Studies on Polymerization and Depolymerization of ε-Caprolactam Polymer. IX. Reformation Reaction of ε-Caprolactam from Poly-ε-capramide*

By Naoya OGATA

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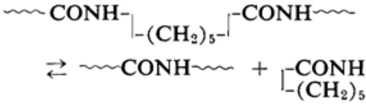
The mechanism of the polymerization reaction of ε-caprolactam in the presence of water has been studied in detail by many investigators[1-6]. It has been generally accepted that the initial reaction of the polymerization is caused by the hydrolysis of ε-caprolactam and that the chain growth occurs mainly through the addition of ε-caprolactam to $-NH_2$ end-groups, being catalyzed by $-COOH$ end-groups. If this mechanism is correct, ε-caprolactam is reformed in the depolymerization reaction rolling out successively from $-NH_2$ end-groups of the polymer chain because the polymerization is an equilibration reaction. Therefore, no ε-caprolactam can be expected from poly-ε-capramide having modified end-groups. In the previous paper[6], however, it was presumed that the addition reaction of ε-caprolactam would take place even on amide groups near the center of the polymer chain. In this case the reverse process of this intramolecular amide-interchange reaction called "Einrollung Reaktion"[1] as shown below is responsible for the reformation of ε-caprolactam from poly-ε-capramide.



$$\sim\sim CONH\text{-}\underbrace{}_{-(CH_2)_5-}\text{-}CONH\sim\sim \rightleftarrows \sim\sim CONH\sim\sim + \left[\begin{matrix}-CONH-\\-(CH_2)_5-\end{matrix}\right]$$

Experimental

TABLE I. THE ANALYTICAL RESULTS OF THE POLYMERS

Kind of end-group	Basic group mol./mol.	Acidic group mol./mol.	$[\eta]$
$NH_2—NH_2$	9.8×10^{-2}	3.9×10^{-4}	0.21
	16.5×10^{-2}	7.2×10^{-4}	0.16
$HOOC—COOH$	11.8×10^{-4}	9.5×10^{-2}	0.20
	8.2×10^{-4}	7.8×10^{-2}	0.20
$NaOOC—COONa$	0	0	0.22
	2.7×10^{-4}	0	0.27
	0	0	0.41
	0	0	0.50
$ClH\cdot H_2N—NH_2\cdot HCl$	0	—	0.25
$AcHN—NHAc$	8.8×20^{-4}	2.3×10^{-4}	0.23
	9.3×10^{-4}	2.7×10^{-4}	0.27
	0	0	0.43
	3.4×10^{-4}	0	0.52

ε-Caprolactam with water content less than 0.01% was polymerized in the presence of 1/20, 1/50 or 1/100 mol./mol. of hexamethylenediamine or adipic acid at 257°C. Polymers were washed with boiling water, and then heated in a solid phase at 180°C for 10 hr. at 1 mmHg pressure. The analytical results of the polymers having almost exclusively $-NH_2$ or $-COOH$ end-groups thus obtained are shown in Table I. The polymer having $-NH_2$ end-groups was heated in refluxing acetic anhydride for 4 hr. and $-NH_2$ end-groups were acetylated almost completely. The polymer having $-NH_2$ end-groups was also dissolved in phenol and $-NH_2$ end-groups in the polymer were neutralized by titrating with aqueous hydrochloric acid in the presence of thymol blue as an indicator. The polymer having $-COOH$ end-groups was dissolved in hot benzyl alcohol and the solution was neutralized by titrating with alcoholic sodium hydroxide solution in the presence of phenolphthalein. The polymers having $-NH_3^+Cl^-$ or $-COONa$ end-groups were precipitated by adding methanol to the neutralized solutions.

Each of the polymers was washed with refluxing methanol and dried at 110°C in vacuo of 2 mmHg for 24 hr. in order to decrease the water content to less than 0.01%. The polymer samples, each 2 g. in weight, were sealed within glass tubes under a nitrogen atmosphere and heated for a certain period of time at 230 or 257°C in a vapor bath of thymol or Dowtherm A. The amount of ε-caprolactam reformed from the polymers was determined for the extract in chloroform. The number of end-groups in the polymers was determined and the intrinsic viscosity $[\eta]$ for the polymers was measured in 98% sulfuric acid. The polymerization degree $\bar{P}_n$ of the polymers was calculated by the following equation[7].

$$\bar{P}_n = 124[\eta] - 5$$

Results

The rates of reformation of ε-caprolactam from the polymers are shown in Tables II—V.

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* VIII, This Bulletin, 33, 1584 (1960).

[1] F. Wiloth, *Kolloid-Z.*, 144, 58 (1955); *Z. physik. Chem.*, 11, 78 (1957).

[2] P. H. Hermans, D. Heikens and P. F. van Velden, *J. Polymer Sci.*, 30, 81 (1958): 44, 437 (1960).

[3] A. V. Tobolsky and A. Eisenberg, *J. Am. Chem. Soc.*, 81, 2302 (1959).

[4] H. Yumoto, This Bulletin, 28, 94, 101 (1955).

[5] H. Yumoto and N. Ogata, *Makromol. Chem.*, 25, 71 (1957).

[6] N. Ogata, ibid., 30, 212 (1959).

[7] A. Matthes, ibid., 5, 165 (1950).

TABLE II. THE RATE OF REFORMATION OF ε-CAPROLACTAM FROM THE POLYMER OF $\overline{P}_n \fallingdotseq 20$

Kind of end-group	Temp. °C	Time hr.	Lactam %	Basic group mol./mol.	Acidic group mol./mol.	[η]
$H_2N—NH_2$	230	0	0	9.8×10^{-2}	3.9×10^{-4}	0.21
		1	0.51	8.9 〃	7.2 〃	0.32
		2	1.33	8.9 〃	7.2 〃	0.33
		5	3.34	—	8.6 〃	—
		10	4.53	8.9 〃	10.0 〃	0.22
		25	4.94	8.4 〃	10.4 〃	—
		50	5.32	9.7 〃	8.5 〃	—
	257	0	0	16.5×10^{-2}	7.2×10^{-4}	0.16
		1	4.60	11.9 〃	9.6 〃	0.14
		2	6.74	12.0 〃	6.7 〃	0.16
		5	8.45	12.0 〃	5.4 〃	0.16
		10	8.97	12.1 〃	8.8 〃	0.17
		25	9.85	11.4 〃	9.6 〃	0.16
		50	10.23	11.5 〃	10.8 〃	0.17
HOOC—COOH	230	0	0	11.8×10^{-4}	9.5×10^{-2}	0.20
		1	0.02	7.8 〃	9.5 〃	0.20
		2	0.11	8.0 〃	9.2 〃	0.24
		5	0.70	9.2 〃	9.0 〃	0.24
		10	0.80	9.2 〃	9.0 〃	0.23
		25	2.02	9.2 〃	9.5 〃	0.22
		50	4.48	9.0 〃	9.5 〃	0.21
	257	0	0	8.2×10^{-4}	7.8×10^{-2}	0.20
		1	1.40	6.3 〃	6.8 〃	0.20
		2	2.22	6.3 〃	6.7 〃	0.21
		5	4.69	6.9 〃	6.8 〃	0.20
		10	6.72	6.5 〃	6.7 〃	0.23
		25	7.84	6.7 〃	6.8 〃	0.20
		50	7.75	6.3 〃	6.7 〃	0.20
NaOOC—COONa	230	0	0	—	0	0.22
		25	0.22	—	0	0.22
		50	0.63	—	0	0.21
	257	0	0	—	0	0.22
		1	5.51	—	0	0.24
		2	5.58	—	0	0.26
		5	5.80	—	0	0.27
		10	7.05	—	0	0.20
		25	14.65	—	0	0.27
		50	16.69	—	0	0.26
$ClH\cdot H_2N—NH_2\cdot HCl$	230	0	0	0	—	0.24
		1	1.74	0	—	0.24
		2	2.06	0	—	0.23
		5	3.40	0	—	0.24
		10	4.74	0	—	0.22
		25	9.35	0	—	0.21
		50	11.21	0	—	0.22
	257	2	7.18	0	—	0.23
		10	11.43	0	—	0.23
		25	13.60	0	—	0.22
		50	13.80	0	—	0.22
AcHN—NHAc	230	0	0	8.8×10^{-4}	2.3×10^{-4}	0.23
		2	0.07	2.4 〃	2.9 〃	—
		5	0.08	2.2 〃	2.9 〃	0.23
		10	0.26	2.2 〃	2.4 〃	0.22
		25	0.11	3.0 〃	2.5 〃	0.23
		50	0.59	3.7 〃	2.9 〃	0.23
	257	0	0	8.6×10^{-4}	4.2×10^{-4}	0.23
		1	0.31	6.9 〃	0.2 〃	0.24
		5	0.87	9.2 〃	0.3 〃	0.25
		10	1.57	15.0 〃	0.3 〃	0.25
		25	2.50	15.0 〃	0.3 〃	0.25
		50	4.98	17.7 〃	0.3 〃	0.24

TABLE III. THE RATE OF REFORMATION OF ε-CAPROLACTAM FROM THE POLYMER OF $\bar{P}_n=30$

Kind of end-group	Temp. °C	Time hr.	Lactam %	[η]
AcHN—NHAc	230	0	0	0.27
		50	0	0.28
		100	0	0.28
		150	0	0.28
	257	0	0	0.27
		25	3.64	0.28
		50	8.75	0.27
		75	10.00	0.27
		100	10.00	0.27
		150	10.88	0.27
NaOOC—COONa	230	0	0	0.27
		50	0	0.28
		100	0	0.28
		150	0	0.28
	257	0	0	0.27
		25	5.79	0.28
		50	7.61	0.28
		75	8.60	0.28
		100	8.29	0.28
		150	9.25	0.28

TABLE IV. THE RATE OF REFORMATION OF ε-CAPROLACTAM FROM THE POLYMER OF $\bar{P}_n=40$

Kind of end-group	Temp. °C	Time hr.	Lactam %	[η]
AcHN—HNAc	230	0	0	0.43
		50	0	0.46
		100	0	0.43
		150	0.63	0.44
	257	0	0	0.43
		25	2.96	0.43
		50	3.90	0.41
		75	7.07	0.42
		100	7.72	0.42
		150	8.17	0.42
NaOOC—COONa	230	0	0	0.41
		50	0	0.47
		100	0	0.45
		150	0	0.43
	257	0	0	0.41
		25	2.89	0.38
		50	6.06	0.37
		75	8.66	0.37
		100	8.93	0.37
		150	8.58	0.37

TABLE V. THE RATE OF REFORMATION OF ε-CAPROLACTAM FROM THE POLYMER OF $\bar{P}_n=50$

Kind of end-group	Temp. °C	Time hr.	Lactam %	[η]
AcHN—NHAc	230	0	0	0.52
		50	0	0.54
		100	0	0.54
		150	0.70	0.51
	257	0	0	0.52
		25	4.41	0.53
		50	3.98	0.50
		75	6.51	0.51
		100	8.52	0.51
		150	8.90	0.51
NaOOC—COONa	230	0	0	0.50
		50	0	0.57
		100	0	0.53
		150	0	0.52
	257	0	0	0.50
		25	3.03	0.43
		50	6.87	0.43
		75	7.41	0.44
		100	8.30	0.44
		150	7.75	0.44

No change in the number of end-groups was observed during the heat treatment. As shown in Tables II—V, at 230°C, ε-caprolactam is reformed from the polymer of which the end-groups are exclusively $-COOH$ or $-NH_2$ while no ε-caprolactam is reformed from the polymer having $-NHAc$ or $-COONa$ end-groups. However, at 257°C, ε-caprolactam is reformed even from the polymer having $-NHAc$ or $-COONa$ end-groups. The rate of the reformation of ε-caprolactam is not influenced by the polymerization degree of the modified polymers. The rate of the reformation of ε-caprolactam from the polymer having $-NH_3^+$ end-groups is very fast.

Discussion

The re-equilibration of poly-ε-capramide has been studied[8-11] on the dry polymers having modified end-groups. It has been reported[8,9] that the rate of reformation of ε-caprolactam from the acetylated polymer is very much slower than that of normal polymer. From these results, it seems very probable that no re-equilibration would take place in a dry polymer having all its end-groups modified.

As shown in the experimental results, no ε-caprolactam is formed at 230°C from the polymer having COONa or $-NHAc$ end-groups. However, above 230°C, it is presumed that the addition or reformation of ε-caprolactam must take place on the amide groups in the polymer chain through the intramolecular amide-interchange reaction. As the rate of the reformation of ε-caprolactam from the polymer having $-NH_3^+$ end-groups is very fast, it is ascertained[2,5] that the addition or the reformation of ε-caprolactam on the $-NH_2$ end-groups, catalyzed by the hydrogen ion, occurs fast.

Assuming that reformation reaction of ε-caprolactam from the polymer having modified end-groups may be caused by the intramolecular interchange reaction between two adjacent

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8) S. Smith, *J. Polymer Sci.*, **30**, 459 (1958).

9) G. M. Van der Want, ibid., **37**, 547 (1959).

10) D. Heikens, P. H. Hermans and S. Smith, ibid., **38**, 265 (1959).

11) N. D. Katorzhnow and A. A. Strepikeev, *Zh. priklad Khim.*, **32**, 625 (1959).

amide groups in polymer chain, it can be expressed as follows:

$$\mathrm{M}_n \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{M}_{n-1}+\mathrm{L} \qquad (1)$$

where M_n and M_{n-1} are polymer chains, L is ε-caprolactam, k_1, k_2 the rate constant of the reformation or addition reactions, respectively. The rate of the reformation reaction of ε-caprolactam can be expressed as follows, when the concentration of polymer chain is expressed in mole fraction of structural unit:

$$\mathrm{d}x/\mathrm{d}t=k_1(1-x)-k_2x \qquad (2)$$

where x is the mole fraction of ε-caprolactam reformed at t hr. At equilibrium,

$$k_2=k_1(1-x_\infty)/x_\infty \qquad (3)$$

where the equilibrium concentration of ε-caprolactam x_∞ is about 0.07⁴⁾ and $(1-x_\infty)$ can be fixed as equal to 1. Then, from Eqs. 2 and 3,

$$\mathrm{d}x/\mathrm{d}t=k_1(1-x/x_\infty) \qquad (4)$$

Integration of Eq. 4 gives Eq. 5.

$$2.303\log x_\infty/(x_\infty-x)=k_1t/x_\infty \qquad (5)$$

From Eq. 5, the rate constant of the reformation reaction of ε-caprolactam can be calculated for the polymer having modified end-groups, as shown in Table VI. The values of k_1 are roughly the same, being independent of the polymerization degree of the polymer. The mean value of k_1 is 0.23×10^{-2} mol./mol.hr. Yumoto⁴⁾ reported that the rate constant of the reformation of ε-caprolactam from the polymer $[\eta]_{\text{cresol}}=1.1$ was 2.26×10^{-2} mol./mol.hr. at 257°C. In this case, as the number of amino- or carboxyl-groups in the polymer is $(0.5\sim0.7)\times10^{-2}$ mol./mol., it is presumed that the reformation of ε-caprolactam may be caused mainly by the reaction rolling out ε-caprolactam succesively from the ends of the polymer chain.

TABLE VI. THE VALUES OF k_1 AT 257°C

Kind of end-group	$\bar{P}_n$	Time hr.	k_1 mol./mol.hr.
AcHN—NHAc	26	1	0.33×10^{-2}
		5	0.18 〃
		10	0.18 〃
		25	0.12 〃
		50	0.18 〃
AcHN—NHAc	29	25	0.18 〃
		50	0.42 〃
NaOOC—COONa	30	25	0.36 〃
		50	0.32 〃
		75	0.33 〃
		100	0.21 〃
AcHN—NHAc	48	25	0.15 〃
		50	0.11 〃
		75	0.20 〃
		100	0.20 〃
NaOOC—COONa	46	25	0.14 〃
		50	0.20 〃
		75	0.42 〃
AcHN—NHAc	59	25	0.24 〃
		50	0.11 〃
		75	0.16 〃
		100	0.28 〃
NaOOC—COONa	57	25	0.15 〃
		50	0.32 〃
		70	0.30 〃
Mean value			0.23×10^{-2}

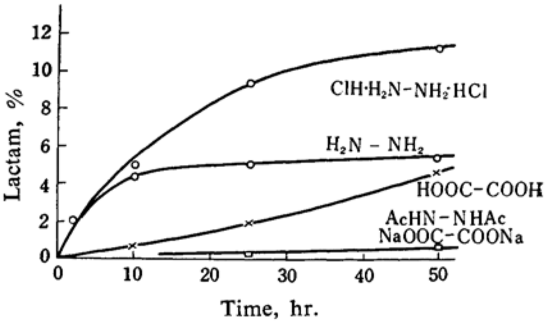

Fig. 1. The rate of reformation of ε-caprolactam from the polymer of $\bar{P}_n=20$ at 230°C.

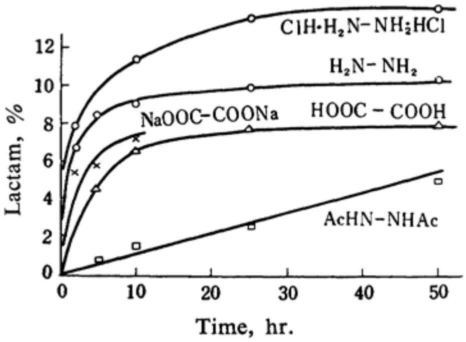

Fig. 2. The rate of reformation of ε-caprolactam from the polymer of $\bar{P}_n=20$ at 257°C.

Compared with this value, the reformation velocity of ε-caprolactam from the polymer having modified end-groups is about 1/10 and it can be found that the end-groups of the polymer play a very important role for the addition or the reformation reactions of ε-caprolactam. However, the rate of the reformation of ε-caprolactam from the polymer having modified end-groups is independent of the polymerization degree of the polymer and it is presumed that ε-caprolactam is reformed also by the reaction between two adjacent amide groups in the polymer chain.

In the previous paper⁶⁾, it was reported from the results of the amide-interchange reaction of an N-alkyl acid amide and ε-caprolactam, that the rate constant of the reformation reaction of ε-caprolactam at 252°C was 3.6×10^{-2} mol./mol.hr. This value is considerably greater than that for the polymer having modified end-groups. This is probably due to the difference in activity of the components.

It is concluded for the polymerization and reformation reactions in the system of ε-caprolactam and poly-ε-capramide that the reaction occurs predominantly on the end-groups of the polymer and that the intramolecular amide-interchange reaction between two adjacent amide groups in the polymer chain occurs slowly.

Summary

The reformation reaction of ε-caprolactam from poly-ε-capramide having modified end-groups has been studied. It was found that no ε-caprolactam was reformed at 230°C from the polymer of which all of the end-groups were -COONa or -NHAc groups, while ε-caprolactam was reformed slowly at 257°C. The rate of the reformation of ε-caprolactam from the polymer having -COONa or -NHAc end-groups is about 1/10 of that from the polymer having normal end-groups at 257°C and it is independent of the polymerization degree of the polymer.

The polymerization and the depolymerization reactions of ε-caprolactam polymer occur predominantly on the end-groups and the interchange reaction between two adjacent amide groups in the polymer chain occurs slowly.

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Research Department
Toyo Rayon Co., Ltd.
Minato-ku, Nagoya