

board inserted below the distilling pan. The heater leads (F) are brought up through the support (C) and out as shown. Connection with the heater is made with spring clamps which make the heater readily demountable. The lower part of the apparatus is the regular distilling tube provided with the Pyrex vacuum distilling apparatus (Catalogue No. 56). The rubber stoppers at the top and bottom of the apparatus are well covered with a suitable wax such as picein. A thermocouple (not indicated in the drawing) is led in through the lower wax seal and the junction placed under the pan (E). The slight bulges on the condenser and the pan support where they enter the apparatus are necessary to obviate the danger of these parts sucking in when the apparatus is evacuated.

Summary

In reversible reactions involving the simultaneous formation of volatile and non-volatile products, the use of molecular evaporation makes it possible to realize chemical effects that cannot be achieved with the aid of the usual distillation equipment. A new design of molecular still is described.

WILMINGTON, DELAWARE

[COMMUNICATION NO. 75 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

STUDIES OF POLYMERIZATION AND RING FORMATION. XII. LINEAR SUPERPOLYESTERS¹

BY WALLACE H. CAROTHERS AND JULIAN W. HILL

RECEIVED NOVEMBER 12, 1931

PUBLISHED APRIL 6, 1932

In previous papers we have described polyesters having molecular weights ranging from 800 to 5000 derived from dibasic acids of the series $\text{HOOC}(\text{CH}_2)_x\text{COOH}$ and glycols of the series $\text{HO}(\text{CH}_2)_y\text{OH}$.² These esters are microcrystalline solids that dissolve readily in appropriate solvents. Their solutions are not highly viscous and they show no signs of inherently colloidal behavior. In the present paper we describe polyesters of the same series having much higher molecular weights. They exhibit colloidal behavior and simulate to a remarkable degree some of the properties of certain naturally occurring high polymers. For the sake of brevity and convenience we use the designation α -ester or α -form for the polyesters having molecular weights ranging from 800 to 5000 and the designation ω -ester or ω -form for the new superpolyesters.

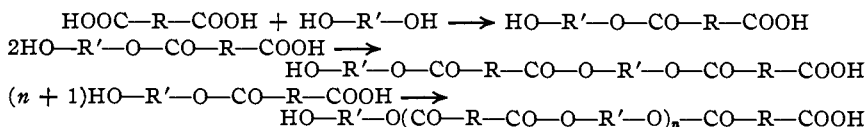
Nature of the Polyesterification.—The mutual esterification of dibasic acids and dihydric alcohols is a bifunctional reaction.³ As such it presents

¹ The term "superpolymer" is applied to linear polymers having molecular weights above 10,000.

² (a) Carothers and Arvin, *THIS JOURNAL*, **51**, 2560 (1929); (b) Carothers and Van Natta, *ibid.*, **52**, 314 (1930); (c) Carothers and Dorough, *ibid.*, **52**, 711 (1930); (d) Carothers, Arvin and Dorough, *ibid.*, **52**, 3292 (1930).

³ Carothers, *ibid.*, **51**, 2548 (1929).

the formal possibility of yielding (1) cyclic monomeric esters, (2) cyclic polyesters, and (3) open-chain polyesters. Studies already reported have proved that the first possibility is ordinarily realized only in those comparatively rare instances where the nature of the starting material permits the formation of a ring of five or six atoms. Otherwise reaction generally is intermolecular and the product is of the third type. The polyesterification thus consists in a series of intermolecular couplings resulting in the formation of progressively longer chains as indicated by way of illustration in the following equations.



The reaction is reversible and an exceedingly large number of entities are involved in the ester equilibrium. The equilibrium can be displaced by the removal of the liberated water, and the more nearly complete the reaction the longer are the molecules of the polyester product. The reaction becomes formally complete when all the molecules of the initial reactants are combined into a single molecule.

A complicating circumstance arises from the fact that the glycol and the acid need not react in precisely equivalent ratio: at any particular stage n molecules of acid may be involved with $n + 1$ molecules of glycol or, conversely, n molecules of glycol may be involved with $n + 1$ molecules of acid. In the former case the product molecules will bear hydroxyl groups at both ends; in the latter they will bear carboxyl groups at both ends. In either event no further progress is possible by esterification. Under favorable conditions, however, coupling may continue nevertheless. Two molecules may unite by a process of ester interchange involving their terminal ester linkages. This mechanism is realized experimentally² when di-(β -hydroxyethyl)-succinate (I) is heated *in vacuo*. Glycol is liberated

$$\text{(I) HO(CH}_2)_2\text{OCO(CH}_2)_2\text{COO(CH}_2)_2\text{OH} + \text{HO(CH}_2)_2\text{OCO(CH}_2)_2\text{COO(CH}_2)_2\text{OH} \longrightarrow \text{HO(CH}_2)_2\text{OCO(CH}_2)_2\text{COO(CH}_2)_2\text{OCO(CH}_2)_2\text{COO(CH}_2)_2\text{OH} + \text{HO(CH}_2)_2\text{OH, etc.}$$

and the final product of prolonged heating is the same as one obtained by similarly heating succinic acid with a very small excess of glycol.

The only factor that could theoretically preclude the possibility of producing exceedingly long molecules as the result of bifunctional esterifications is the loss of terminal groups through ring formation. Since in the polyesters thus far examined the terminal groups are still present, it appears that such ring formation does not occur.⁴

⁴ Valuable indications in this connection are furnished by Lycan and Adams' studies [THIS JOURNAL, 51, 625, 3450 (1929)] of the polyesters derived from ω -hydroxydecanoic acid. We should add that our generalization to the effect that no intramolecular reaction occurs in bifunctional esterifications involving compounds whose

Another factor that might be expected to have the same effect is the mutilation of terminal groups, *e. g.*, through the loss of carboxyl as carbon dioxide. But our experience indicates that the loss of terminal groups in this fashion occurs only when patently inappropriate conditions are adopted. More important than this is the fact demonstrated by the behavior of di-(β -hydroxyethyl)-succinate cited above that the coupling can progress through a process of ester interchange involving the last ester linkage. The possibility of further coupling therefore does not absolutely depend upon the integrity of the terminal groups as such.

As a matter of fact, however, as such reactions have been carried out in the past an apparent limit is reached at a comparatively low molecular weight. Thus the glycol and the acid are heated together in a distilling flask provided with a receiver to collect the liberated water, and heating is finally continued at low pressure and considerably elevated temperature. The molecular weight of the polyester product increases during the progress of the heating and finally reaches a value of 3000 to 5000. This value is not noticeably increased if the period of heating is greatly prolonged.

We ascribe the failure of the reaction to progress further under these conditions to the following factors. The concentration of reactive (terminal) groups in esters having molecular weights as high as 3000 is rather low; moreover, such esters are very viscous even at a temperature of 200°. This implies a restricted mobility of the molecules, and a low rate of diffusion of the volatile products to the surface. Beyond this, macromolecular materials, perhaps because of their exaggerated molecular cohesions,⁵ have a very powerful tendency to retain dissolved or adsorbed liquids or vapors—several days' heating in high vacuum are required to remove benzene completely from macromolecular polystyrenes or water from resinous esters. All these factors affect either the position of the equilibrium or the rate at which the equilibrium is approached, and one may suppose that if some more drastic and effective means could be found for the removal of water or other volatile reaction products, it would be possible to force the reaction further.

Methods of Producing Superpolyesters.—The molecular still, first used by Brönsted and Hevesy⁶ for the separation of the isotopes of mercury and later by Washburn⁷ for the separation of petroleum hydrocarbons, provides a means for continuously displacing physical equilibria involving structural units are longer than seven atoms is not altogether free from exceptions. Dr. Van Natta of this Laboratory in preparing polyesters of ω -hydroxydecanoic acid has recently observed the formation of appreciable amounts of the dimeric lactone already obtained by Lycan and Adams by a different method.

⁵ Dunkel, *Z. physik. Chem., Abt. A*, **138**, 42 (1928).

⁶ Brönsted and Hevesy, *Phil. Mag.*, **43**, 31 (1922).

⁷ Washburn, *Bur. Standards J. Research*, **2**, 476 (1929); see also Burch, *Proc. Roy. Soc. (London)*, **123**, 271 (1929); and Hickman, *Chem. Ind.*, **48**, 365 (1929).

very minute vapor pressures, and the application of this to the chemical equilibrium under consideration led to the desired result.

Some of the experiments described below were made in stills of the type described by Washburn⁷ and others in a modified still described in the preceding paper,⁸ where the principles involved are also briefly discussed.

For reasons of a theoretical nature that need not be discussed, our first experiments were made with an ester which has not been described previously, namely, the trimethylene ester of hexadecamethylene dicarboxylic acid. This was obtained from the acid and the glycol by the method used for other α -polyesters.^{2a}

It was then placed in the molecular still and heated by a bath at 200° for a total time of twelve days. During the first seven days a small amount of distillate collected on the condenser. No distillate was observed during the remaining five days. The viscosity of the molten polyester increased progressively during the heating, and the final product showed an apparent molecular weight of about 12,000.

The same treatment applied to ethylene succinate, ethylene sebacate, and to polyesters derived from ω -hydroxydecanoic acid and from ω -hydroxypentadecanoic acid, led to similar transformations.

A part of the effect of the molecular still treatment is evidently due to the greatly prolonged time of heating, and it was found later that a similar, if somewhat less pronounced, effect could be produced by merely heating polyesters such as ethylene sebacate in thin layers at ordinary pressure in a stream of nitrogen for a long period of time, or by bubbling a stream of nitrogen through the molten polyester.

Physical Properties of Superpolyesters.—Linear α -polyesters are microcrystalline powders (in certain cases resins) that dissolve readily in certain solvents such as cold chloroform and yield solutions which are quite mobile. The crystalline esters melt fairly sharply and when molten they are exceedingly viscous. On cooling they solidify to opaque masses which range from rather hard, brittle, porcelain-like masses to soft, waxy solids as the length of the polymethylene chain in the acid or glycol from which they are derived increases.

The superpolyesters in the massive state are harder and much tougher. They also dissolve in cold chloroform but the process is slow; they first imbibe solvent and swell, and their solutions are highly viscous. They separate from solution as more or less coherent powdery or curdy masses. When heated they melt at approximately the same temperatures as the α -polyesters from which they are derived. The phenomena associated with the melting, however, are quite different from those observed in the α -polyesters. The solid ester at the melting point suddenly becomes transparent, but it does not lose its shape; a tendency to flow appears only at a

⁸ Paper XI.

considerably higher temperature. In the solid state the superpolyesters furnish sharp x-ray powder diffraction patterns that closely resemble similar patterns obtained from the corresponding α -polyesters. At a temperature a few degrees below the melting point the patterns lose their sharpness. At the melting point the pattern is a diffuse halo characteristic of a liquid. The most remarkable property of the superpolyesters is their capacity to be drawn out into very strong, pliable, highly oriented fibers, and this is discussed in detail in a subsequent paper.⁹

By way of summary, the properties of the α - and ω -polyesters from trimethylene glycol and hexadecamethylene dicarboxylic acid are listed in Table I. Similar relations exist between the α - and the ω -forms of other polyesters. One curious property of the ω -esters deserves special mention. They adhere very firmly to the glass vessel (in the molecular still) in which they are prepared, and the force of contraction during cooling often causes the vessel to be completely shattered if the layer of ester is more than two or three millimeters thick.

TABLE I
PROPERTIES OF α - AND ω -POLYESTERS FROM TRIMETHYLENE GLYCOL AND HEXADECAMETHYLENE DICARBOXYLIC ACID

	α -Ester	ω -Ester
Apparent mol. wt.	3000	12,0000
At 100° C.	Viscous liquid	Soft, sticky resin
At room temperature	White, opaque, brittle wax; d_{20}^{20} 1.061	Cream colored, opaque, horny, elastic; d_{20}^{20} 1.058
Melting point, °C.	75-76	Becomes transparent at 75, but does not flow
Solubility	Very soluble in cold CHCl_3 . Readily soluble in hot ethyl acetate; separates on cooling as a micro- crystalline powder	Swells in cold CHCl_3 , then dissolves. Swells and slowly dissolves in hot ethyl acetate; separates on cooling as a white, amorphous, curdy pre- cipitate
Relative viscosity of 7.3% weight solution in chloro- form (chloroform, 2.16 seconds = 1 unit)	8.6 units	166 units

Structure of the ω -Polyesters

The simplest and most reasonable assumption concerning the superpolyesters is that they are formed by a continuation of the same bifunctional esterification that first results in the formation of the α -polyesters, and that they are exceedingly long polymeric chains bearing hydroxyl or carboxyl groups at the ends. Their physical, chemical and analytical behavior is completely consistent with this assumption, but no actual data

⁹ Paper XV.

on the presence of terminal groups are yet available. The average length of the molecules also is still very uncertain. The molecular weights quoted in Table I were obtained by ebullioscopy and in view of the fact that the observed elevations did not greatly exceed the experimental error they can be accepted as signifying only that the molecular weights are quite large—at least as high as 10,000. Comparison of physical properties indicates that molecular weights of the ω -polyesters probably lie in the neighborhood of 20,000. Further work on the determination of the molecular weights of the superpolyesters is in progress.

ω -Trimethylene Ester of Hexadecamethylene Dicarboxylic Acid.—This ester was obtained in its α -form by heating the acid together with a 10% excess of the glycol in a distilling flask at 180–200° for three hours, and then heating the residue to 200° for six hours at a pressure less than 1 mm. It was thus obtained in the form of a very viscous liquid which on cooling solidified to a hard, waxy mass. It was readily soluble in cold chloroform and in hot ethyl acetate, from which it separated on cooling as a white microcrystalline powder. It melted rather sharply at 75–76°. Its apparent molecular weight was about 3300.

Anal. Calcd. for $-\text{O}-(\text{CH}_2)_3-\text{O}-\text{CO}-(\text{CH}_2)_{16}-\text{CO}- = \text{C}_{21}\text{H}_{38}\text{O}_4$: C, 71.13; H, 10.81; saponification equivalent, 177.2; mol. wt. 354.3. Calcd. for $\text{H}(-\text{O}-(\text{CH}_2)_3-\text{O}-\text{CO}-(\text{CH}_2)_{16}-\text{CO}-)_{10}-\text{O}(\text{CH}_2)_3-\text{OH} = \text{C}_{213}\text{H}_{358}\text{O}_{42}$: C, 70.63; H, 10.80; saponification equivalent, 181; mol. wt. 3619. Found: C, 70.34, 70.40; H, 10.60, 10.69; saponification equivalent, 175.2; mol. wt. (in boiling benzene), 3600, 3200.

A sample (8.5 g.) of this recrystallized ester was placed in a molecular still of the type described by Washburn.¹⁰ The condenser was cooled with running tap water, and a trap between the mercury diffusion pump and the still was cooled with liquid air. The still was heated by means of a metal bath kept at about 200°. The pressure of the system as measured by a McLeod gage between the trap and the pump was always less than 10^{-6} mm. Heating was continued for seven days. During the first two days of heating, 0.4 g. of distillate collected on the condenser. This was removed and the heating of the residue was continued for five days more. No distillate collected during this period.

The analytical composition and the saponification equivalent of the residual ester were the same as those of the starting material. Its molecular weight, however, was much greater.

Anal. Calcd. for $-\text{O}-(\text{CH}_2)_3-\text{O}-\text{CO}-(\text{CH}_2)_{16}-\text{CO}- = \text{C}_{21}\text{H}_{38}\text{O}_4$: C, 71.13; H, 10.81; saponification equivalent, 177.2; mol. wt. 354.3. Calcd. for $\text{H}(-\text{O}-(\text{CH}_2)_3-\text{O}-\text{CO}-(\text{CH}_2)_{16}-\text{CO})_{34}-\text{O}-(\text{CH}_2)_3-\text{OH} = \text{C}_{717}\text{H}_{1300}\text{O}_{258}$: C, 70.89; H, 10.83; saponification equivalent, 178.2; mol. wt., 12,122. Found: C, 70.38, 70.52; H, 10.56; 10.53; saponification equivalent, 178.4; mol. wt. (in boiling benzene) 12,100.

The distillate was not homogeneous. By crystallizing it from alcohol there was obtained an apparently homogeneous fraction composed of needles melting sharply at 124–125°. It depressed the melting point of hexadecamethylene dicarboxylic acid (which melts at 122–123°) and was neutral. A single ultimate analysis indicated that it was possibly a monomeric form of the trimethylene ester of hexadecamethylene dicarboxylic acid.

Anal. Calcd. for $\text{O}-(\text{CH}_2)_3-\text{O}-\text{CO}-(\text{CH}_2)_{16}-\text{CO}$; C, 71.13; H, 10.81. Found: C, 70.06; H, 10.63.

¹⁰ Washburn, *Bur. Standards J. Research*, **2**, 480 (1929).

A sample of the α -ester and heated at 200–250° for thirty-two hours with a current of dry nitrogen bubbling through the molten mass. The viscosity of the molten polymer increased very greatly and the product exhibited the phenomenon of cold-drawing described in paper XV.

ω -Polyethylene Succinate.—A sample of polyethylene succinate having the approximate formula $\text{HO}-(\text{CH}_2)_2-\text{O}(\text{CO}-(\text{CH}_2)_2-\text{CO}-\text{O}-(\text{CH}_2)_2-\text{O})_{21}-\text{H}^{11}$ was heated in the molecular still as described above for the trimethylene ester of hexadecamethylene dicarboxylic acid. From the very small amount of distillate no homogeneous fraction could be isolated. The residue was a tough, horny, somewhat elastic mass (the original material was hard, brittle, rather porcelain-like). On being heated to 97° it softened to a very viscous and somewhat rubbery mass. Fibers prepared from this material were short and rather brittle.

Anal. Calcd. for $\text{C}_8\text{H}_{16}\text{O}_4$: C, 50.00; H, 5.50. Found: C, 50.30; H, 5.70.

ω -Polyester from ω -Hydroxydecanoic acid.— ω -Hydroxydecanoic acid was prepared by the method of Lycan and Adams.¹² Five grams was heated under a moderate vacuum for ten hours to bring about incipient polymerization. If this is neglected and the acid heated directly in the molecular still, it distills practically completely before polymerization sets in. The material after the preliminary heating was transferred to the molecular still and heated at 150° for twenty-four hours. Two and four-tenths grams of distillate (m. p. 60–65°) collected. This was not further examined. The residue was a hard brittle wax which was heated for four days more at 150° and then at 200° for two days. The final residue was a light gray, translucent, tough, flexible mass. On being heated it suddenly became transparent at 65° but did not lose its shape. At higher temperatures it could easily be drawn into threads which could be cold drawn.

Microscopic Observation at a Magnification of 180 Diameters.—A thin hazy film was obtained by placing a small specimen of the ester on a slide and covering it with a cover glass. Between crossed nicols the field appeared as an aggregate of very small, irregular anisotropic particles, each of which showed two extinction positions. The slide was then warmed to melt the ester and the cover glass moved about 5 mm. The middle region of the specimen when cold was now transparent and homogeneous; the surrounding portions were unchanged. This effect is apparently due to the action of stress in moving the slide. The transparent section showed brilliant interference colors between crossed nicols and extinction parallel and normal to the direction of the stress applied.

Anal. Calcd.: C, 70.59, H, 10.59. Found: C, 70.24, 70.21; H, 10.74, 10.79; mol. wt. in boiling ethylene chloride, 24,600.

ω -Ester from ω -Hydroxypentadecanoic Acid.—One gram of "exaltolide" (the lactone of ω -hydroxypentadecanoic acid) was refluxed with 0.5 g. of sodium hydroxide in 12 cc. of water and 5 cc. of alcohol for five hours. The solution was evaporated to dryness on a steam-bath, dissolved in 450 cc. of water, acidified with dilute sulfuric acid, and extracted with ether. The ether solution was dried over magnesium sulfate, filtered, and evaporated to dryness; yield, 1.075 g. The product was recrystallized from benzene; m. p. 83–84°. The acid was put in the molecular still and heated overnight at 150°. It distilled completely except for a very small residue of hard wax. The distillate was heated for six hours at 150° at 1 mm. and again placed in the still and heated for seven days. A small amount of distillate which melted at 70–75° was not further examined.

The residue consisted of 0.65 g. of a flexible, translucent mass. It became transparent at 95°, yielding a stiff mass which held its shape up to 200°. It could be drawn into thin fibers and cold drawn.

¹¹ Carothers and Dorough, *THIS JOURNAL*, **52**, 711 (1930).

¹² Lycan and Adams, *ibid.*, **51**, 625 (1929).

Ethylene Sebacate.—101 g. (0.5 mole) of sebacic acid and 32.5 g. (0.525 mole) of ethylene glycol were heated together at atmospheric pressure in a Claisen flask at 175°.

The aqueous distillate was discarded. The residue was then heated at 250° for five hours at 2 mm. pressure. The light gray-buff product was a hard wax. Threads drawn from the molten ester, if pulled immediately while still warm, yielded transparent fibers. The product after recrystallization from ethyl acetate melted at 75° (copper block) and still exhibited the cold drawing phenomenon; molecular weight by cryoscopic method in benzene, 4800, 6000.

Summary

By prolonged heating in a molecular still or in a stream of inert gas, the previously described linear polyesters derived from dibasic acids and glycols or from higher ω -hydroxy acids are caused to react with themselves to produce polyesters of much higher molecular weight. The new superpolyesters (ω -polyesters) are tough, opaque solids which exhibit sharp x-ray powder diffraction patterns and become transparent at a definite temperature. They dissolve in chloroform to form highly viscous solutions. The mechanism of the reaction is discussed.

WILMINGTON, DELAWARE

[COMMUNICATION No. 76 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

STUDIES OF POLYMERIZATION AND RING FORMATION. XIII. POLYAMIDES AND MIXED POLYESTER-POLYAMIDES

BY WALLACE H. CAROTHERS AND JULIAN W. HILL

RECEIVED NOVEMBER 12, 1931

PUBLISHED APRIL 6, 1932

Above its melting point ϵ -aminocaproic acid undergoes dehydration with the simultaneous formation of two different products.¹ One of these is the cyclic lactam, a seven-membered ring. The other is a polyamide having the formula



This compound is analogous to the polyesters obtained by the self-esterification of higher hydroxy acids or by the action of glycols on dibasic acids. The binding atom between the units in the case of the esters is —O— and in the case of the polyamide —NH—. In comparison with the esters the polyamide is harder, tougher, less easily fusible and much less soluble. The difference lies in the direction required by the much higher molecular cohesions of amides as compared with esters.²

The polyamide prepared by dehydration of the amino acid at atmospheric pressure or under diminished pressure in the usual distillation equipment has an apparent molecular weight of about 1000 (the actual value probably

¹ Carothers and Berchet, *THIS JOURNAL*, **52**, 5289 (1930); Gabriel and Maass, *Ber.*, **32**, 1266 (1899); Braun, *ibid.*, **40**, 1835 (1907).

² Dunkel, *Z. physik. Chem., Abt. A*, **138**, 42 (1928).