Studies on Synthetic Polyamides (VI)[1] Dimeric ε-Caprolactam.

By Kôhei HOSHINO.

(Received March 12, 1946.)

ε-Caprolactam $HN(CH_2)_5CO$ (I) (m. p. 68°) on being heated in an autoclave, reacts with itself and yields linear polycapramide — $HN(CH_2)_5CO \cdot HN(CH_2)_5CO \cdot HN(CH_2)_5CO$ — (II) (m. p. 210–220°)[2] and a small quantity (below 0.01%) of fluffy byproduct sublimes to adhere to the upper part of the autoclave. The sublimate is slightly soluble in water and alcohol, insoluble in ether and petroleum ether, and soluble in formamide and hot water from which it separates as a microcrystalline powder melting at 341–342° on cooling. Its analytical composition agrees very closely with that required for the structural unit — $NH(CH_2)_5CO$—.

Anal. (Submicro-Kjeldhal). Found: N, 12.31. Calculated for $C_6H_{11}ON$: N, 12.38.

It is quantitatively hydrolyzed in six hours by boiling with concentrated hydrochloric acid to ε-aminocaproic acid. This was identified by conversion into the benzoyl derivative (melting point and mixed melting point, 78–80°), and by measurement of the weight increase of hydrochloride, 48.6% (calculated for the conversion from $(HN(CH_2)_5CO)_n$ (III) to n

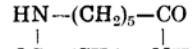
(1) The fifth paper: this Bulletin, **19** (1944), 171.

(2) Hosino and Noisiki: this Bulletin, **18** (1943), 105.

[$HCl \cdot H_2N(CH_2)_5COOH$]: 48.2%). By oxidizing the sample with concentrated nitric acid, adipic acid $HOOC(CH_2)_4COOH$ was obtained.

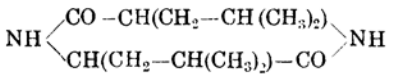
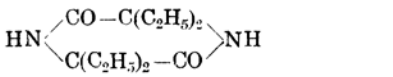
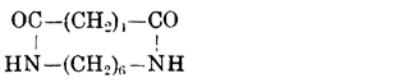
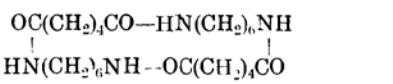
On heating the sample in a sealed tube at 280° with two hundred-parts of water for five hours, it yielded a transparent solution, then by continued heating in an open tube, it was converted to a polyamide melting at 215°, i. e. the linear polycapramide (II). By these facts, it is proved that it retains the structural unit of ε-caprolactam.

This compound is sufficiently soluble in camphor to determine the molecular weight when the quantity of the solvent is increased to about a hundred fold of the solute. The value obtained of n corresponding to the formula (III) was 2. Therefore its structure may be represented by the formula (IV), i. e. neutral cyclic dimeric capramide (a 14-membered ring compound).



(IV)

It is conceivable that the high melting point of this compound is due to two amide groups of high molecular cohesion in one ring. The following compounds (V), (VI), (VII) and (VIII) are some examples of substances with similar structure.

Cyclic amide	Ring size	Formula	M.p., °C.
3,6-Dioxo-2,5-diisobutyl-piperazine (V) (lactam of leucylleucine)	6		271[3]
3,6-Dioxo-2,2,5,5-tetraethyl-piperazine (VI)	6		346[3]
Neutral cyclic monomeric hexamethylene adipamide (VII)	14		248[4]
Neutral cyclic dimeric hexamethylene adipamide (VIII)	28		238[4]

Summary.

The fluffy sublimate (m. p. 341–342°), byproduct of the polymerization of ε-caprolactam, is shown to be neutral cyclic dimeric capramide (IV) (a 14-membered ring compound).

Research Department, Toyo Rayon Kaisha, Otsu, Japan.

---

(3) Beilsteins Handbuch der Org. Chem. Bd. 24. Ergänzbd. 311–312.
(4) Greenewalt, U.S.P. 2,241,323.