Studies on Synthetic Fibers (II)(1). Polycapramide.

By Kôhei HOSINO and Kisaburo NOISIKI.

(Received December 20, 1942.)

Introduction. On the polymerization process of ε-caprolactam, the following patents are presented:

(1) It. P. 373977. Aug. 9, 1939. (I.G.). For producing a polyamide, one mole of ε-caprolactam is continuously heated at 180–250° (usually at 225°) with a catalyst, e. g. $\frac{1}{100}-\frac{1}{200}$ mole of ε-aminocaproic acid hydrochloride, until polymerization is effected to such an extent that the product can be continuously spun from melt into uniform thread. With catalyst the polymerization is effected in 36–64 hours at 225°, while without catalyst it requires 96–102 hours.

(2) Swed. P. 99037, June 4, 1940. R. M. Joyce and D. M. Ritter (du Pont). ε-Caprolactam is heated at 120–150° with 1/50 mole of alkali metal, e.g. Na or Li, per mole of the lactam till all alkali metal brings into reaction and heating is continued at 250° under vacuum.

(3) B.P. 535421.(2) April 9, 1941. ε-Caprolactam is heated with water at a temperature of 180–300°C. under 200–280 lb. per sq. in. to effect partial polymerization. When most of the monomer has been converted to a low polymer, the water is allowed to distil gradually from the reaction mixture while polymerization continues. The pressure is finally reduced to atmospheric and polymerization is completed by heating in the range of 180–300°.

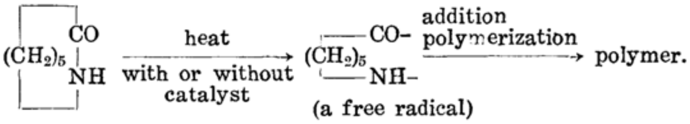
(4) A.P. 2241321.(3) May 6, 1941. Paul Schlack. (I.G.). This is identical to (1).

(5) A.P. 2241322.(4) May 6, 1941. Wm. E. Hanford (du Pont). A process is employed which involves heating ε-caprolactam under superatmospheric pressure with water of at least 0.1 mole of water per mole of the cyclic amide and continuing the heating under superatmospheric pressure with retention of water until the cyclic amide has been mostly converted to polyamide.

(6) A.P. 2241323.(4) May 6, 1941. Crawford H. Greenwalt (du Pont). A process which involves heating to a temperature above the melting point of the cyclic amide and below the temperature at which substantial pyrolysis of the resultant polyamide takes place, and continuing the heating until the polyamide obtained is capable of being spun into oriented fibers.

(7) A.P. 2251519.(5) Aug. 5, 1941. Robert E. Joyce and David M. Ritter (du Pont). This is identical to (2).

It is conceivable from these patents that the polymerization of ε-caprolactam may proceed as in the following manner:



---

(1) *J. Chem. Soc. Japan*, **62**(1941), 1202.
(2) *J. Text. Inst.*, 1941, A 314.
(3) *Chem. Abst.*, **35**(1941), 5128.
(4) *Chem. Abst.*, **35**(1941), 5129.
(5) Text. Colorist, 1941, 550.

But on the mechanism of polymerization and the structure of the polymer no information has been reported, so the present study was attempted and the results obtained were the following.

Mechanism of Polymerization. ε-Caprolactam does not polymerize by heating at 250–300° at atmospheric pressure to a polymer which has spinnability. When ε-aminocaproic acid is heated it is partly converted to the monomeric lactam (about 30%) and partly to polyamide (about 70%). According to Carothers' description(6), these are not directly convertible. But by heating ε-caprolactam under superatmospheric pressure of inert gas, it is converted to linear superpolyamide. This polymerization is effected in a vessel of glass, porcelain, brass, aluminium, stainless steel or iron, and addition of a small quantity of potassium carbonate or magnesium metal or magnesiumoxide or stannouschloride does not give better results in a glass vessel. As ε-caprolactam is hygroscopic in moist atmosphere, it is conceivable that a smaller amount of water catalyzes polymerization. This was proved by the following procedure: The freshly distilled ε-caprolactam in a dry glass tube equipped in an autoclave from which any moisture remained was removed by heating at 300° was heated continuously for 24 hours at 250–260° under the pressure 20 kg./cm². of hydrogen, but no evidence of polymerization was recognized; the lactam remained unchanged and could be distilled in vacuum. Then the interior of the autoclave was wiped with moist cloth, by the same procedure as before the polyamide of intrinsic viscosity $[\eta]_{20}=1.21$ was obtained. It is evident from this fact that a small quantity of water is indispensable for the effective polymerization of ε-caprolactam(7). What is the rôle of water in this process? The following experiments answer this question. By heating 5 g. of ε-caprolactam with 1 c.c. of water at 270° for 7 hours, white waxy mass was obtained and this can be shaved in thin flakes with a knife. Next by heating 5 g. of ε-caprolactam with 5 c.c. of water in the same way, the polymer precipitates as white powder when cooled. In both cases the product was insoluble in water or alcohol, m.p. 207–213°. When 2 g. of ε-caprolactam dissolved in 10 c.c. of water was heated at 275° for 2 hours under the pressure 70 kg./cm². of hydrogen, a clear solution was obtained after cooling. By evaporating this solution, 2.15 g. of ε-aminocaproic acid (Found: N, 10.36. Calculated for $C_6H_{13}O_2N$: N, 10.68%) was obtained. Therefore it is true that ε-caprolactam hydrolyzes in ε-aminocaproic acid in the presence of water. In fact, ε-caprolactam polymerizes in the presence of ε-aminocaproic acid instead of water.

As reaction mechanism, the following two cases are conceivable.

(i) ε-Caprolactam first reacts with water forming ε-aminocaproic acid, then this polymerizes to polyamide by the process of condensation polymerization.

---

(6) Carothers and Berchet, *J. Am. Chem. Soc.*, **52** (1930), 5289; van Natta, Hill and Carothers, *J. Am. Chem. Soc.*, **56** (1934), 455.

(7) Oda and Mokudai obtained similar results from a different experiment. *Bull. Inst. Phys. Chem. Research* (Tokyo), **20** (1941), 1046.

$$\underline{\mathrm{NH-R-CO}}+\mathrm{H_2O} \longrightarrow \mathrm{H_2N-R-COOH}$$

$$\mathrm{H_2N-(R-COHN)_m-R-COOH+H_2N-(R-CONH)_n-R-COOH}$$
$$\longrightarrow \mathrm{H_2N-(R-CONH)_{m+n+1}-R-COOH},$$

where $\mathrm{R=(CH_2)_5}$, m, n = 0, 1, 2, 3, ...

(ii) ε-Aminocaproic acid which is produced by the interaction of ε-caprolactam and a small quantity of water reacts with ε-caprolactam,

$$\mathrm{H_2N-R-COOH+}\underline{\mathrm{HN-R-CO}} \rightarrow \mathrm{H_2N-R-CO-NH-R-COOH}.$$

The amino-acid dimer reacts with the lactam forming amino-acid trimer, and so on,

$$\mathrm{H_2N-(R-CONH)_m-R-COOH+}\underline{\mathrm{HN-R-CO}} \rightarrow \mathrm{H_2N-(R-CONH)_{m+1}-R-COOH}.$$

If the reaction between two polymers may be neglected and the number of amino-acid molecule is constant, the molecular distribution is represented by Poisson's distribution formula. Denoting the number-average or weight-average degree of polymerization as $P_{n.1}$ or $P_{w,1}$ in the case (i) and as $P_{n.2}$ or $P_{w.2}$ in the case (ii), and assuming that the Flory's theory⁽⁸⁾ is applicable, the following relations are obtained.

$$P_{w.1}=P_{n.1}\left(2-\frac{1}{P_{n.1}}\right)$$

$$P_{w.2}=P_{n.2}+1-\frac{1}{P_{n.2}}$$

When the intrinsic viscosity of the polyamide synthesized by the mechanism (i) is equal to that of the polyamide synthesized by the mechanism (ii),

$$P_{w.1}=P_{w.2}\,;\ P_{n.1}=\frac{P_{n.2}}{2}+1-\frac{1}{2P_{n.2}}$$

When $P_{n.1}$ and $P_{n.2}$ are sufficiently large,

$$P_{n.1}\fallingdotseq\frac{P_{n.2}}{2}$$

While the breaking strength F of a fiber is represented by the following formula⁽⁹⁾, which is derivable from Kanamaru-Hata's theory⁽¹⁰⁾ under some assumption,

$$F=a-\frac{b}{P_n},\qquad \text{where } a \text{ and } b \text{ are constants.}$$

---

(8) Flory, *J. Am. Chem. Soc.*, **62**(1940), 1561; **58**(1936), 1877.
(9) Hosino and Aikawa, *J. Chem. Soc. Japan*, **63**(1942), 1187.
(10) Kanamaru and Hata, *Science (Japan)*, **11**(1941), 458.

But the strength of the fiber spun from condensation polymer derived from ε-aminocaproic acid is equal to that of the fiber spun from ε-caprolactam polymer, when the intrinsic viscosity of both polymer is equal. Therefore, the reaction mechanism (ii) excluding the reaction between two polymers is improbable. Either the reaction mechanism (i) or the reaction mechanism (ii) including the amide group exchange process is probable.

Structure of the Polymer. The structure of ε-caprolactam polymer molecule excluding end groups may be concluded to be identical to that of condensation polymer of ε-aminocaproic acid, i.e. polycapramide, on the basis of the following evidences.

(1) The product by hydrolysis of the ε-caprolactam polymer is ε-aminocaproic acid. 5.00 g. of the ε-caprolactam polymer are decomposed by means of 100 c.c. of 5N. H_2SO_4 on a water-bath, and SO_4^{--} ion are removed by means of 65 g. of barium carbonate,and by evaporating the filtrate, 5.53 g. of crystals (m.p. 193–195°) are obtained, this corresponds to 97% yield of the theoretical amount. Recrystallized from 85% alcohol, m.p. 200–202° (benzoyl derivative, m.p. 79–80°). ε-Aminocaproic acid, which is obtained by hydrolysising of ε-caprolactam, m.p. 202–203°. Mixture of the both substances are of m.p. 201–202° (benzoyl derivative, m.p. 78–80°).

(2) Fiber period of extended fiber is 8.84 A. The X-ray diagram of fully extended cold drawn fiber is shown in Fig. 1. In equator there are shown two intensive spots, corresponding to the plane distance 4.32 A. and 3.76 A. respectively. The fiber period along the fiber axis is 8.84 A. on the basis of the layer line distance. If it is assumed that C–N or C–C distance along the paraffine chain axis is 1.27 A., the number of chain atoms in the structural unit=8.84/1.27= 6.97 ≒ 7, this result corresponds to the structure of $[NH(CH_2)_5CO]$. Therefore, among the conceivable structures of the polymer,

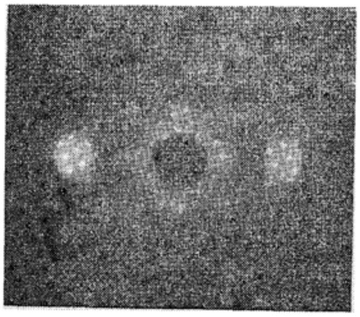


Fig. 1.

(a) $-NH(CH_2)_5CO-CO(CH_2)_5NH-$

(b) $-CO(CH_2)_5NH-NH(CH_2)_5CO-$

(c) $-NH(CH_2)_5CO-NH(CH_2)_5CO-$,

(a) and (b) and the mixture of two or three of (a) (b) (c) must be excluded as its structure.

(3) The melting points of ε-caprolactam polymer, ε-aminocaproic acid polymer and copolymer of the lactam-amino acid mixture in molar ratio are identical, 209–212°.

(4) Analysis. Found; N, 12.21. Calculated for $[NH(CH_2)_5CO]$, N, 12.38%.

Experimental.

(1) *Cyclohexanoneoxime*. (i) Hydroxylamine hydrochloride method. Cyclohexanone used was of 85% grade. By Bousquet's method(11), yield: 83%.

(ii) Hydroxylamine disulphonate method.

$$Na_2CO_3+SO_2+H_2O \rightarrow 2\,NaHSO_3+CO_2$$

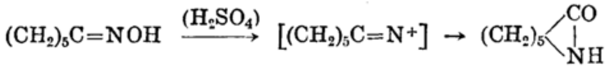
$$NaNO_2+NaHSO_3+SO_2 \rightarrow HON(SO_3Na)_2$$

$$(CH_2)_5CO+HON(SO_3Na)_2+H_2O \rightarrow (CH_2)_5C{=}NOH+2\,NaHSO_4$$

By Marvel and Eck's method(12), using 0.01–0.02% of sodium cetyl sulphate as emulsifier of cyclohexanone in water instead of alcohol as solvent, the yield of recrystallized oxime was 64.5% of the calculated amount. We also found that hydroxylamine disulphonate hydrolyzes to hydroxylamine sulphate in 30 minutes at 75°, and this hydrolysate can be used with good results for obtaining oxime; yield: 74.6% of the theoretical amount.

(iii) When hydroxylamine and iso-mono-sulphoxylamine were used, which were obtained by means of electrolytic reduction of nitric acid, the yield of oxime was about 50% with current efficiency of 60%.

(2) *ε-Caprolactam (2-Ketohexamethyleneimine, Cyclohexanoreisoxime)*.



$$(CH_2)_5C{=}NOH \xrightarrow{(H_2SO_4)} [(CH_2)_5C{=}N^+] \rightarrow (CH_2)_5\left\langle\begin{matrix}CO\\ |\\ NH\end{matrix}\right.$$

ε-Caprolactam was synthesized by Beckmann rearrangement of cyclohexanone oxime. By Marvel and Eck's method(13), it yields 79% of the theoretical. Using the method, which consists in adding the powder of oxime into heated concentrated sulphuric acid(14), several factors were examined. The mole ratio of sulphuric acid to oxime is sufficient, when this ratio exceeds 2.5. As to the relation between concentration of sulphuric acid and the yield of lactam, 95% H_2SO_4 is superior to less concentrated acid. To neutralize the sulphuric acid after rearrangement, ammonia was the best, potassium hydroxide or sodium hydroxide was less convenient. Using 300 c.c. of extracting solvent per 200 g. of oxime, the amount of lactam obtained was as follows: chloroform, 77%; benzene, 10%; ethylene chloride, 54%; trichloroethylene, 28%; carbon tetrachloride, 2%. The quantity of chloroform was sufficient, when 300 c.c. per 200 g. of oxime was used. Our best procedure was as follows: A 2000 c.c. porcelain beaker was charged with 250 c.c. of 95% sulphuric acid. The acid was stirred and heated to 95–100°C. and then maintained at that temperature by the gradual addition of 200 g. of cyclohexanoneoxime. The solution was then held at 100°C. for one hour, followed by addition of the oxime, then cooled to 20°C., and then neutralized with 20% aqueous ammonia. The resulting solution was extracted with 300 c.c. of chloroform; the chloroform was then evaporated and the residual oil was then distilled under reduced pressure, discarding a small forerun of unchanged oxime and collecting the fraction boiling at 122–124°/5 mm., 165–167°/19 mm., m.p. 65–68°, was collected; this corresponds to a yield of 77%.

(3) *Polymerization*. (i) Temperature. The optimum temperature for polymerization is 245° in the case of polymerization condition of Table 1. Intrinsic viscosity is defined as $(\ln \eta_r)/c$, in which η_r is the viscosity of a dilute solution (e.g., 0.5%

---

(11) "Organic Syntheses", XI, 56.
(12) "Organic Syntheses," XIX, 20.
(13) "Organic Syntheses," XVIII, 60; XIX, 20.
(14) Cass, A.P. 2221369, Belg. P. 436765.

concentration) of the polymer in *m*-cresol divided by the viscosity of *m*-cresol and c is the concentration in grams of polymer per 100 c.c. of solution.

Table 1. Intrinsic viscosity $[\eta]_{20}$ of the polymer.

Initial Pressure of Hydrogen: 20 kg./cm^2., heating: 24 hours.

Temp. (°C.)	225±5	245±5	265±5	285±5	305±5	325±5
Lactam	1.130	1.185	0.886	0.699	0.525	0.127
Lactam+1% ε-amino acid	1.154	1.156	0.874	0.736	0.510	0.158

Thermal decomposition begins at about 300°; in the case of the reaction temperature at 320° the polymer is soft and sticks to glass wall.

(ii) Time (Table 2).

Table 2.

Initial Pressure of Hydrogen: 15 kg./cm^2., temperature: 250-260°.

Heating Duration, hour	3	6	10	18	28	43	52	67
$[\eta]_{20}$	0.013	0.059	0.333	0.738	0.820	0.937	0.876	0.866

A 30 hour's heating is sufficient for the effective polymerization.

(iii) Effect of water added (Table 3).

Table 3.

Initial Pressure of Hydrogen: 15 kg./cm^2., temp. 250-260°, heating hour: under superatmospheric pressure 2 hours, then gradually reduced to atmospheric during 1 hour, and then under atmospheric pressure 2 hours.

Added water in mol per 1 mole of lactam	0	0.1	0.2	0.5	1	2	5	10
Intrinsic viscosity, $[\eta]_{20}$	0.696	0.764	0.795	0.796	0.891	0.840	0.833	0.844

There is an obvious difference between the case in which no water is added and the case in which water is added more than 0.1 mole per 1 mole of lactam.

(iv) Effect of added adipic acid as viscosity stabilizer (Table 4).

Table 4.

Temp. 230-240°, heating hour under shaking: 32 hours.

Adipic acid, mole ratio	0	1/800	1/400	1/200	1/100	1/50	1/25	1/12.5	1/6.25	1/3.125
$[\eta]$ of the polymer	0.878	0.887	0.821	0.728	0.523	0.380	0.267	0.184	0.127	0.101

(v) 113 g. (1 mole) of ε-caprolactam is heated for 16 hours under initial pressure of hydrogen 15 kg./cm.^{2} at 240–250° with 2 c.c. of N-HCl (HCl: 1/500 mole, water: 0.11 mole). The intrinsic viscosity of the product is 0.926, and its viscosity is stable in melt state.

(4) *Spinning*. Polycapramide was heated at about 230° in a small brass apparatus provided by a electric heater and the melt of polyamide was extruded through a small spinnerette at constant speed. The spinning conditions and properties of resultant fibers are shown in Table 5.

Table 5.

Exp. No.	[η] of the polymer	Dia. of jet hole, mm.	Temp. (°C.)	Sp. speed. m./min.	Cold drawing (%)	Denier	D.T./D. g.	W.T./D. g.	D.E. (%)	W.E. (%)
44	0.9061	1.5	230	26	300	256.0	4.26	4.12	15.3	20.0
61–a	1.050	1.0	230–245	52	300	200.3	3.97	3.73	16.5	17.3
76–4	1.026	1.0	230–240	61	300	110	4.07	3.39	27.1	46.6
84–3	0.9141	1.5	207–215	13	300	972.0	3.12	2.62	59.4	50.2

In conclusion, the authors wish to express their sincere gratitude to Mr. A. Karasima and Dr. T. Ozawa for the permission of the publication and for the encouragement and to Dr. K. Tanemura for kind guidance throughout this work, and the authors also desire to thank Messrs. A. Aikawa, T. Okura, S. Tuda, H. Turusima and Miss I. Kameda for the assistance in the experimental work.

Research Department, Tôyô Rayon Kaisya,
Otu, Japan.