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

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The rapid polymerization of ε-caprolactam catalyzed by alkali metal behaves in a manner quite different from the polymerization by water, acids or amino acids. W. Griehl[1,2] found that the molecular weight distribution of poly-ε-capramide obtained in the presence of alkali metal or its salt is very sharp just after reaching the ring-chain equilibrium and then gradually changes into Flory's distribution. O. Wichterle[3] and D. Heikens[4] proposed the mechanism of ε-caprolactam polymerization catalyzed by alkali metal salt.

Experimental

(1) The Initial Reaction between ε-Caprolactam and Alkali Metal.—The Mixture of equal moles of ε-caprolactam and alkali metal was heated together at 100°C. The generated gas was brought to copper oxide heated at 400°C with a stream of nitrogen. It was found as shown in Table I that 1/2 mole of hydrogen molecule to 1 mole of alkali metal is produced.

TABLE I

THE REACTION DEGREE OF SODIUM TO ε-CAPROLACTAM AT 100°C

Sodium (mole)	Produced water (mole)	Molar ratio of hydrogen to sodium
1.34×10^{-2}	6.1×10^{-3}	2.2
1.58 〃	7.2 〃	2.2
1.49 〃	9.7 〃	1.6

The infrared spectrum of the reaction product is shown in Fig. 1. The absorption bands of =NH group at 3.16 μ and 3.28 μ is very weak. After the product was exposed in the atmosphere for only 5 minutes, the spectrum came to be similar to that of ε-caprolactam (Fig. 2). Therefore the reaction product is thought to react easily with water moisture in the atmosphere and to change into ε-caprolactam. By dissolving the reaction product in the heavy water, the solution

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* IV. *Makromolekulare Chem.*, **25**, 91 (1958).

** Presented at the 3rd Autumn Meeting of the Chemical Society of Japan in Tokyo, Nov. 24, 1957.

1) W. Griehl, *Faserforsch. u. Textiltech.*, **6**, 260 (1955).

2) W. Griehl, ibid., **7**, 207 (1956).

3) O. Wichterle, ibid., **6**, 237 (1955).

4) D. Heikens, *Makromolekulare Chem.*, **18**, 62 (1956).

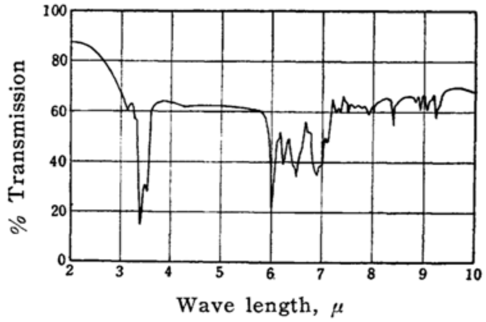


Fig. 1. The infrared spectrum of the reaction product of ε-caprolactam and sodium.

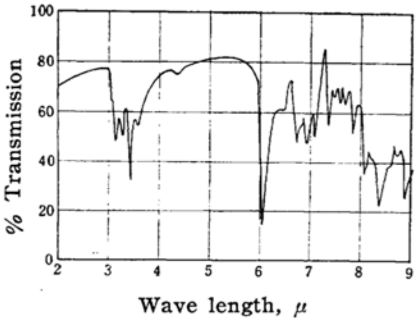


Fig. 2. The infrared spectrum of ε-caprolactam.

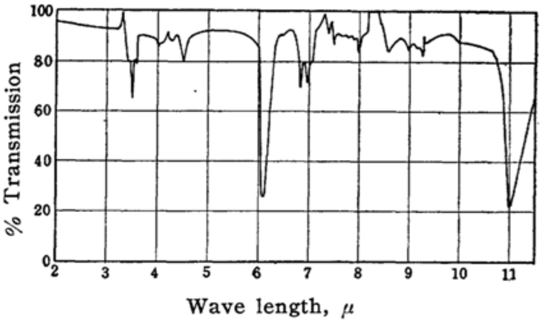


Fig. 3. The infrared spectrum of the product in the lower layer of the heavy water solution.

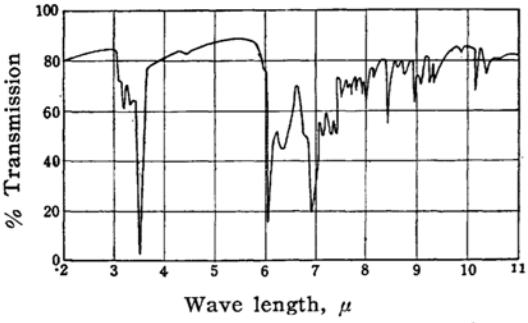
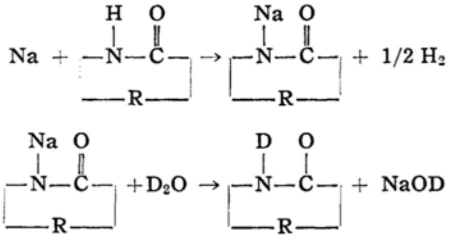


Fig. 4. The infrared spectrum of the reaction product of ε-caprolactam and lithium.

was separated into two layers. The substance extracted in chloroform from the lower layer has the absorption band of =N—D group at 4.46 μ as shown in Fig. 3 and that from the upper layer has both absorption bands of =N—H and =N—D. It was ascertained in an experiment that the hydrogen of the amide group in ε-caprolactam cannot be substituted by deutrium, when it was only dissolved in the heavy water. It is concluded that the following reactions take place:



$$\mathrm{Na} + \underbrace{-\overset{\overset{\mathrm{H}}{|}}{\mathrm{N}}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-}_{\mathrm{R}} \rightarrow \underbrace{-\overset{\overset{\mathrm{Na}}{|}}{\mathrm{N}}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-}_{\mathrm{R}} + 1/2\,\mathrm{H_2}$$

$$\underbrace{-\overset{\overset{\mathrm{Na}}{|}}{\mathrm{N}}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-}_{\mathrm{R}} + \mathrm{D_2O} \rightarrow \underbrace{-\overset{\overset{\mathrm{D}}{|}}{\mathrm{N}}-\overset{\overset{\mathrm{O}}{|}}{\mathrm{C}}-}_{\mathrm{R}} + \mathrm{NaOD}$$

The reaction product of equal moles of ε-caprolactam and lithium has absorption bands at 8.75 μ and 9.05 μ (Fig. 4), which are expected to be assigned to =N—Li.

(2) The Rate of Polymerization. — The mixture of sodium and dried ε-caprolactam (water content of 0.01% or less) at the molar ratio of 1/25, 1/50, 1/100 or 1/200, was heated in a sealed glass tube at 232°C and the quantity of ε-caprolactam in product was determined from the soluble fraction in chloroform. The result is shown in Table II and Fig. 5. Similar experiments using lithium were carried on and the

TABLE II

THE RATES OF POLYMERIZATION OF ε-CAPROLACTAM WITH SODIUM

Sodium (mole/mole)	Time (min.)	Quantity of ε-caprolactam (%)	$[\eta]^{25^\circ\mathrm{C}}_{\mathrm{cresol}}$ of polymer
1/25	2.5	40.0	
	5	14.6	
	10	8.9	
	15	9.1	
	20	7.5	
	30	6.4	0.602
1/50	5	61.3	
	10	9.0	
	15	7.8	
	20	5.0	
	30	4.9	0.809
1/100	5	84.4	
	10	13.6	
	15	10.5	
	20	5.0	
	30	4.7	1.085
1/200	5	91.4	
	10	81.0	
	15	55.9	
	20	30.8	
	30	5.3	1.435

TABLE III
THE RATE OF POLYMERIZATION OF ε-CAPROLACTAM WITH LITHIUM

Lithium (mole/mole)	Time (min.)	Quantity of ε-caprolactam (%)	$[\eta]^{25°C}_{cresol}$ of polymer
1/50	1	94.5	
	2	89.3	
	3	68.4	
	6	4.3	
	9	4.8	0.824
1/100	2	90.7	
	3	83.1	
	4	48.5	
	5	32.2	
	6	6.1	2.110
1/200	2	98.4	
	4	86.0	
	5	72.3	
	6	49.6	
	10	5.6	2.210

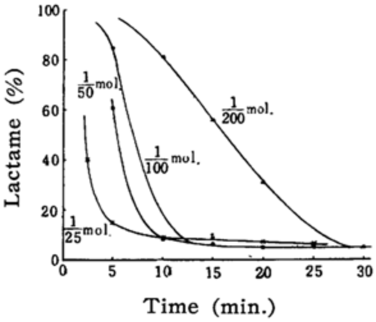


Fig. 5. The rate of polymerization of ε-caprolactam with sodium at 232°C.

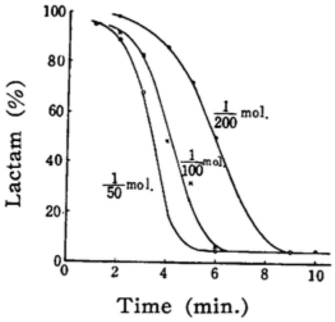


Fig. 6. The rate of polymerization of ε-caprolactam with lithium at 232°C

result is shown in Table III and Fig. 6. The catalytic effect is greater in case of lithium than sodium. Induction periods for the polymerization appear in both cases. The rate of polymerization increases with the quantity of catalyser as shown in Fig. 7.

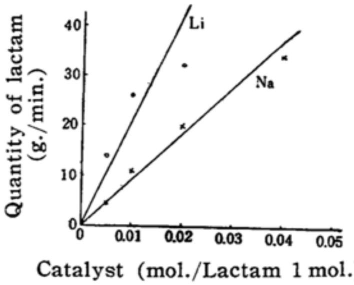


Fig. 7. The rates of polymerization at various quantities of catalyst.

A mixture of 0.041 g. of sodium and 5 g. of ε-caprolactam was heated at 280°, 255°, 238° or 230°C for 10 minutes and then 95 g. of dry ε-caprolactam heated previously at the same temperature was mixed to polymerize. The rate of polymerization is given in Table IV. The induction period disappears in such a case.

TABLE IV
THE RATE OF POLYMERIZATION OF ε-CAPROLACTAM WITH 1/200 MOLES OF SODIUM AT VARIOUS TEMPERATURES

Temp. (°C)	Time (min.)	Quantity of ε-caprolactam (%)
280	1	6.8
	5	7.6
255	0.3	86.2
	1.5	54.9
	1.75	51.9
	3.5	6.4
238	1	78.7
	2	65.0
	2.5	59.2
	2.75	54.7
	3.5	45.2
	4.5	31.0
	10.0	5.7
230	0.5	91.0
	1.5	85.3
	2.5	81.2
	3.5	73.1
	4.0	67.5
	4.5	63.6
	5.0	55.8
	5.5	54.5
	7.0	44.7
	8.0	34.4
	9.0	22.8
	11.0	21.0
	15.0	15.0
	30.0	5.4

The rate of polymerization decreases with the increase in the water content as shown in Fig. 8. When the water content is less than 0.01%, its influence on polymerization can be assumed to be negligible. The acidic substance in trace makes the polymerization retard. The ε-caprolactam used in experiments, therefore, was once distilled in the presence of 0.1% of sodium hydroxide to remove volatile acidic substances.

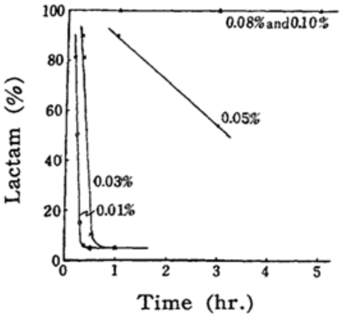


Fig. 8. The rate of polymerization at various water contents.

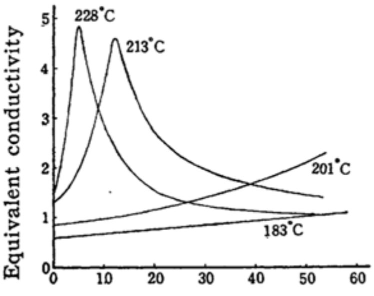


Fig. 9. The electric conductivities of ε-caprolactam during the polymerization in the presence of 0.5 mole % of sodium.

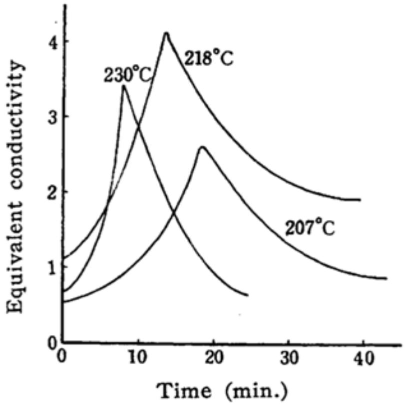


Fig. 10. The electric conductivities of ε-caprolactam during the polymerization in the presence of 0.5 mole % of lithium.

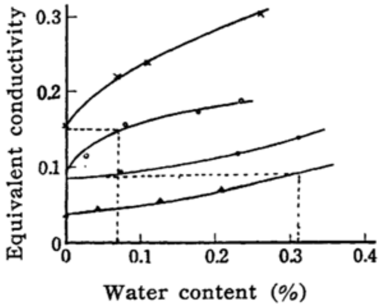


Fig. 11. The electric conductivity of ε-caprolactam at 100°C.

× 0.2 mole % of sodium hydroxide
○ 0.2 mole % of sodium
● 2 mole % of sodium hydroxide
△ 2 mole % sodium

(3) Electric Conductivities. — The change of electric conductivity during polymerization was measured. The results are shown in Figs. 9 and 10. It increases to maximum and then decreases to the equilibrium. It is seen in Fig. 11 that the electric conductivity of ε-caprolactam containing 0.5 or 2 mole percents of sodium and water together is almost the same as that of

TABLE V

ANALYTICAL VALUES OF POLYMER OBTAINED BY HEATING ε-CAPROLACTAM WITH 1/4 MOLES OF SODIUM

Time of polymerization (min.)	Mole of added sodium (mole/mole)	Condition of extraction	Quantity of alkali in water (mole/mole)	Number of acidic groups (mole/113 g.)	Number of basic groups (mole/113 g.)	Quantities of water-soluble chain oligomers (%)	Quantities of ring monomer (%)	Quantities of ring oligomers (%)
5	0.252	25°C, 2 hrs.	0.268	4.0×10^{-2}	9.90×10^{-2}	—	—	
		100°C, 2 hrs.	0.262	2.99 〃	8.65 〃	—	—	
10	0.218	25°C, 2 hrs.	0.210	3.90×10^{-2}	9.92×10^{-2}	12.7	28.8	0
		100°C, 2 hrs.	0.191	2.20 〃	8.65 〃	—	—	—
20	0.247	25°C, 2 hrs.	0.273	3.24×10^{-2}	11.2×10^{-2}	9.7	13.7	1.2
		100°C, 2 hrs.	0.246	3.28 〃	9.1 〃	—	—	—
		25°C, 5 hrs.	0.244	3.40 〃	11.3 〃	—	—	—
		100°C, 5 hrs.	0.245	3.11 〃	10.5 〃	—	—	—

ε-caprolactam containing 0.5 or 2 mole percent of sodium hydroxide. It is expected in the presence of water, therefore, that sodium transforms into its hydroxide before it reacts with ε-caprolactam and loses the catalytic effect. Sodium hydroxide has only a catalytic effect on the ε-caprolactam polymerization in a boiling[3,5] state.

(4) Quantitative and Qualitative Determination of End Groups of polymer.—The polymer was steeped in water and then the number of acidic and basic groups were measured[6]. The quantities of alkali, water-soluble chain-oligomers, ring-monomer and oligomers were determined from the analyses of water extracts. The results are shown in Table V. Sodium bonded to polymer is dissolved easily in water. The number of acidic groups of polymer is hardly changed by the polymerization time and the condition of water steeping. It is always about one-third of the number of basic groups.

As concerns the polymer heated in 0.2 N sodium hydroxide solution at 70°C, the number of acidic groups did not change at all as shown in Table VI. The polmer was steeped in absolute methanol, aqueous ammonia solution or isopropyl amine, for 5 hours at room temperature and then washed repeatedly with methanol and water until the washing did not show alkaline. The results are given in Table VII. The number of acidic groups in case of isopropyl amine was very small and isopropyl amine was found on the hydrolysis.

TABLE VI

THE NUMBER OF ACIDIC GROUPS IN POLYMER BEFORE AND AFTER HYDROLYSIS BY 0.2 N SODIUM HYDROXIDE

Time of polymerization (min.)	Number of acidic groups before hydrolysis (mole/113 g.)	Number of acidic groups after hydrolysis (mole/113 g.)
5	4.00×10^{-2}	3.87×10^{-2}
10	3.00 〃	3.32 〃
20	3.24 〃	3.12 〃

TABLE VII

THE NUMBER OF ACIDIC AND BASIC GROUPS IN POLYMERS STEEPED IN VARIOUS SOLUTIONS

Time of polymerization (min.)	Kind of solution	Number of acidic groups (mole/113 g.)	Number of basic groups (mole/113 g.)
10	Water	2.28×10^{-2}	10.1×10^{-2}
	Methanol	—	—
	Ammonia	1.70×10^{-2}	10.4×10^{-2}
	Isopropyl amine	0.40 〃	10.5 〃
20	Water	1.96 〃	12.4 〃
	Methanol	0.10 〃	12.7 〃
	Ammonia	0.25 〃	10.8 〃
	Isopropyl amine	0.36 〃	11.1 〃

The polymer and its water extract were colorized reddish yellow by the diazo reaction and grey by the Nessler's reagent, while ε-aminocaproic acid was not. On the paperchromatogram of the water extract, a spot having the same Rf value as that of 6-aminohexanol appear as shown in Table VIII, besides those corresponding to ε-aminocaproic acid, di- and tri-ε-aminocaproic acids. In the infrared spectrum of the water extract, the absorption bands of hydroxyl and free =N—H group appear at 2.8 μ and 2.98 μ.

TABLE VIII

R_f VALUES OF PRODUCTS OBTAINED BY EXTRACTION OF POLYMER WITH WATER

Sample	R_f values of spots				
Product	0.19	0.37	0.46	0.54	0.94
ε-Aminocaproic acid	0.19				
Di-ε-aminocaproic acid		0.37			
Tri-ε-aminocaproic acid			0.46		
6-Aminohexanol					0.94

The polymer, of which basic groups had previously been acetylated, was steeped in 1% alkaline solution of potassium permanganate for 2 hours at room temperature. The number of acidic groups increases to the number of basic groups as shown in Table IX.

TABLE IX

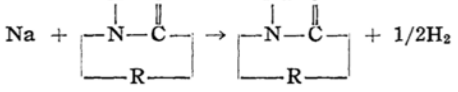
THE NUMBER OF END GROUPS OF POLYMER OXIDIZED BY 1% ALKALINE POTASSIUM PERMANGANATE SOLUTION

Sample	Number of carboxyl groups (mole/113 g.)	Number of amino groups (mole/113 g.)
Polymer at first	2.50×10^{-2}	10.2×10^{-2}
Acetylated polymer	3.50 〃	0
Oxidized polymer	7.50 〃	0

From these experimental results, it is expected that the end groups of polymer steeped in water are carboxyl, amino and hydroxyl groups. The third is probably produced by the reduction. No decarboxylation occures because neither carbon monoxide nore dioxide was found during the polymerization.

Discussion

It is expected that the catalytic polymerization of ε-caprolactam by alkali metal is an ionic reaction and the reaction proceeds through the following mechanism:



$$\mathrm{Na} + \underbrace{-\overset{\mathrm{H}}{\overset{|}{\mathrm{N}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-}_{\mathrm{R}} \rightarrow \underbrace{-\overset{\mathrm{Na}}{\overset{|}{\mathrm{N}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-}_{\mathrm{R}} + 1/2\mathrm{H}_2 \qquad (1)$$

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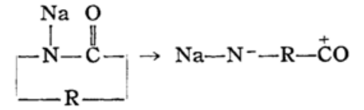
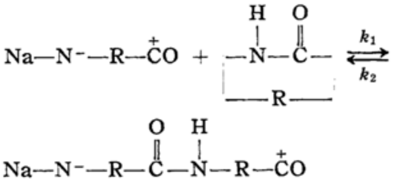
5) H. Yumoto and N. Ogata, to This Bulletin, 31, 913 (1958).

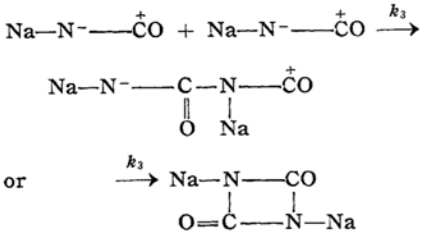
6) J. E. Walz and G. B. Taylor, *Anal. Chem.*, 91, 448 (1947).

7) H. Zahn and H. Wolf, *Melliand Textilber.*, 32, 317 (1951).


(2)


(3)

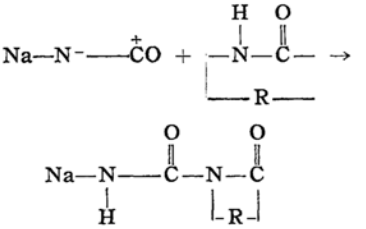
As the number of amino groups is about 40 percent of the mole number of added sodium, the reactions between chain molecules may also occur as shown below;


(4)

$$\text{Na—N}^-\text{——}\overset{+}{\text{C}}\text{O} + \text{Na—N}^-\text{——}\overset{+}{\text{C}}\text{O} \xrightarrow{k_3} \text{Na—N}^-\text{——}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{—}\underset{\underset{\text{Na}}{|}}{\text{N}}\text{——}\overset{+}{\text{C}}\text{O} \quad (4)$$

$$\text{or} \quad \xrightarrow{k_3} \begin{array}{l}\text{Na—N——CO}\\ \quad\ \ |\qquad\ \ |\\ \text{O=C——N—Na}\end{array}$$

If the following termination reaction occured, the number of carboxyl groups should be increased by boiling the polymer in the aqueous solution of acid or base, because the bond such as $-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{N}-\overset{\overset{\text{O}}{\|}}{\text{C}}-$ is easily hydrolyzed. The number of carboxyl groups was scarely changed. It is expected therefore that the termination reaction such as shown in equation 5 does not occur.


(5)

Sodium combined to polymer dissolves in water because the bond >N—Na is affected by water and amino groups are formed. On the other hand carbonyl cations react with water to form carboxyl groups. When polymer is steeped in an amine, carbonyl cations are changed into acid amides.

When dry ε-caprolactam is added to the molten polymer catalyzed by sodium, reactions 3 and 4 may occur and the following equations can be derived, where $[\sum M_1]$ and $[L]$ are chain molecule and lactam monomer and k_1, k_2 and k_3 are rate constants of reactions shown by arrows and A is the mole number of the Brownian motion unit in whole reaction phase[8].

$$d[L/A]/dt=k_2([\sum M_{i+1}]/A) - k_1([\sum M_i][L]/A^2) \quad (6)$$

$$-d[\sum M_i/A]/dt=k_3([\sum M_i]^2/A^2) \quad (7)$$

Suppose $d[L/A]/dt=0$ at equilibrium and $[\sum M_i] \fallingdotseq [\sum M_{i+1}]$ in high polymeric system, then

$$k_2=k_1([L_\infty]/A) \quad (8)$$

where $[L_\infty]$ represents $[L]$ at equilibrium. Substituting Eq. 8 into Eq. 6, the following equation is obtained;

$$d[L/A]/dt=k_1([\sum M_i]/A^2)([L_\infty]-[L]) \quad (9)$$

Integreating Eq. 7 under the conditions that $[\sum M_i]$ is $[\sum M_i^0]$ at $t=0$ and A is invariable.

$$[\sum M_i]/A=[\sum M_i^0]/(k_3[\sum M_i^0]t+A) \quad (10)$$

Substituting Eq. 10 into Eq. 9 and integrating it under the condition that $[L]$ is $[L^0]$ at $t=0$:

$$\begin{aligned}\ln\{([L_\infty]-[L^0])/([L_\infty]-[L])\} &= (k_1/k_3)\ln\{(k_3[\sum M_i^0]t/A)+1\}\\ &= (k_1/k_3)\{k_3[\sum M_i^0]t/A\\ &\quad -(1/2)(k_3/A[\sum M_i^0])^2t^2+\cdots\}\\ &= k_1[\sum M_i^0]t/A\\ &\quad -(k_1/k_3/2)([\sum M_i^0]/A)^2t^2+\cdots \quad (11)\end{aligned}$$

When $\ln\{([L_\infty]-[L^0])/([L_\infty]-[L])\}$ are plotted against t a linear relation is obtained from the data of Table IV (Fig. 12). Therefore, the rest below the second term can be assumed to be negligible. Then

$$\ln([L_\infty]-[L^0])/([L_\infty]-[L]) \fallingdotseq k_1[\sum M_i^0]t/A \quad (12)$$

The value of $k_1[\sum M_i^0]/A$ can be determined from Fig. 12, as shown in Table X.

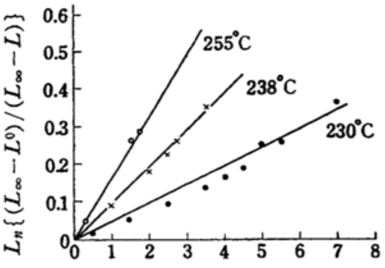


Fig. 12. The relation between $L_n\{(L_\infty-L^0)/(L_\infty-L)$ and time.

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[8] H. Yumoto, This Bulletin, **28**, 101 (1955).

TABLE X

Temp. (°C)	$k_1 \sum M_i^0 / A$ (mole/mol, min.)	L_∞ (%)	K/A
230	0.14	5.4	18.4
238	0.27	—	—
255	0.38	6.4	15.6
280	—	7.2	13.9

The logarithm of $k_1[\sum M_i^0]A$ is plotted against the reciprocal of the absolute temperature in which $\Delta E_{act.}$ of about 22 kcal./mole is estimated. This value is greater than the activation energy of 8.7 kcal./mole for the polymerization of ε-caprolactam in the presence⁷⁾ of water.

Summary

When alkali metal reacts with ε-caprolactam, it was found experimentally that hydrogen and *N*-alkali metal ε-caprolactam are produced at first. The rate of polymerization of ε-caprolactam in the presence of *N*-alkali metal derivative was studied. The change in the electric conductivity during polymerization was also measured. In this case the polymerization is expected to proceed by an ionized molecule.

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