*Studies on Polymerization and Depolymerization of ε-Caprolactam. I. The Formulation of Amide-Interchange Reaction, the Heat of Reaction and the Activation Energy**)

By Hirosuke YUMOTO

(Received May 20, 1954)

Introduction

Considering possible reactions in ε-caprolactam polymerization, they are a sort of reaction expressed by the amide-interchange formula. The equations capable of treating the reaction rate are introduced under such a consideration, and simplified by the approximation peculiar to the super high polymeric system. The main object of this study is to elucidate the reality of the supposed reaction formulas, experimentally.

From the results of this study, polymerization reaction of ε-caprolactam is considered to be the equilibration process by amide-interchange reactions, in which two series of polymerizates, namely chain- and ring-molecules, such as supposed by Jacobson and Stockmayer,[1] are expected to exist. Herein a series of chain-molecules should be the series of condensation polymerizate which had been primarily introduced by Flory.[2]

Furthermore the heat of polymerization and the activation energies of amide-interchange reactions are estimated under these suppositions. The former is apparently coincident with the value determined calorimetrically by S. M. Skurator et al.[3]

The Formulas of the Reactions

As the catalyst of ε-caprolactam polymerization, water, acids, bases, alkali metals, etc. have been reported. Now for the sake of argument, it is assumed that benzoic acid is alone used as the catalyst and the lactam is completely free of water. In the poly-

* Presented at the Symposium of Polymer Science at Nagoya November 9, 1953.

1) H. Jacobson and W. H. Stockmayer, *J. Chem. Phys.*, 18, 1600 (1950).

2) P. J. Flory, *J. Am. Chem. Soc.*, 58, 1877 (1938).

3) S. M. Skuratov, A. A. Stepikheev and E. N. Kanarskaya, *Kolloid Zhur.*, 14, 185—91 (1952); *C. A.*, 46, 8506c (1952); *Faserforschung und Textiltechnik*, 4, 390 (1953).

merizing reaction from such ε-caprolactam and benzoic acid, the monomer, dimer, trimer, ... , m-mer, ...in the series of chain- and ring (lactam)-molecules are designated by the notations of M_1, M_2, M_3, ... , M_m. ..... and L_1, L_2, L_3, ...L_m, ... , respectively. Two end-groups of chain-molecules must always be benzoyl and carboxylic acid groups. M_1 corresponds to the benzoylaminocaproic acid, and L_1 corresponds to the ε-caprolactam. Besides the molecule of free benzoic acid is designated by the notation B.

1. Reactions between ring- and chain-molecules
   - (i) About lactam-monomer
     $L_1+B \rightleftarrows M_1$, $L_1+M_n \rightleftarrows M_{n+1}$
   - (ii) About lactam-dimer
     $L_2+B \rightleftarrows M_2$, $L_2+M_n \rightleftarrows M_{n+2}$
   - (iii) Generally about lactam-m-mer
     $L_m+B \rightleftarrows M_m$ (1)
     $L_m+M_n \rightleftarrows M_{m+n}$ (2)
2. Reactions between two chain-molecules
   $M_n+M_m \rightleftarrows M_{n+m}+B$ (3)
   $M_{n+i}+M_m \rightleftarrows M_{n+m}+M_i$ (4)

Formula (3) represents the condensation reaction and formula (4) represents what is called amide-interchange reaction.

It was already found by K. Hoshino[4] that the completely dried pure ε-caprolactam cannot be polymerized merely by means of heating it. The lactam-dimer or -trimer should be similar in such behavior. These chemical properties make it possible to suppose that the reaction between two lactam-molecules should not arise; e.g. the reaction $L_1+L_1 \rightleftarrows L_2$ does not occur. When amide linkage and the carboxylic acid group collide, the amide-interchange reaction is expected to ensue; but when two amide linkages collide, the amide-interchange reaction is not expected to ensue for the same reason. Consequently

$M_{n+m}+M_{i+j} \rightleftarrows M_{n+j}+M_{m+i}$ is not conceivable.

All of the reactions which arise from caprolactam and benzoic acid can be represented by any of the above formulas (1), (2), (3), and (4). Those reactions can be regarded as the amide-interchange reaction which is indicated by the following formula.

$R_1CONHR_2+R_2COOH \rightleftarrows R_3CONHR_2+R_1COOH$

In the case of ring-molecule, two radicals R in one molecule are linked together. Carboxyl group in chain-molecule can react with the amide linkage in the lactam-molecule, in the own chain-molecule or in the other chain-molecule. As the result of such reaction, polymerization, depolymerization or what is called amide-interchange reaction is expected to arise respectively.

Now consider the reaction where only lactam-monomer (L_1) is related. Hereafter, notations of L, M, B shall represent the mol. no. of each molecule. In this case it is sufficient to consider the following equations,

$$L_1+\sum M_i \rightleftarrows \sum M_{i+1}, \quad (5)$$

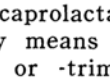
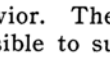
$$L_1+B \rightleftarrows M_1. \quad (6)$$

(In this paper $\sum$ represents $\sum_{i=1}^{\infty}$,)

As for the super high polymeric system where the degree of polymerization is about 100, $B \ll \sum M_i$[a] and $M_1 \ll \sum M_i$[b]. Therefore the following equations are approximately applicable to the super high polymeric system,

$$\left.\begin{aligned} &L_1+\sum M_i \rightleftarrows \sum M_{i+1} \\ &\sum M_i \approx \sum M_{i+1}. \end{aligned}\right\} \quad (7)$$

Generally, insofar as B, $M_1 \ll \sum M_i$ is effective, the equilibrium and the rate[c] of reaction can be discussed with Eq. (7) in approximation.

a) As for the super high polymeric system where the degree of polymerization P is about 100, B is too small to make quantitative analysis by extraction, and also from equilibrium between amide linkages and carboxyl groups, i.e. [-CO-NH-]+  -COOH$\rightleftarrows$[-COOH]+[-NH-CO-  , B will be about one hundredth of $\sum M_i$, because the equilibrium constant will be the magnitude of nearly 1.

b) As for the super high polymeric system where P is about 100, M_1 is too small to make quantitive analysis by extraction and also according to Flory's molecular weight distribution[2] $M_1=(1-p)\sum M_i$ derived from the probability law, M_1 will be about one hundredth of $\sum M_i$, if $p=0.99$.

c) The applicability of eq. (7) for rate process depends on the constancy of $\sum M_i$ in reaction. Considering the general reaction formulas (1), (2), (3), (4), there is no change of $\sum M_i$ in (1), (2), (4), and no change of $\sum M_i+B$ in (3). Accordingly, insofar as $B \ll \sum M_i$ is effective, the change of $\sum M_i$ resulting from reaction (3) will be negligible, and therefore Eq. (7) can be applied to the rate process.

Depolymerizing Process

Polycapramide filament of about 3 denier, which was completely free of water soluble components, i.e. lactam-monomer, -dimer, -trimer, through scouring in boiling water, was dried to be used for experiments. It was sealed in a glass tube and melted by heat for a definite time in a salt bath. Thereafter the content was analysed. The temperature of the salt bath was maintained constant (±1°C) by means of a mercury re-

4) K. Hoshino, *J. Chem. Soc. Japan* (in Japanese), **64**, 628 (1943).

gulator. Analytical procedures were as follows. The sample was chipped and water soluble components were throughly extracted into boiling water. Then the nitrogen content in this extract-solution was estimated by micro-Kjeldahl's method. Besides this analysis, part of this extract-solution was evaporated and dried up completely until the weight of the residue became constant. The nitrogen content of this residue was determined as decribed above.

The filament yarn used for experiments was super high polymer whose degree of polymerization was seemingly about 110[d] estimated from the intrinsic viscosity, i.e. $[\eta]$ (25°C cresol)≈1.1. Those polymers which have such high degree of polymerization contain negligibly small quantities of low molecular weight chainmolecules soluble in water. Therefore one may practically consider the water soluble substances to be only low molecular weight ring-molecules, i.e. monomer, dimer and trimer of lactam. As the lactam-monomer is much more volatile than the two others the quantity of lactam-monomer can be estimated from the above mentioned two nitrogen contents.[5]

The temperatures of reaction were 230, 257, 280, 295 and 310°C. For the purpose of comparison caprolactam was heated to polymerize with ε-aminocaproic acid[e] at the same temperatures. Polymeric systems which had been equilibrated through such a polymerization process were similarly analysed as the polymeric systems obtained by the above mentioned depolymerizing process.

The results of these experiments are shown in Tables I and II, and by dots in Fig. 1.

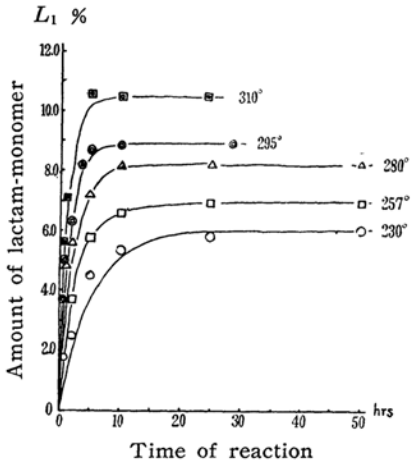


Fig. 1. Amounts of lactam-monomer in depolymerizing process at varying temperatures (Dots represent experimental values, and real lines represent deduced lines from the supposed equation.).

TABLE I

AMOUNTS OF LACTAM-MONOMER IN DEPOLYMERIZING PROCESS AT VARYING TEMPERATURES

Temp. °C	hrs.	L_1 (%) weight/weight
230	1	1.9
	2	2.5
	5	4.5
	10	5.3
	25	5.8
	50	6.0
257	1	2.5
	2	3.7
	5	5.8
	10	6.6
	25	6.9
	50	6.9
280	1	4.9
	2	5.6
	5	7.2
	10	8.2
	25	8.2
	50	8.3
295	0.5	3.7
	1	5.0
	2	6.3
	3.5	8.2
	5	8.7
	10	8.8
	27	8.9
310	1	5.6
	2	7.1
	5	10.6
	10	10.5
	24	10.5

TABLE II

AMOUNTS OF LACTAM-MONOMER AND -DIMER PLUS -TRIMER AT EQUILIBRIUM STATE IN HIGH POLYMERIC SYSTEMS

Temp. °C	L_1° (%)	$L_2^\circ+L_3^\circ$ (%)
230	6.2	2.0
257	7.0	2.2
280	8.3	2.3
295	8.9	2.4
310	10.6	2.5

The rate of reaction in such high polymers can be discussed by Eq. (7). From Eq. (7) following equation may be supposed.

$$\frac{d(L_1/A)}{dt}=\kappa\sum M_i/A-kL_1\sum M_i/A^2, \qquad (8)$$

where L_1=mol. no. of lactam monomers, M_i=mol. no. of the end groups in i-mer chain

5) W. E. Hanford and R. M. Joyce, *J. Polym. Sci.*, 3, 167 (1948). Independently O. Fukumoto in Research Laboratory of Toyo Rayon Co. had established the analysis of lactam-monomer discriminating lactam -dimer and -trimer.

molecules relating to amide-interchange reaction,[6] A = mol. no. of the Brownian motion unit in whole reaction phase. κ = the rate constant of lactam-monomer appearing from chain molecule (depolymerization), k = the rate constant of lactam-monomer disappearing into chain molecule (polymerization). At equilibrium, $d\left(\frac{L_1}{A}\right)/dt=0$; therefore

$$\kappa\sum M_i/A - kL_1^\circ\sum M_i/A^2=0$$

$$k=\kappa A/L_1^\circ, \qquad (9)$$

where L_1° represents L_1 at equilibrium. Substituting Eq. (9) into Eq. (8),

$$d(L_1/A)/dt=(\kappa/A)\sum M_i\left(1-\frac{L_1}{L_1^\circ}\right)$$

$$=(\kappa/L_1^\circ)\ (\sum M_i/A)\ (L_1^\circ-L_1). \qquad (10)$$

It is necessary to give an explanation about A, the mol. no. of average unit of the Brownian motion in the whole reaction phase. For the kinetics of polymerization in the melt phase or in the particularly concentrated solution one cannot simply take "(the number of mol.)/(the volume of whole reaction phase)" as the concentration of the reaction component. It is more reasonable to take "the molar fraction"; the "molar fraction" in this case shall be "(the number of mol.)/(the number of mol. of average unit of the Brownian motion in whole reaction phase)". For the polymer molecule the unit of flow or segment must be taken into consideration; it is apparently doubtful to consider this unit to be a structural unit of the chemical formula.[7] The unit of flow in linear polyamide had not been estimated by melt viscosity measurements. Nevertheless, the assumption that A does not change in reaction is approximately allowable in the case of these depolymerizing processes, because the fairly high polymerized molecules always hold more than 90 percent of the system during the course of the reaction. The particular studies of the value of A shall be reported in next paper.

Integrating Eq. (10) under assumption that A and $\sum M_i$ are invariable with time and the initial condition that $L_1^\circ=0$ at $t=0$,

$$(L_1^\circ/\kappa\sum M_i)\{\ln L_1^\circ-\ln(L_1^\circ-L_1)\}=t \qquad (11)$$

i.e.

$$(2.303\ L_1^\circ/\kappa\sum M_i)\{\log L_1^\circ-\log(L_1^\circ-L_1)\}=t. \qquad (11')$$

If $L_1^\circ\{\ln L_1^\circ-\ln(L_1^\circ-L_1)\}$ are plotted against t, a straight line through the origin is expected to be obtained in case that Eq. (11) is suitable. Values of $\kappa\sum M_i/2.303$ of Table III were estimated from the slope of these lines which were roughly found from the experimental data of Table I and II. The curve L_1 vers. t, recalculated from L_1° and these values of $\kappa\sum M_i/2.303$ by means of Eq. (11) is the real line in Fig. 1. The experimental data fall on this real line within the limit of experimental error. This is evidence to confirm the supposed reaction formulas.

Furthermore, because the values of $\sum M_i/A$ may be approximately assumed hardly to change with temperature, the activation energy $\Delta E_{act.}$ of depolymerization reaction, i.e.

$$\sum M_{i+1}\rightarrow\sum M_i+L_1$$

can be obtained from these values of $\kappa\sum M_i/2.303$ and $\kappa\propto\exp\left(-\frac{\Delta E_{act.}}{RT}\right)$. Logarithms of $\kappa\sum M_i/2.303$ are plotted against reciprocals of the absolute temperature in Fig. II which is linear and then leads to $\Delta E_{act.}$ of 12.5 kcal./mol.

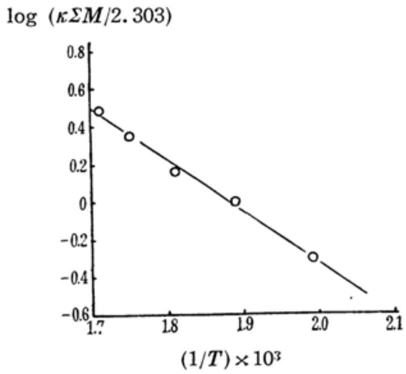


Fig. 2. Ratio of depolymerizing rate plotted against the reciprocal of absolute temperature.

Eq. (9) takes the form,

$$\kappa/k=K=L_1^\circ/A. \qquad (12)$$

The ratios of equilibrium constants K of varing temperatures, relating to the amide-interchange reaction about lactam monomer, can be found from values of L_1°. Therefore one could determine the energy difference ΔE between a lactam-monomer and a structural unit of chain-molecule, because no change of A with temperature may be assumed for the first approximation. ΔE of 3.8 kcal./mol. was estimated from Fig. 3 where log KA is plotted against reciprocals of the absolute temperature.

In conclusion, the thermochemical equation

$$\underline{CO-(CH_2)_5-NH}+3.8\ \text{kcal.}$$

$$=[-CO-(CH_2)_5-NH-]$$

6) K. Hoshino and M. Watanabe, *Scientific Reports of Toyo Rayon Co.* (in Japanese) Vol. 3, No. 4, 110 (1948).

7) A. Matthes, *Makromol. Chem.*, 5, 197 (1951).

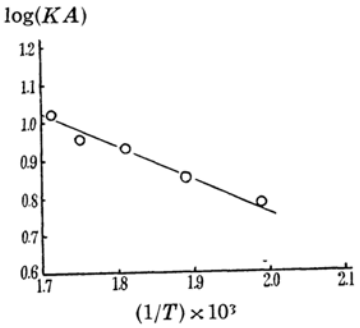


Fig. 3. Ratio of equilibrium constant plotted against the reciprocal of absolute temperature.

and Fig. 4 which illustrate energy levels in such reaction can be obtained.

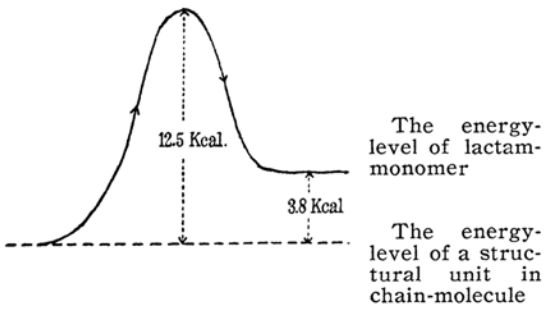


Fig. 4. Illustraction of energy levels in polymerizing and depolymerizing reaction.

The values of $\kappa\sum M_i$ and $(\kappa/k)A$ afford the ratio of rate constant k in Table IV by means of equation

$$\kappa\sum M_i/(\kappa/k)A=k\sum M_i/A. \qquad (13)$$

As the absolute values in Table IV should be changed by units of concentration and time, only their ratio can be criticized here.

TABLE III
THE RATE OF DEPOLYMERIZING AT VARYING TEMPERATURES FROM EXPERIMENTS

Temp. °C	$L_1°$ (mol. no.)	$\kappa\sum M_i/2.303$ (mol. no./hr.)
230	6.0	0.50
257	7.0	0.98
280	7.8	1.46
295	8.9	2.25
310	10.6	3.10

d) $\overline{M}_n=10400[\eta]^{1.51}$ [6], where $\overline{M}_n$ denotes number-average molecular weight. Molecular weight was estimated by this relation.

e) 5% aminocaproic acid was added to caprolactam for the purpose of accelerating the reaction.

f) A linear chain molecule can have two groups affecting amide-interchange reaction. Accordingly it is reasonable to consider the mol. no. of groups capable of affecting amide-interchange reaction rather than the number of chain-molecules. In the case of lactam and benzoic acid reaction, M_i coincides with mol. no. of chain-molecules.

Polymerizing Process

20 g. of ϵ-caprolactam and 100 g. of polycapramide filament from which water soluble components are removed by extraction, were sealed in a tube and heated at 257°C. The decrease of caprolactam was analysed. The methods of heating and analyses were identical with the above mentioned experiments. The results are shown by circles in Fig. 5.

Eliminating κ from Eqs. (8) and (9)

$$d(L_1/A)/dt=(k\sum M_i/A^2)(L_1°-L_1). \qquad (14)$$

Integrating eq. (14) under the initial condition that $L_1=L_1^*$ at $t=0$,

$$\frac{A}{k\sum M_i}\ln\{(L_1°-L_1^*)/(L_1°-L_1)\}=t. \qquad (15)$$

L_1 plotted against t, calculated from Eq. (15) using values that $L_1^*=16.7$, $L_1°=7.0$, and $2.303A/k\sum M_i=1/0.14$ shown in Table IV, is represented by a real line in Fig. 5.

TABLE VI
THE RATE OF POLYMERIZING AT VARYING TEMPERATURES

Temp. °C	$\kappa\sum M_i\frac{1}{2,303}$ (mol. no./hr.)	$\frac{\kappa}{k}A$ (mol. no.)	$k\frac{\sum M_i}{A}\frac{1}{2.303}$ (mol. no./mol. no. hrs.)
230	0.50	6.0	0.083
257	0.98	7.0	0.14
280	1.46	7.8	0.19
295	2.25	8.9	0.25
310	3.10	10.6	0.29

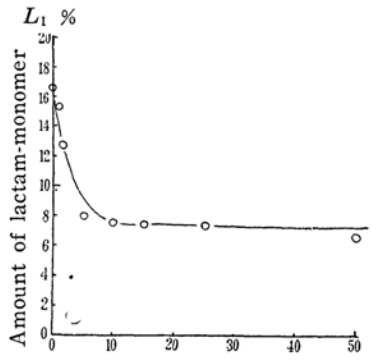


Fig. 5. Amounts of lactam-monomer in polymerizing process at 257°C (Circles represent experimental values and the real line represents deduced line from supposition.)

Experimental data are in accordance with the calculated curve within the limit of ex-

perimental error. This accordance assures the reality of assumed reaction formulas. For this means that two equilibrium constants, derived from the ratio of rate constants of polymerization and depolymerization and directly obtained from the amount of lactam-monomer at equilibrium state, are coincident.

Discussion

One of the results of this study is that the difference of energy (ΔE) between the lactam-monomer (closed ring) and the structural unit in chain-molecule (opened chain) is 3.8 kcal./mol. and the reaction is exothermic in ring-opening. Recently a calorimetric measurement on polymerization heat of caprolactam under the existence of water has been reported.[3] According to this report, the reaction is exothermic and the heat of polymerization is 28.5–29.0 cal./g. independent to the amount of water. This value corresponds to 3.28 kcal./mol. lactam. As the polymeric system contains ca. 10% of low molecular weight lactam-molecules, the reaction heat of the ring-opening of caprolactam,

$$CO-(CH_2)_5-NH \rightarrow [-OC-(CH_2)_5-NH-],$$

becomes to 3.6 kcal./mol. and this value apparently agrees to the value of ΔE deduced from this equilibrium experiments.

However this value seems to be too small as a heat of chemical reaction, but because the difference of entropy of reaction with temperature change is considered to be negligibly small, this heat of reaction is probably due to the potential which restricts the intramolecular bond rotation. In chain-molecules all of the paraffine bonds can take the *trans* or the *gauche* configurations.[8] But in the comparatively small numbered ring each of these bonds cannot take the *trans* nor even the correct *gauche* configurations: only in cyclohexane can the correct *gauche* configurations be taken. ε-Caprolactam ring contains five methylene- and one amide-linkages. For the present we cannot calculate quantitatively the configuration of these linkages. Suppose that cycloheptane ring can be taken as the substitute of caprolactam ring. The potential energy of this ring is $V_r(=\alpha+\beta)$ higher than the minimum energy belonging to the configuration that all of bonds take the *trans*, namely α and β components are respectively the energy difference between *trans* and *gauche* configurations and the additional energy due to the deviation of the correct *gauche* configuration. Being 0.8 kcal./mol. (butane)[9] or 0.5 kcal./mol. (from pentane to cetane)[10,11,12] the energy difference between *trans* and *gauche* configurations in normal paraffin, the value of the latter will be applied here: then α is $(0.5\times7=)3.5$ kcal./mol. Above 500°K even a chain molecule contains a considerable ratio of the *gauche* configurations; the corresponding increment (V_c) of potential energy from the level of all *trans* configurations can be presumed to be 1.9 kcal./mol.[8] (V_r-V_c) shall be compared with the heat of reaction ($\Delta E=3.6$ kcal./mol.). Neglecting the differences of the oscillation and the molecular rotation energies, $V_r-V_c=\Delta E$. Then $\beta=2.0$ kcal./mol. is obtained; this value is considered to be conceivable. For the interpretation of the heat of reaction the idea above described is fairly probable. An analogous treatment of data for the sum of lactam-dimer (14-membered ring) and -trimer (21-membered ring) leads to the energy difference between chain and ring whose value was about 1/2–1/3 of the value for monomer. As the large numbered ring contains a large ratio of the *trans* configuration or small deviation from the correct *trans* and *gauche* configurations, it seems reasonable in accordance with the above opinion. The larger the ring is, the smaller these effects are, and the ring becomes more stable.

Activation energies, 12.5 kcal./mol. for the depolymerization where a lactam-monomer appears from the chain-molecule, and 8.7 kcal./mol. for the polymerization where a lactam-monomer is converted to the chain-molecule were estimated. But there have been no results of studies directly referable for discussing these values of activation energies. Nevertheless, because these are comparatively small (about 10 kcal./mol.) and effective catalysts have tendencies to ionize easily, the amide-interchange reaction is seemingly the reaction where the ionization occurs. As the rate or the activation energy of the pure amide-interchange reaction is being further investigated, such discussions will be treated in detail in subsequent reports.

The view that the lactam-polymerization is an amide-interchange reaction, may be conjectured from the early patent.[13] D'Alelio imaginatively explained it through the carbonium ion under similar consideration.[14]

8) "Physical Chemistry 1" Ed. S. Mizushima (in Japanese) Kyoritsu Publisher, Tokyo (1948), pp. 272—6.

9) K. S. Pitzer, *J. Chem. Phys.*, 8, 711 (1940).

10) S. Mizushima, Y. Morino and M. Takeda, *J. Chem. Phys.*, 9, 826 (1941).

11) S. Mizushima and H. Okazaki, *J. Am. Chem. Soc.*, 71, 3411 (1949).

12) N. Sheppard and J. G. Szasz, *J. Chem. Phys.*, 17, 86, 93 (1949).

13) P. Schlack, *U.S.P.*, 2,241,321 (1941).

14) G. E. D'Alelio, "Fundamental Principles of Polymerization" New York, John Wiley & Sons. Inc. pp. 441—6 (1952).

Mark and Tobolsky[15] also considered this interchange reaction.

But recently it was reported by Wiloth[16] that caprolactam-polymerization is a bimolecular condensation reaction; i.e. any caprolactam is always hydrolyzed into ε-aminocaproic acid

"$\underline{HN(CH_2)_5CO}+H_2O\rightarrow H_2N(CH_2)_5COOH$"

and it is polymerized by the dehydration with other chain molecule "$H_2N(CH_2)_5COOH+H[HN(CH_2)_5CO]_nOH\rightarrow H[HN(CH_2)_5CO]_{n+1}OH+H_2O$" therefore the lactam-monomer is equilibrated with the aminocaproic acid only. And also Wiloth has taken the position that for the completely dried lactam benzoic acid cannot act as a catalyst: water is necessary for benzoic acid to be a catalyst. The experimental bases of these descriptions are seemingly doubtful and the kinetics on his consideration was not investigated. If water is coexistent with benzoic acid both may be catalysts. By Matthes[7] comprehensive research was accomplished and the addition-theory about the radical $-NH(CH_2)_5CO-$ was represented. His experimental data are very useful, but his theory is questionable. The author, like D'Alelio, has considered the amide-interchange reaction and revealed its reality: the "amide-interchange reaction" shall probably be "an ionic reaction".

g) If N_{C2h} and N_{C2} represent the number of *trans* and *gauche* configurations in chain molecule respectively,

$K_p=N_{C2}/N_{C2h}=\text{constant}\cdot e^{-\Delta E/RT}$, where ΔE is the energy difference between both configurations. From values at various temperatures about dichloroethane[17] the value of this constant is roughly presumed to be about 2. Substituting $\Delta E=0.5$ kcal./mol. and $T=530°K$ (257°C) into the above equation, $K_p=1.24$. Then the ratio of the *gauche* configurations in chain molecule is obtained and the increment of the potential energy is 1.9 kcal./mol. (0.5 kcal×7×1.24/2.24).

15) H. Mark, A. V. Tobolsky, "Physical Chemistry of High Polymeric Systems", Interscience Publishers, Inc., New York p. 382 (1950).
16) F. Wiloth, *Angew. Chem.*, 65, 351 (1953).
17) H. A. Stuart, "Die Struktur des freien Moleküls," Springer Verlag (1952) pp. 219—21.

Conclusion

All possible reactions in lactam-polymerization are brought to reactions of a sort, i.e. amide-interchange reaction, and the equation enabling us to discuss the reaction rate by measurable value is derived by the approximation peculiar to super high polymeric system. The experimental results on polymerizing and depolymerizing processes show the reality of this reaction formula. All reactions relating to the lactam-monomer can be indicated by the amide-interchange equation,

$$L_1+M_n\rightleftarrows M_{n+1}$$

where L_1, M_n are the lactam-monomer and n-mer-chain molecules respectively. The heat of polymerization of caprolactam was 3.8 kcal./mol. exothermically, which coincides with the calorimetrically measured value. The ratios of the reaction rates were derived. Activation energy of depolymerizing is 12.5 kcal./mol. and that of polymerizing is 8.7 kcal./mol., which suggest that the ionization will participate in these reactions. The unit of Brownian motion in the molten linear high polymer presented in this paper was not determined but will be deduced from experiments about dilution in a subsequent paper.

The author wishes to thank Dr. K. Hoshino and Dr. H. Kobayashi who instructed him in these studies and permitted this publication.

Research Laboratory of Toyo Rayon Co. Ltd.