in its physical properties. The behavior of these anhydrides toward aniline is described and discussed. The prefixes α, β, γ and ω used above have been adapted arbitrarily to designate the anhydrides of different origins.

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STUDIES OF POLYMERIZATION AND RING FORMATION. XV. ARTIFICIAL FIBERS FROM SYNTHETIC LINEAR CONDENSATION SUPERPOLYMERS

BY WALLACE H. CAROTHERS AND JULIAN W. HILL

The linear condensation superpolymers described in the three preceding papers of this series[1] can easily be drawn out into strong, pliable, transparent, permanently oriented[2] fibers. So far as we are aware no strictly synthetic material has hitherto been obtained in the form of fibers which thus simulate natural silk.

The superpolyester derived from hexadecamethylene dicarboxylic acid and trimethylene glycol is for brevity referred to below as the 3–16 ω-ester.

Methods of Producing Filaments.—Continuous filaments can be obtained from the molten 3–16 ω-ester by touching it with a stirring rod and drawing the stirring rod away. More uniform filaments are obtained by dissolving the ester in chloroform and extruding the viscous solution through an ordinary rayon spinneret into a chamber warmed to permit the evaporation of the chloroform. The filaments can be picked up and continuously collected on a motor-driven drum at the bottom of the chamber. The production of filaments having a diameter of less than 0.001 inch presents no difficulties. It is also possible to extrude the molten ester through a spinneret that is provided with a heating coil to maintain the ester in a sufficiently fluid condition. When this method is used it is easy to apply considerable tension to the filaments as they are collected on the drum.

Properties of the Filaments.—The properties of the filaments produced by any of these methods depend upon the amount of tension or stress applied during the spinning operation. If no stress is used the filaments closely resemble the massive ester from which they are produced. They melt at 74–75° and, like the initial mass, they are opaque and devoid of luster. But if sufficient tension is applied during the spinning operation

[1] Papers XII, XIII and XIV.

[2] The orientation implied in this use of the term is general orientation, with reference to the fiber axis, of the molecules or of some ordered units involving the molecules.

the filaments are very different from the initial mass in their physical properties.   Instead of being opaque they are transparent, and they have a
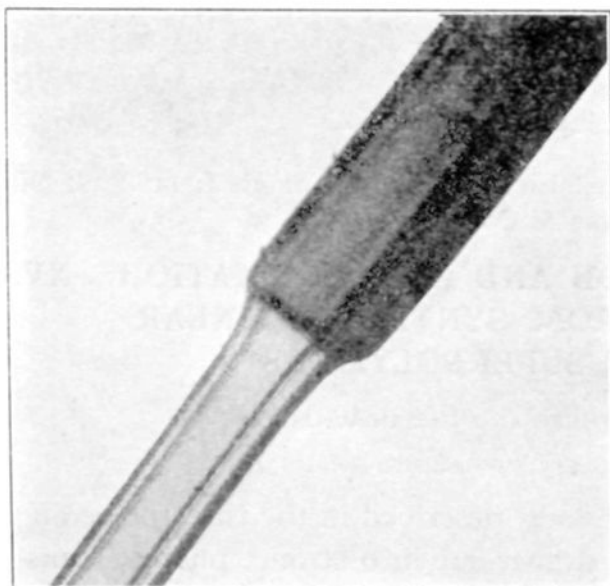

Fig. 1.—Filament from 3–16 ω-ester showing opaque and transparent sections with boundary.

very high luster. They also have a very much higher breaking strength than the initial mass, and they are sufficiently pliable to be tied into hard knots, whereas the opaque filaments produced without stress are so fragile that they can hardly be bent without breaking. The opaque polyester and the transparent filaments produced from it by spinning under tension furnish very different x-ray diffraction patterns. The pattern for the opaque ester (Fig. 4) indicates that it is crystal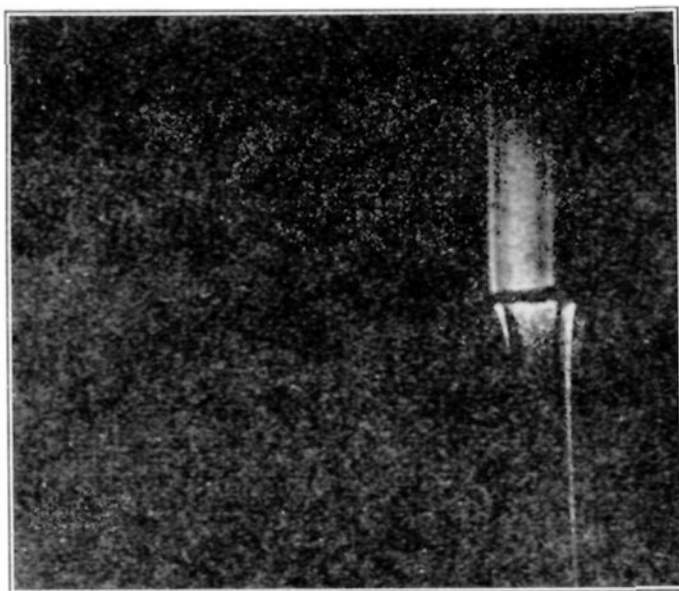line, but there is no sign of general orientation. The transparent filaments on the other hand furnish a fiber pattern (Fig. 5) such as one obtains from certain natural silk and cellulose fibers and rayon filaments that have been spun under tension. The character of this pattern indicates a very considerable degree of molecular orientation along the axis of the filament.[3]

Cold Drawing.—In connection with the formation of fibers the ω-polymers exhibit a rather spectacular phenomenon which we call cold drawing. If stress is gently applied to a cylindrical sample of the opaque, unoriented 3–16 ω-polyester at room temperature or at a slightly elevated tempera-

Fig. 2.—Same as Fig. 1 under crossed Nicols showing parallel extinction of oriented section.

[3] According to some preliminary calculations made by Dr. A. W. Kenney of this Laboratory, the identity periods in the oriented fibers derived from ethylene sebacate and from the 3–16 ester lie within about 10% of the calculated lengths for one structural unit of the chain.

ture, instead of breaking apart, it separates into two sections joined by a thinner section of the transparent, oriented fiber. As pulling is continued this transparent section grows at the expense of the unoriented
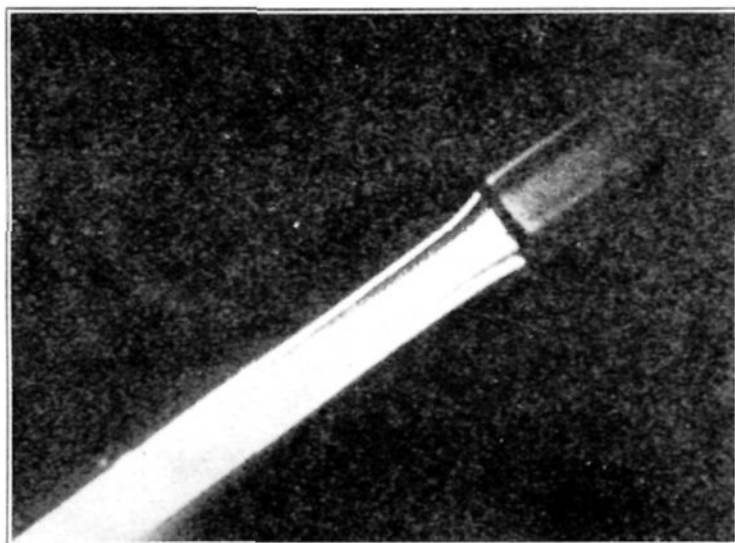

Fig. 3.—Same as Fig. 2, 45° to cross hairs.

sections until the latter are completely exhausted. A remarkable feature of this phenomenon is the sharpness of the boundary at the junction between the transparent and the opaque sections of the filament (Fig. 1).
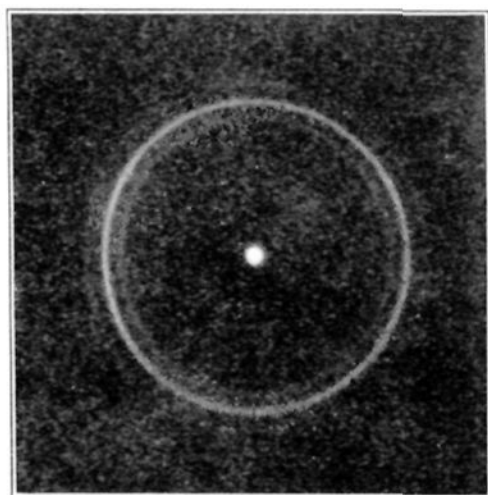

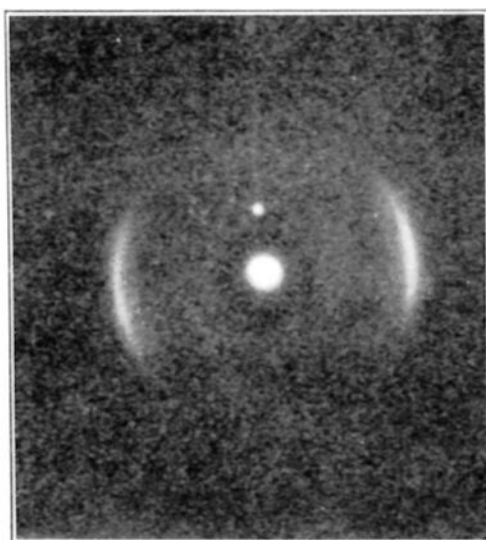Fig. 4.—x-Ray diffraction pattern of unoriented 3–16 ω-ester.

Fig. 5.—x-Ray diffraction pattern of oriented 3–16 ω-ester.

During the drawing operation the shape of this boundary does not change; it merely advances through the opaque sections until the latter are exhausted. This operation can be carried out very rapidly and smoothly, and it leads to oriented fibers of uniform cross section. The oriented and

unoriented forms of the polyester are different crystalline states, and in the cold drawing operation one crystalline form is instantly transformed into the other merely by the action of very slight mechanical stress.

Photomicrographs of filaments of the 3–16 ω-ester are reproduced in Figs. 1, 2, 3 and 6. The opaque filament shown in Fig. 1 was obtained by pulling out a specimen of the molten ester, and the transparent section attached to it was produced by cold drawing this filament. This figure shows clearly the sharpness of the boundary between the oriented and the unoriented sections. Figures 2 and 3 represent the same sample under polarized light. The oriented fiber is birefringent and shows parallel extinction. The opaque filaments of Fig. 6 were obtained by spinning a

Fig. 6.—Filaments of 3–16 ω-ester spun from chloroform solution showing transparent fibers produced by cold drawing ($\times$ 15).

23 weight per cent. solution in chloroform of the 3–16 ω-ester through a spinneret having 0.0045 inch holes into a chamber four feet deep heated to about 30°. At the bottom of the chamber the filaments were caught and collected on a motor driven drum. The filaments had a diameter between 0.001 and 0.002 inch. No attempt was made to stretch them during the spinning operation, and they were opaque, devoid of luster and very fragile. Nevertheless they furnished a fiber x-ray diffraction pattern practically identical with that shown in Fig. 5. Thus the x-ray data indicate a high degree of orientation while the physical properties indicate that scarcely any orientation was effected during the spinning operation. When a bundle of the filaments was warmed to about 35° and pulled it was drawn out into thin, transparent fibers which were strong and pliable. Rough determinations of the tenacity of the partially oriented opaque filaments and the oriented transparent filaments prepared from them by cold drawing indicated that the breaking strength of the transparent filaments was about six times that of the opaque filaments. This specimen of oriented fibers was used in some of the physical tests described in the next paragraph.

Tenacity and Elasticity.—Rough determinations of the tensile strength of rather thick fibers of 3–16 ω-ester prepared by pulling filaments from the molten ester and subsequently orienting them by cold drawing gave values ranging from 16 to 24 kg./sq. mm. (24,000 to 36,000 lb./sq. in. These values compare well with those for cotton fibers (*ca.* 28 kg./sq. mm.) and silk (*ca.* 35 kg./sq. mm.). Under gradually increasing stress the

fibers show a more or less definite flow point, and then, after considerable elongation, a point of increased resistance to stress. The fibers are sufficiently tough and flexible to be tied into hard knots; thick fibers are sufficiently stiff to be bristle-like.

We are indebted to Dr. W. H. Charch of the du Pont Rayon Company for a series of physical tests on fibers of the 3–16 ω-ester spun from chloroform solution and subsequently oriented by cold drawing. The observed tenacity was about 1.1 g. per denier, but this value is believed to be too low owing to the fact that no account was taken of the considerable number of broken filaments in the specimens tested. The wet tenacity is fully equal to the dry tenacity. (In the actual tests the fibers gave consistently higher values when wet than dry, but the differences probably lay within the experimental error.) A clump of filaments rolled into a small ball and compressed showed a remarkable springiness resembling wool. In their elastic properties these fibers are very much superior to any known artificial silk. In Fig. 7 are presented some slightly idealized curves taken from drawings made by a modified Richards dynamometer. Bundles of filaments of viscose rayon, natural silk and fibers from the 3–16 ω-ester were stretched for one minute and the curves show the extent and rate of recovery from stretch during the first minute after release from

Fig. 7.—x-Ray diffraction pattern of oriented ethylene sebacate.

tension. These curves indicate that the synthetic product is even superior to natural silk, but it is possible that the silk specimen was somewhat deteriorated.
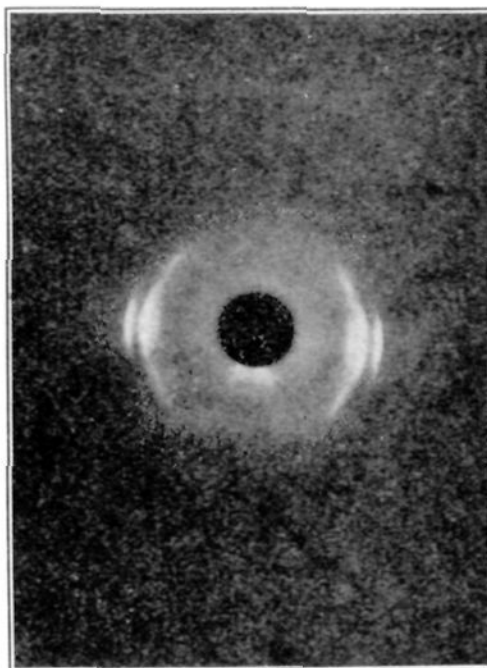
Fibers from Other Linear Condensation Superpolymers.—Fibers closely resembling those described in the preceding section have been obtained in the same way from a variety of other linear condensation polymers in the ω- or superpolymeric state. The polyesters thus far examined are those derived from ω-hydroxydecanoic acid, ω-hydroxypentadecanoic acid, ethylene glycol and sebacic acid, trimethylene glycol and adipic acid, and ethylene glycol and succinic acid. All of these materials clearly exhibit the phenomenon of cold drawing. Wide differences in the nature of the structural unit naturally have a considerable effect on the capacity to form fibers and on some of the properties of the fibers. Thus ethylene succinate in its α-form has a higher melting point and is more brittle than

most other α-polyesters derived from dibasic acids and glycols,[4] and fibers derived from ω-ethylene succinate are somewhat short and brittle.   On the other hand, α-polyesters derived from adipic acid have rather low melting points, and ω-polyesters derived from the same acid show a tendency to collapse at slightly elevated temperature.

Polyamides such as that derived from ϵ-aminocaproic acid can also be got in the superpolymeric state.[5]   Owing to the very high polarity of the amide group and the consequent high molecular cohesion, such polyamides are exceedingly hard and insoluble in most common solvents.   They show signs of melting only at temperatures sufficiently high to produce considerable decomposition.   These refractory qualities make it very difficult to draw satisfactory filaments from pure polyamides.   On the other hand, mixed polyester-polyamides of the type already described[5] yield filaments that are easily cold drawn and, when oriented, have very high tenacity and pliability.
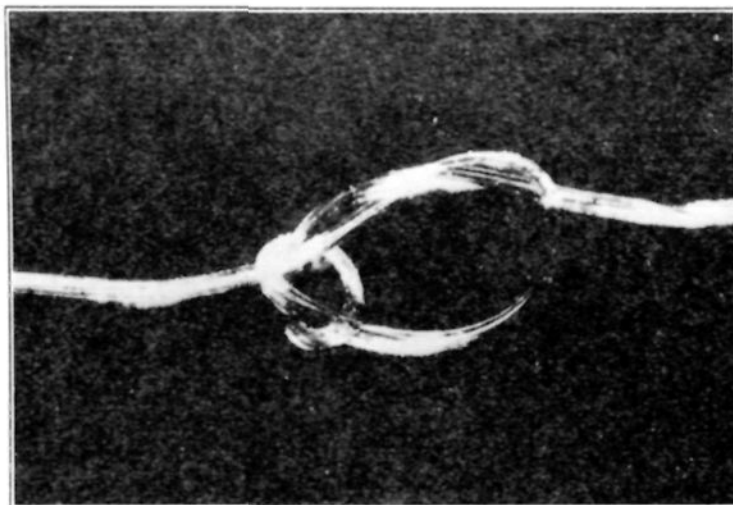

Fig. 8.—Cold drawn fiber from ω-anhydride of decamethylene dicarboxylic acid.   The lack of definition is due to specular reflection caused by high luster.
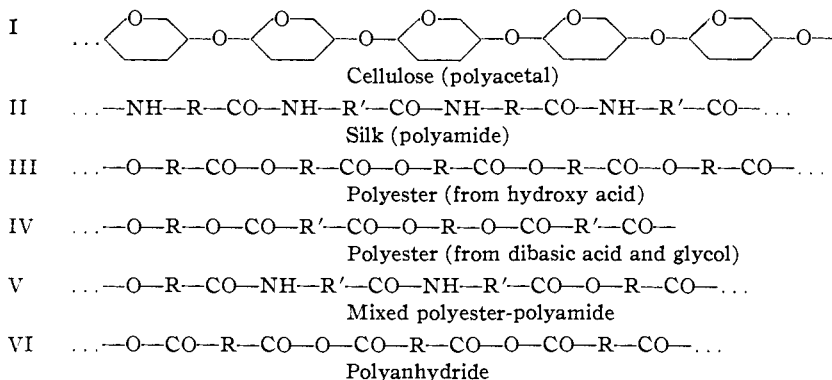
Polyanhydrides derived from dibasic acids of the series $HOOC(CH_2)_x$-$COOH$ are especially easy to obtain in the superpolymeric state.   The technique involved and the nature of the reaction is discussed in detail for sebacic acid ($x = 8$) in paper XIV.   The behavior described there is characteristic (so far as the formation of superpolyanhydride is concerned) for those acids in which x is greater than 4.   (Actual observations thus far include those in which x is 5, 6, 7, 8, 9, 10, 11, 12 and 16.)   The fibers obtained from the anhydrides have an especially high degree of strength, pliability and luster (*cf.* Fig. 8) but they gradually disintegrate on standing owing to hydrolytic degradation.

[4] Carothers and Arvin, THIS JOURNAL, **51,** 2560 (1929).
[5] Paper XIII.

Discussion

Our studies of polymerization were first initiated at a time when a great deal of scepticism prevailed concerning the possibility of applying the usually accepted ideas of structural organic chemistry to such naturally occurring materials as cellulose; and its primary object was to synthesize giant molecules of known structure by strictly rational methods. The use of synthetic models as a means of approach to this problem had already been undertaken by Staudinger, but the products studied by him (polyoxymethylene, polystyrene, polyacrylic acid, etc.) although unquestionably simpler than naturally occurring polymers, were produced by reactions of unknown mechanism, and their behavior, except in the case of polyoxymethylene, was not sufficiently simple to furnish an unequivocal demonstration of their structure. On the other hand, the development of the principles of condensation polymerization described in preceding papers of this series has led to strictly rational methods for the synthesis of linear polymers, and the structures of the superpolymers III to VI follow directly from the methods used in their preparation. Meanwhile the weight of authoritative opinion has shifted; further evidence has been accumulated,[6] and cellulose has been assigned a definite and generally accepted structure.[7] Like the synthetic products III to VI it falls in the class already defined as linear superpolymers.

I   Cellulose (polyacetal)

II   ...—NH—R—CO—NH—R'—CO—NH—R—CO—NH—R'—CO—...
         Silk (polyamide)

III   ...—O—R—CO—O—R—CO—O—R—CO—O—R—CO—...
         Polyester (from hydroxy acid)

IV   ...—O—R—O—CO—R'—CO—O—R—O—CO—R'—CO—
         Polyester (from dibasic acid and glycol)

V   ...—O—R—CO—NH—R'—CO—NH—R'—CO—O—R—CO—...
         Mixed polyester-polyamide

VI   ...—O—CO—R—CO—O—CO—R—CO—O—CO—R—CO—...
         Polyanhydride

Addition polymers of very high molecular weight have been synthesized in the past, but the capacity to yield permanently oriented fibers of any considerable strength has not been observed hitherto. Why is this,

[6] Haworth, Long and Plant, *J. Chem. Soc.*, **129**, 2809 (1927); Freudenberg, *Ber.*, **54**, 767 (1921); *Ann.*, **461**, 130 (1928); Freudenberg and Braun, *ibid.*, **460**, 288 (1929); Freudenberg, Kuhn, Durr, Bolz and Steinbrunn, *Ber.*, **63**, 1528 (1930).

[7] Sponsler and Dore, *Colloid Symposium Monograph*, **4**, 174 (1926). Chemical Catalog Company, New York; Sponsler, *Nature*, **125**, 633 (1930); Meyer and Mark, *Ber.*, **61**, 593 (1928); Mark and Meyer, *Z. physik. Chem.*, [B] **2**. 115 (1929); Mark and Susich, *ibid.*, **4**, 431 (1929).

and what conditions of molecular structure are requisite for the production of a useful fiber? We regret that the limitations of space prohibit a detailed discussion of these and accessory questions, and permit only the baldest statement of our conclusions.
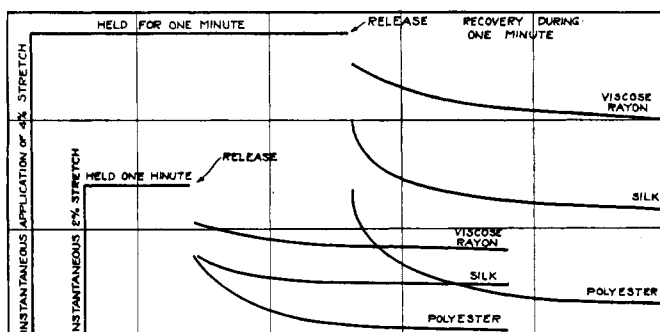

Fig. 9.—Elastic recovery of various fibers.

We picture a perfectly oriented fiber as consisting essentially of a single crystal in which the long molecules are in ordered array parallel with the fiber axis (Fig. 10). (In actual fibers a considerable number of the molecules fail to identify themselves completely with this perfectly ordered structure.) The high strength in the direction of the fiber axis and the pliability are accounted for by the high cohesive forces of the long molecules

Fig. 10.—Lattice from molecules of unequal length.

and by the absence of any crystal boundaries along the fiber axis.[7a] Fiber strength should depend upon molecular length, and recent work by Dr. Van Natta in this Laboratory indicates that it is not possible to spin continuous filaments from the polyester of hydroxydecanoic acid until its molecular weight reaches about 7000. The property of cold drawing does not appear until the molecular weight reaches about 9000. From these and other facts we conclude that a useful degree of strength and pliability in a fiber requires a molecular weight of at least 12,000 and a molecular length not less than 1000 Å. (The limits for polyamides may perhaps lie at somewhat lower values.)

Besides being composed of very long molecules, a compound must be capable of crystallizing if it is to form oriented fibers, and orientation is probably necessary for great strength and pliability. Linear condensation polymers are quite generally crystalline unless bulky substituents are

[7a] Cf. Meyer and Mark, "Der Aufbau der hochpolymeren organischen Naturstoffe," Akademische Verlagsgesellschaft, Leipzig, Germany, 1930.

present to destroy the linear symmetry of the chains; addition polymers, especially those produced from vinyl compounds, are more rarely crystalline. Possible reasons for this have already been discussed in part.[8] Three dimensional polymers are obviously unsuited for fiber orientation, and synthetic materials of this class are besides invariably amorphous. Glyptal resins belong to this class.[9] It has been proposed[10] to use glyptal resins for the production of artificial silk, but our attempts to carry out the proposed process led to exceedingly fragile (though lustrous) threads which showed no signs of orientation when examined by x-rays.

Although one will not expect oriented fibers to arise by any process of spontaneous crystallization under the ordinary conditions, the phenomenon of cold drawing is perhaps only accidentally associated with the capacity to yield oriented fibers; it apparently requires a certain degree of softness and suppleness in the molecules; and its mechanism is doubtless analogous to that involved in the mechanical orientation of cellulose preparations.[11] (Perhaps however, in the unoriented polyesters the molecules are in spiral form and become extended during orientation.)

It has been suggested repeatedly by Staudinger that the great sensitivity of cellulose and rubber to degradation by heat and by certain reagents is due to the fact that the upper limit of thermal stability of the very long molecules lies close to room temperature. It is of interest in this connection that the synthetic linear superpolyesters, in spite of their very high molecular weights, are formed at 200 to 250°, and that they show no signs of being degraded by repeated exposure to elevated temperature.

Acknowledgment

Summary

The linear condensation ω-polyesters, polyanhydrides, and mixed polyester-polyamides described in preceding papers are easily drawn out into very strong, pliable, highly oriented fibers which closely simulate natural silk and cellulose fibers. These materials also resemble cellulose and silk in the essential details of their molecular structure. The significance of these analogies is discussed.

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[8] Carothers, *Chem. Reviews*, **8**, 415 (1931).

[9] Ref. 8, p. 402.

[10] British Patents 303,867 and 305,468.

[11] Ref. 8, p. 418.