

indicating an increase in molecular weight. By heating together  $\epsilon$ -aminocaproic acid with hexadecamethylene dicarboxylic acid and trimethylene glycol, mixed polyester-polyamides are obtained. These materials in their physical properties lie between the polyesters and the polyamides and like the superpolyesters described in the preceding paper they can be drawn out into strong, pliable, transparent fibers.

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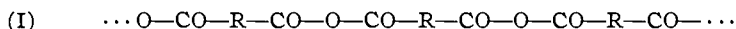
### STUDIES OF POLYMERIZATION AND RING FORMATION. XIV. A LINEAR SUPERPOLYANHYDRIDE AND A CYCLIC DIMERIC ANHYDRIDE FROM SEBACIC ACID

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In a previous paper<sup>1</sup> it has been shown that adipic anhydride as ordinarily prepared is a linear polymer of the type formula represented by I and that under the action of heat *in vacuo* it is broken down to the cyclic monomer, a seven-membered ring.



Observations have now been extended to sebacic anhydride, and it is shown that the anhydride ( $\alpha$ -anhydride) prepared by the action of acetic anhydride or acetyl chloride on sebacic acid is also polymeric. No smooth depolymerization of this polymer can be effected under ordinary conditions, but in the molecular still<sup>2</sup> at elevated temperatures two processes occur simultaneously. The  $\alpha$ -anhydride is transformed into a polyanhydride of much higher molecular weight ( $\omega$ -anhydride) and at the same time depolymerization occurs with the formation of a crystalline product ( $\beta$ -anhydride), which is shown to be not the eleven-membered cyclic monomer, but the twenty-two membered cyclic dimer. At its melting point the dimer reverts to a higher polymer ( $\gamma$ -anhydride). The anhydrides of different origins are arbitrarily assigned the prefixes  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\omega$  to designate them for the purposes of discussion.

**Sebacic  $\alpha$ -Anhydride.**—Voerman<sup>3</sup> obtained this as a microcrystalline solid melting at 74.5° by the action of acetyl chloride on sebacic acid. He seemed unable to decide whether to regard it as monomeric or polymeric. Compared with succinic and glutaric anhydrides (known to be monomeric) it showed a diminished solubility and ability to crystallize, and molecular weight determinations in boiling benzene and boiling acetone gave ab-

<sup>1</sup> J. W. Hill, THIS JOURNAL, 52, 4110 (1930).

<sup>2</sup> Paper XI.

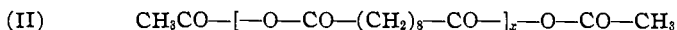
<sup>3</sup> Voerman, *Rec. trav. chim.*, 23, 265 (1904).

normally high values. The doubt concerning its polymeric character arose from the fact that freezing point determinations in phenol gave values agreeing with those calculated for the monomer, but Voerman overlooked the fact that sebacic anhydride reacts very rapidly with phenol to give phenyl esters of sebacic acid.

We prepared the  $\alpha$ -anhydride by heating sebacic acid with excess acetic anhydride, distilling off the volatile material, and precipitating a benzene solution of the residue with petroleum ether. The melting points varied somewhat from one preparation to another and a typical specimen melted at 79–80°. The molten anhydride is exceedingly viscous; on cooling it crystallizes: minute doubly refracting spherulites first separate and grow to what appear to be star-like clusters of needles. This behavior is highly characteristic of crystalline linear high polymers and is observed with such diverse materials as polyesters,<sup>4</sup> trimethylcellulose,<sup>5</sup> and triacetylulinin.<sup>6</sup>

At a temperature of 200° and under a pressure of 0.1 mm. the  $\alpha$ -anhydride shows no tendency to distil, and this behavior is also consistent with a highly polymeric structure.

We tentatively assign to sebacic  $\alpha$ -anhydride the formula II.



This represents it as a linear polymer and the chains are terminated by acetyl groups derived from the reagent used in bringing about the anhydride formation. It reacts with water to form sebacic acid and acetic acid. The latter may conceivably represent adsorbed acetic acid or acetic anhydride not removed in the purification process, but we are inclined to the view that it arises from acetyl groups that actually form a part of the polyanhydride molecule. This assumption together with the estimation by distillation and titration of the amount of acetic acid formed on hydrolysis furnished a value of 5260 for the molecular weight of a typical specimen of the polymer.

A specimen of the recrystallized  $\alpha$ -anhydride which had been stored for three days in a vacuum desiccator over phosphorus pentoxide, potassium hydroxide, and paraffin was refluxed with 3 g. of sodium hydroxide in 40 cc. of water, diluted, acidified with sulfuric acid, and distilled with the occasional addition of water. A total of 415 cc. of distillate was collected and titrated with 0.1 *N* sodium hydroxide. Sodium acetate was identified in the resulting neutralized solution by microscopic observation of the highly characteristic crystals of sodium uranyl acetate formed upon adding uranyl nitrate. We are indebted to Mr. W. D. M. Bryant for this identification. Since it was found that sebacic acid itself tends to steam distil very slowly, a correction was made by repeating the above determination using 6 g. of pure sebacic acid.

*Anal.* Subs. 5.51 g.: 0.0999 *N* NaOH, 26.35 cc. Blank: 0.0999 *N* NaOH, 5.35 cc. Found: (assuming two acetyl groups per molecule) mol. wt., 5260.

<sup>4</sup> Carothers and Arvin, *THIS JOURNAL*, **51**, 2560 (1929).

<sup>5</sup> Hess, "Die Chemie der Cellulose," Akademische Verlagsgesellschaft, Leipzig, 1928, p. 432.

<sup>6</sup> Pringsheim and Hensel, *Ber.*, **63**, 1096 (1930).

A different though not strictly independent estimate of molecular weight is found in the quantitative analysis of the behavior of the polymer toward aniline, which is described in the next section, and this method gives a value of 5500. Attempted molecular weight determinations in boiling benzene gave much lower values than this (as low as 650), but their lack of constancy and reproducibility deprives them of any significance.<sup>7</sup> On the other hand, the  $\alpha$ -anhydride in its physical properties closely resembles polyesters derived from sebacic acid and known to have molecular weights in the neighborhood of 5000.

The analytical data presented below are consistent with the suggested structure for the  $\alpha$ -anhydride.

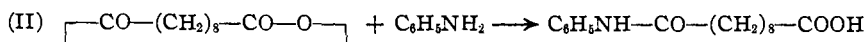
	Calcd., %		Found, %	
	C	H	C	H
$(C_{10}H_{16}O_3)_n$	65.18	8.75	64.19	9.07
$CH_3COO(C_{10}H_{16}O_2)_2COCH_3$	62.35	8.31	64.22	9.01
$CH_3COO(C_{10}H_{16}O_2)_8COCH_3$	64.00	8.57		
$CH_3COO(C_{10}H_{16}O_2)_{30}COCH_3$	64.84	8.71		

**Behavior of Sebacic Anhydrides toward Aniline.**—Theory requires a difference, both qualitative and quantitative, between cyclic monomeric anhydrides and linear polymeric anhydrides in their behavior toward unsymmetrical reagents such as aniline. This requirement was first pointed out by one of us and experimentally verified in the case of adipic anhydrides.<sup>1,8</sup> The analysis has now been extended and further observations made with sebacic anhydrides.

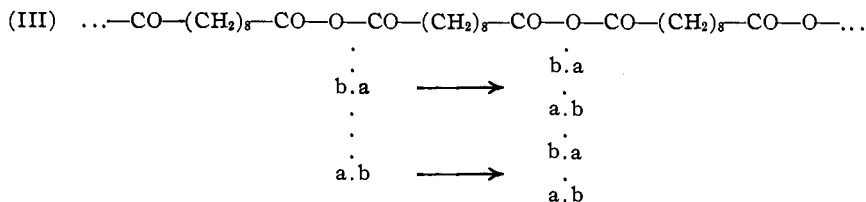
The monomeric anhydride (II) can react with aniline to form only a single product, namely, the monoanilide of sebacic acid.

<sup>7</sup> The low and inconsistent molecular weight values obtained for the polymeric anhydrides in boiling benzene are probably due to progressive degradation by hydrolysis. Greer has lately shown [THIS JOURNAL, 52, 4191 (1930)] that completely dry benzene seizes with great avidity sufficient moisture to provide 0.000229 g. of water for one gram of benzene. In a molecular weight determination this would be sufficient to furnish more than one gram of water for each 100 g. of anhydride. The hydrolytic absorption of water in this proportion (1:100) would reduce the average molecular weight of the anhydride by 75% if the initial value were 5400 and the polymer were an open chain. If the initial value were 396 the reduction would be only 14%. If the polymer were cyclic its molecular weight might actually be slightly increased by partial hydrolysis.

<sup>8</sup> We now find that Étaix [*Ann. chim.*, [7] 9, 356 (1896)] has recorded the fact that the anhydrides of adipic, suberic, azelaic and sebacic acids react with ammonia to give the diamides as well as the amic acids. Einhorn and Diesbach [*Ber.*, 39, 1222 (1906)] have also observed that the anhydrides of diethylmalonic acid react with ammonia and with diethylamine to form both diamides and amic acids. But apparently none of these investigators recognized the bearing of this behavior on the structure of the anhydrides. Incidentally, it seems certain in view of this behavior that Einhorn and Diesbach's tetrameric diethylmalonic anhydride is actually a sixteen-membered ring. On the other hand, their dodecamer is probably a high polymeric mixture rather than a definite individual.



In the polymeric form, however, as soon as one anhydride linkage reacts with aniline, reaction at the next linkage will give different products depending upon which side of the oxygen is involved with the reagent. In III we symbolize aniline (RNH—H) as b—a.



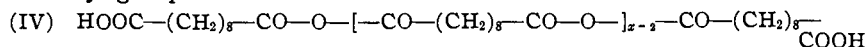
Considering the two linkages of an interior unit of the chain, if reaction occurs in the direction b—a at the first one it may occur in the directions b—a, and a—b at the second; and if the direction is a—b at the first it may be either b—a or a—b at the second. If we assume that reaction is random, *i. e.*, that the direction of reaction at the second linkage is not affected by the direction that the reaction has already taken at the first linkage, then the probability of each of these four possibilities is the same, and the terminal groups attached to the reaction product derived from the unit under consideration are (1) a b, (2) a a, (3) b b and (4) b a. The first and fourth of these represent monoanilide, and the second and third represent, respectively, dibasic acid and dianilide. Thus each interior unit of the anhydride chain will yield

$$\begin{aligned} & \frac{1}{4} \text{ molecule of dibasic acid} \\ & \frac{1}{4} \text{ molecule of dianilide, and} \\ & \frac{1}{2} \text{ molecule of monoanilide} \end{aligned}$$

and this total product will contain one atom of acid hydrogen.

If the polyanhydride is cyclic, all the units are interior units, and the ratio of products indicated above will be maintained so long as the anhydride is polymeric (*i. e.*, not monomeric). But if the chains are open this ratio will be modified.

We consider the case IV in which the chains are open and terminated by carboxyl groups.



The total number of units in the chain is  $x$ . Of these, the  $x-2$  interior units will furnish acid, monoanilide and dianilide in the ratios already indicated, while the terminal units will each furnish one-half molecule of acid and one-half molecule of monoanilide. Thus the total products are

$$\begin{aligned} & (x-2)/4 + 1 \text{ molecule of dibasic acid} \\ & (x-2)/2 + 1 \text{ molecule of monoanilide, and} \\ & (x-2)/4 \text{ molecules of dianilide} \end{aligned}$$

and the number of atoms of acidic hydrogen in the product is

$$[(x - 2)/4 + 1] 2 + (x-2)/2 + 1 = x + 1$$

If  $M$  is the gram molecular weight of the polymer, then, since the molecular weight of the structural unit is 184

$$184x + 18 = M \quad (1)$$

and this weight after reacting with aniline will furnish  $x + 1$  mole of hydrogen ion. Thus the weight of anhydride required to furnish one mole of hydrogen ion is

$$M/(x + 1) \quad (2)$$

Let  $g$  represent the weight of a sample of polyanhydride of the formula IV which is treated with aniline and  $cc$  represent the volume in cubic centimeters of normal alkali required to neutralize the product. Then from (2)

$$M/(x + 1) = 1000 \text{ g}/(cc) \quad (3)$$

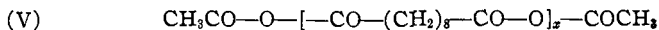
and from (1)

$$x = (M - 18)/184 \quad (4)$$

Substituting and solving for  $M$ , we have

$$M = 166,000 \text{ g}/(184 \text{ cc} - 1000 \text{ g}) \quad (5)$$

If the terminal groups are acetyl as in V



$M = 184 + 102$ , and this weight after reacting with aniline will furnish

$$\begin{aligned} &x/4 \text{ moles of dibasic acid} \\ &x/4 \text{ moles of dianilide} \\ &x/2 \text{ moles of monoanilide} \\ &1 \text{ mole of acetic acid, and} \\ &1 \text{ mole of acetamide} \end{aligned}$$

The moles of available hydrogen ion in this product are

$$2x/4 + x/2 + 1 = x + 1$$

In this case equation (5) becomes

$$M = 82,000 \text{ g}/(184 \text{ cc} - 1000 \text{ g}) \quad (6)$$

The manner in which the calculated available acid from the aniline reaction product varies with the molecular weights of different sebacic anhydrides is indicated in Table I.

From the data of Table I it is evident that even if one allows an error of 2% in the titration it should be possible to distinguish an open chain terminated by carboxyl and having a molecular weight of 7500 or less from a cyclic anhydride. If the terminal groups of the chain are acetyl, a similar distinction is possible only if the molecular weight lies below about 3500.

TABLE I  
ACID FURNISHED BY ANILINE REACTION PRODUCT OF SEBACIC ANHYDRIDES

Structural units	Mol. wt. (for cyclic anhydride)	Millimoles of available H <sup>+</sup> in reaction product from one gram of anhydride		
		Cyclic anhydride	Chain terminated by carboxyl	Chain terminated by acetyl
1	184	5.44	9.9	6.95
2	368	5.44	7.75	6.39
3	552	5.44	7.02	6.12
4	736	5.44	6.62	5.97
6	1,104	5.44	6.24	5.82
10	1,840	5.44	5.92	5.66
15	2,760	5.44	5.76	5.59
20	3,680	5.44	5.68	5.55
40	7,360	5.44	5.56	5.49
60	11,040	5.44	5.52	5.48
100	18,400	5.44	5.49	5.46
200	36,800	5.44	5.46	5.45

The data from which the molecular weight of the  $\alpha$ -polyanhydride described in the preceding section were calculated are as follows.

Weighed samples of the reprecipitated anhydride, which had been stored for several days in an evacuated desiccator over solid potassium hydroxide, were added to 5 to 8 cc. of aniline and triturated with a stirring rod until a smooth cream was formed. The mixture was then diluted with about 30 cc. of 95% alcohol and titrated with 0.1 *N* sodium hydroxide using phenolphthalein as the indicator.

*Anal.* Subs. 0.5869, 0.4814, 0.5632: 0.0999 *N* NaOH, 32.40, 26.55, 31.12 cc. Calcd. by equation (6):  $M = 5532, 5891, 5248$ .

**Sebacic  $\omega$ -Anhydride.**—Attempts to depolymerize sebacic  $\alpha$ -anhydride by heating it under greatly diminished pressure in a Claisen flask resulted merely in thermal decomposition with the formation of tarry products. But in the molecular still,<sup>9</sup> at 200° change occurred simultaneously in two directions: a crystalline distillate gradually accumulated on the condenser, and the residue became more viscous. The rate of distillation was about one gram in twenty-four hours (from 8 g. of  $\alpha$ -anhydride, and an evaporating surface of about 40 sq. cm.). The final residue when cold was very much harder and tougher than the  $\alpha$ -anhydride. It was opaque and when heated to about 83° it suddenly became transparent but remained very stiff. At 130° it was soft enough to be drawn into continuous filaments. These filaments exhibited the phenomenon of cold drawing described in a subsequent paper.<sup>10</sup> The resulting fibers were lustrous and exceedingly strong and pliable, but after standing for a few days in a vacuum desiccator they became brittle and fragile. Massive specimens of the  $\omega$ -anhydride also become brittle under the same conditions and lose their capacity to be drawn out into filaments. No data concerning the molecular weight of  $\omega$ -polyanhydride are available, but its toughness and

<sup>9</sup> Carothers and Hill, paper XI.

<sup>10</sup> Paper XV.

viscosity indicate a considerably higher molecular weight than for the  $\omega$ -polyesters described in paper XII.

The brittleness and loss of tenacity that develop when the  $\omega$ -polyanhydride is stored are apparently due to hydrolysis. When a sample of the anhydride was stored at ordinary temperature in the still in which it was prepared, it retained its strength and toughness for six days. When the still was opened and the anhydride transferred to a desiccator containing anhydrous calcium chloride, brittleness developed within twenty-four hours.

The  $\omega$ -anhydride adheres very firmly to the glass dish in which it is prepared; and if the specimen is more than 2 or 3 mm. deep the dish is completely shattered by the force of contraction during cooling. The  $\omega$ -polyesters manifest the same behavior.

*Anal.* Calcd. for  $(C_{10}H_{16}O_3)_n$ : saponification equivalent, 92. Found: 92.0, 92.3.

**Sebacic  $\beta$ -Anhydride.**—The distillate formed from the  $\alpha$ -anhydride during the treatment in the molecular still is a definitely macrocrystalline solid melting sharply at  $68^\circ$ . It dissolves readily in most of the common organic solvents with the exception of petroleum ether and ligroin. When recrystallized from a mixture of petroleum ether and benzene it separates in the form of fine needles and the melting point remains unchanged. The analytical behavior of this material identifies it as the twenty-two-membered cyclic dimer.

*Anal.* Calcd. for  $(C_{10}H_{16}O_3)_2$ : C, 65.18; H, 8.75; mol. wt., 368; saponification equivalent, 92. Found: C, 65.08, 64.85; H, 8.90, 8.77; mol. wt. in boiling benzene, 386, 393; saponification equivalent 91.9.

Still more decisive support for the cyclic dimeric structure for sebacic  $\beta$ -anhydride is found in the analysis of its behavior toward aniline when treated in the manner already described for the  $\alpha$ -anhydride.

*Anal.* Subs. 0.939 (after treatment with aniline): 0.0992 *N* NaOH, 51.2 cc.

Thus one gram of the anhydride furnished 5.41 millimoles of hydrogen ion. The calculated value for a cyclic anhydride is 5.44, and, as the data of Table I show, this agreement demonstrates that the  $\beta$ -anhydride cannot be an open chain unless its molecular weight lies above 3500. But the volatility of the compound indicates that its molecular weight must lie below 1000.<sup>11</sup>

The neutral solution from the above titration contained both monoanilide and dianilide. The alkali used in the titration was neutralized with an equivalent amount of hydrochloric acid; the alcohol was evaporated; the residue was treated with excess hydrochloric acid to dissolve the aniline, and filtered. The residue on the filter was repeatedly extracted with boiling water until no more material dissolved. The combined filtrates on cooling deposited handsome lustrous platelets of the monoanilide, m. p.  $122$ – $123^\circ$ . This compound appears not to have been described before. Recrystallization from water did not raise its melting point.

<sup>11</sup> Carothers, Hill, Kirby and Jacobson, *THIS JOURNAL*, **52**, 5284 (1930).

*Anal.* Calcd. for  $C_{16}H_{23}O_4N$ : C, 69.26; H, 8.37. Found: C, 69.51, 69.58; H, 8.26, 8.48.

The insoluble dianilide was transferred to a Gooch crucible and weighed: yield, 0.450 g.; theory requires 0.450 g. After recrystallization from alcohol it melted at 201–202°.<sup>12</sup>

*Anal.* Calcd. for  $C_{22}H_{23}O_2N_2$ : C, 74.96; H, 8.01. Found: C, 74.49, 74.67; H, 8.34, 8.05.

The fact that dianilide was produced in this reaction demonstrates decisively that the anhydride is not monomeric, and the close agreement between the dianilide calculated and found indicates again that the structure is cyclic.

The  $\beta$ -anhydride is not present as such in more than traces in the  $\alpha$ -anhydride before the molecular still treatment. The  $\beta$ -anhydride is exceedingly soluble in cold carbon tetrachloride, whereas rough determinations indicated that the  $\alpha$ -compound at 25° dissolves to the extent of only about 0.04 g. in 100 cc. of carbon tetrachloride.

**Sebacic  $\gamma$ -Anhydride.**—When the  $\beta$ -anhydride is heated to its melting point, cooled and then heated again, its melting point is found to have changed from 68 to 82°. This change is due to polymerization. Samples of the new anhydride were prepared by sealing the  $\beta$ -anhydride in carefully dried glass tubes and heating them in a water-bath. The specimens melted at 68° to an exceedingly mobile fluid which almost instantly became so viscous that it failed to flow when the tube was inverted. When cold, the product was an opaque (or translucent) microcrystalline wax that resembled the  $\alpha$ -anhydride. It melted at 82°, and heating at 90–100° for five hours did not raise the melting point.

When the  $\gamma$ -anhydride is heated in the molecular still it behaves in the same manner as the  $\alpha$ -anhydride and is converted to the  $\beta$ - and  $\omega$ -anhydrides.

Determinations of the molecular weight of the  $\gamma$ -anhydride in boiling benzene gave values in the neighborhood of 600, but for reasons already discussed in connection with the  $\alpha$ -anhydrides we think that these values merely signify that the material is not monomeric or dimeric.

The behavior of the  $\gamma$ -anhydride toward aniline fails to reveal the presence of terminal carboxyl groups in detectable amounts.

*Anal.* Subs. 0.2234, 0.2707, 0.1925: (after treatment with aniline) 0.0999 *N* NaOH, 12.15, 14.70, 10.50 cc. These values correspond to 5.43, 5.43, 5.45 cc. of *N* NaOH per gram of sample.

Thus one gram of the anhydride furnishes 5.44 millimoles of hydrogen ion, and from Table I it appears that if the polymer is an open chain bearing carboxyl groups at the ends, its molecular weight must lie above 7500.

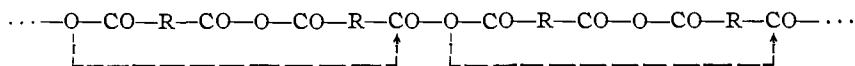
<sup>12</sup> Pellizzari, *Gazz. chim. ital.*, **15**, 555 (1885), gives 198°; Barnicoat, *J. Chem. Soc.*, 2926 (1927), gives 200°.



### Discussion

The  $\alpha$ -anhydride probably bears terminal groups in the manner already indicated. We suppose that it is made up of chains of slightly differing lengths. Our idea in heating this product in the molecular still was that under these conditions it would condense or couple with itself by a process of dehydration or anhydride interchange involving the elimination of terminal groups between adjacent molecules.

A similar mechanism had already been established<sup>13</sup> for the transformation of the  $\alpha$ -polyesters into  $\omega$ -polyesters. The available facts are all consistent with this mechanism for the transformation of the  $\alpha$ -polyanhydride into the  $\omega$ -polyanhydride. The molecules of the latter compound therefore are very long open chains. Their molecular weights lie perhaps in the neighborhood of 30,000, certainly at not less than 15,000. The transformation of this compound into the  $\beta$ -anhydride evidently involves a process of anhydride interchange.



An analogous transformation occurs by heating polyesters derived from six-membered cyclic esters.<sup>14</sup> But among polyesters smooth depolymerization in this fashion can be effected only if the structural unit is six atoms long. Polyesters whose units are longer than six atoms yield cyclic degradation products only in small amounts and only when they are heated to a temperature sufficiently high to produce complete thermal decomposition.<sup>15</sup> The much smoother degradation of the anhydride is consistent with the much greater mobility and reactivity of anhydrides as compared with esters.

A peculiarity of this transformation lies in the fact that the product is not the eleven-membered cyclic monomer but the twenty-two membered cyclic dimer. A similar peculiarity exists in the nature of the cyclic degradation products from the polyesters.<sup>15</sup> The significance of this fact will be discussed in connection with data concerning cyclic anhydrides from other dibasic acids which will be presented in a future publication.

The formation of the  $\gamma$ -anhydride from the  $\beta$ -anhydride apparently involves merely the mutual coalescence of the cyclic molecules of the latter compound. At any rate this transformation occurs under fairly rigorously anhydrous conditions, and, since no terminal groups could be detected in the resulting  $\gamma$ -anhydride, one is almost impelled to conclude that the  $\gamma$ -anhydride is initially a very large ring. This conclusion is a little difficult to reconcile with the fact that in the molecular still the  $\gamma$ -anhydride

<sup>13</sup> Paper XII.

<sup>14</sup> Carothers, Dorough, and Van Natta *THIS JOURNAL*, **54**, 761 (1932).

<sup>15</sup> Carothers, *Chem. Reviews*, **8**, 381 (1931).

behaves just like the  $\alpha$ -anhydride. According to our hypothesis the transformation of  $\alpha$ -anhydride depends upon the presence in this compound of terminal groups capable of being eliminated by condensation between adjacent molecules. There is of course nothing theoretically to preclude the possibility of the mutual coalescence of very large anhydride rings to produce still larger rings. Moreover, it is possible that the  $\omega$ -anhydride derived from the  $\alpha$ -anhydride and that derived from the  $\gamma$ -anhydride are structurally different: the former may be an open chain and the latter a large ring. On the other hand, it appears that mere heating does not bring about the further polymerization of the  $\gamma$ -anhydride. The conditions of molecular distillation are required for this transformation. It is a little difficult to see just why the further growth of the  $\gamma$ -anhydride molecules, if they are rings, should occur only under conditions that favor the simultaneous elimination of smaller cyclic ( $\beta$ -anhydride) residues. Perhaps the resulting rupture leaves fragments (*e. g.*, bivalent radicals) that are especially prone to unite with one another.

We think it more likely, however, that traces of moisture inevitably acquired by the  $\gamma$ -polymer during its transfer to the molecular still may suffice to transform its molecules into open chains terminated by carboxyl groups. Coupling could then occur by the elimination of water between adjacent molecules.

One further feature of the behavior of the  $\alpha$ -anhydride in the molecular still remains to be mentioned. It has already been indicated that degradation to the  $\beta$ -anhydride and growth to the  $\omega$ -anhydride occur simultaneously. The latter process however reaches an apparent limit after a short time, *e. g.*, twelve hours. But this does not interrupt the formation and distillation of  $\beta$ -anhydride, which continues at an only slightly diminished rate until only a trace of residue remains.

### Summary

Sebacic  $\alpha$ -anhydride formed by the action of acetyl chloride or acetic anhydride on the acid is a linear polymer. The chains are probably open and the molecular weights in the neighborhood of 5000. No smooth depolymerization of this anhydride can be effected by ordinary vacuum distillation, but in the molecular still two different transformations occur: (1) coupling of the  $\alpha$ -anhydride with itself yields  $\omega$ -anhydride, a polymer of much higher molecular weight; (2) depolymerization of the  $\alpha$ - and  $\omega$ -compounds, which occurs at the same time, yields the definitely crystalline volatile  $\beta$ -anhydride melting at 68°. The  $\omega$ -anhydride is very tough and hard and it can be drawn out into exceedingly strong, pliable, lustrous, highly oriented fibers. The  $\beta$ -anhydride is a cyclic dimer (twenty-two-membered ring). When heated above its melting point it instantly polymerizes, yielding a  $\gamma$ -anhydride which closely resembles the  $\alpha$ -anhydride

in its physical properties. The behavior of these anhydrides toward aniline is described and discussed. The prefixes  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\omega$  used above have been adapted arbitrarily to designate the anhydrides of different origins.

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[COMMUNICATION No. 78 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & Co.]

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

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The linear condensation superpolymers described in the three preceding papers of this series<sup>1</sup> can easily be drawn out into strong, pliable, transparent, permanently oriented<sup>2</sup> 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  $\omega$ -ester.

**Methods of Producing Filaments.**—Continuous filaments can be obtained from the molten 3-16  $\omega$ -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

<sup>1</sup> Papers XII, XIII and XIV.

<sup>2</sup> 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.