

sulfuric acid. The 1,3-diphenyl-2-butanone²¹ (143 g.) was distilled at 152–153 (2 mm.), n_D^{25} 1.5597.

The ketone (50 g.) in 40 ml. of dioxane with 8.5 g. of ammonia was shaken with Raney nickel (5 g.) for five hours under 100 atm. of hydrogen at 150°. The dioxane was distilled, the residue taken up in ether and treated with concentrated hydrochloric acid until it was acid to congo red. The acid solution was extracted with two 150-ml. portions of ether, whereupon the amine hydrochloride crystallized out of the acid layer. The latter was made alkaline with a 50% solution of potassium hydroxide and extracted with 250 ml. of ether. The ether layer was washed with alkali, dried over potassium hydroxide and distilled.

The 1,3-diphenyl-2-aminobutane (24 g., n_D^{25} 1.5657) distilled at 133–138°. The amine partially crystallized upon standing, m. p. 50–51°. When recrystallized from petroleum ether (b. p. 60–68°) the melting point was as high as 54°. The 3-nitrophalimide had a melting point 152–153° (from alcohol).

Hydrogenations.—In general 30 to 40 g. of an iminonitrile dissolved in 80 ml. of ether or dioxane was allowed to react with hydrogen at 200 to 300 atm., over about 5 g. of Raney nickel, for two to three hours at 120 to 150°. The steel reaction vessel (270 ml. void), catalyst and procedures, were those ordinarily used in this Laboratory. The products were separated by fractionation and the formation of salts or other derivatives of the amines. The types of derivative used for characterization (and in some cases for isolation of small amounts of an amine) are indicated in Table I.

Summary

Five iminonitriles of the type $RCH_2C=NH$.

(21) Levy and Jullien, *Bull. soc. chim.*, [4] **45**, 941 (1929).

CHRCN have been prepared by the Thorpe reaction from nitriles RH_2CN where R was hydrogen, methyl, ethyl, *n*-propyl or phenyl, and submitted to hydrogenation over Raney nickel. The corresponding diamines were obtained in yields averaging about 60%, but in no case was it possible to selectively hydrogenate the imino group and obtain an aminonitrile.

All of the iminonitriles gave cleavage products upon hydrogenation. In the first four nitriles listed above the predominant cleavage involved the removal of the cyano group, while with $C_6H_5-CH_2C=NHCHC_6H_5CN$ only the nitrogen of the cyano group was lost to any considerable extent.

Two substituted iminonitriles, 3-(phenylimino)-butyronitrile and 3-piperidinocinnamonitrile underwent cleavage almost exclusively at the imino group.

Molecular weight determinations in benzene indicated that the compound $C_8H_7CH_2C=NH$ (C_8H_7)CN exists as a trimer at the freezing point of benzene and as a dimer at the boiling point of benzene. In an alcohol solution di- or trimerization does not occur, but the alcohol adds to the iminonitrile.

The behavior of the iminonitriles upon hydrogenation lends support to the concept that they have the structure $RC(NH_2)=CRCN$.

MADISON, WISCONSIN

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[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES]

Chain Structure of Linear Polyesters—Trimethylene Glycol Series

BY C. S. FULLER, C. J. FROSCH AND N. R. PAPE

In previous papers^{1,2,3} results have been reported on the crystalline nature and the chain molecule configurations of linear polyesters of high molecular weight. These results have been based on the measurement of X-ray fiber patterns obtained from oriented fibers. In the case of the crystalline members of the ethylene glycol and decamethylene glycol series, it has been shown that the chain molecules are arranged parallel to the fiber axis and are essentially planar zigzag in configuration. In addition it was found that in these series the molecules exhibit typical paraffinic packing in the plane perpendicular to the chain

axes.⁴ At the same time there is good evidence that the mutual alignment of the chemical repeating units in adjacent chain molecules is sometimes variable within the same compound (polymeric mixture), so that several apparently stable arrangements of the planar chains, corresponding to various angles of "tilt" of the dipole layers, may co-exist in a given polycrystalline aggregate. As might be expected this is particularly true in the decamethylene series² where the dilution of the polar ester groups is great and the energy between different arrangements is therefore small.⁵

(1) C. S. Fuller and C. L. Erickson, *THIS JOURNAL*, **59**, 344 (1937); **61**, 3601 (1939).

(2) C. S. Fuller and C. J. Frosch, *ibid.*, **61**, 2575 (1939).

(3) C. S. Fuller and C. J. Frosch, *J. Phys. Chem.*, **43**, 323 (1939).

(4) Polyethylene succinate appears to be an exception to this rule. However, evidence has been found¹ which indicates that under certain conditions it also can be made to exhibit paraffinic packing.

(5) T. Schoon, *Z. physik. Chem.*, **B39**, 385 (1938); *Ber.*, **72**, 1821 (1939).

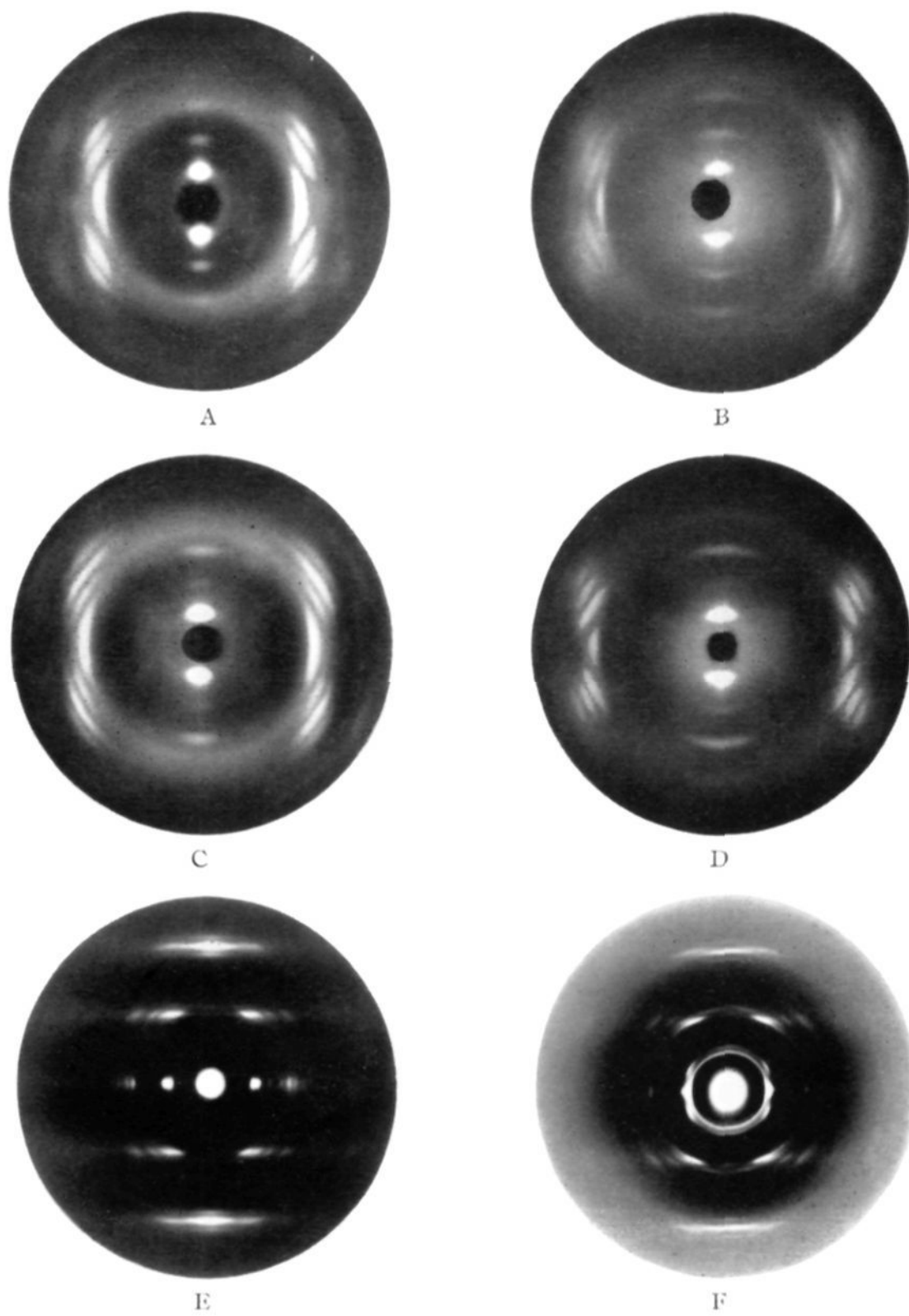


Fig. 1.—Fiber patterns of oriented trimethylene polyesters: A, azelate, 4 cm.; B, sebacate, 5 cm.; C, 1,9-dicarboxylate, 4.5 cm.; D, 1,10-dicarboxylate, 5 cm.; E, electron diffraction photograph of oriented 1,9-dicarboxylate (stretched film); F, electron diffraction photograph of oriented 1,9-dicarboxylate (relaxed film), fiber axis vertical, $L\lambda = 2.34 \times 10^{-6}$ sq. mm. for electron photographs.

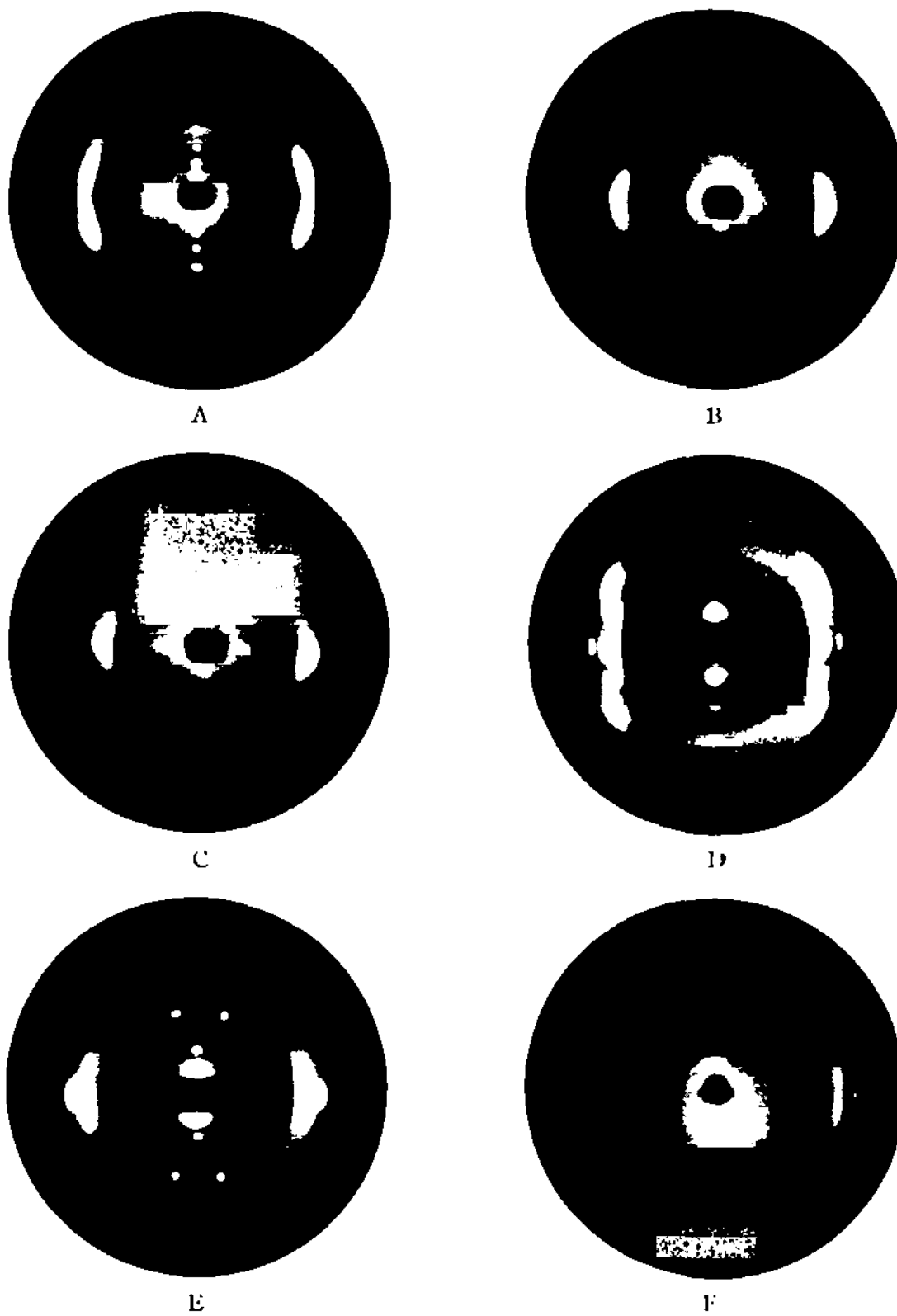


Fig. 4.—A, fiber pattern of oriented trimethylene 1,16-dicarboxylate, 4 cm.; B, same as A stretched 10%, 3.8 cm.; C, same as A stretched 20%, 3.8 cm.; D, partially oriented trimethylene azelate, 4 cm.; E, oriented trimethylene 1,10-dicarboxylate maximum stretch, 4 cm.; F, same as E but short exposure showing fine structure of meridian reflection, 5 cm., fiber axis vertical.

Members of the trimethylene series considered in the present report exhibit a considerably different crystalline behavior from those of the ethylene and decamethylene series mentioned above. For example, different fiber patterns are obtained depending on the manner in which the samples are prepared. Particularly, the application of stress to the specimens often has a profound effect on the type of arrangement assumed by the chain molecules. Although there are a number of possible interpretations, the results support the conclusion that the chain molecules in the trimethylene series of polyesters, at least over the length of one chemical repeating unit, are essentially planar zigzag in configuration and in the oriented samples are tilted to the fiber axis at an angle of approximately 30 degrees. This is unexpected since in all other synthetic fibers heretofore examined the axes of zigzag chain molecules lie parallel to the fiber direction. Results obtained on stretched samples also support this view and further indicate that in these polymeric systems the chain molecules assume different degrees of orderliness of arrangement. Evidence that the ester group dipoles play an important role in the determination of the type of crystalline arrangement has likewise been obtained.

Materials and Method

The trimethylene polyesters were prepared by condensing redistilled trimethylene glycol with various dibasic acids at 200° in a stream of dry oxygen-free hydrogen. The reaction was continued until thin rods of the materials solidified from the melt could be oriented by cold drawing⁶ into fibers exhibiting a high degree of X-ray orientation. The succinic (187–187.4°) and adipic (151.8–152°) acids were reagent grade recrystallized from nitric acid. The 1–16 dicarboxylic (126–127°) acid was obtained from Fränkel and Landau. The pimelic (105–106°), glutaric (94–96°) and suberic (138–140°) acids were obtained from the Eastman Kodak Company. The sebacic acid (132–133°) was prepared by distillation of a pure grade of commercial acid. The azelaic (107–108°), 1,9-dicarboxylic (109.5–110°) and 1,10-dicarboxylic (124–126°) acids were prepared by standard organic syntheses.⁷ Table I lists the trimethylene polyesters studied, together with their approximate melting points.

The technique of preparing the specimens for exposure and the X-ray method employed were the same as have already been described. Single oriented fibers (0.4–0.8 mm. diameter) were employed to secure the fiber diagrams using sodium chloride dusted directly on the samples as a refer-

(6) W. H. Carothers and J. W. Hill, *THIS JOURNAL*, **54**, 1568 (1932).

(7) The authors are indebted to Mr. W. S. Bishop and Dr. B. S. Biggs for the preparation and purification of the acids employed in this report.

ence standard. In the case of the unstressed specimens, the fibers were placed directly on the insert containing the pinhole. When stretched samples were examined, the fibers were held in a clamp attached to the insert. By means of a screw the desired elongation could be applied to the fibers. It was found impossible to prepare fibers from the succinate, glutarate, adipate, pimelate and suberate polyesters, which were all slow to crystallize. The succinate and glutarate esters in particular required several months before they were sufficiently crystalline to photograph. However, a comparison of the Debye-Scherrer patterns of these compounds with those of the higher members, which could be obtained in fibrous form, usually established the rings corresponding to the meridian or repeating length spacings⁸ and hence made it possible to determine the fiber periods for these compounds. The fiber periods for these esters are followed by the letter D in Table I. All patterns were taken at 20–25°. Filtered copper radiation was employed.

Results and Discussion

A. Unstretched Fibers.—The fiber patterns obtained from the oriented trimethylene polyesters show a distinct similarity to one another, but are considerably different in appearance from those given by the polyesters of the ethylene or decamethylene series. Figure 1 shows typical fiber patterns normally observed for the higher trimethylene polyesters. Contrary to the behavior of the ethylene series, in which only the esters containing odd acids show meridian reflections, such reflections are observed for both the even and odd members of the trimethylene series. The appearance of only the even orders of the basal plane reflection suggests twofold screw axes along the fiber direction. The best values of the fiber periods and lengths of the chemical units projected along the fiber axis for the various members are given in the third and fourth columns of Table I, respectively, with the estimated error in the case of the latter. The patterns show a single side spacing of 4.55 and 4.65 Å. for the odd and even esters, respectively. There is thus a difference in structure between the odd and even esters although this does not appear to be very pronounced.

It is not immediately evident how many chemical repeating units are contained in the fiber period distances of Table I. However, the assumption that the innermost meridian reflection corresponds in each case to the length of the chemical repeating unit measured in the fiber direction ap-

(8) The rings corresponding to the meridian reflections in the case of the succinate and glutarate were difficult to measure and fall below the curve in Fig. 2. The chain molecules in these esters may therefore possess a different structure from those of the higher esters.

TABLE I

Trimethylene polyester	M. p., °C.	Fiber period, Å.	Projected chemical repeating unit length, Å.
Succinate ⁸ (D)	47	15.2	7.6 ± 0.3
Glutarate ⁸ (D)	39	15.4	7.7 ± .2
Adipate (D)	38	21.5	10.8 ± .1
Pimelate (D)	37	23.6	11.8 ± .1
Suberate (D)	41	26.1	13.1 ± .1
Azelaate	50	27.7	13.9 ± .1
Sebacate ⁹	53	31.3	15.7 ± .1
1,9-Dicarboxylate	59	32.4	16.2 ± .1
1,10-Dicarboxylate	61	35.8	17.9 ± .2
1,16-Dicarboxylate ¹⁰	76	51.6	25.8 ± .4

D = Debye-Scherrer pattern.

pears to be justified on the basis of the results obtained and discussed in detail below. In Fig. 2 are plotted the lengths of the chemical repeating units of Table I for the various trimethylene esters against the number of chain atoms in these units.

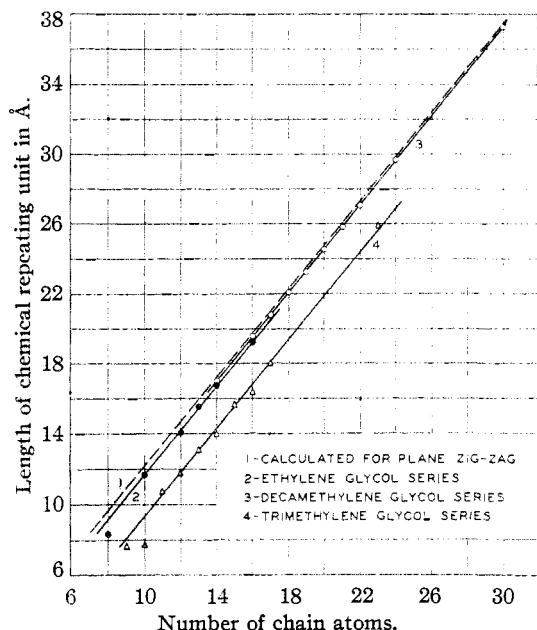


Fig. 2.—Lengths of chemical repeating units in the fiber direction plotted against number of chain atoms in the units for various polyester series.

The same data for the ethylene and decamethylene polyesters have also been plotted, to which, in addition to measurements already reported,¹¹ have been added values for polyethylene 1,9-dicarboxylate, polydecamethylene pimelate, polydecamethylene 1,9-dicarboxylate and polydecamethylene 1,16-dicarboxylate. It is evident that the

(9) The value for the fiber period in this case is somewhat greater than that previously reported.¹

(10) Carothers and Hill,⁸ page 1581, give a fiber pattern of this polyester, but do not calculate the fiber period.

(11) C. S. Fuller, *Chem. Rev.*, 26, 143 (1940).

increase in length per carbon atom added to the acid portion of the ester is essentially the same for the esters in all three series.⁴ However, the trimethylene esters show a nearly constant difference in the lengths of the repeating units of approximately 2.8 Å. less than the members in the other two series which have the same number of chain atoms. The accuracy of the results, however, does not justify the conclusion that this difference is actually constant for the various trimethylene esters.

There are obviously a number of chain configurations for the chemical repeating units of the trimethylene esters which are capable of reproducing the observed fiber periods given in Table I. The following possibilities need to be considered.¹² (1) The chains are uniformly kinked or coiled about the fiber axis direction by suitable rotations on the bonds so as to result in the proper repeating distances. (2) The chains are partly planar zigzag and partly coiled and are parallel to the fiber axis. (3) The chains are essentially planar zigzag but lie at an angle to the fiber axis such that the projection of the zigzag length of the repeating units on the fiber axis gives the observed fiber periods.

The first possibility requires a variable amount of rotation per bond in the case of the different compounds of the series in order to account for the almost constant amount of shortening shown in Fig. 2. However, there does not appear to be any logical reason to postulate such a behavior. In addition, chains of this helical structure would be difficult to construct so as to reproduce the reflections observed on the meridian lines of the various patterns. Other considerations such as the difficulty of accounting for the layer-line spacings on the basis of such a chain model and the similar behavior of odd and even esters make the presence of a uniformly coiled chain structure improbable.

The slope (1.26 Å. per CH₂) of the line in Fig. 2, giving the length of the chemical repeating units as the acid portion of the chain is progressively increased, suggests that perhaps the acid part of the esters is planar zigzag and that the chains are parallel to the fiber axis. This would require the shortening to be restricted to the glycol portion

(12) A folded configuration such as suggested in ref. 1, Fig. 2c, is considered now to be eliminated since such an arrangement is unable to account for the fluctuation of meridian intensities observed in the various esters of the series or the intensity and spacings of the strong layer-line reflections.

of the molecule and thus would favor the second possibility mentioned above. However, the slope observed in Fig. 2 can also be obtained with fully extended zigzag chains inclined at progressively steeper angles to the fiber axis. In fact (with the exception of the 1,16-dicarboxylate, which is poorly crystalline) a variation in "tilt" from only 36.5 to 32.0° is sufficient to allow the adipate and 1,10-dicarboxylate to fall on the observed line. It is not possible on the basis of the partly folded chain arrangement to account for the meridian intensities and the intense reflections which occur on the third and fourth layer-lines. It is therefore necessary to consider the third possibility mentioned above.

The intense layer-line reflections referred to as well as others appearing on higher layer-lines have d -values agreeing closely with interplanar distances found on the equator in the case of the ethylene and decamethylene polyesters, and hence suggest planar extended chains inclined to the fiber direction. As already mentioned, this is not incompatible with the slope observed in Fig. 2. However, in order to account for the observed fiber patterns, it is necessary in addition that the chains be rotated about the fiber direction in the manner illustrated in Fig. 3. A paraffinic¹³ type of packing of the inclined zigzag chains is able to account for the observed spacings at various angles between the equatorial and meridian lines depending on the tilt, the orientation of the cell about the axis and the interplanar spacing of the plane reflecting. In agreement with the (110) and (200) reflections from low molecular chain compounds, the strongest spacings observed are the 4.0 and 3.7 Å. planes. These occur at angles to the equatorial line of approximately 22.5 and 30° , respectively. In addition, other spacings characteristic of such extended chains (3.0 , 2.5 , 2.2 and 2.1 Å.) are observed in the layer-line area as would be expected. The 4.55 and 4.65 Å. equatorial spacings for the odd and even esters are more difficult to explain. It is possible that they arise from vertical planes marked by the C=O groups.

Further evidence that the chains of the trimethylene esters are tilted to the fiber or cold drawing direction is furnished by an examination of the meridian reflections arising from the dipole layers. In Table II, columns 2-5 give the observed intensities as estimated from the fiber patterns.

(13) A. Müller, *Proc. Roy. Soc. (London)*, **A120**, 455 (1928).

TABLE II

Polyester	II ₀	IV ₀	VI ₀	VIII ₀	
Azelaate	VS	S	M	..	0.42
Sebacate	VS	M	S	..	.39
1,9-Dicarboxylate	VS	W	M	..	.35
1,10-Dicarboxylate	VS	W	S	..	.33
1,16-Dicarboxylate	VS	M	W	M	.24

The last column lists the values of f , the ratio of the distance of the intermediate carbonyl plane (Fig. 3) to the chemical repeating distance assuming a planar zigzag chain. It is evident that when f is near $1/2$, as in the case of the azelaate, IV₀ is stronger than VI₀. On the other hand, when f becomes one third as for the 1,10-ester, VI₀ becomes stronger. Finally, when f is near one-fourth, the VIII₀ reflection is strong as in the case of the 1,16-ester. The planar zigzag chain, therefore, accounts for the fluctuation observed in the meridian intensities, whereas a chain kinked in the glycol portion is unable to account for these observations. It is evident that tilting the extended chains does not alter the ratios of the distances between the dipole layers.

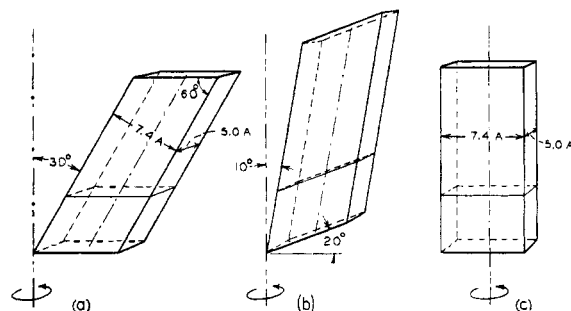


Fig. 3.—Elementary volumes comprising two chemical repeating units. (a) unstretched oriented 1,10-dicarboxylate; (b) stretched (20%) oriented 1,10-dicarboxylate; (c) stretched (20%) oriented 1,9-dicarboxylate, fiber axis vertical.

In Fig. 3A, the chain molecules are considered to lie along the edges and center lines of the cell shown. The dipole layers formed by the ends of the repeating units and the one formed by the intermediate carbonyl groups are perpendicular to the fiber axis. The molecules, considered as planar zigzag, then assume a tilt of approximately 30° to reproduce the required spacing (35.8 Å.) between corresponding dipole layers. Only one chemical repeating unit has been shown in the figure since it cannot be uniquely determined from the data whether the next succeeding units are co-linear or assume an opposite tilt. If they are co-linear it is difficult to explain the orientation since it is expected that the crystallites would

follow molecular lines in their habit and would orient with their long axes parallel to the fiber axes. A structure with alternately tilted repeating units has the advantage of progressing in the fiber direction and in addition more readily explains the fact that the structure repeats every second chemical unit whether it contains an even or odd number of atoms. On the other hand, it is difficult to imagine crystallites constructed of chains possessing such a configuration. It is therefore not possible to reconcile the tilted chain structure with the orientation observed in other chain polymers at the present time.

A possible explanation for the structure may reside in the fact that the dipole interactions require the chains to pack in the tilted fashion. If we consider the chain molecules as planar zigzag structures, it is evident that the dipoles in the trimethylene portion are similarly directed and will interact on one another with an energy of μ^2/r^3 ergs where μ is the component of the ester dipole vector perpendicular to the chain, and r is the distance between the dipole centers. Although this energy cannot be calculated exactly it probably lies in the neighborhood of 0.1×10^{-13} ergs.¹⁴ This, together with the thermal energy at the melting point (0.5×10^{-13} erg), approximates that (0.7×10^{-13} erg or 1000 calories per mole)

estimated as the barrier to rotation about the $\text{C}-\overset{\text{O}}{\parallel}\text{C}$ bonds¹⁵ but is somewhat less than the value of approximately 2000 calories or 2500 calories required to cause rotation on $\text{C}-\overset{\text{H}_2}{\text{O}}$ or $\text{C}-\overset{\text{H}_2}{\text{C}}$ bonds, respectively.¹⁶ No energy data seem to be available in regard to the $\text{C}-\overset{\text{O}}{\parallel}\text{C}$ bond barrier. If the

value is less than 1000 calories per mole, as seems probable, a rotation on alternate bonds of this type could result in an opposed dipole arrangement and at the same time explain the tilted chain structure. It is also possible that rotations about several weak bonds persist in amorphous parts of the solid esters and in some way impose a tilt on the linear chains in the crystalline parts.

That carbon-to-carbon linkages do oppose rotation is supported by the fact that little shorten-

(14) Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalogue Company, New York, N. Y., 1931, p. 81.

(15) Schumann and Aston, *J. Chem. Phys.*, **6**, 485 (1938).

(16) Kistiakowsky and Nazmi, *J. Chem. Phys.*, **6**, 18 (1938); J. H. Howard, *ibid.*, **5**, 451 (1937); Kistiakowsky and Rice, *ibid.*, **8**, 618 (1940).

ing apparently occurs in decamethylene glutarate polyester.² Also, evidence that bond rotation occurs in other polyesters which contain $\text{C}-\overset{\text{H}_2}{\text{O}}$ bonds between similarly directed dipoles is given in Table III, which shows that shorter repeating units result under these circumstances. Trimethylene 1,10-dicarboxylate is included in Table III for comparison.

TABLE III

	Observed chemical repeating unit length, Å.	Difference from planar length (21.0 Å.)
Decamethylene glutarate	20.8 ± 0.1	0.2
Nonamethylene adipate	20.3 ± .3	.7
Trimethylene 1,10-dicarboxylate normal form	17.8 ± .1	3.2
Diethylene sebacate	17.7 ± .1	3.1
Decamethylene diglycolate	18.7 ± .1	2.1

The last column gives the difference between the observed length and that calculated assuming a planar form of chain. It is evident as mentioned above that no appreciable shortening occurs in the case of decamethylene glutarate where the dipoles are similarly directed but are separated by carbon-to-carbon bonds. In the other cases, however, a shortening is observed which qualitatively bears out the above predictions.

B. Stretched Fibers.—Although in the case of previously reported polyesters^{2,3} the method of preparing and exposing the specimens has slight effects on the resulting fiber patterns, these are much more evident in the case of the trimethylene compounds. There is no doubt that considerable amounts of supercooled amorphous material are present in some of these compounds. This is particularly true if, prior to cold drawing, the samples are rapidly quenched from the melt. When samples containing both amorphous and crystalline matter are subjected to stress, mixed fiber patterns are often obtained. Thus, when a 1,9-dicarboxylate was quenched, cold drawn and exposed stretched, the two equatorial reflections characteristic of planar zigzag chains parallel to the fiber direction were evident superimposed on the pattern normally given by the unstretched fiber. The same is observed for the azelate ester (see Fig. 4D), and is no doubt due to the extension of amorphous, rubber-like chains into parallel paraffinic arrangement.

When, however, a sample of the 1,10-dicarboxylate ester showing only the normal, unstretched fiber pattern was subjected to stretch-

ing, a mixed pattern of a wholly different kind was obtained. Figures 4E and 4F show the type of pattern when the maximum stress (just short of breaking) is applied. The sample slowly elongated under the stress and a second stretch was given resulting in a total elongation of approximately 20%.

There appear to be three superimposed patterns: (1) A remnant of the old normal (unstretched) pattern which has not completely transformed as a result of stretching. (2) A new meridian reflection (10.25 Å.) corresponding to an identity period of 41.0 Å. which is within experimental error equal to the planar zigzag length (42.0 Å.). (3) The chief pattern, which consists of a transformation pattern of the normal one as a result of stretching. Its period is 38.8 Å. in agreement with a tilt of the molecules of about 18 degrees to the fiber axis. The peculiarity of this pattern is the splitting of the 4.2 and 2.5 Å. reflections about the equator and the breaking up of the original meridian reflections. This behavior is precisely what is expected if stretching results in a tilting of the dipole layers originally perpendicular to the fiber axis so that they form an angle of about 20° with this axis (see Fig. 3B). The effects are analogous to those observed when a monoclinic crystal is rotated about an axis inclined slightly to the crystallographic axis. It is inferred that the main effect of the stretching is to decrease the angle of tilt of the molecules from about 30° for the normal trimethylene form to 10° found in the present case. It is probable also that some rotation as well as gliding of the chains occurs. The final result is probably a monoclinic cell tilted in such a way as to maintain the 3.7 Å. plane parallel to the fiber axis. The uni-axial orientation originally present in the normal crystalline form still persists, as is shown by patterns taken perpendicular to the fiber axis and to each other. That the stretching has rearranged the chains into another stable form, rather than caused a disruption of crystals already present, is suggested by the fact that releasing the stress allows the normal pattern to return slowly.

It is not clear to what to attribute the 10.25 Å. meridian reflection mentioned above in 2. The value suggests extended chains parallel to the fiber direction, but the carbonyl layers of such chains require a very weak reflection for this order. All that can be said is that the reflection appears to originate from the alignment of chains which

were amorphous prior to stretching, and may correspond to a translation of one-half a chemical repeating unit between adjacent chains.

Since the 1,16-dicarboxylate ester provides rather unusual results particularly when stretched, its treatment has been postponed until now. As Fig. 4A shows, the fiber pattern obtained from this ester when solidified at room temperature, does not exhibit a normal pattern even in the absence of stress. Unlike the other esters no reflections characteristic of a three dimensional lattice structure are evident but rather a set of meridian spots and a single broad layer-line reflection having a spacing of 4.16 Å. This suggests a layer-like structure in which the layers are tilted at an angle of about 25° to the fiber direction but in which the repeating units maintain planes perpendicular to the fiber axis, *i. e.*, dipole layers form perpendicular to this axis. Apparently the long polymethylene chain present favors this mesomorphic chain arrangement. That this form is unstable is shown by annealing the ester at 60° for several days. It then could no longer be cold drawn, and Debye-Scherrer photographs showed a number of sharp rings indicating that crystallization had occurred.

Figures 4A-C show the effect of stretching a fiber drawn from the 1,16-dicarboxylate ester. Figure 4B represents an intermediate (about 10%), and Fig. 4C a maximum stretch (about 20%). Not only do the intense layer-line reflections coalesce on the equator, but an ordering of the chains to the extent of causing a new reflection (3.7 Å.) to appear apparently occurs. A definite decrease in the intensities of the higher order meridian reflections takes place also, indicating the formation of strong intermediate planes as a result of chain parallelization in the fiber axis direction.

Electron Diffraction Results.—In order to explore more fully the correctness of the interpretations of the X-ray fiber patterns as discussed above, Mr. K. H. Storks of these Laboratories kindly examined both the 1,9- and the 1,10-dicarboxylate ester by means of electron diffraction. His results are shown in Figs. 1E and F. Figure 1E is the transmission pattern from a film of the 1,9-dicarboxylate which was prepared by melting a thin film (about 1000 Å.) on a glass plate, quenching in liquid nitrogen and cold drawing on a water surface. The film was maintained in the stretched form during exposure. The significant point is that the pattern shows a typical paraffinic

zigzag chain structure in which the chains are fully extended along the fiber direction. The observed fiber period of 19.9 Å. agrees well with that calculated of 19.76 Å. Figure 3C illustrates the chain arrangement.

Figure 1F is a pattern obtained from the same film which has been allowed to relax. It is a mixed pattern of the normal tilted and the vertical zigzag form produced by stretching. For this reason it is difficult to analyze. However, there are certain significant effects which have a direct bearing on the X-ray conclusions drawn above. Broad, weak, fuzzy lines are noted in the upper and lower regions of the pattern inclined to the fiber axis at an angle of about 60°. (These are not noticeable in the reproduction.) These lines suggest that in the normal form which arises on relaxing the film the chains are zigzag and are inclined at an angle of about 30° to the fiber axis as concluded above. As to the reason for the presence of both patterns in the relaxed sample, we can only speculate. However, microscopic examination of the specimen shows definitely two types of crystal regions. It appears that in the fully stretched film the chains are behaving, at least in part, like the chains in natural rubber, with the difference that instead of relaxing to an amorphous state they relax to a second more stable crystalline state. The value of 32.1 Å. for the fiber period of the normal form deduced from this photograph agrees well with the X-ray value (32.6 Å.).

In addition to the above patterns, a stretched film of 1,10-dicarboxylate was prepared from chloroform. It was initially about 400 Å. thick and was exposed in the fully stretched state. As in the case of the X-ray results on the stretched ester, a pattern intermediate between the vertical and tilted forms of pattern is obtained. The fiber period observed (40.8 Å.) agrees with a nearly vertical extended chain. The arcing in the meridian reflection at 1.20 Å. fits the picture previously presented of zigzag chains inclined to the

fiber axis and rotated about it. The angle required (11°), is practically identical with the X-ray case. No doubt the value varies with the stress. The evidence from the electron photographs therefore agrees well with the X-ray results in favoring the tilted chain arrangements mentioned above for the normal forms of the trimethylene polyesters.

Summary

1. A number of trimethylene glycol polyesters of high molecular weight have been prepared, and a study of their fiber patterns has been made.

2. Fiber patterns produced by stretching oriented fibers of the polyesters have also been examined in order to obtain further information on the nature of the chain molecule organization and configuration in the solid esters.

3. The results favor the presence in the crystalline regions of essentially planar zigzag chain molecules inclined to the fiber axis, rather than coiled or kinked chains parallel to this axis. Evidence of amorphous regions containing disordered kinked chains has been obtained. Intermediate (mesomorphic) states of order have also been observed in which the chains are parallel but otherwise are unordered. The latter is particularly the case when long hydrocarbon chains are present as in the 1,16-dicarboxylate ester.

4. Although the structure in the crystalline regions is undetermined, evidence has been found in support of randomly rotated crystallites containing dipole layers and extended chains inclined at approximately 60° to these layers. In the oriented state in the absence of external stress, the crystallites are disposed so that the dipole layers lie perpendicular to the fiber direction. Stretching along the fiber direction decreases the angle of inclination of the chains to the fiber axis and causes the formation of dipole layers lying at an angle to this axis. This, under certain conditions, results in a complete parallel alignment of the chain molecules.

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