural studies of polymerized substances is thus demonstrated.

3. *Unstretched films of gutta-percha* are found to be composed of relatively large crystallites which are precisely oriented with their fiber axis directions normal to the film surface. It is presumed that the macromolecules are folded back and forth upon themselves in such a way that adjacent sections remain parallel.

4. *Unstretched films of polyethylene sebacate* consist of relatively small crystals which are believed to be oriented with their fiber axis directions approximately in the plane of the film, but with limited rotation around the fiber axis directions.

NEW YORK, N. Y. RECEIVED MAY 4, 1938

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 392]

Note on a Corresponding-States Equation of Practical Interest for General Physicochemical Computations

BY FREDERICK G. KEYES

During the last few years the desire to compute equilibrium physicochemical quantities under conditions removed from the range of validity of the ideal gas laws has led to a renewed interest in the search for an empirical relation of the corresponding-states character.

One form of this effort has been to test the relation of the fugacity–pressure ratio, γ, to the pressure–critical pressure ratio, π, using the existing p–v–T data for gases, to form a graph of constant temperature–critical temperature, θ, lines. The iso-reduced temperature lines of necessity start from $\gamma = 1$ on the vertical axis[1] and are approximately linear in π for θ large, but become increasingly convex relative to the horizontal, or π, axis for θ small. A chart of this sort for hydrocarbons was prepared and its uses discussed by J. D. Cope, W. K. Lewis and H. C. Weber; W. K. Lewis and C. D. Luke and others.[2] Recently[3] R. H. Newton brought together the data for twenty-four substances and found that within a range of 4%, with some exceptions, the data for the substances in the form $(\gamma)_\theta$ *versus* π fell together. A ficticious critical temperature and pressure, however, had to be selected for H_2 and He to bring the data for these substances into line with other substances.

The existence of an exact, universal correspondence in terms of a relation between θ, π, and φ has, however, good reason to be doubted. The cases of H_2 and He at higher temperatures are well-known examples of how badly the concept works out at ordinary temperatures when the form of the equation of state is based on the van der Waals concept of the molecular field.[4] There does exist, however, a range of temperature for all substances, perhaps, where the van der Waals concept leads to a fair approximation in representing the behavior of individual gases.

---

[1] See G. Tunnel's article, *J. Phys. Chem.*, **35**, 2885 (1931), for a comprehensive discussion of the definition and evaluation of the fugacity [G. N. Lewis, *Proc. Am. Acad. Arts Sci.*, **37**, 95 (1901)]. Also, L. H. Adams, *Chem. Rev.*, **19**, 1 (1936).

[2] J. D. Cope, W. K. Lewis and H. C. Weber, *Ind. Eng. Chem.*, **23**, 887 (1931); W. K. Lewis and C. D. Luke, *Trans. Am. Soc. Mech. Eng.*, **54**, 55 (1932); and *Ind. Eng. Chem.*, **25**, 725 (1933); C. W. Selheimer, M. Souders, Jr., R. L. Smith and G. G. Brown, *ibid.*, **24**, 515 (1932); G. G. Brown, W. K. Lewis and H. C. Weber, *ibid.*, **26**, 325 (1936); W. K. Lewis and W. C. Kay, *Oil Gas J.*, **32**, 40, 45 (1934).

[3] R. H. Newton, *Ind. Eng. Chem.*, **27**, 1 (1935). See also, R. H. Newton and B. F. Dodge, THIS JOURNAL, **56**, 1 (1934).

[4] F. G. Keyes, *Chem. Rev.*, **6**, 175 (1929).