

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

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

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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).

lies somewhat higher than this, perhaps in the neighborhood of 3000). It corresponds, therefore, in molecular weight with the α -polyesters that have been described in previous papers.³ The polyesterification reaction can be forced further toward completion by the use of molecular distillation, and this process leads to the formation of superpolyesters described in the preceding paper.⁴ One of the objects of the experiments described in the present paper was to examine the possibility of forcing the amide reaction in a similar manner so as to obtain a polyamide of very high molecular weight.

The polyamide already described was placed in the molecular still and heated for forty-eight hours at 200°. A very small amount of the crystalline cyclic lactam distilled from the reaction mixture and the residue was considerably changed in its properties. It was harder and tougher than before and in thin sections was flexible and elastic. It softened at 210° with considerable decomposition. Like the initial amide it was insoluble in common organic solvents with the exception of hot phenol and hot formamide.

Anal. Calcd. for $C_6H_{11}ON$: C, 63.71; H, 9.73. Found: C, 63.94, 63.94; H, 9.72, 9.76.

The change in properties indicates a considerable increase in molecular weight but no actual measurements of molecular weight are available owing to the lack of any method of sufficient reliability.

The superpolyesters described in the preceding paper are especially interesting because of their ability to furnish strong, pliable, highly oriented fibers. This property is discussed in detail in Paper XV. As synthetic silk, however, these materials suffer from the defect of low melting point and considerable solubility in various organic solvents. On the other hand, the polyamide described above is too infusible and insoluble to allow a ready test of its ability to furnish fibers. In the hope of obtaining a compromise between the properties of the polyesters and the polyamides we prepared mixed polyester-polyamides. These compounds were obtained by heating together trimethylene glycol, hexadecamethylene dicarboxylic acid and ϵ -aminocaproic acid. The glycol was used in a 5% excess over the amount equivalent to the dibasic acid and the amino acid was varied in different experiments in the proportion of 1, 2, 3 and 5 moles per mole of dibasic acid. The mixtures were separately heated in a Claisen flask for three hours in a current of dry nitrogen by means of a bath kept at 200–220°. Heating was continued for five hours more at a pressure of 1 mm. with the bath at 250–260°. The very viscous residue was then removed from the flask and transferred to the molecular still, where it was heated for three days at 200°. So far as could be inferred from the

³ Carothers and Arvin, *THIS JOURNAL*, 51, 2560 (1929); Carothers and Van Natta, *ibid.*, 52, 314 (1930).

⁴ Paper XII.

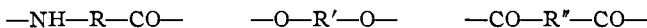
physical appearance of these products the molecular still treatment produced very little effect although in each experiment a small amount of the cyclic lactam from the amino acid was obtained as a distillate.

The products were opaque or translucent solids, hard, very tough, and in thin sections flexible and elastic. As the proportion of amino acid increased, the polymers increased in brittleness, hardness, transparency and melting point. The effect of the composition on melting point is indicated below:

1 mole of amino acid	<i>ca.</i> 73°	3 moles of amino acid	125°
2 moles of amino acid	100°	5 moles of amino acid	145°

The melting points were determined on a copper block. In the two polymers of lowest amino acid content the temperatures at which the specimens became transparent were taken as the melting points. In the other two cases where the high degree of transparency when cold made this determination extremely uncertain the temperatures at which the sample first began to adhere slightly to the block were taken as the melting points.

The solubility of the mixed polyester-polyamides also diminished with increasing amino acid content. The first member of the series was swelled by hot ethyl acetate and finally completely dissolved. It separated from the cold solution in the form of soft powder. The second was very slightly soluble in hot ethyl acetate, and the higher members were practically insoluble. Since the polyamide derived from ϵ -aminocaproic acid is not dissolved by hot ethyl acetate, the mixed polyester-polyamides are evidently not merely physical mixtures. From the nature of the reaction also it seems likely that all the components participate in forming each molecule of the product. The different units that may be present in the product molecules are



which may be joined in any order that leads to ester or amide linkages.

The mixed polyester-polyamides when molten can readily be drawn out into filaments by touching a specimen with a rod and drawing the rod away. The successful production of continuous filaments by this method requires a degree of plasticity in the molten mass that appears only at a temperature somewhat above the melting point. Filaments obtained in this way are brittle and opaque. When slightly warmed (*e. g.*, to 40 to 50°) they can be drawn out by the action of stress into transparent fibers which are exceedingly pliable. Purely qualitative observations indicate that these fibers are considerably stronger than similar fibers derived from the ω -polyesters.

Summary

The polyamide derived from ϵ -aminocaproic acid when heated in the molecular still undergoes a considerable change in its physical properties,

indicating an increase in molecular weight. By heating together ϵ -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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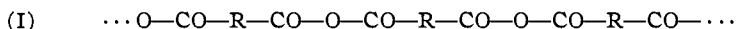
STUDIES OF POLYMERIZATION AND RING FORMATION. XIV. A LINEAR SUPERPOLYANHYDRIDE AND A CYCLIC DIMERIC ANHYDRIDE FROM SEBACIC ACID

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In a previous paper¹ 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 (α -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 still² at elevated temperatures two processes occur simultaneously. The α -anhydride is transformed into a polyanhydride of much higher molecular weight (ω -anhydride) and at the same time depolymerization occurs with the formation of a crystalline product (β -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 (γ -anhydride). The anhydrides of different origins are arbitrarily assigned the prefixes α , β , γ and ω to designate them for the purposes of discussion.

Sebacic α -Anhydride.—Voerman³ 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-

¹ J. W. Hill, THIS JOURNAL, 52, 4110 (1930).

² Paper XI.

³ Voerman, *Rec. trav. chim.*, 23, 265 (1904).