*On the Ring Opening Reaction of ε-Caprolactam Derivatives**

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It must be considered for the condensation polymerization whether ring-monomer and -oligomers are stable or not; if ⌊–A–⌋ or ⌊–A–A–⌋ is considerably stable in comparison with –A– or –A–A–, such a large quantity of the ring-monomer or -dimer may be produced that the polymer molecule can not be found in the reaction product. δ-Aminovaleric acid or δ-valerolactam is an instance of the former case and α-amino-acid dimer or diketopiperazine is that of the latter case. Thus the ring-chain equilibrium is not only interesting in the structural chemistry but also important for the purpose of polymer manufacturing. It is the object of this paper to study experimentally the influence of side chains on ε-caprolactam polymerization.

Results

Monomethyl-ε-caprolactam. — Methyl cyclohexanone (b. p. 160~170°C) was obtained from cresol (b. p. 190~200°C) through methyl cyclohexanol (b. p. 165~175°C) by the usual method. Methyl-ε-caprolactam (b. p. 123~124°C/5mmHg) was prepared from methyl cyclohexanone with a yield of 75 % by Schmidt's method using sodium azide[1]. This monosubstituted caprolactam, which was a mixture of α, β, γ, δ and ε-derivative, was used for the polymerization experiment; the melting point of the polymer is 164~166°C. Methyl-ε-aminocaproic acid was prepared by the hydrolysis of methyl-ε-caprolactam.

About 3 g. of monomethyl-ε-caprolactams was previously polymerized, with 0.1~0.05 g. of monomethyl-ε-aminocaproic acid as the catalyst, by heating in a glass tube at 230°C for 100 hr. Then, after the tube was sealed, heating was continued at 280°C for 15 hr., at 257°C for 25 hr., at 215°C for 30 hr. or at 182°C for 30 hr. to reach the equilibrium at each temperature. The quantities of lactam-monomer and -oligomers were measured by the same procedure with that for the unsubstituted polycapramide[2]. The intrinsic viscosity of polymerized contents was also measured in the cresol solution at 25°C. The obtained results are shown in Table I.

TABLE I

ANALYTICAL VALUES OF POLY-MONOMETHYL-ε-CAPRAMIDE

($L_1°$ or $L_2°$ = mole of lactam-monomer or -oligomers in the product in the case that 1 mol. of monomer is initially used for polymerization)

Temp. of polymerization °C	$L_1°$ mol.	$L_2°$ mol.	$[\eta]^{25°C}_{cresol}$
280	0.198	0.022	0.56
257	0.164	0.023	0.57
230	0.150	0.021	0.64
205	0.129	0.021	0.69
182	0.119	0.018	0.74

The equilibrium of the reactions concerning lactam-monomer,

$$\mathrm{NH\cdot CO\cdot C_5H_9(CH_3)} + [\text{——}\mathrm{NH_3^+}] \underset{\kappa}{\overset{k}{\rightleftarrows}} [\text{——}\mathrm{NH\cdot CO\cdot C_5H_9(CH_3)\cdot NH_3^+}] \quad (1)$$

can be expressed by the following equation for the high polymeric system[2];

$$L_1° = A\kappa/k = AK \quad (2)$$

where $L_1°$ is the mole number of lactam-monomer at equilibrium, A the whole mole number of the average unit of the Brownian motion in the reaction phase, k the rate constant of ring-opening reaction, κ that of ring-closuring one and K the chain-ring equilibrium constant.

The values of A were determined by the experiment which follows. Monomethyl-ε-caprolactam was diluted with thymol at various ratios and polymerized at 230°C for 100 hr.; analytical results for products are given in Table II. The following equation can be applied to the increase of $L_1°$ with dilution as shown in the previous paper[3];

$$L_1°/(1-L_1°) = \kappa/k\{(S+L_1°)/(1-L_1°)\} + (\kappa/k)\alpha \quad (3)$$

where the mole number of the diluent per 1 mol. of the initial lactam-monomer is denoted by S and, on assuming that 1 mol. of lactam polymerizes completely into a chain molecule, the mole number

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1) T. Hoshino, Y. Iwakura and H. Iwasaki, *J. Polymer Chem.* (*Japan*), **2**, 280 (1945).

2) H. Yumoto, This Bulletin, **28**, 94 (1955).

3) H. Yumoto, ibid., **28**, 101 (1955).

of the average unit of the Brownian motion by α. The data in Table II are used for Fig. 1, which satisfy the equation 3. From Fig. 1, α is estimated to be ca. 0.6 and consequently the average unit of the Brownian motion of chain macromolecules corresponds to 1.66(=1/0.6) structure units, i.e. 13.3(=8×1.66) skeleton atoms or 11.6(=7×1.66) ring-forming atoms. This value is smaller than 19 skeleton atoms for the unsubstituted one[3]; it means that the side chain such as methyl group makes the chain-molecules more kinky and activities of reaction components larger.

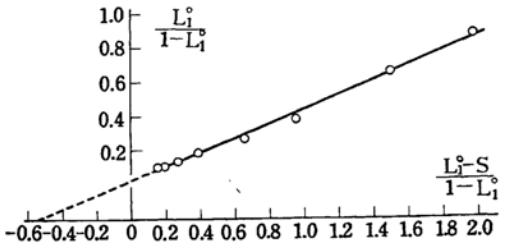

Fig. 1. The effect of dilution on the polymerization of monomethyl-ε-caprolactam.

TABLE II

ANALYTICAL VALUES OF PRODUCTS IN THE CASE THAT MONOMETHYL-ε-CAPROLACTAM IS POLYMERIZED UNDER THE DILUTION IN THYMOL AT 230°C

Initial Monomer mol.	Thymol mol.	L_1° mol.	L_2° mol.	$[\eta]^{25°C}_{cresol}$
1.00	0.846	0.349	0.027	—
〃	0.675	0.297	0.029	0.35
〃	0.507	0.229	0.027	0.39
〃	0.338	0.189	0.025	0.41
〃	0.169	0.155	0.023	0.51
〃	0.085	0.141	0.022	0.60
〃	0.043	0.132	0.021	0.65
〃	0.000	0.133	0.021	0.59

When there is no diluent,

$$A = L_1^\circ + (1 - L_1^\circ)\alpha \qquad (4)$$

The value of α for unsubstituted poly-ε-capramide is hardly changed at all with the temperature in the range from 200 to 250°C[3]. On the assumption that α is 0.6, equilibrium constants $K(=\kappa/k)$ can be found by equations 4 and 2; they were calculated as given in Table III. The relation between K and the absolute temperature T in Fig. 2 is expressed as follows:

$$\log K = 0.39 - 500/T \qquad (5)$$

Then the heat of the ring-opening reaction was estimated to be 2.3 kcal/mol., which is smaller than the value 3.5 kcal/mol. for the unsubstituted one[3].

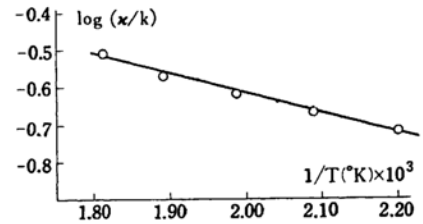

Fig. 2. The effect of temperature on the polymerization of monomethyl-ε-caprolactam.

TABLE III

EQUILIBRIUM CONSTANTS ON RING-CHAIN EQUILIBRIA AT VARIOUS TEMPERATURES FOR MONOMETHYL-ε-CAPROLACTAM

Temp. °C	L_1° mol.	A mol.	K
280	0.198	0.639	0.310
257	0.164	0.624	0.263
230	0.150	0.617	0.237
205	0.129	0.608	0.212
182	0.119	0.603	0.197

(1 mol. of lactam monomer is used for polymerization)

The relation between the intrinsic viscosities in the cresol solution ($[\eta]$) and the number average degrees of polymerization ($\overline{P}$), which were calculated from the numbers of the carboxyl end-group, is shown in Fig. 3. The following equation can be derived approximately,

$$\overline{P} = K_m[\eta]^a$$

where K_m is 214 and a is 1.67; these are

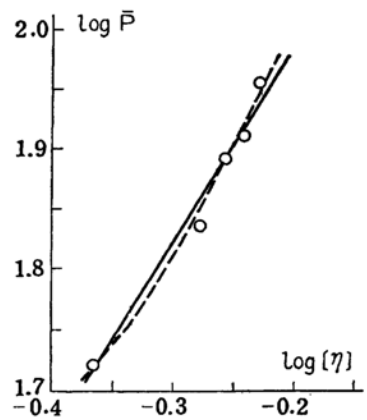

Fig. 3. The relation between the degree of polymerization of poly-monomethyl-ε-capramide and its intrinsic viscosity in cresol solution at 25°C.

TABLE IV

ANALYTICAL VALUES FOR POLY-MONOMETHYL-ε-CAPRAMIDE USING ACETIC ACID TO CONTROL THE DEGREE OF POLYMERIZATION

Acetic acid mol./1mol. of lactam monomer	-COOH mol./127 g of polymer	$-NH_2$ mol./127 g of polymer	$[\eta]^{25°C}_{cresol}$
0.0200	1.89×10^{-2}	0.27×10^{-2}	0.431
0.0100	1.44 〃	0.45 〃	0.526
0.0066	1.30 〃	0.51 〃	0.554
0.0050	1.21 〃	0.53 〃	0.569
0.0033	1.11 〃	0.60 〃	0.584

greater than the values of K_m(=127) and a(=1.44) for the unsubstituted one.[4]

N-Methyl-ε-caprolactam. — N-methyl-ε-caprolactam (b. p. = 124°C/123 mmHg and $n_D^{25} = 1.428$) was prepared from ε-caprolactam by dimethyl sulfuric acid[5], and N-methyl-ε-aminocaproic acid containing 2 moles of the water of crystallization (m. p. 69°C) was obtained by the acid hydrolysis of N-methyl-ε-caprolactam[5]. On heating N-methyl-ε-caprolactam at 230°C with water, water and benzoic acid, or water and ε-aminocaproic acid, no polymer molecules were obtained. N-methyl-ε-aminocaproic acid transformed into N-methyl-ε-caprolactam on heating at 230°C. N-methylol-ε-caprolactam, prepared from ε-caprolactam and formladehyde[5], did not polymerize, either.

These results agree with J. Prochazka's, that N-substituted caprolactam does not polymerize[6]. Poly-N-methyl-ω-hendecanamid or -undecanamid has been known[7]. Then the reason, why N-derivatives of ε-caprolactam can not polymerize, seems to be ascribed to their small ring size.

Dimethyl-ε-caprolactam.—The mixture of α, δ and β, ε-dimethyl ε-caprolactam (m. p. 95~98°C, b. p. 110~115°C/5 mmHg) was prepared from p-xylenol through p-dimethyl cyclohexanol (b. p. 179°C), p-dimethyl cyclohexanone(b.p. 80°C/25 mmHg) and its oxime (m. p. 97°C) by a process similar to that for the caprolactam manufacturing. Dimethyl-ε-aminocaproic acid (m. p. 173~175°C) was obtained by the hydrolysis of dimethyl ε-caprolactam.

Dimethyl ε-caprolactam was heated with catalysts at 230°C for five hours but did not polymerize at all. When dimethyl ε-aminocaproic acid was heated at 230°C for five hours, it only transformed into dimethyl ε-caprolactam and no polymer was obtained.

It is suggested, therefore, when two hydrogen atoms on the different carbon atoms in ε-caprolactam ring are replaced by methyl groups, the ring-chain equilibrium shifts extremely to the ring-form. Even by the use of amino acid for the starting material, it changes into lactam ring by the intramolecular condensation; the contribution of the intermolecular condensation is too small to give the polymer molecule.

Hoshino has already published in 1941[8] the experiment that menton isoxime (methyl isopropyl ε-caprolactam) does not polymerize at all.

Conclusion

The experimental results on the ring-chain equilibria for monomethyl ε-caprolactam can be analyzed through the same procedure with that for the unsubstituted one; the substitution shifts the equilibrium to the ring-form. The heat of reaction, i. e. the energy difference between the chain and the ring form for the monomethyl derivative is 2.3 kcal/mol., which is smaller than 3.5 kcal/mol. for the unsubstituted one.

For dimethyl and N-methyl or -methylol derivatives the equilibria shift too much in favor of the ring-form to give polymer molecules at high temperatures. When amino acids, which are prepared from these lactams by hydrolysis, are heated, they transform into lactam. The theoretical interpretation on these behaviors can be made by the intramolecular rotational isomers[9], which will be reported subsequently. The average unit of the Brownian motion of chain molecules, i. e. the segment, for the monomethyl derivative is 13.3 skeleton atoms which is smaller than 19 skeleton atoms for the unsubstituted polycapramide; the substitution makes it easier for chain molecules to be kinky.

Summary

The ring-chain equilibria,

$$-CO-R-NH- \rightleftharpoons \underset{\lfloor\_\_\_\_\_\rfloor}{CO-R-NH}$$

were investigated experimentally for ε-caprolactam derivatives and their results

4) O. Fukumoto, *J. Polymer Sci.*, **22**, 263 (1956).
5) R. E. Benson and T. L. Cairns, *J. Am. Chem. Soc.*, **70**, 2115 (1948).
6) J. Procházka, *Chem. Listy.*, **37**, 202 (1943); *Chem. Abst.*, **40**, 2113 (1946).
7) G. Champetier and R. Aelion, *Bull. soc. chim. France*, 683 (1948); *Chem. Abst.*, **42**, 7099 (1948).
8) K. Hoshino, *J. Chem. Soc. Japan Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **63**, 1184 (1942).
9) H. Yumoto, Presented at the Symposium on the Structural Chemistry of the Chemical Society of Japan in Nagoya, October 16, 1956.

could be analyzed by the method similar to that for ε-caprolactam. For the monomethyl derivative the equilibrium shifts to the ring-form and ΔH has been estimated to be 2.3 kcal/mol. which is smaller than ΔH(=3.5 kcal/mol.) for the unsubstituted. For dimethyl and *N*-methyl or -methylol derivatives equilibria shift too much to the ring-form to give polymers at high temperatures. The average unit of the Brownian motion of polymer chain molecules, i. e. the segment, for the monomethyl derivative is 13.3 skeleton atoms which is smaller than 19 skeleton atoms for unsubstituted polycapramide; the substitution makes it easier for chain molecules to be kinky.

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