The Cyclic Oligomers of ε-Caprolactam[*]

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Introduction

The cyclic oligomers of ε-caprolactam, extractable from polycapramide with boiling water or methanol are here studied.

One of the cyclic dimers was found by K. Hoshino[1] from the sublimate which was obtained during the polymerisation of ε-caprolactam. The brief notes of the cyclic oligomers were also described by German investigators[2].

In addition to the cyclic dimer which was found by K. Hoshino, there are also the dimeric isomer and the cyclic trimer in the extracts of polycapramide. Recently H. Hermans reported the isomers of the cyclic dimers of ε-caprolactam independently[3].

* This work was presented at the Symposium of Polymer Science at Nagoya, Nobember 11, 1954.
** Research Department of Toyo Rayon Co., Ltd.
1) K. Hoshino, This Bulletin, 19, 171 (1944).

2) PB. 44806.
3) H. Hermans, *Rec. Trav. Chim. Pays-Bas*, **72**, 798 (1953).

Experiments

(1) Separation of Cyclic Oligomers

The greater part of ε-caprolactam is removed by vacuum distillation from the hot water extracts of polycapramide, then the residue is extracted with acetone to remove the still remaining monomer and other extractable impurities. The residue can be fractionated in three parts by the difference of the solubility of oligomers in water (cold or hot). The following results are finally obtained.

	m. p.	yield from the residue
[I]	234~236°C	32.8 %
[II]	343~345°C	30.4 %
[III]	231.4~237.2°C	30.1 %

The solubility in water increases in the series [I]<[II]<[III]. No carboxyl group is contained in them.

(2) Identification of the Cyclic Dimer (α-Dimer)

It is confirmed by the mixed examination of melting point that [II] is the cyclic dimer which was found by K. Hoshino.

(3) Confirmation of the Isomer of Cyclic Dimer (β-Dimer)

It is confirmed that [III] is the isomer of the cyclic dimer from the following results.

Mol. Wt. (Rast's method) Found: 225. Calcd. for $(C_6H_{11}N_1O_1)_2$: 226.

When [III] is hydrolysed in boiling concentrated hydrochloric acid and then dried up, the weight increase is 47.6 %. (Calculated for the conversion from $[NH(CH_2)_5CO]_n$ to $n[HCl.NH_2(CH_2)_5COOH]$: 48.2 %). ε-Benzoylaminocaproic acid is obtained from the hydrolysed [III] by the reaction with benzoyl chloride.

Since [III] is different from [II] in regard to the water solubility and melting point, it seems that [III] is an isomer of the cyclic dimer which was found by K. Hoshino.

(4) Confirmation of the Cyclic Trimer

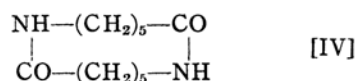It is confirmed that [I] is the cyclic trimer of ε-caprolactam from the following results.

Mol. Wt. (Rast's Method) Found: 339. Calculated for $(C_6H_{11}N_1O_1)_3$: 339.

Anal. Found: C, 63.45; H, 10.15; N, 12.59; O, 13.81. Calcd. for $(C_6H_{11}N_1O_1)_3$: C, 63.65: H, 9.81; N, 12.38; O, 14.15.

This can be hydrolysed quantitatively in boiling concentrated hydrochloric acid to ε-aminocaproic acid, which is identified by conversion to the benzoyl derivative (m.p. 76.5~78.0°C). Its melting point agrees with that of ε-benzoylaminocaproic acid (78~80°C).
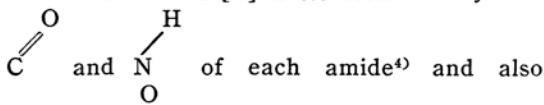
Discussion

K. Hoshino gave the following constitutional formula [IV] (cyclic dimer of ε-caprolactam) for the sublimate which was obtained during the polymerisation of ε-caprolactam.

4) M. Tsuboi, This Bulletin, **22**, 255 (1949).

$$\begin{array}{c} NH-(CH_2)_5-CO \\ | \qquad\qquad | \\ CO-(CH_2)_5-NH \end{array} \quad [IV]$$

3,6-Dioxopiperazine [V] which has a comparatively high melting point (311°C), has a similar constitutional formula and considerable high sublimation pressure.

$$\begin{array}{c} CH_2 \\ NH \quad\quad CO \\ CO \quad\quad NH \\ CH_2 \end{array} \quad [V]$$
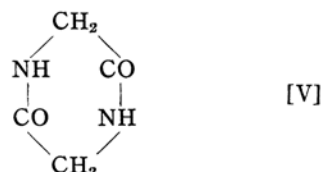
The structure of [V] is *cis* form for adjacent $\overset{O}{\underset{\diagup}{C}}$ and $\overset{H}{N}$ of each amide[4] and also its two $\overset{O}{\underset{\diagup}{C}}$ are symmetrical to the plane which is perpendicular to the line between two carbonyl C atoms and contains the median of its line. Studying the cyclic dimers with the molecular structural model, there must be at least two geometrical isomers. The one is composed of the special arrangement of carbon atoms by which the intramolecular free rotation is hindered, such as by double bond. (Fig. 1).
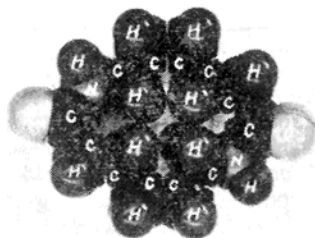

Fig. 1. α-Dimer.

It has probably the same structure as 3,6-dioxopiperazine, which has two methylene groups instead of two pentamethylene groups. It seems that the crystal structure of [III] is also the same as that of 3,6-dioxopiperazine, which has been already known.

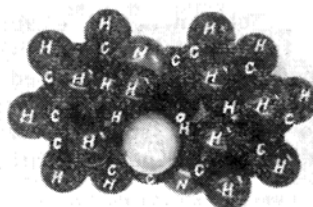Rearranging these carbon atoms of pentamethylene groups, another structural model
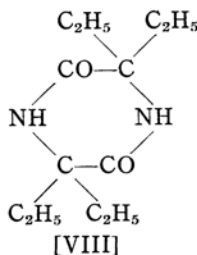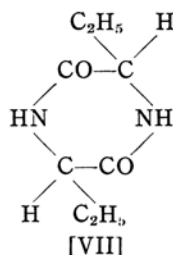

Fig. 2. β-Dimer.

can be obtained which is able to rotate freely, for instance, as Fig. 2.

Conversion between these two configurations which are derived from the study of the molecular structural model, will require a considerable amount of energy and really the mixture of [II] and [III] cannot be obtained by the fusion of [II].

Since the melting point of cyclic hexamethylene adipamide [VI] is similar to that of the β-dimer of ε-caprolactam, and besides the isomer of [VI] has not been found, the α-dimer of ε-caprolactam which has an unusually high melting point should be composed of the special arrangement of atoms.

$$OC—(CH_2)_4—CO$$
$$HN—(CH_2)_6—NH \quad\quad (VI)$$
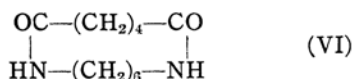
E. Fischer reported that 3, 6-dioxo-2, 5-diethyl-piperazine [VII] had two isomers[5]. But unlike the cyclic dimer of ε-caprolactam these isomers may exist because of the asymmetric carbon atoms at 2 and 5 position. 3, 6-Dioxo-2, 2, 5, 5-tetraethylpiperazine [VIII] which was found by Freytag[5] is the constitutional isomer of caprolactam dimer and it melts at 346~346. 5°C and dissolves 0. 11 g. in 100 cc. of water at 26°C. These physical properties of [VIII] are exactly similar to those of the α-dimer of ε-caprolactam.

$$\begin{array}{ccc} C_2H_5 & H \\ & CO—C \\ HN & NH \\ & C—CO \\ H & C_2H_5 \\ & [VII] \end{array} \quad\quad \begin{array}{ccc} C_2H_5 & C_2H_5 \\ & CO—C \\ NH & NH \\ & C—CO \\ C_2H_5 & C_2H_5 \\ & [VIII] \end{array}$$

In the case of [VIII], owing to the tension of the dioxopiperazine ring, hydrogen bonds

formed by $\overset{C}{\underset{}{\overset{\parallel}{C}}}$ and $\overset{H}{\underset{}{N}}$ should be inter-

molecular. Then the hydrogen bonds of the α-dimer may be also intermolecular. ε-Caprolactam trimer has a 21-membered ring and considering the idea of closely packed atom groups in molecular lattices and its lower melting point, the structure of the trimer may be a type such as its three hydrogen bonds are all intramolecular. Regarding a benzene ring as one atom, the cyclic trimer of polyethylene terephthalate which has recently been discovered (m. p. 325~327°C)[7] has also a 21-membered ring, and in this

case, owing to the steric hindrance of benzene rings, the probability of the cyclic dimer formation may be less than that of the trimer formation.

W. H. Stockmayer gave the following formula[8] for the configulation of the cyclic polymer, which is obtained during the polymerisation of ω-hydroxyundecanoic acid type monomer.

$$R_n = BVn^{-\frac{5}{2}}x^n$$

$$B = \left(\frac{3}{2\pi r}\right)^{\frac{3}{2}}/b^3$$

R_n:　The number of n mer rings.
V:　The volume of the system.
r:　The number of chain atoms per molecular unit.
b:　The effective link length.
x:　The fraction of reacted end-groups in the chain fraction.

For the case of oligomers the following expression is derived.

$$R_1 : R_2 : R_3 = x : \frac{2^{-\frac{5}{2}}x^2}{8} : \frac{3^{-\frac{5}{2}}x^3}{27},$$

where V, r are constant.

For $x = 0. 99$, the weight ratios of the cyclic oligomers are as follows.

$$R_1 : 2R_2 : 3R_3 = 1 : 0. 35 : 0. 19$$

Since the weight ratios of the oligomers actually measured are 1: 0. 17: 0. 08, the calculated value agrees with that observed for the ratio of the dimer (α-type+β-type) to the trimer. Then Stockmayer's equation which is reasonable when ring molecules are long enough (15 skeltal atoms and up) so that short-range steric effects are not dominant, is applicable in this case. The hot water or methanol extracts from polycapramide having an average polymerisation degree of about 100~150, mostly consist of the cyclic monomer and oligomers. There are very few linear oligomers in such high polymers.

Conclusion

From the extracts of polycapramide, two kinds of cyclic dimers and one trimer are obtained. One of the dimers which was found by K. Hoshino may be the diketopiperazine type. The ratio of the dimer to the trimer which is experimentally observed, agrees with the calculated value by Stockmayer's equation.

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5)　E. Fischer, Ber., 39, 3985 (1906).
6)　Freytag, Ber., 48, 651 (1915).
7)　Sidney D. Ross, J. Polymer Sci., 13, 406 (1954).

8)　W.H. Stockmayer, J. Chem. Phys., 18, 1600 (1950).