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Studies of Polymerization and Ring Formation. XVIII. Polyesters from ω-Hydroxydecanoic Acid

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The obvious importance of simple synthetic models as an aid in studying macromolecular materials has been emphasized repeatedly by Staudinger,[1] who has used polystyrene, polyoxymethylene, polyacrylic acid, etc., for this purpose. Our own researches on condensation polymers were started with the idea that the fact of a proposed model's being synthetic is of little value unless the method of synthesis is rational, *i. e.*, unless it is sufficiently clear-cut to leave no doubt concerning the structure of the product. Polystyrene may, for example, serve as a simplified model of rubber, but it has the disadvantage that the method used in its synthesis (a spontaneous polymerization of unknown mechanism) furnishes no certain clue to its structure. The independent demonstration of its structure presents the same difficulties as does rubber; in fact today the formula of rubber can be written with more assurance than that of polystyrene.

In the first paper of this series[2] it was pointed out that bifunctional condensations frequently proceed by known mechanisms. In the second paper[3] it was shown for polyesters derived jointly from dibasic acids and glycols that the reaction consists exclusively in esterification while the average size of the product molecule increases progressively with the completeness of the reaction. Rational, deliberate control over the average molecular weight is thus made possible, and, as was shown later,[4] by using more drastic conditions molecules of average weight greater than 20,000 can be obtained. Meanwhile a study of the self-esterification of ω-hydroxydecanoic acid was presented by Lycan and Adams,[5] who concluded that the products must be formulated like the polyesters referred to above.

We have now greatly extended the range of polyesters derived from ω-hydroxydecanoic acid and have obtained the series of fractions of different average molecular weights shown in Table I. The structure of these polyesters $HO[—(CH_2)_9CO—O—]_n(CH_2)_9CO—OH$ follows from the method used in their synthesis (see Experimental Part) and the fact that they can be hydrolyzed quantitatively to ω-hydroxydecanoic acid. The only important uncertainty is the distribution, in a given sample, of the molecular weight about the observed average (*i. e.*, the degree of homogeneity). However, since these esters are all crystalline solids and since the mer or unit of the chain is quite long, the homogeneity is probably better than

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(1) Staudinger, "Die hochmolekularen organischen Verbindungen," Julius Springer, Berlin, 1932.

(2) Carothers, THIS JOURNAL, **51**, 2548 (1929).

(3) Carothers and Arvin, *ibid.*, **51**, 2560 (1929).

(4) Carothers and Hill, *ibid.*, **54**, 1559 (1932).

(5) Lycan and Adams, *ibid.*, **51**, 625, 3450 (1929).

in the case of such materials as polystyrene which can be purified only by fractional precipitation or extraction. Moreover, a determination of the molecular weight of the highest member of the series by the Svedberg ultracentrifugal method indicates that the weight of most of the molecules lies fairly close to the observed average. It is indeed our opinion that this series of polyesters is more definitely and certainly established in identity and structure than any similar series of macromolecular compounds yet described.

TABLE I

POLYESTERS FROM ω-HYDROXYDECANOIC ACID

Mol. wt.	M. p., °C.	d_4^{25}	n_D^{85}	Spinnability	Tensile strength
780	66–67	1.0957	1.4494	Absent	
1720	72–74	1.0935	1.4506	Absent	
3190	74–75	1.0877	1.4517	Absent	
4170	74–76	1.0814	1.4517	Absent	
5670	73–75	1.0751	1.4518	Very short fibers. No cold drawing	
7330	74–75	1.0715	1.4517	Long fibers, but cold drawing absent	Very weak
9330	75–76	1.0668	1.4518	Long fibers which cold draw	Very weak
16900	77–78	1.0627	....	Easily spins and cold draws	13.1 Kg./mm.^{2}
20700	77–78	1.0632	....	Spins with difficulty but easily cold draws	12.3 Kg./mm.^{2}
25200	75–80	1.0621	1.4515	Spins above 210° and cold draws	7.0 Kg./mm.^{2}

TABLE II

MOLECULAR WEIGHTS OF POLYESTERS

Observed mol. wts. (by titration)			Average	Observed mol. wts. (by other methods)	Calculated length of molecule in Å.
776	784		780	930 (in boiling benzene)	60
1707	1722		1720	1620 (in boiling benzene)	123
3188	3201		3190	Not measured	188
4114	4226		4170	Not measured	313
5626	5717		5670	Not measured	440
7327	7329		7330	Not measured	570
9331	9335		9330	Not measured	730
16890	17110	16790	16900	Not measured	1320
20380	20930		20700	Not measured	1610
24240	25760	25660	25200	26700 (ultracentrifuge)	1970

Molecular Weights.—Molecular weights were estimated by titration with standard alcoholic potash of the polyesters dissolved in a chloroform–alcohol mixture. Phenolphthalein was used as an indicator. This method applied to pure lauric acid gave values agreeing sharply with the theoretical (200.4, 199.6 and 199.2 as against 200.2). Observed values for the polyesters are shown in Table II. It is interesting to note that no difficulty was encountered in titrating the highest member of the series where the acid hydrogen is only one part in 25,000.

The average equivalent weight measured by titration will of course be identical with the average molecular weight only if each molecule bears a terminal carboxyl in the manner required by the indicated structure.

The accidental loss of terminal carboxyls under the conditions of preparation used seems rather improbable, but indication of the absence of such loss is provided by independent estimations of molecular weight. The boiling point method furnished values for the first two members agreeing, within the probable experimental error, with the much more sharply reproducible values determined by titration. For compounds above molecular weight 3000, in our experience, boiling-point or freezing-point methods are not self-consistent within 10%, and above 10,000 they are practically worthless. We were, however, very fortunate in being able to obtain a value for the highest polymer by the Svedberg ultracentrifugal method.[6] The agreement is all that could be desired.

Physical Properties.—The polyesters below 10,000 dissolve rapidly and completely in cold chloroform or benzene and in hot acetone, ethyl acetate and acetic acid. They are practically insoluble in hot alcohol, ligroin or water. The highest members show diminished solubility in benzene and in hot acetone and ethyl acetate. They dissolve copiously in chloroform, but solution occurs only slowly and is preceded by some swelling. At *ca.* 110° the first member of the series is a highly viscous liquid while the highest member is a transparent resin that is too stiff to flow and sufficiently elastic to offer resistance to permanent deformation.

Lycan and Adams have pointed out[5] that the melting point of self-esters of hydroxydecanoic acid increases with increasing molecular weight up to 1000, but changes little between 1000 and 9000. As the data of Table I show, there is also no further increase between 9000 and 25,000. The polyesters separate from solution in the form of white powders which give sharp x-ray powder diffraction patterns. At least in the lower members of the series crystallinity can also be demonstrated by microscopic observation. A very dilute solution of the 3190 ester in butyl acetate, when examined at a magnification of 400, showed the separation of tiny flat glittering plates. The molten esters in thin layers crystallize very rapidly, but with the lower members one can observe the crystallization to start with the emergence and growth of innumerable doubly refracting centers, apparently spherulites. At a magnification of 900 the growth appears to involve the intermeshing of radiating clusters of needles.

The masses resulting from crystallization of the molten polyesters are opaque solids. The lower members are waxy and brittle; when fractured they show no planes of cleavage. The highest members are harder and so horny and tough that they can scarcely be fractured.

In Table I are listed the densities of the solid esters at 25°. The values *diminish* as the molecular weight rises, quite rapidly at first and then more slowly until at a molecular weight of 16,900 they become almost constant.

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(6) Kraemer and Lansing, THIS JOURNAL, **55**, 4319 (1933).

This at first sight is very surprising. Polymerization usually involves an increase in density. There is, for example, an increase of 23% in passing from chloroprene to polychloroprene.[7] The interpretation of the present case can scarcely be attempted in the absence of data on the molten esters, which are not yet available; but it is easy to imagine that the longer the molecules are the more difficulty they will have in lining themselves up perfectly in the crystal lattice. The refractive indices of the molten esters at 85° are presented in Table I. There is a slight increase from 780 to 1720, a smaller increase from 1720 to 3190, and beyond that no further change.

Fiber Formation.—In a previous paper[8] it was shown that linear polyesters of molecular weight above 10,000, when melted or dissolved, can be spun into fibers. The initial filaments are opaque and fragile, but when stress is applied to them they are readily elongated several fold and then remain *permanently extended*. The stretching is accompanied by a loss of opacity, and an enormous increase in tensile strength and pliability. Examination by x-rays shows the presence of fiber orientation.

These fibers are, we believe, the first examples of a synthetic material being obtained in the form of fibers having any considerable degree of strength, orientation and pliability. The analogies in chemical structure with cellulose and silk are especially interesting, and the esters of the present paper provide some data (Table I) on the relation between molecular weight and fiber-forming ability. Until a molecular weight of 5670 is reached, the viscosity and coherence of the molten esters are so low that they do not yield continuous filaments. The ester of molecular weight 7330 furnished continuous filaments which, however, could not be stretched and oriented. The 9330 ester could be stretched, but the oriented fibers were too weak to permit the determination of tensile strength. Oriented fibers from the 16,900 ester had a tensile strength of 13.1 kg./sq. mm. or 1.36 g. per denier, which is in the same range as good regenerated cellulose fibers. The value for the 20,700 ester (12.3 kg./sq. mm.) differs from that for the 16,900 ester by an amount that probably lies within the experimental error. The tensile strength of the 15,200 ester is, however, definitely much lower. It is exceedingly improbable that the fiber strength of completely oriented molecules rises to a maximum and then falls off as the length of the molecule increases. On the other hand, the degree of orientation that can be produced by cold-drawing probably depends upon other factors besides molecular weight. An unusually high temperature (210°) was required to soften the 25,200 ester sufficiently to permit spinning, and its relatively low tensile strength may therefore reasonably be ascribed to factors associated with orientation. It may be observed that the ability to form strong, highly oriented fibers does not appear until the molecular length reaches some value lying between 700 and 1300 Å.

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[7] Carothers, Williams, Collins and Kirby, THIS JOURNAL, **53**, 4203 (1931).

[8] Carothers and Hill, *ibid.*, **54**, 1579 (1932).

Viscosity and Other Properties.—The viscosities of dilute solutions of these polymers in tetrachloroethane have been carefully measured. The results already reported and discussed[9] show that Staudinger's simple empirical equations relating viscosity to molecular weight[1] are satisfied fairly well until the molecular weight reaches 16,900; beyond this point the viscosities rise more rapidly than the equations require. Staudinger has assumed that the relations between viscosity and molecular weight established for compounds below 10,000 will hold for compounds of higher molecular weight. The data referred to above provide the first experimental test of this assumption, and for the polyesters under consideration it is shown to be not strictly valid. Molecular weights that have been assigned to cellulose, rubber, high polystyrenes, etc., on the basis of viscosity measurements must therefore be considered as subject to considerable uncertainty.

Study of the physical properties of polyesters derived from hydroxydecanoic acid is being continued, and further results will be reported in future papers.

Experimental Part

Preparation of Polyesters.—The lowest members of the series were obtained by heating ω-hydroxydecanoic acid at 150° in an ordinary distilling flask provided with a receiver. Diminished pressure and higher temperatures were used for higher members of the series; the highest members (above 10,000) were obtained by heating the hydroxydecanoic acid or its lower polyesters in a molecular still consisting essentially of a suction flask into which a water-cooled test-tube was inserted to act as a condenser. The products were crystallized several times to increase their homogeneity. Typical procedures are indicated below.

Polyester of Molecular Weight 4170.—Twenty grams of the acid was heated at 150–175° under atmospheric pressure for one and one-half hours, then at 200° at 1 mm. pressure for eight hours. The resulting waxy product was crystallized by dissolving in a small amount of boiling chloroform and adding several volumes of hot acetone. The product had an apparent equivalent weight of 3906. A second crystallization from hot acetone by slow cooling raised the equivalent weight to 4170. The ester was obtained as a chalky powder, soluble in chloroform and benzene and in hot acetone, ethyl acetate and acetic acid. Hot alcohol, ligroin or water did not dissolve it appreciably.

Anal. Calcd. for $HO—[(CH_2)_9—CO—O]_{24}—H$: C, 70.22; H, 10.66; mol. wt. 4101; saponification equivalent, 170.8. Found: C, 70.35, 70.70; H, 10.69, 10.88; mol. wt. by titration, 4114, 4226; saponification equivalent, 170.7.

Polyester of Molecular Weight 9330.—Thirty-six grams of the acid was heated for seven hours at 120–175° at 1 mm. pressure, then for twenty-five hours at 225° at 1 mm. It was crystallized several times from hot acetone by slow cooling and was obtained as a pure white powder. It did not differ appreciably from polymer 4170 in solubility.

Anal. Calcd. for $HO—[(CH_2)_9—CO—O]_{55}—H$: C, 70.39; H, 10.66; mol. wt. 9376; saponification equivalent 170.5; Found: C, 70.56; H, 10.87; mol. wt. by titration: 9335, 9331; saponification equivalent 169.6.

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(9) Kraemer and Van Natta, *J. Phys. Chem.*, **36**, 3175 (1932).

Polyester of Molecular Weight 20,700.—Fifteen grams of hydroxydecanoic acid was heated at 230° in a molecular still for thirty hours. During the first few hours a considerable amount of distillate (dimer and unchanged acid) collected on the condenser. This was removed and the residue in the flask was stirred frequently. At the end of the reaction the mass was plastic when hot. It was purified by dissolving in a small amount of hot chloroform, then adding several volumes of acetone and allowing the product to crystallize by cooling. This polymer was less soluble than lower members in benzene or in hot acetone or ethyl acetate. Solution was slow and was preceded by some swelling.

Anal. Calcd. for $HO—[(CH_2)_9—CO—O]_{121}—H$: C, 70.47; H, 10.66; mol. wt. 20,605; saponification equivalent 170.3. Found: C, 70.72, 70.29; H, 10.62, 10.47; mol. wt. by titration, 20,380, 20,930; saponification equivalent 170.8.

Saponification of the polyesters by alcoholic alkali always resulted in complete solution, indicating the absence of any appreciable amount of non-ester ingredient, and the following experiment showed that the product of saponification was the initial hydroxydecanoic acid: 0.3097 g. of the 13,600 polyester was saponified with alcoholic sodium hydroxide; the alcohol was removed and the solution was acidified and extracted with ether. Evaporation of the ether yielded 0.34 g. (99.3% of the theoretical amount) of hydroxydecanoic acid.

During the preparation of the polyesters a small amount of the cyclic dimeric lactone, a 22-membered ring $O—(CH_2)_9—CO—O—(CH_2)_9—CO$, was always formed. It was obtained in the form of needles from dilute alcohol; m. p. 95–96°.

Anal. Calcd. for $C_{20}H_{36}O_4$: C, 70.58; H, 10.67. Found: C, 70.07, 70.04; H, 10.53, 10.55.

This lactone has already been prepared by Lycan and Adams[6] indirectly from the potassium salt of hydroxydecanoic acid and acetic anhydride followed by dry distillation at 400–500°.

Summary

A series of polyesters prepared from ω-hydroxydecanoic acid and ranging in molecular weight from 780 to 25,200 is described. Strong, oriented fibers are obtained only from members having molecular weights above 9330. The influence of molecular weight on some other physical properties is discussed.

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