Studies on Polymerization and Depolymerization of ε-Caprolactam Polymer VI. On the Reaction Mechanism of the ε-Caprolactam Polymerization by Alkali Metal Compound.***

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(Received on June 2, 1958)

It is well known that[1,2,3] alkali metal compounds cause the polymerization of ε-caprolactam and the high polymer can be obtained in several minutes. The mechanism of the reaction has been also studied[2]. It is the main object of this paper to elucidate the reaction mechanism and to find the method for giving reproducible results.

Experimental

1. The Reaction Product of ε-Caprolactam and Alkali Metal Compound.—The mixtures of dry ε-caprolactam and sodium hydroxide or sodium carbonate were heated at 270°C for 30 minutes in a nitrogen stream. In this case a stream of nitrogen was passed through a calcium chloride tube or aqueous barium hydroxide solution in order to detect the generated volatile compound. Water in case of sodium hydroxide or water and carbon dioxide in case of sodium carbonate were detected. Since the mixed components were not dissolved completely, the molar ratio of the product to the added sodium hydroxide or carbonate was smaller than 1 as shown in Tables I and II.

TABLE I

MOLAR RATIO OF WATER TO SODIUM HYDROXIDE (270°C)

Molar ratio of NaOH to lactam	reaction time (min.)	Molar ratio of water to NaOH
1	25	0.191
1	45	0.251
1/2	60	0.664
1/2	50	0.588
1/2	20	0.368

TABLE II

MOLAR RATIO OF CARBON DIOXIDE TO SODIUM CARBONATE (270°C)

Molar ratio of Na_2CO_3 to lactam	Reaction time (min.)	Molar ratio of CO_2 to Na_2CO_3
1	60	0.102
1	60	0.250

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* V, This Bulltin, **31**, 907 (1958).

** Presented at the 11 th Annual Meeting of the Chemical Society of Japan in Tokyo on April 5, 1958.

[1] BIOS Final Reports, No. 1472, p. 14.

[2] O. Wichterle, *Faserforsch. und Textiltech.*, **6**, 237 (1955).

[3] W. Griehl, ibid., **7**, 207, (1956).

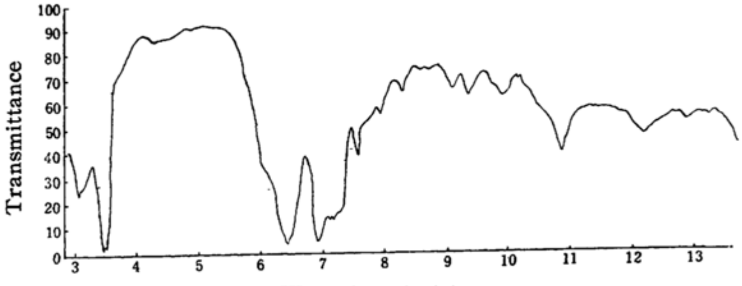

Fig. 1. The infrared spectrum of the reaction product of equal mole of sodium hydroxide and ε-caprolactam (270°C, 30 min.)

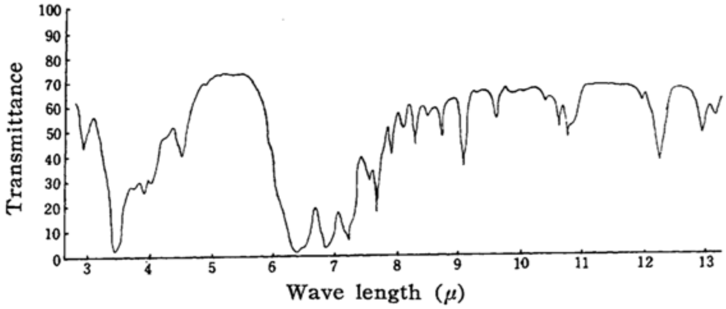

Fig. 2. The infrared spectrum of sodium ε-aminocaproate.

The reaction product of equal moles of sodium hydroxide and ε-caprolactam resembles sodium ε-aminocaproate in the infrared spectrum as shown in Figs. 1 and 2. The quantities of sodium ε-aminocaproate, ε-caprolactam-monomer and -oligomers in the product were analyzed[4,5]. The results are given in Table III.

TABLE III

ANALYSIS OF REACTION PRODUCT OF EQUAL MOLES OF ε-CAPROLACTAM AND SODIUM HYDROXIDE

Product	Yield (%)
Sodium ε-aminocaproate	85
Lactam monomer	15
Lactam oligomers	0

2. Polymerization of ε-Caprolactam by Alkali Metal Compounds.—The alkali metal compound must be added to the boiling ε-caprolactam for the polymerization. ε-Caprolactam was kept boiling at 290°C previously and 0.5 mole percent of sodium -hydroxide, -carbonate, -cyanate, -acetate, -formate, -ε-aminocaproate, potassium -hydroxide or -carbonate, was added subsequently. The rate of polymerization is given in Fig. 3.

When alkali metal compound is mixed previously in ε-caprolactam and then the mixture is boiled, it is difficult to polymerize and the rate of the reaction is not reproducible. When an alcoholic solution of alkali metal hydroxide is added to the boiling ε-caprolactam, the polymerization hardly ever occurs either. It may be said, therefore, that the solid surface must be considered for the catalytic effect.

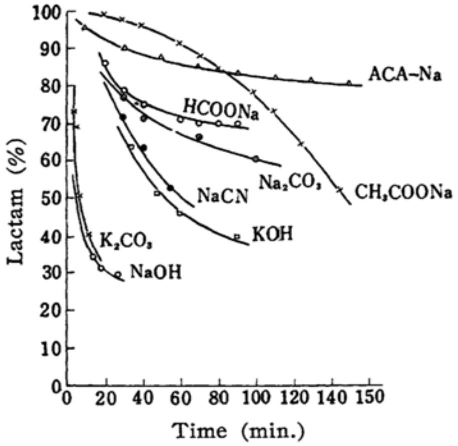

Fig. 3. The rate of polymerization in the presence of various alkali compounds.

In case of the polymerization of pyrolidone (γ-butyrolactam), *N*-acetyl pyrolidone is the promotor in the presence of potassium hydroxide[6]. ε-Caprolactam was heated at 290°C in the presence of 0.5 mole percent of sodium hydroxide and various mole percents of *N*-acetyl-ε-caprolactam.

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[4] H. Zahn and H. Wolf, *Melliand Textilber.*, **32**, 317 (1951).

[5] P. H. Hermans, *J. Appl. Chem.*, **5**, 493 (1955).

[6] W. O. Ney et al., U. S. *Atomic Energy Comm. Nuclear Soc. Abstr.*, 2,739,959 (1956).

TABLE IV

THE RATE OF POLYMERIZATION OF ε-CAPROLACTAM BY COLLOIDAL SODIUM CARBONATE

Na_2CO_3 (mole %)	Time (min.)	Water-soluble component (%)	$\eta_{rel}^{98\%\ H_2SO_4}$	25°C $[\eta]_{cresol}$
0.5	30	15.0	2.10	0.754
0.25	2	98.2	—	
	3	37.2	4.47	
	4	16.5	4.68	2.017
	10	13.5	3.35	
	30	14.0	2.85	
0.10	2.5	19.8	8.69	2·850
	5	21.4	5.35	2.210
	10	17.7	4.56	
	30	13.6	3.09	1.172
0.05	6	49.5	7.45	
	10	38.5	7.77	
	15	22.9	3.92	
	30	29.8	4.18	
0.025	60	68.2	—	

TABLE V

ANALYSES OF POLYMERS OBTAINED BY HEATING ε-caprolactam at 250°C UNDER REDUCED PRESSURE OF 250 mmHg WITH COLLOIDAL SODIUM CARBONATE

Na_2CO_3 (mole %)	Time (min.)	Water-soluble component (%)	$\eta_{rel}^{98\%\ H_2SO_4}$	25°C $[\eta]_{cresol}$
0.1	30	11.0	11.2	3.27
0.05	30	76.9	—	—

TABLE VI

ANALYSES OF POLYMERS OBTAINED BY HEATING ε-CAPROLACTAM WITH 0.1 MOLE % OF COLLOIDAL SODIUM CARBONATE AT VARIOUS CONDITIONS

Polymerization condition	Temp. (°C)	Time (min.)	Water-soluble component (%)	$\eta_{rel}^{98\%\ H_2SO_4}$
with 10% tetralin	290	10	17.3	6.27
with 10% toluene	290	10	14.9	5.69
with 20% xylene	250	120	64.0	2.84
with 30% xylene	250	60	43.7	6.55
with 20% toluene	250	60	100.0	—
with 30% toluene	250	60	41.3	6.59
with 30% xylene	230	60	100.0	—
with 30% toluene	230	60	100.0	—
with blowing dry nitrogen into ε-caprolactam	250	60	13.5	6.69
	250	60	17.6	8.80
	250	37	16.4	—
	230	60	100.0	

TABLE VII

THE RATE OF POLYMERIZATION OF ε-CAPROLACTAM BY COLLOIDAL POTASSIUM CARBONATE (290°C)

K_2CO_3 (mole %)	Time (min.)	Water-soluble component (%)	25°C $[\eta]_{cresol}$
0.2	3	13.5	4.52
	5	14.3	4.18
	10	16.8	3.84
	30	14.4	2.88
0.1	3	25.7	7.57
	5	35.4	5.93
	11.5	20.4	4.78
	30	29.3	3.16
0.05	10	68.8	—
	30	57.4	4.77

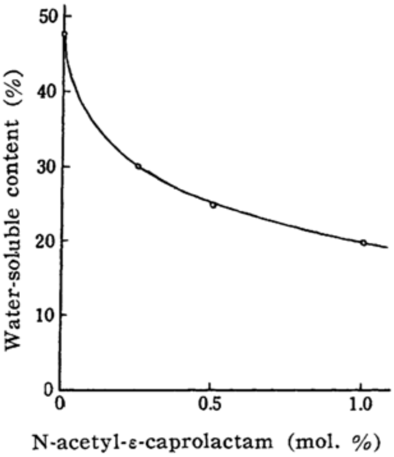


Fig. 4. The quantity of water-soluble content in the polymer in the presence of various mole percents of *N*-acetyl-ε-caprolactam (290°C, 1 hr.)

The quantities of water-soluble contents in the products are shown in Fig. 4.

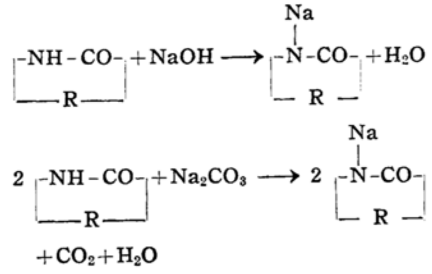
Since the alkali metal compound is assumed to have great catalytic effect at its surface as stated above, it is expected that the greater effect can be obtained in case of dispersing the alkali metal compound colloidally in ε-caprolactam in order to increase the solid surface. Sodium hydroxide is dissolved previously in ε-caprolactam at 100°C and then carbon dioxide is bubbled for about 30 min. to 1 hour. The stable colloidal dispersion of sodium carbonate is obtained. The diameter of sodium carbonate is less than 0.1 μ. ε-Caprolactam containing 0.5 to 0.025 mole percent of colloidal sodium carbonate was boiled at 290°C. The rate of polymerization is given in Table IV. In case of 0.25 to 0.1 mole percent it took 3 to 4 minutes to polymerize. The reaction is reproducible. The degree of polymerization reaches maximum after 2 to 5 minutes and then decreases gradually. Even if sodium carbonate is pulverized finely in a mortar and added to the boiling ε-caprolactam, such a high rate of reaction can not be obtained. When ε-caprolactam was boiled at 250°C under the reduced pressure of 250 mmHg in the presence of the colloidal sodium carbonate, the decrease in the polymerization degree after the maximum is slower than at 290°C as shown in Table V.

When the solvent of low boiling point is dissolved in ε-caprolactam, the boiling can occur under the boiling temperature of ε-caprolactam (263°C). As shown in Table VI, ε-caprolactam containing 0.1 mole percent of colloidal sodium carbonate, polymerizes in the presence of 30% of xylene or toluene for about 20 minutes at 250°C.

When dry nitrogen was bubbled, polymerization also occurred under the boiling temperature as shown in Table VI. The polymerization by the colloidal potassium carbonate is slower than that by sodium carbonate, as shown in Table VII.

Discussion

At first sodium hydroxide or carbonate may react with ε-caprolactam into *N*-sodium ε-caprolactam as follows:



$$\underbrace{-NH-CO-}_{R} + NaOH \longrightarrow \underbrace{-\overset{Na}{N}-CO-}_{R} + H_2O$$

$$2\ \underbrace{-NH-CO-}_{R} + Na_2CO_3 \longrightarrow 2\ \underbrace{-\overset{Na}{N}-CO-}_{R}$$

$$+CO_2+H_2O$$

Water or carbon dioxide is analysed as mentioned above. Sodium ε-aminocaproate is also found in the reaction product practically. It can be assumed that sodium ε-caprolactam is hydrolyzed easily into sodium ε-aminocaproate in the presence of water. The reason why boiling is necessary for the polymerization seems to be ascribed to rapid removal of water or carbon dioxide from the reaction phase. Therefore the salt such as sodium stearate or adipate which yields non-volatile acid can not cause the polymerization. It has been reported that –COONa does not cause the reaction[7].

N-Acetyl ε-caprolactam functions slighlty as a promotor in the presence of alkali metal hydroxide. After *N*-alkali metal ε-caprolactam is formed, the reaction mechanism can be assumed to be similar to that of polymerization in the presence of alkali metal[8]. The catalytic effect of alkali metal compound is expected to be eminent at its solid surface, because the colloidal dispersion is much more effective than the pulverized solid. The degree of polymerization is very large in case of using colloidal alkali metal compound. The polymer has a rubber-like elasticity in a molten state.

Summary

The basic compound of alkali metal reacts with ε-caprolactam and gives at first *N*-alkali metal ε-caprolactam. It can cause the polymerization of ε-caprolactam. The boiling of the reaction phase is necessary for making the reaction proceed. The polymerization is especially rapid and reproducible in case of dispersing alkali

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[7] H. Yumoto and N. Ogata, *Makromolekulare Chem.*, **25**, 91 (1958).

[8] H. Yumoto and N. Ogata, This Bulletin, **31**, 907 (1958).

metal compound colloidally in ε-caprolactam. It is supposed, therefore, that the solid surface of the catalyser is a very important factor in the polymerization.

The authors wish to thank to Dr. K. Hoshino and Dr. H. Kobayashi who instructed them and permitted the publication of this study and Mr. S. Yamauchi et al. who collaborated with them on experiments.

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