Studies on Polymerization and Depolymerization of ε-Caprolactam. II.[*] *The Effects of the Diluent and an Estimation of the Size of the "Segment"*

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Introduction

The polycapramide ordinarily manufactured from ε-caprolactam contains the caprolactam-monomer, -dimer and -trimer which are soluble in water. Even if these lactams (ring-molecule oligomers) are completely removed from the polymer on scouring in hot water, they are always regenerated on melting. It has been found by the author that if the diluent is coexistent on melting, the quantities of the regenerated lactams increase exceedingly. Besides, if ε-caprolactam is polymerized in the presence of a diluent, such prepared polymer contains greater quantities of the lactam oligomers than that prepared from ε-caprolactam only. The diluent has little effect on the polymerization-degree of the chain molecules, but makes the quantities of lactams, especially lactam-monomer, notably increase. These phenomena suggest that the reaction-orders of the lactam-formation (depolymerization) and the lactam-disappearing (polymerization) are different.

Generally when the two reaction-orders of the direct and the reversal reaction are different, the effect of the concentration or the pressure is an important factor for the composition at equilibrium state.

The polymer prepared from the pure caprolactam without the diluent contains still considerable quantities of lactams. This fact should be interpreted as showing that in this case there is also a sort of reaction in the solution, and the problem of how to determine the concentration of the component must be subjected to consideration above everything else.

Usual methods of determining the concentration on the chemical kinetics are suitable to the reaction of gases or in the dilute solutions, but cannot be directly applied to the reactions of liquid especially to those of the molten high polymer-systems. At the reaction in dilute solution the concentration of the component is usually represented by means of the number of mols in unit volume. Polymerization makes little change of volume of system. Then when such a method is applied to the molten polymer system, if only the number of mol. of any component is invariable, the concentration is constant in the whole course of reaction whether polymerization occurs or not: e.g. carboxylic acid group component in this case. But polymerization occurring, even if the number of mol. is invariable, the functional concentration should be truly variable. If the direct and reverse reactions are in the same order, such a complicated problem should not arise.

In view of the classical interpretation, the "molar fraction" is the most adequate expression of the concentration to consider the probability of the molecular collision, and in order to determine the molar fraction, the number of mol. of whole reaction phase must be prescribed. But as it has not yet been known, how to determine the number of mols of the molten high polymer, the author, as the first step, assumed the average unit of macro-Brownian motion for the linear high polymeric molecule, and prescribed the number of mol. of the whole reaction phase according to this unit. As for the viscosity of liquid, Eyring has already considered the "segment" to be the unit of flow in the high molecular weight substance, and this idea has been experimentally approved to be real. Therefore, such a consideration may be seemingly applied to the chemical reaction, namely collisions of molecules, and the author had derived the equation of kinetics on the polymerization and depolymerization of caprolactam in view of the "segment" and the "amide-interchange reaction".[1]

In this study the polymerizations of ε-caprolactam in coexistence of the various amounts of thymol at the various temperature were subjected to the experiments. The experimental data were applied to the deduced equation; the result is that the reaction formulas about the amide-interchange reaction are proved again to be true and also the size of the unit of macro-Brownian motion of the linear polycapramide molecules can be determined. The size of unit determined by such method was of nearly the same magni-

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[1] H. Yumoto, This Bulletin, 28, 94 (1955).

tude as the segments of hydrocarbon[2] and polyester[3] determined by the measurement of the melt viscosities.

As the results of determing the size of such a unit, the equilibrium constants at various temperatures, concerning with the transforming reactions between lactam-monomer $[\underline{\mathrm{CO}-(\mathrm{CH}_2)_5-\mathrm{NH}}]$ and the structural unit of the polycapramide chain-molecule $[-\mathrm{CO}-(\mathrm{CH}_2)_5-\mathrm{NH}-]$, can be estimated; from these equilibrium constants the energy difference between both the above states can be obtained more accurately than that estimated previously[1] for the first approximation, its value giving better coincidence to the value determined calorimetrically by S. M. Skurator et al.[4]

Experiments

10 g. of pure ε-caprolactam, 0.5 g. of ε-aminocaproic acid, and purified thymol were mixed and heated to polymerize in a glass tube at the atmospheric pressure preventing oxidation. The amounts of the mixed thymol were changed from 3/100 to 70/100 by the molar ratio to the sum of mol. of caprolactam and aminocaproic acid. The temperatures of polymerization-reactions were 257, 230 and 200°C. The time of reaction is 50 hrs. at 257 or 230°C and is 100 hrs. at 200°C. The boiling point of thymol being 232°C, the temperature of the system containing a large quantity of thymol cannot rise to 257°C under the atmospheric pressure; the melting point of polycapramide being 215–220°C, a small quantity of thymol could not be used at 200°C because of solidification. ε-Aminocaproic acid is used as the catalyst for the purpose of shortening the time to reach the equilibrium state but also can convert to a structural unit of the polycapramide molecule as the polymerizible component.

The obtained polymer contains the lactam oligomers. The amounts of lactam-monomer and the sum[a] of lactam-dimer and -trimer were found through the micro-Kjeldahl's nitrogen contents of the water-extracted components: the quantities of

TABLE I

THE AMOUNTS OF LACTAM-MONOMER, AND SUM OF LALTAM-DIMER AND -TRIMER

Polymerization temp. °C	The number of mol. of (ε-caprolactam+ε-aminocaproic acid) for polymerization	The number of mol. of thymol as the diluent S	The number of mol. of lactam-monomer in polymer L_1°	The number of mol. of (lactam-dimer +-trimer) in polymer[a] $L_2^\circ+L_3^\circ$
257	1.00	0	0.070	0.010
		0.036	0.079	0.009
		0.072	0.084	0.010
		0.107	0.092	0.010
		0.143	0.096	0.010
230	1.00	0	0.060	0.006
		0.036	0.069	0.006
		0.072	0.068	0.007
		0.107	0.075	0.007
		0.143	0.081	0.007
		0.286	0.106	0.007
		0.572	0.151	0.007
200	1.00	0.072	0.058	0.004
		0.178	0.071	0.006
		0.356	0.098	0.007
		0.572	0.125	0.007
		0.678	0.145	0.007

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2) W. Kauzmann and H. Eyring, *J. Am. Chem. Soc.*, 62, 3113 (1940).

3) P. J. Flory, ibid., 62, 1057 (1940).

4) S. M. Skuratov, A. A. Stepikheev, and E. N. Kanarskaya, *Kolloid. Zhur.*, 14, 185 (1952); *Faserforschung u. Textiltechnik* 4, 390 (1953); *Chem. Abstr.*, 46, 8506 (1952).

a) The weight of the sum of lactam-dimer and -trimer can be found through the analytical value, but the number of moles of the sum of them cannot be determined unless the weight-ratio of them is estimated. The polymeric system of polycapramide contains two series of chain and ring molecules. Such polymeric system being in equilibrium, the ratio of the numbers of the ring molecules in their series will be presumed from the probability. The order of apporoximation for the value of the ratio calculated from the probability may increase for the large rings, e.g. the 14-membered ring of lactam-dimer or the 21-membered ring of lactam-trimer. Therefore, by means of this presumption,[7] the ratios of numbers of moles of lactam-dimer to that of -trimer were determined as follows;

$$L_n^\circ \approx A(7n)^{-3/2}n^{-1},\quad L_n^\circ \propto n^{-5/2}$$

$$\therefore\quad L_2^\circ/L_3^\circ \approx 1.5^{5/2} = 2.8$$

where L_n°=the number of moles of the n-mer ring (lactam) molecule at the equilibrium state, A=a constant. Using this relation the values of $(L_2^\circ+L_3^\circ)$ were obtained.

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

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

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

the water-soluble chain oligomers are negligibly small.(b) 8) These analytical procedures were similar to that described in the preceding paper.1) The results of the experiments are shown in Table I.

The degree of polymerization of the chain molecules were estimated from the intrinsic viscosity of the cresol solution about the polymer prepared at the temperature of 230°C. The results is presented in Table II.

TABLE II
THE DEGREE OF POLYMERIZATON OF THE CHAIN MOLECULE IN THE POLYMER, PREPARED AT 230°C IN COEXISTENCE OF THYMOL

The no. of mol. of thymol for 1 mol. of (ε-caprolactam+ε-aminocaproic acid)	0	0.075	0.188	0.376	0.603
$[\eta]$ 25°C cresol	1.13	1.10	1.08	0.87	0.94
The number-average(c) degree of polymerization (P)	112	107	102	73	94

Discussions

Assuming the number of mol. of the unit of macro-Brownian motion in the whole reaction phase to be A, the equilibration about lactam-monomer in the case of the super-high polymeric system was represented by Eq. (9) in the previous paper.1) The reactions about lactam-monomer are

$$M_n+L_1 \underset{\kappa}{\overset{k}{\rightleftarrows}} M_{n+1},\ B+L_1 \rightleftarrows M_1 \tag{1}$$

where L_1 = lactam-monomer, $M_n = n-$mer chain molecule, B = the catalyst unbound. For the super-high polymeric system, $B \ll \sum_{n=1}^{\infty} M_n$, $M_1 \ll \sum_{n=1}^{\infty} M_n$,1) so that approximately $\sum_{n=1}^{\infty} M_n + L_1 \rightleftarrows \sum_{n=1}^{\infty} M_{n+1}$, $\sum_{n=1}^{\infty} M_n \approx \sum_{n=1}^{\infty} M_{n+1}$. Consequently polymerizing 1 mol. of ε-caprolactam, in equilibrium

$$L_1^{\circ} = A\kappa/k \tag{2}$$

where L_1° = the number of mol. of lactam-monomer at the equilibrium state, κ = the rate constant of lactam-monomer to be formed from the chain-molecule, k = the rate constant of lactam-monomer to transform into a structural unit of the chain-molecule. In the previous paper A in Eq. (2) was treated approximately as a constant, but in this study on the reactions in coexistence of the diluent A is the most important function.

The larger the value of A is, namely the reaction which arises in the more dilute state, the more lactam-monomer in equilibrium is. Even if the diluent increases, the degree of polymerization of the chain-molecules could hardly change; for it is only directly affected by the quantity of the reagent that possibly reacts to the amide-linkage.

It is experimentally required as the diluent to choose a substance which is a solvent of polycapramide and also chemically stable at the temperature of about 250°C. Thymol (m. wt. 150) was chosen among the usually obtainable substances. The reactiveness of thymol to the amide-linkage is shown by P (the degree of polymerization of the chain-molecules) which is represented in Table II. The larger the dilution was, the smaller P was. The dilution brought increase of the lactam (ring)-molecules so that the chain-molecules were decreased. Considering this effect, however, the observed P is still smaller than the calculated value on the assumption that thymol is a pure diluent. Nevertheless the decrease of the value of P is too slight to assume that thymol reacts on the amide-linkage, considering that the experimental error of intrinsic viscosity measuring is about 5%. Although 0.6 mol. of thymol was used to 1 mol. of lactam, P was about 90; if 0.6 mol. of benzoic acid was used to 1 mol. of lactam, P would be less than 2.(d) Consequently the main effect of thymol must be the dilution. If P is about 80, Eq.(2) may be enough applied approximately because $M_1 \ll \sum_{n=1}^{\infty} M_n$, $B \ll \sum_{n=1}^{\infty} M_n$: so that Eq. (2) is able to be used in the case of discussing the equilibrium about lactam-monomer, assuming thymol as merely

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(b) As for the super-high polymeric system where the degree of polymerization P is about 100, the amounts of water-soluble chain oligomers are too small to make quantitative analysis by extraction. Besides, according to Flory's molecular weight distribution,5) they are negligibly little.

8) P. H. Hermans, *Rec. trav. chim. Pay-Bas*, 72, 798 (1953).

(c) The number-average molecular weight $\overline{M}$ was estimated by the following relation;6)

$$\overline{M}_n = 10400[\mu]^{1.61}$$

where $[\eta]$ is the instrinsic viscosity on the cresol solution at 25°C. It is enough to make a rough estimation.

(d) Polymerizing 1 mol. of ε-caprolactam with 0.5 mol. of benzoic acid at the temperature of 257°C, the number-average degree of polymerization about the chain-molecules was 2.4 and the number of moles of lactam-monomer remaining in the sysrem was 0.11. Benzoic acid effects the reaction not only as the diluent but also as the component that possibly reacts to the amide-linkage.

the diluent.

The size of the unit of macro-Browian motion of the polycapramide molecule has not yet been known. Then it was assumed as follows;

"if 1 mol. of caprolactam were to be entirely polymerized into the polycapramide chain-molecule, the number of mols of the average unit of macro-Browian motion would be α."

In the high polymeric system the quantities of the chain-oligomers are negligibly small b)8) and so only the ring-oligomers are well considered quantitatively as the oligomers. Assume that 1 mol. of caprolactam is polymerized together with S mol. of the diluent, and in equilibrium L_1°, L_2° and L_3° mol. of lactam-monomer,-dimer and-trimer, respectively, are of existence in the polymer. Consequently

$$A=S+L_1^\circ+(1-L_1^\circ)\alpha \tag{3}$$

or

$$A=S+L_1^\circ+L_2^\circ+L_3^\circ+(1-\overline{L_1^\circ+2L_2^\circ+3L_3^\circ})\alpha \tag{4}$$

Eq. (3) is the case that only lactam-monomer besides the diluent is taken into account as the molecule of the low molecular weight in the phase of reaction; Eq. (4) is the case that also lactam-dimer and -trimer are considered. $L_2^\circ+L_3^\circ$ is far less than L_1° as is shown in Table I, so that also Eq. (3) is approximately applicable. Substituting Eq. (3) or Eq. (4) into Eq. (2),

$$L_1^\circ/(1-L_1^\circ)=(\kappa/k)\{(S+L_1^\circ)/(1-L_1^\circ)\}+(\kappa/k)\alpha \tag{5}$$

or

$$L_1^\circ/(1-\overline{L_1^\circ+2L_2^\circ+3L_3^\circ})=(\kappa/k)\{(S+L_1^\circ+L_2^\circ+L_3^\circ)/(1-\overline{L_1^\circ+2L_2^\circ+3L_3^\circ})\}+(\kappa/k)\alpha \tag{6}$$

Plotting $L_1^\circ/(1-L_1^\circ)$ or $L_1^\circ/(1-\overline{L_1^\circ+2L_2^\circ+3L_3^\circ})$ against $(S+L_1^\circ)/(1-L_1^\circ)$ or $(S+L_1^\circ+L_2^\circ+L_3^\circ)/(1-\overline{L_1^\circ+2L_2^\circ+3L_3^\circ})$ about the experimental values of Table I, Fig. 1 or Fig. 2 resulted. As a straight line through the dots is obtainable, these experimental data seemingly satisfy the Eq. (5) or Eq. (6). The values of κ/k and α can be found from the gradient of this straight line and from the coordinate at the point of this straight line to cut across the horizontal axis, respectively. Three straight lines at the temperatures of 200, 230 and 257°C seem apparently to converge to a point on the horizontal axis in the limit of experimental error. The difference between Fig. 1 and Fig. 2 is very small: but Fig. 2 shall be preferred in spite of the assumption to determine $L_2^\circ+L_3^\circ$. The values of α and κ/k from Fig. 2 are shown in Table III.

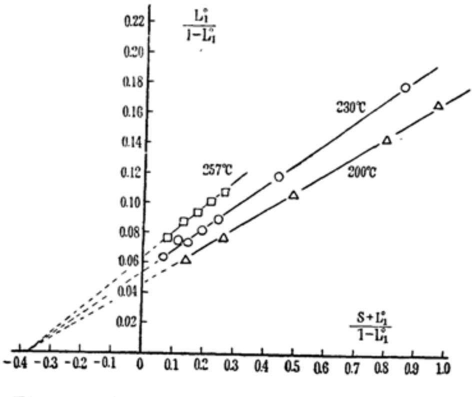


Fig. 1. Application of the experimental data (Table I) to Eq. (3).

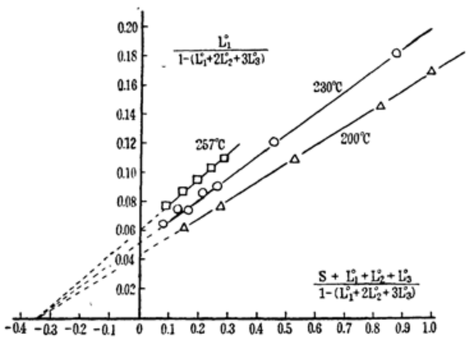


Fig. 2. Application of the experimental data (Table I) to Eq. (4).

TABLE III

THE EXPERIMENTAL VALUES OF α AND κ/k FROM FIG. 2

Temp. °C	257	230	200
α	0.36	0.36	0.36
κ/k	0.170	0.147	0.125

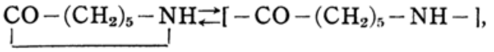
(i) **The Size of the "Segment".**—According to the experimentally obtained value of α and the above assumption about α, if 1 mol. of caprolactam were to be entirely polymerized into the polycapramide chain-molecule, 0.36 mol. of the average unit of macro-Browian motion would be presented in the phase. And so the magnitude of the average unit of macro-Browian motion is of $(1/0.36\approx)$ 2.8 mol. of the structural unit. Expressing the magnitude by the number of atoms of the skeleton, because the structural unit is a 7-atoms member, it is $(7\times2.8\approx)$ 19.5 atoms.

The unit of macro-Brownian motion should be equivalent to the unit of flow discussed on the liquid-viscosity; so it is also equivalent to the "segment" which Eyring put forward about the motion of macromolecule. The magnitude of the "segment" has been hitherto exclusively presumed from the activation energy of flow, and two examples are known. Kauzmann and Eyring[2] measured the activation energies of flow about the various normal hydrocarbons and so estimated the size of the unit of flow by extrapolation to be about 20–25 atoms for the macromolecule. Flory[3] also measured the activation energies of flow on the polyesters and presumed under some suppositions the unit of flow to be 28–34 atoms.

The value here estimated of about 20 atoms on the polycapramide is somewhat smaller than these values on the hydrocarbon and the polyesters, but is roughly equal to them. The method described here to presume the size of a segment is more direct and less hypothetical than the method from the viscosity measurement. As far as these three linear macromolecules are concerned, it is almost approved that the size of the "segment" in molten state has no intimate relation to the intermolecular strength of cohesion.

(ii) **Equilibrium Constant.**—κ/k is the constant which governs whether the structural unit close into ε-caprolactam or open into chain through the amide-interchange reaction.

The value of α is not changed between 200 and 257°C and then it will be possibly applied to 310°C. When ϵ-caprolactam is polymerized without dilution at the temperatures of 230, 257, 280, 295 and 310°C, the amounts of lactam-monomer and (-dimer+-trimer) at the equilibrium state are analysed; these values were presented in Table II of the previous paper.[1] The values of L_1° and $(L_2^\circ+L_3^\circ)$ to denote the numbers of mols of each molecules are deduced by calculation.[a] The value of A in the case of no diluent ($S=O$) at each temperature can be calculated by Eq. (4), and substituting it into Eq. (2), the value of κ/k is obtained. The results of such calculations are Table IV. Plotting the logarithms of κ/k against the reciprocals of the absolute temperature, Fig. 3 is obtained. The energy difference between the ring and the chain states, i.e.



$$\underbrace{CO-(CH_2)_5-NH}\rightleftarrows[-CO-(CH_2)_5-NH-],$$

may be estimated through Fig. 3; its value is 3.4–3.6 kcal./mol. In the previous paper[1] the values of A could not be determined, so A was treated as a constant under the first approximation. Therefore, there is nothing for estimation of the energy difference but to use $A(\kappa/k)$ instead of κ/k. Practically the values of A at the various temperatures are slightly different as are shown in Table IV. Considering this effect for the second approximation, slightly smaller value is obtained; this value coincids better with the heat of polymerization calorimetrically measured by Skurator et al. [4,1]

TABLE IV

THE VALUES OF THE EQUILIBRIUM CONSTANT κ/k AT THE VARIOUS TEMPERATURES

$$\left(\begin{array}{l}\kappa/k=L_1^\circ/A,\ A=S+L_1^\circ+L_2^\circ+L_3^\circ\\ +(1-\overline{L_1^\circ+2L_2^\circ+3L_3^\circ})\alpha,\ S=0,\ \alpha=0.36\end{array}\right)$$

Temp. °C	L_1° mol.	$L_2^\circ+L_3^\circ$	A mol.	κ/k
200	—	—	0.400	0.125
230	0.062	0.009	0.406	0.153
257	0.070	0.010	0.411	0.170
280	0.083	0.010	0.420	0.197
295	0.089	0.011	0.424	0.210
310	0.106	0.011	0.435	0.244

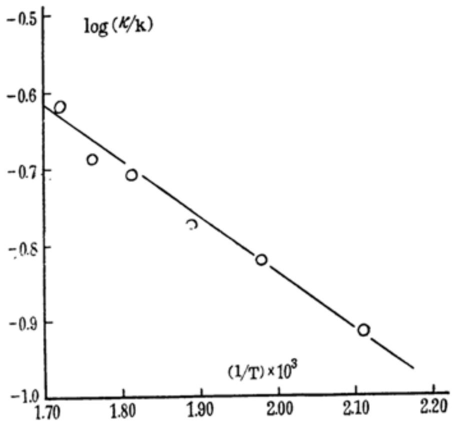


Fig. 3. Logarithms of the equilibrium constants vers. reciprocals of the absolute temperatures.

Conclusion

In the previous paper the author deduced the equation of kinetics about polymerization and depolymerization of ε-caprolactam in the super-high polymeric system through the amide-interchange reaction, and investigated the formulas experimentally. In succession, the experiments about the polymerization of ε-caprolactam with thymol as the diluent were carried out at 200, 230 and 257°C and their results were discussed in view of the deduced equations. The quantities of lactam oligomers in the polymeric systems containing the diluent were larger than those containing no diluent. Such inclination shows the reaction-orders of polymerization and depolymerization to be different. The increase of lactam-monomer satisfied the deduced equation quantitatively. Then from this relation the size of unit of macro-Browian motion, i.e. a "segment", about the polycapramide chain-molecules could be estimated to be ca. 20 atoms. The method described here to estimate unit of macromolecule's macro-Brownian motion contains less assumption than the method from the melt viscosity measurement. The number of mol. of the unit of macro-Brownian motion in the whole reaction phase, A, being assumed in the derived equation, was calculated. Consequently the equilibrium constants, concerned with the transforming reactions between a structural unit (opened state) and a lactam monomer (closed state), could be found at the various temperatures, and so the heat of the above reactions can be estimated to be 3.4–3.6 kcal./mol.

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