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On the Mechanism of the Polymerization of ϵ-Caprolactam.* II. The Polymerization in the Presence of Water

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1. INTRODUCTION

The polymerization of ϵ-caprolactam (CL) in the presence of water leads to equilibrium. The present kinetic evaluation of the process requires knowledge of the equilibrium constants. These are borrowed from a previous study of the equilibrium published in an earlier paper.[9]

The results of our kinetic investigation (almost finished in 1954) have only been briefly surveyed in a lecture.[5a] This work has proceeded simultaneously with corresponding efforts by a group of workers in the Central Laboratory TNO in Delft and by Dr. F. Wiloth in Germany with whom reports have been frequently exchanged. Wiloth, who has published several papers on the subject[10b,c,d] has ultimately reached conclusions[10d] which in major points are almost identical with those presented here. His approaches, however, are sufficiently different from ours to justify a comprehensive publication of our work.

Carothers[1] has reported that pure caprolactam (CL) does not polymerize when heated in a sealed vessel, and we have confirmed this in an earlier phase of our work. If the material is very pure and carefully dried, heating at 250° for 600 hr. in a closed and evacuated tube effects hardly any change.

Though the repeating unit in the linear nylon 6 polymer has the same composition as caprolactam, polymer formation from the latter requires the presence of some other substance (often called "initiator" in patent literature) responsible for endgroup formation.

In simple preliminary experiments we have convinced ourselves that, under rigorously anhydrous conditions, addition of about 1 mole per cent of the following substances does not effect significant polymerization after heating during 100–150 hr. at 250°: adipic acid, benzoic acid, hexamethylene diamine, benzylalcohol, *N*-*n*-caproyl-*n*-amylamide.

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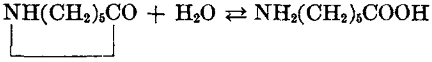
This excludes carboxylic acids, primary amines, alcohols, and amides as possible initiators. Skuratov[8b] reported the same observations for carboxylic acids and amines, and Wiloth for benzoic acid[10b] and recently also for several amines and amides.[10d] If, however, a mixture of equal parts (0.5 mole per cent) of benzoic acid and benzyl alcohol was added, fairly rapid polymerization ensued. This also holds for combined additions of an acid plus an amine (nylon salt) or of an amino acid (ε-aminocaproic acid) alone. Since these additions can produce water through esterification or amidation, it was strongly suggested that water is a powerful initiating agent.

In the polymerization of CL in the presence of a small quantity of water (as is the usual practical procedure), the first reaction step is likely to be the formation of aminocaproic acid (ACA) by hydrolysis:



$$NH(CH_2)_5CO + H_2O \rightleftarrows NH_2(CH_2)_5COOH$$

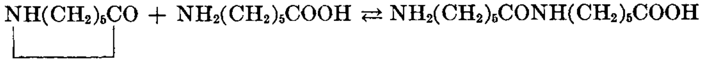
followed by other reactions to be established in detail. Among these the linear polycondensation of ACA acting as a bifunctional monomer can be expected to occur.

From earlier experimental work of the TNO group in Delft on the reaction of dry CL to which a small amount of ACA had been added, unmistakable evidence has been derived that hydrolysis followed by polycondensation alone can never account for the rate of CL conversion and that another, much faster reaction is involved. This was suggested to be a growth of chains by direct addition of CL onto endgroups.[13] This type of reaction has also been advocated by Matthes,[7] one of the first authors who published experimental work on the subject. However, Matthes' considerations were rather unclear and his experiments and analytical methods are open to criticism.

Matthes relied on extraction values for CL determination, a method giving considerable error at low degrees of polymerization. Furthermore, he claims that CL is readily polymerized in the presence of some benzoic acid alone, and he evaluates the kinetics of this system, not accounting for the water which must have been present in order to effect reaction rates as reported by him. It should be admitted, though, that Matthes has sensed the essentials of the actual reaction through which polymerization mainly occurs.

For want of conclusive kinetic experiments, considerations of a more or less speculative character have also been advanced by other authors.[11] The polymerization of CL in the presence of water has been investigated systematically by Skuratov et al.[8a] by direct calorimetry.

Flory[2] in his book writes that in the formation of condensation polymers from a cyclic "monomer," such as lactide or caprolactam, which is accelerated by small amounts of water, the mechanism is most probably as follows: Through hydrolysis by water a small amount of a linear product bearing OH and COOH or NH_2 and COOH endgroups is formed. The polymerization then proceeds by successive addition of the cyclic compound onto the OH or the NH₂-group of the chain, lengthening the chain per one unit. This reaction comes down to an ester or amide interchange reaction:



$$\mathrm{NH(CH_2)_5CO + NH_2(CH_2)_5COOH \rightleftarrows NH_2(CH_2)_5CONH(CH_2)_5COOH}$$

In the present work this general picture is confirmed.

In a following paper conclusive evidence will be presented that the addition actually takes place onto the NH₂-group while it is catalyzed by COOH-groups.

2A. EXPERIMENTAL METHODS

In each kinetic run, a large number of small Pyrex tubes (of exactly measured inside diam. 6–8 mm.) were filled up to a mark (see Fig. 1-1) with a previously prepared mixture of pure CL and water in known proportion. The filling was performed inside a specially designed hot chamber in which the storage vessel containing the mixture was also kept ready. (The temperature was 80–90° in order to keep the mixture liquid.) With the aid of a valve mechanism, the required portion of the mixture (0.5–2 g. according to requirements) could be allowed to flow into the reaction tube through a small funnel (*3*), the tip of which remained slightly above the mark and was kept centered by means of three glass nipples. This enabled us to withdraw the funnel while keeping the inside wall of the tube clean.

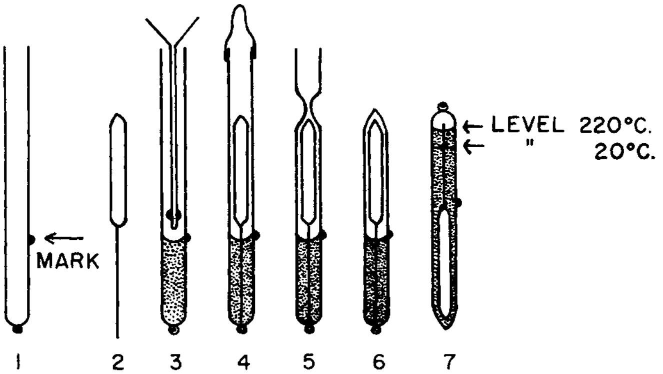


Fig. 1. Filling of reaction tubes.

After removal of the funnel, a glass dummy (*2*) of diameter selected to fit closely inside the tube was inserted, the thin glass rod pointing downwards (*4*). By keeping the body of the dummy at some distance from the liquid level, the rod prevented the liquid from creeping into the capillary space between dummy and tube wall. The tube was closed with a rubber cap and its lower part quickly cooled (Dry Ice in ethanol) to avoid condensation of water from the hot reaction mixture on the upper tube wall. After conditioning to the laboratory atmosphere, the tube and its contents were weighed. The tube was then narrowed just above the dummy body (*5*), the lower part was cooled again and the tube evacuated, washed with nitrogen, and evacuated again. The tube was then sealed off at the narrowed part (*6*), and was weighed again with the glass molten off. From these weighings and the weight of the tube before filling, the weight of the contents was known and there was a check that no loss of material occurred during evacuation.

TABLE I. Numerical Values of Experimental Data
(Concentrations in millimoles (or milli val.) per gram mixture

t	$-\dot{x}$	$\dot{c}$	x	c	$w = w_0 - c$	z	u_1
Series A, $w_0/x_0 = 0.10$, $w_0 = 0.87$, $x_0 = 8.71$, temp. 221.5°							
1.0	0.125	0.012	8.6	0.005	0.866	0.055	0.0029
1.5	0.31	0.026	8.5	0.022	0.849	0.188	0.0039
2.0	0.51	0.040	8.3	0.040	0.831	0.35	0.0044
2.5	0.82	0.048	7.95	0.065	0.806	0.7	0.0045
3.0	1.46	0.051	7.4	0.090	0.781	1.2	0.0045
3.5	2.65	0.058	6.35	0.117	0.754	2.25	0.0042
4.0	2.69	—	4.9	0.142	0.729	3.65	0.0038
4.5	2.05	0	3.75	0.146	0.725	4.8	0.0032
6.0	0.73	−0.012	1.75	0.124	0.747	6.85	0.0016
7.0	0.36	−0.008	1.31	(0.114)	0.757	7.3	0.0011
10.0	0.10	−0.004	0.75	(0.096)	0.775	7.85	0.0008
Series B, $w_0/x_0 = 0.067$, $w_0 = 0.59$, $x_0 = 8.75$, temp. 221.5°							
1.5	0.15	0.012	8.65	0.011	0.576	0.1	0.0018
2.0	0.20	0.0175	8.55	0.019	0.568	0.2	0.002
2.5	0.32	0.021	8.4	0.029	0.558	0.3	0.0021
3.0	0.52	0.028	8.2	0.042	0.545	0.5	0.0022
3.5	0.84	0.039	7.9	0.060	0.527	0.8	0.0022
4.0	1.18	0.040	7.4	0.081	0.506	1.25	0.0022
4.5	1.51	0.038	6.7	0.100	0.487	1.95	0.0021
5.5	2.00	0	4.85	0.119	0.468	3.8	0.0019
7.0	0.93	−0.0155	2.7	0.108	0.479	5.95	0.0014
7.5	0.70	−0.014	2.3	0.100	0.487	6.35	0.0013
8.0	0.54	−0.009	1.95	0.094	0.493	6.7	0.0012
9.0	0.34	−0.005	1.55	0.087	0.500	7.1	0.0011
10.0	0.23	−0.0035	1.25	0.083	0.504	7.4	0.001
Series C, $w_0/x_0 = 0.05$, $w_0 = 0.44$, $x_0 = 8.78$, temp. 221.5°							
2.0	0.23	0.010	8.55	0.010	0.429	0.22	
3.0	0.44	0.0175	8.2	0.024	0.415	0.55	
4.0	0.61	0.0275	7.7	0.049	0.390	1.05	
5.0	0.80	0.018	7.0	0.072	0.367	1.7	
6.0	0.93	0.014	6.1	0.088	0.351	2.6	
7.0	1.0	—	5.15	0.100	0.339	3.55	
8.0	1.05	—	4.1	0.101	0.338	4.6	
9.0	1.0	−0.007	3.0	0.094	0.345	5.7	
10.0	0.86	−0.0065	2.05	0.087	0.352	6.65	
12.0	0.31	−0.004	0.95	0.077	0.362	7.75	
Series D, $w_0/x_0 = 0.05$, $w_0 = 0.44$, $x_0 = 8.78$, temp. 253.5°							
0.5	0.26	0.029	8.65	0.010	0.42	0.12	
0.75	0.455	0.050	8.60	0.019	0.41	0.16	
1.0	0.94	0.070	8.42	0.032	0.40	0.33	
1.25	1.53	0.087	8.10	0.051	0.38	0.63	
1.50	2.08	0.087	7.65	0.073	0.36	1.06	
1.75	3.17	0.087	7.0	0.095	0.335	1.68	
2.0	5.0	0.031?	6.0	0.110	0.31	2.67	
2.25	4.26	~0	4.8	0.113	0.31	3.87	
3.0	2.0	−0.019	2.05	0.105	0.325	6.62	
3.5	1.08	−0.0213	1.85	0.095	0.335	6.83	
4.0	0.56	−0.0135	1.4	0.086	0.345	7.29	
5.0	0.29	−0.007	1.05	0.077	0.35	7.65	

The tubes were heated in inversed position (7) at the required temperature and for the required length of time in an aluminum block thermostated to ±0.5°.

The dummy served to keep the vapor phase in the reaction tube as small as possible in order to reduce to a minimum the fraction of water present in the vapor phase at the reaction temperature.[9] It could be shown that the quantity of water vapor in the remaining dead space was small enough as to be negligible in the case of the low water contents of the reaction mixtures employed in the present work.[9]

The change in volume of the reaction mixture with time appeared to be smaller than could be detected with the method of volume determination employed (for details see ref. 9). For convenience, all concentrations were therefore expressed in millimoles/gram.

The analytical procedures applied for the determination of endgroups, unconverted CL, total weight of chain fraction, and fraction of cyclic oligomers were essentially the same as those previously described.[5,9]

For the kinetic analysis it became imperative to have additional data available on the course of the concentration of ε-aminocaproic acid (ACA) during the reaction. Since this substance occurs in but promille concentrations, a paper chromatographic method for its determination was worked out which has been described in detail elsewhere.[5b]

2B. EXPERIMENTAL RESULTS

The following runs were investigated:

Series	Molar ratio, water/Cl	Temperature, °C.	ACA	Higher rings
A	0.10	221.5	+	+
B	0.067	221.5	+	
C	0.05	221.5		+
D	0.05	253.5		

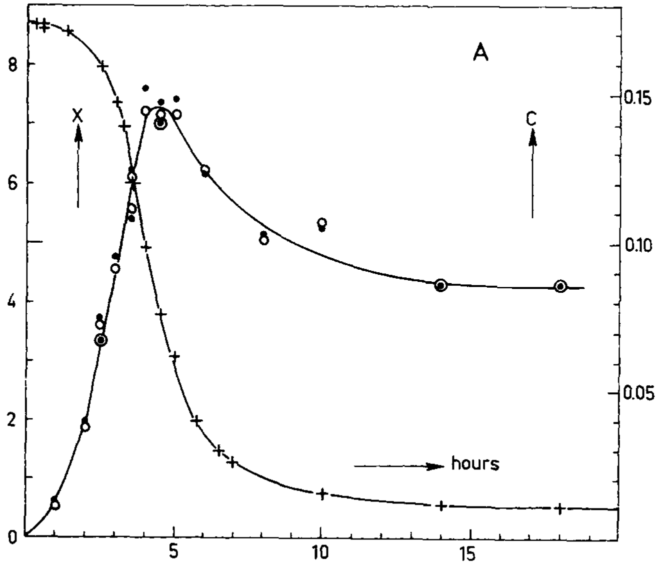


Fig. 2A. Experimental series A, $w_0/x_0 = 0.10$, temp. 221.5°. x = unconverted lactam (mmoles/g.). c = endgroups (meq./g.). (O) COOH. (●) NH_2.

Determination of ACA and of higher ring oligomers (requiring separate runs) were carried out only in the cases indicated by +.

We refrain from giving all the experimental results in extenso. As an example, those of series A and B are graphically shown in Figures 2A and 2B (unconverted CL and endgroup concentration). It is seen that the endgroup titrations always yielded a practically equal concentration of COOH- and NH_2-groups.

In Figure 3 are given the ACA concentrations observed in series A and B. (For determinations of ACA having an estimated error of ±10%, numerous points have been determined.)

Figure 4 gives the total weight of the higher ring oligomers (dimer, trimer, and tetramer) produced in the series A and C.

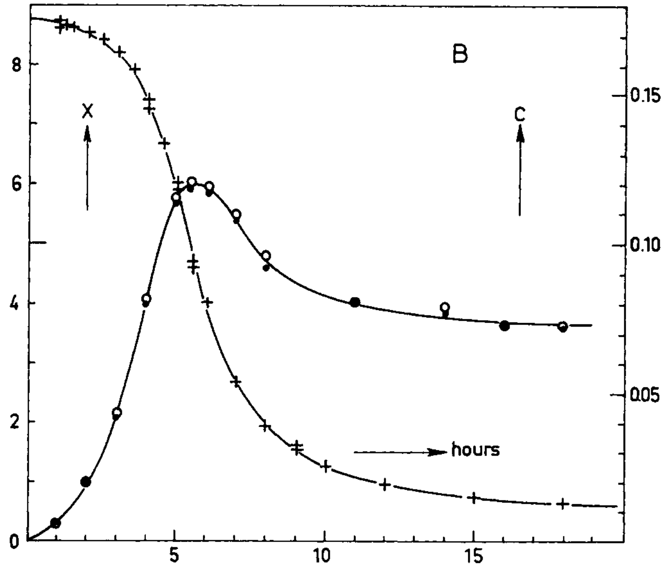


Fig. 2B. Experimental series B, w_0/x_0 = 0.067, temp. 221.5°. Symbols as in Fig. 2A.

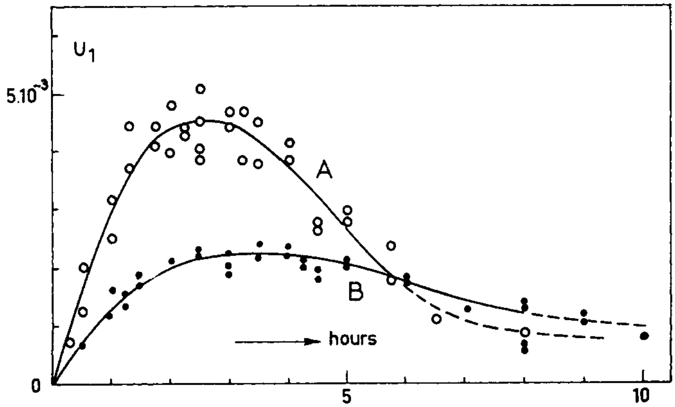


Fig. 3. ACA concentration μ_1 in meq./g. for series A (O, molar ratio water/lactam 0.1) and B (●, molar ratio 0.067) at 221.5°.

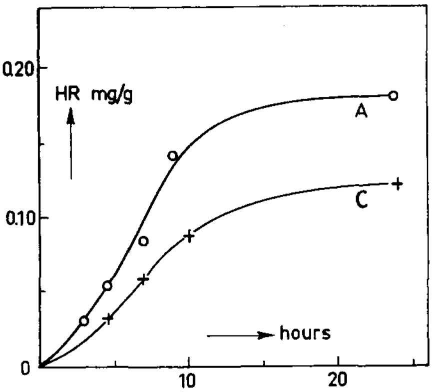


Fig. 4. Total production of cyclic oligomers HR (di, tri, and tetramer) in mg./g. for the series A and C (221.5°).

The results have been evaluated by the differential method as in the preceding paper. This means that the slopes of the conversion curves were determined in order to evaluate dx/dt and dc/dt (symbols $\dot{x}$ and $\dot{c}$) at suitably chosen reaction times. The corresponding concentrations were read from the curves.

This procedure has led to the establishment of a set of experimental reference data as given in Table I on which the kinetic evaluation has been mainly based.

In the evaluation of the hydrolysis reaction, experimental readings at smaller reaction times than those recorded in Table I were also required. These are separately dealt with in Table II.

TABLE II

Data Pertaining to Short Reaction Times for the Series A and B

Time t in hours, concentrations in millimoles/g.

t	$\dot{c} \times 10^3$	x	w	RO ($xw - 400u_1$)	($\dot{c}$/RO) $\times 10^3$	$c \times 10^3$
			Series A, $w_0/x_0 = 0.10$			
0.5	11.5	8.65	0.865	6.86	1.68	5
1.0	15	8.60	0.858	6.22	2.41	11.5
1.5	25	8.50	0.848	5.65	4.42	22.5
2.0	37	8.30	0.830	5.13	7.21	40
2.5	50	7.95	0.805	4.56	10.96	65
3.0	50	7.45	0.779	4.00	12.50	91
			Series B, $w_0/x_0 = 0.067$			
0.25	5	8.75	0.586	4.988	1.00	1.2
0.50	5	8.73	0.585	4.827	1.04	2.5
0.75	6	8.72	0.584	4.692	1.28	3.5
1.00	9.5	8.70	0.581	4.535	2.09	6
1.50	12	8.65	0.576	4.282	2.80	11.5
2.00	17.5	8.55	0.568	4.068	4.30	19
2.50	21	8.42	0.559	3.847	5.46	28.5
3.00	28	8.20	0.546	3.585	7.81	41.5

3. SURVEY OF SYMBOLS USED

The concentrations will be designated as follows:

	Initial	After time t (hours)	Unit
ε-Caprolactam	x_0	x	mmoles/g.
Water	w_0	w	mmoles/g.
COOH		c	meq./g.
NH_2		a	meq./g.
Amide groups in chains		z	meq./g.
ε-Amino caproic acid		u_1	mmoles/g.
Linear dimer		u_2	mmoles/g.

In the systems dealt with in this paper, both kinds of endgroups were always present in equal amounts, thus $c = a$.

The following relations based upon stoichiometry were used: $w = w_0 - c$ and $z = x_0 - x - c$. In the latter the amide groups present in cyclic oligomers are neglected. The error involved in this neglection remains quite unimportant.

The molecule of a linear n-mer will be designated by S_n (S_1 = ACA); S_2 = linear dimer, etc.).

4. DISCUSSION

We shall first list the three principal reactions tested in the evaluation. The symbols below the reaction equations give the total concentration of the molecules or groups involved in the reaction.

(*a*) Hydrolysis of lactam represented by the equation

$$\underset{x}{\text{Lactam}} + \underset{w}{H_2O} \underset{k_1'}{\overset{k_1}{\rightleftarrows}} \underset{u_1}{\text{ACA}} \tag{I}$$

designated as RO (ring opening).

(*b*) Formation of amide groups by condensation

$$S_n + S_m \rightleftarrows S_{n+m} + H_2O \tag{II}$$

Assuming equal reactivity of all endgroups irrespective of the length of the molecule to which they belong, we can simplify this reaction as follows:

$$\underset{c}{-NH_2} + \underset{c}{-COOH} \underset{k_2'}{\overset{k_2}{\rightleftarrows}} \underset{(x_0-x-c)}{-CONH-} + \underset{w}{H_2O} \tag{IIa}$$

designated as PC (polycondensation).

(c) Addition of lactam onto endgroups

$$\underset{x}{\text{CL}} + \underset{c}{S_n} \underset{k_3'}{\overset{k_3}{\rightleftarrows}} \underset{c-u_1}{S_{n+1}} \tag{III}$$

designated as PA (polyaddition). This is the amide interchange reaction referred to in section 1.

Now let us first consider the conversion curves in Figure 2. If reaction (I) were alone responsible for the initial rate of endgroup production, then $\dot{c}$ at the start would be proportional to xw and decrease with time as x and w diminish. Actually $\dot{c}$ rapidly increases with time, suggesting an autocatalytic process. It is thus reasonable to suppose hydrolysis catalyzed by endgroups.

As can be appreciated from the fact that the concentration of endgroups remains very small as compared to the rapid rate of lactam conversion $\dot{x}$, and as will be clearly shown below by quantitative evaluation, only a very small fraction of lactam conversion can be explained by the hydrolysis reaction.

This fact, together with the observation that the maximum rate of lactam conversion practically coincides with the maximum endgroup concentration, suggests that the lactam is predominantly converted in reaction (III) representing a reversible polyaddition of lactam to endgroups of chains.

Mutual comparison of the series with different initial proportion of water to lactam shows an increase of reaction rates and of the maximum concentrations of endgroups (and ACA) with increasing water content (Fig. 3).

In the following it will be shown that the polymerization process can be described rather satisfactorily by differential equations containing the terms for both the catalyzed and uncatalyzed forms of reactions (I)–(III).

Since the concentrations of COOH- and NH_2- groups are invariably equal ($c = a$), the present experiments do not offer a decision on the question of whether catalysis is effected by only one kind of endgroup, or by both.

Thus we get from (I), (II), and (III):

$$-\dot{x}_{RO} = ({}_0k_1 + k_1c)xw - ({}_0k_1' + k_1'c)u_1 \qquad (1)$$

$$\dot{c} = ({}_0k_1 + k_1c)xw - ({}_0k_1' + k_1'c)u_1 + ({}_0k_2 + k_2c)c^2 - ({}_0k_2' + k_2'c)(x_0 - x - c)w \qquad (2)$$

$$-\dot{x}_{PA} = ({}_0k_3 + k_3c)xc - ({}_0k_3' + k_3'c)(c - u_1) \qquad (3)$$

The equilibrium constants of reactions (1)–(3) are known from previous work[9] to be 360 mmoles ml.$^{-1}$, 720 (dimensionless), and 2 mmoles ml.$^{-1}$, respectively, at 221.5°. The density of the system at this temperature being estimated to remain practically constant and equal to 0.9, the equilibrium constants are replaced by 400 mmoles g.$^{-1}$, 720, and 1.8 mmoles g.$^{-1}$. The equations then simplify to:

$$-\dot{x}_{RO} = ({}_0k_1 + k_1c)(xw - 400u_1) \qquad (1a)$$

$$\dot{c} = ({}_0k_1 + k_1c)(xw - 400u_1) - ({}_0k_2 + k_2c)c^2 - 0.00139(x_0 - x - c)w \qquad (2a)$$

$$-\dot{x}_{PA} = ({}_0k_3 + k_3c)\ [xc - 0.555(c - u_1)] \qquad (3a)$$

We shall further abbreviate (1a) and (2a) as follows:

$$-(\dot{x})_{\mathrm{RO}} = ({}_0k_1 + k_1c)(\mathrm{RO}) \tag{1b}$$

$$\dot{c} = ({}_0k_1 + k_1c)(\mathrm{RO}) - ({}_0k_2 + k_2c)(\mathrm{PC}) \tag{2b}$$

where (RO) and (PC) represent numerical values which can be calculated from the experimental values of x, w, c and u_1. Since u_1 is only known for series A and B (Table I), we shall confine the present part of the evaluation to these two runs.

a. Evaluation of Endgroup Concentration

In the right-hand side of equation (2b), the first term accounts for the production of endgroups by lactam hydrolysis (RO) and the second for their consumption by polycondensation (PC). At short reaction times the first term dominates while the second can be neglected. Thus we can write for short reaction times:

$$\dot{c}/(\mathrm{RO}) = {}_0k_1 + k_1c \tag{2c}$$

A plot of $\dot{c}/(\mathrm{RO})$ against c yields values for ${}_0k_1$ and k_1. Substitution of the latter in the rearranged unabbreviated equation for $\dot{c}$:

$$-\dot{c}/(\mathrm{PC}) + ({}_0k_1 + k_1c)(\mathrm{RO})/(\mathrm{PC}) = {}_0k_2 + k_2c \tag{2d}$$

should similarly yield values for ${}_0k_2$ and k_2.

In Table II are given the relevant data at short reaction times, and Figure 5 gives the corresponding plots of $\dot{c}/(\mathrm{RO})$ against c.

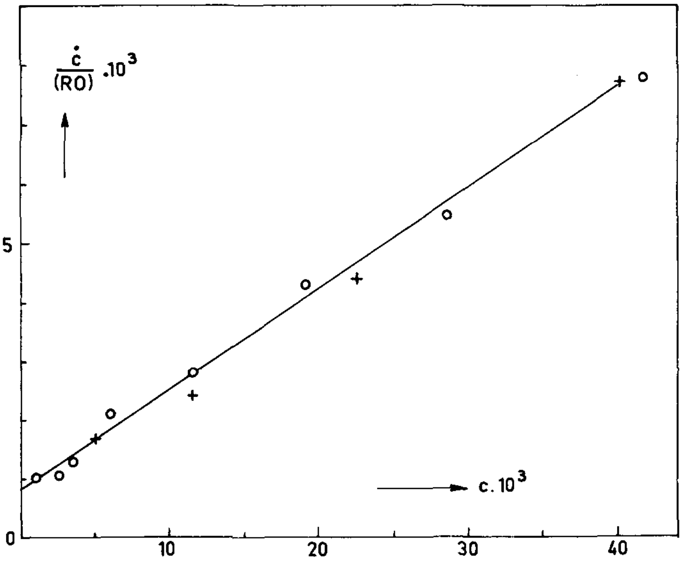


Fig. 5. Plot of $\dot{c}/(\mathrm{RO})$ against c. (+) For series $w_0/x_0 = 0.1$, and (O) for series $w_0/x_0 = 0.067$, leading to ${}_0k_1 = 8 \times 10^{-4}$ and $k_1 = 0.17$.

It is seen that the data of both kinetic series yield practically the same linear relation from which can be derived:

$$_0k_1 = 8 \times 10^{-4} \text{ kg. hr}^{-1} \text{ mole}^{-1} \qquad k_1 = 0.17 \text{ kg.}^2 \text{ hr.}^{-1} \text{ mole}^{-2}$$

In the beginning, when no endgroups are present, the reaction starts with a slow uncatalyzed hydrolysis of lactam. After that, further hydrolysis is more and more accelerated by endgroup catalysis.

The evaluation at long reaction times after equation (2d), which should give information on the polycondensation reaction, does not permit precise conclusions. This is due to reasons associated with the nature of the system.

In the neighborhood of the maximum in c, the nature of the medium is changing very rapidly from one containing caprolactam as the principal component into one in which polymer is the dominant constituent. Nevertheless, in this region the value of $\dot{c}$ is still mainly determined by the ring opening reaction. It does not seem surprising that application of the rate constants of the latter, as derived from an early state of the reaction to its final phase, does not lead to consistent information on the polycondensation. Accordingly, the available data do not permit precision analysis of the contributions of the catalyzed and uncatalyzed polycondensation.

The order of magnitude of the rate constants found, if either uncatalyzed or catalyzed reactions are assumed exclusively, is:

	Rate constant of PC $_0k_2$	k_2
$w_0/x_0 = 0.10$	either ~ 3 kg. hr.$^{-1}$ mole^{-1} or	~ 25 kg.^{2} hr.$^{-1}$ mole^{-2}
$w_0/x_0 = 0.067$	either ~ 3 kg. hr.$^{-1}$ mole^{-1} or	~ 40 kg.^{2} hr.$^{-1}$ mole^{-2}

The controversy in the literature as to whether polyamidation proceeds through second- or third- order reactions cannot be solved by the present experiments.

However, from the positive result that in lactam-hydrolysis the catalyzed and uncatalyzed reactions both occur, it would seem logical to conclude, by analogy, that the same also holds for polycondensation. Fortunately, the rather uncertain evaluation of the polycondensation reaction is of no importance to the subject matter of the following sections.

In another approach to evaluate k_1 and k_2 we used equation (2c) and assumed catalyzed reactions only:

$$\dot{c}/(\text{RO}) = k_1c - k_2(\text{PC})/(\text{RO}) \tag{2e}$$

In view of the very small value of $_0k_1$ given above, this seems permissible for not too small times. By substituting the experimental values of (RO) and (PC) over the whole reaction time, a set of equations, each containing the two unknowns k_1 and k_2, are obtained. Evaluating these equations in various combinations, average values of k_1 and k_2 are obtained.

This procedure yielded values of k_1 between 0.22 and 0.29 (k_2 between 26 and 50).

In the evaluation of lactam conversion in section 4b, where k_1 is used, it is of no importance whether its value is precisely known, only the right order of magnitude being required. Consequently, the value of $k_1 = 0.25$ has been adopted as a sufficient approximation (including both the catalyzed and uncatalyzed reactions at not too short reaction times). As shown in section 4c, this value is also a sufficient approximation to demonstrate that the course of the ACA concentration is also in accordance with the proposed reaction scheme.

b. Evaluation of Lactam Conversion

Since k_1 is known from the previous section, equation (1a) permits calculation of the contribution of $\dot{x}_{\mathrm{RO}}$ to lactam conversion.

By substraction from the experimental values of $\dot{x}$, we find $\dot{x}$ pertaining to lactam conversion by the supposed polyaddition expressed in eq. (3a):

$$\dot{x}_{\mathrm{exp}} - \dot{x}_{\mathrm{RO}} = \dot{x}_{\mathrm{PA}} \tag{4}$$

The values of $\dot{x}_{\mathrm{RO}}$ and $\dot{x}_{\mathrm{PA}}$ thus calculated are listed in the third and fourth columns of Table III. It is seen that lactam conversion by hydrolysis (RO) represents but a small fraction of the total conversion. The major part of the latter is due to $\dot{x}_{\mathrm{PA}}$.

In order to investigate whether the course of this quantity can be represented by equation (3a), the values calculated for ${}_0k_3 + k_3c$ as listed in the last column of Table III are plotted against c in Figure 6 for the two series A and B.

It is seen that there is conformity between the two series, but that the points of observation cannot be well represented by a straight line. Moreover, observations are only represented up to times of reaction lying 1–2 hr. beyond the endgroup maximum (those at longer reaction times fall out of range, being systematically too high). Nevertheless, if the fully drawn line in Figure 6 is taken to represent the observations, values of the reaction constants are arrived at which enable us to describe the rate of lactam conversion over the entire process rather satisfactorily. From the intercept and slope of the line follows

$${}_0k_3 = 1.0 \text{ kg. hr.}^{-1} \text{ mole}^{-1} \qquad k_3 = 21 \text{ kg.}^2 \text{ hr.}^{-1} \text{ mole}^{-2}$$

In Figure 7 the crosses represent the values of log ($\dot{x}_{\mathrm{PA}}$) in function of time as calculated from (3a) when substituting these constants. The fully drawn line in this figure stands for the corresponding experimental values of log ($\dot{x}_{\mathrm{PA}}$). As such were taken the figures from the fourth column of Table III. (The latter represent the actually observed values of $\dot{x}$ after subtraction of the calculated very small contribution of $\dot{x}_{\mathrm{RO}}$.)

Logarithms of $\dot{x}$ have been plotted in order to bring out directly on scale the relative values of the deviations between theory and experiment.

TABLE III

Data Relevant to Lactam Conversion

t	$-10^2 \times$ $\dot{x}_{\text{exp}}$	$-10^2 \times$ $\dot{x}_{\text{RO}}$	$-10^2 \times$ $\dot{x}_{\text{PA}}$	$[xc - 0.555$ $(c - u_1)] \times$ 10^2	${}_0k_3 +$ k_3c
Series A, w_0/x_0 = 0.10					
1	12.5	1.6	10.9	9.3	1.17
1.5	31	2.4	28.6	17.8	1.61
2	51	3.6	47.5	31	1.53
2.5	82	5.0	77	48	1.60
3.0	146	6.0	142	63	2.25
3.5	265	6.0	259	69	3.75
4.0	269	4.8	264	61.7	4.27
4.5	205	3.5	201	47.4	4.24
5.0	135	2.3	133	32.2	4.13
6.0	73	1.4	72	15.6	4.42
Series B, w_0/x_0 = 0.067					
1.5	15	1.22	14.8	9.3	1.59
2	20	1.69	18.3	14.0	1.31
3	52	2.92	49.1	31.7	1.55
3.5	84	3.73	80	44.2	1.81
4	118	4.31	114	54.8	2.08
4.5	151	4.51	146	62.2	2.34
5.5	200	3.36	197	51.8	3.80
6.0	160	2.50	157	40.1	3.90
7.0	93	1.46	91.5	23.2	3.94

It is seen that the conformity is reasonable and seems right in first approximation at least. A similar plot for series B is given in Figure 8B (compare crosses with curve).

In both series the systematic deviations between theory and experiment are of the same kind. Despite many attempts, no simple way has been found to reach a better fit. It is felt that this may be associated with the nature of the system and the inherent possibility of variation of activity

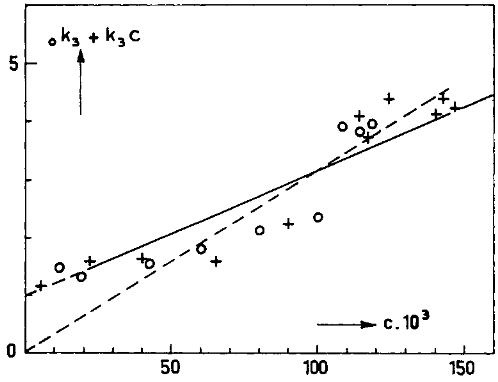


Fig. 6. Plot of ${}_0k_3 + k_3c$ calculated after (3a) against c. (+) Series A. (O) Series B.

coefficients with the changing composition of the system in the course of time requiring a more refined approach.

In view of the transformation of non-ionized substances (lactam and water) into products with ionizable endgroups, it is not surprising that application of simple kinetic expressions does not lead to very precise results.

In Figure 7 are also plotted the values calculated for a still simpler approximation in which the contribution of the uncatalyzed reaction in (3a) is neglected and only the dominating catalyzed reaction is used to describe the process. In this case the observations in Figure 6 are taken to be represented by the dotted line from which follows $k_3 = 32$ kg.^{2} hr.$^{-1}$ mole^{-2}.

It is seen that for reaction times longer than 2 hr. the simplified approach (open circles in Fig. 7) describes the lactam conversion practically just as well as the previous one (crosses). Only at low conversion times is the latter significantly better.

This still simpler and thus more convenient approximation of lactam conversion will be applied in the evaluation of series C and D and also in a subsequent paper.

The principal conclusion from the foregoing is that the bulk of lactam conversion can be represented in fair approximation by a catalyzed polyaddition reaction with rate proportional to xc^2 and that this representation is sufficient except in the very beginning of the reaction.

In the series C and D ($w_0/x_0 = 0.05$) measured at 221.5° and 253.5°, respectively, where no determinations of ACA are available, we cannot calculate $(dx/dt)_{RO}$. Neglecting its very small contribution to total CL

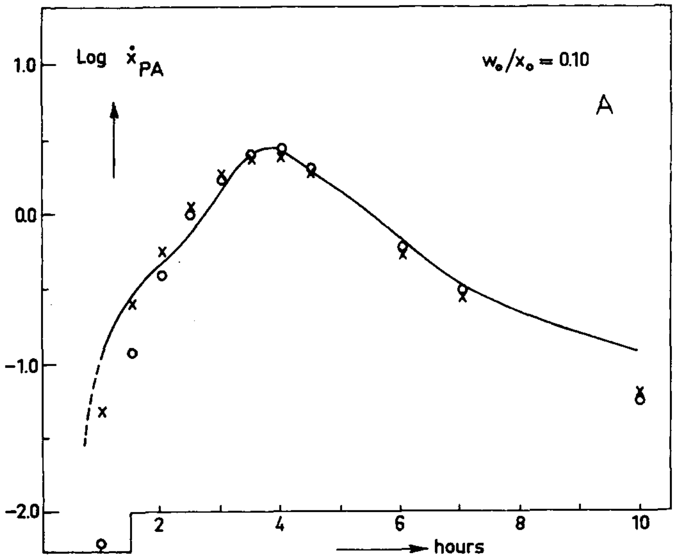


Fig. 7. Logarithms of experimental values of $\dot{x}_{PA}$ as function of time for series A (fully drawn curve) and those calculated after eq. (3a). (X) $_0k_3 = 1.0$ and $k_3 = 21$. (O) $_0k_3 = 0$ and $k_3 = 32$.

conversion, however, still enables us to compute k_3 with reasonable approximation by setting $\dot{x}_{\mathrm{PA}}$ equal to $\dot{x}_{\mathrm{exp}}$.

Applying equation (3a) and taking $_0k_3 = 0$, we find the values for k_3 as listed in Table IV.

TABLE IV

Computed Values of k_3 for series C and D (contribution of hydrolysis to lactam conversion neglected)

Series C (221.5°)		Series D (253.5°)	
t	k_3	*t*	k_3
4	36	1.0	98
5	24	1.25	52
6	22	1.50	40
7	22	1.75	48
8	29	2.0	69
9	49	2.25	87
	—	3.0	123
Average (4–9 hr.)	*30*	3.5	89
		4.0	103
			—
		Average (1–4 hr.)	*77*

It is seen that series C (221.5°) leads to a value of k_3 having the correct magnitude. At 253.5°, k_3 assumes about 2.5 times that figure. This value is in conformity with the estimation arrived at in section 3.2 of the preceding paper.

In view of the previously discussed nature of the systems, it is felt (as can also be appreciated from Fig. 7) that no more detailed information will be accessible from the present experiments.

In the next section it will be shown, though, that the general interpretation given is also in line with the observations on the ACA concentration in the series A and B.

Finally, it should be remarked that the catalyzed reaction with rate proportional to xc^2 does not necessarily require a trimolecular collision or could on that ground be deemed improbable. The formation of complexes either between two different endgroups or between CL and an endgroup is within possibility. (Complex formation between CL and carboxylic acids has been reported by Van Velden.[12])

In a later paper we will show that addition of lactam takes place on NH_2-groups and is catalyzed by COOH groups. Thus, the essential process in the polyaddition reaction (in this paper also referred to as a "transamidation") actually represents *aminolysis of the amide bond* and is better designed as such.

c. Evaluation of Aminocaproic Acid Concentration

If lactam is added onto endgroups, it will also add onto ACA, and the concentration of the latter in the reaction mixture will thus remain very much lower than in case such a reaction would be absent, particularly in the first half of the reaction when the CL concentration is still high.

In the light of the foregoing, the rate expression of ACA formation and conversion is:

$$\dot{u} = k_1c(xw - 400u_1) - 2k_2c[u_1c - (c - u_1)w/720] - k_3c(xu_1 - 0.555u_2) - k_4c[u_1(x_0 - x - 2c + u_1) - K_{\text{IV}}(c - u_1)^2] \quad (6a)$$

or simplified:

$$\dot{u}_1 = k_1p - k_2q - k_3r - k_4s \quad (6b)$$

where p, q, r, and s are known from experiments.

k_1p = contribution from lactam hydrolysis (RO)
k_2q = contribution from polycondensation (PC)
k_3r = contribution from polyaddition (PA)
k_4s = contribution from transamidation (TA)

For an explanation of the last term, k_4s, we refer to the next section. Since its numerical value as compared to that of the other terms remains negligible, it can also be omitted.

From (6a) and (6b) follows:

$$-k_3 = [\dot{u}_1 - k_1p + k_2q]/r \quad (6c)$$

Abbreviated: $-k_3 = B/r$.

To compute r, the concentration u_2 of linear dimer is required. It is arbitrarily taken as $0.9u_1$. The term $0.555u_2$ being very small as compared to xu_1, this approximation is sufficient.

In Table V the relevant data are listed.

TABLE V

Data Required after (6c) for Evaluation of k_3 from Aminocaproic Acid Concentration

t	$\dot{u}_1 \times 10^3$	$k_1p \times 10^3$	$k_2q \times 10^3$	$B \times 10^3$	$r \times 10^3$	k_3
		Series A, $w_0/x_0 = 0.10$				
2.0	0.6	36	0.3	−35.1	1.39	25
2.5	0.15	50	1.0	−48.8	2.20	22
3.0	−0.5	60	1.9	−58.6	2.83	21
4.0	−1.0	48	3.7	−45.3	2.52	19
4.5	−1.1	35	3.7	−32.4	1.53	21
					Average	*22*
		Series B, $w_0/x_0 = 0.067$				
3.0	0.1	29.2	0.3	−28.8	0.71	40
4.0	−0.1	43.1	1.0	−42.2	1.23	34
5.0	−0.2	41.1	1.3	−40.0	1.17	34
6.0	−0.3	25.0	1.5	−23.8	0.77	31
					Average	*35*

Comparing k_1p (ACA formation through lactam hydrolysis) with $-B = k_3r$ (ACA consumption through polyaddition), it is seen that in the region considered the latter is the major reaction in which ACA is transformed. ACA consumption by polycondensation (k_2q) is negligibly small.

Table V also shows that the rate constants k_3 as found for the polyaddition reaction come out with the same magnitude as those previously arrived at from lactam consumption (although those in the series A are rather on the low side).

This means that in the addition reaction with lactam the monomeric chain ACA does not behave significantly different from any other chain.

In our opinion, there are no indications for a particular role played by ACA such as assumed by Wiloth in his tenth communication[10d] (see also section 5).

d. The Transamidation Reaction as a Consequence of the Foregoing

As the amide group in lactam can react with the endgroup of a chain S_n to form a chain S_{n+1}, an analogous reaction will also occur between amide groups build into chains with the endgroup of another chain under formation of two other chains

$$S_{p+q} + S_r \rightleftarrows S_{p+r} + S_q$$

This is a transamidation (which, of course, will then also be catalyzed by endgroups). Since the number of endgroups remains unchanged, this reaction escapes experimental detection.

Its equilibrium constant K_{IV} must be $= 1$. The rate constants k_4 and k_4' can be estimated when making the reasonable assumption that the following rate-relation holds:

$$\frac{\text{transamidation}}{\text{polyaddition}} = \frac{\text{hydrolysis of amide in chain}}{\text{hydrolysis of lactam}}$$

Consequently $k_4/k_3 = k_2'/k_1$ or $k_4 = \sim 5$. Transamidation will certainly play a significant role in the process and have a very considerable bearing on the distribution of chain lengths during the reaction.

Whereas in a pure polycondensation based on the principle of equal reactivity, maintenance of the normal Flory-Schulz (random) distribution during the reaction is assured, it can be shown that this will be otherwise if the starting product is not the linear monomer but a cyclic compound, the more so if a reaction of the polyaddition type is also involved. Transamidation will, however, tend to accelerate attainment of the normal distribution.

Reports which have thus far appeared in the literature on the occurrence of other molecular weight distributions in technical nylon 6 polymers (like those of Korschak[6]) should be taken with the utmost reserve. Fractionation experiments by Wiloth,[10a] as well as work from our laboratory, have confirmed the existence of random distribution in caprolactam polymerisates.

e. Cyclic Oligomers

Figure 4 gives the overall formation of cyclic oligomers for series A and C. Since the concentration of the individual substances remains unknown, quantitative evaluation is impossible.

From Figure 4 it is seen, however, that the maximum in the overall rate of formation coincides with the maximum in the endgroup concentration of the corresponding series. It is felt that the formation of cyclic oligomers will be governed by equations of the same type as those pertaining to lactam conversion, though with smaller and different rate constants for each oligomer. Hence, the cyclic oligomers will be formed for the major part through splitting off from linear chains by transamidation and for the minor part through ring closure and condensation from linear molecules of corresponding chain length.

A paper on the equilibrium constants of the separate cyclic oligomers has been recently published.[4]

5. COMPARISON OF RESULTS WITH THOSE PUBLISHED BY WILOTH

Since several papers on the same subject have been published by Wiloth,[10b,c,d] it seems necessary to give a brief comparative discussion. We shall only consider the tenth communication of this author[10d] in which he also disposed of our aminocaproic acid determinations through private information. In Wiloth's seventh communication [*Kolloid-Z.*, **144,** 58 (1955)] quite different rate constants are proposed and the course of aminocaproic acid concentration assumed is entirely different from the actual one.

TABLE VI

Rate Constants Proposed by Wiloth and Those from the Present Work

	Wiloth (220°)			
Reaction[a]	Rate constant	Conversion factor	Comparable constant	Present work (221.5°)
RO	${}_0c_1 = 7 \times 10^{-3}$	8.7^{-1}	$\underline{8 \times 10^{-4}}$	${}_0k_1 = \underline{8 \times 10^{-4}}$
	$c_1 = 16$	8.7^{-2}	$\underline{0.21}$	$k_1 = \underline{0 \times 17}$
PC	${}_0c_3 = 8.0$	8.7^{-1}	0.9	either ${}_0k_2 \sim 3.0$
	$c_3 = 960$	8.7^{-2}	13	or $k_2 \sim 30$
PA	${}_0c_5 = 0.5$	8.7^{-1}	0.06	${}_0k_3 = 1.0$
	$c_5 = 1500$	8.7^{-2}	$\underline{20}$	$k_3 = \underline{21}$
[PA]$_{\text{ACA}}$	$\tilde{c}_5 = 5.5$	8.7^{-1}	0.63	
BI	${}_0c_7 = 10^{-2}$	8.7^{-1}	10^{-3}	—
	$c_7 = 500$	8.7^{-3}	0.8	—

[a] RO = lactam hydrolysis (ring opening), PC = polycondensation, PA = polyaddition (lactam onto endgroups), [PA]$_{\text{ACA}}$ = addition of lactam on to aminocaproic acid, BI = "building in" of lactam.

With regard to the principal features of the process consisting of lactam hydrolysis followed by catalyzed polyaddition as the dominant factor in lactam conversion, there is general conformity between this author's and our conclusions.

There is even a gratifying conformity between the value of his rate constants and ours for these reactions, as can be seen from Table VI where a survey of the rate constants proposed by Wiloth and in the present paper are given. (The constants in question are underlined.)

Since Wiloth expresses lactam conversion per mole as initial lactam, his rate constants have to be multiplied by $(8.7)^{-n}$ in order to express them on the base of our concentration units, where 8.7 is the initial lactam concentration in mole/kg, and n depends on the dimension of the rate constant. These dimensions are:

reverse reaction of RO and PA uncatalyzed	hr.$^{-1}$
the same reactions catalyzed	kg. hr.$^{-1}$ mole^{-1}
all other uncatalyzed reactions	kg. hr.$^{-1}$ mole^{-1}
all other catalyzed reactions	kg.^{2} hr.$^{-1}$ mole^{-2}

For reasons outlined in section 4a, the difference in rate constants pertaining to PC is considered as being of little importance and not worthy of discussion. (It is felt that experimental data on other systems than lactam-water would be required in order to arrive at more reliable figures.)

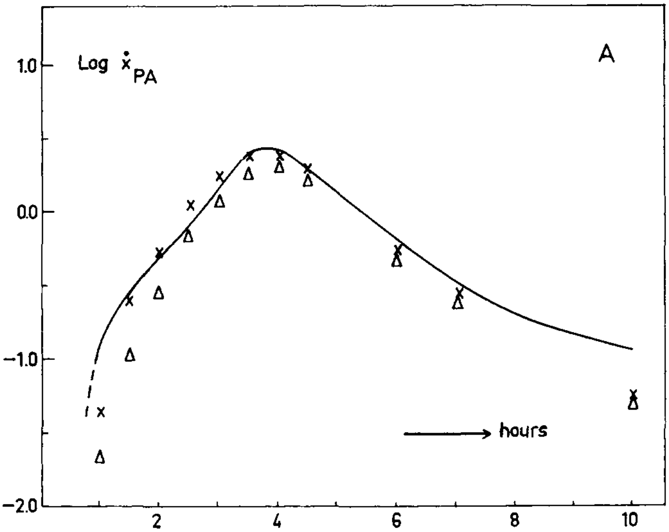


Fig. 8A. Rate of lactam conversions in series A. Curve and crosses as in Fig. 7. (Δ) Calculated from Wiloth's system.

The main point demonstrated by Table VI is that Wiloth ascribes a much smaller rate constant to uncatalyzed polyaddition (0.06 against 1.0 in the present paper).

Since this would entail a much too slow lactam conversion, in particular at the start of the process, Wiloth finds a compensation through the assumption of two other special reactions, one particularly effective in the initial phase of the process and the other in its further course. These are:

1. A specific uncatalyzed reaction $[PA]_{ACA}$ between amino caproic acid and lactam in which both substances are consumed in a process with rate proportional to u_1x (instead of u_1xc as in analogy to addition of lactam onto other chains). In this reaction ACA would then react in the form of a cyclic ionic complex and thus not require catalysis by another endgroup. Its effect being only significant in the initial phase of the process, it is emphasized by Wiloth as the "treibende Reaktion."

2. The "building in" (BI) of lactam into chains by transamidation with a chain amide group catalyzed by a complex of two endgroups and with rate proportional to xzc^2 (z being the concentration of amide groups in chains).

Figures 8A and 8B serve to demonstrate that Wiloth's and our systems of rate constants lead to a practically equivalent description of lactam conversion.

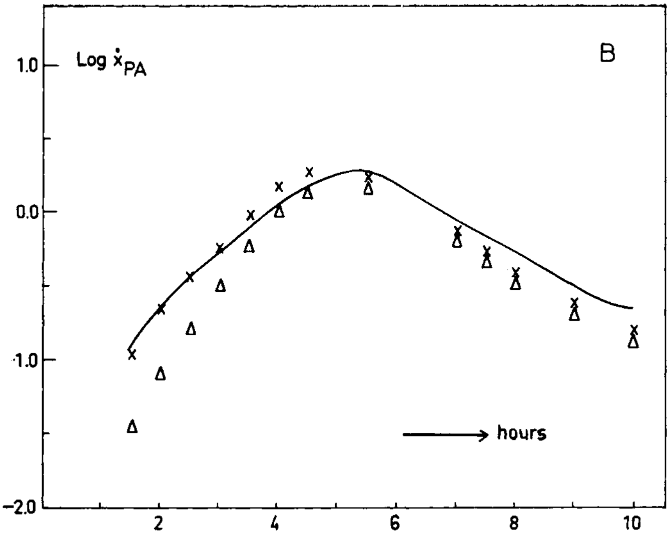


Fig. 8B. Rate of lactam conversion in series B. The curve is from our experimental work. (×) Calculated from eq. (3a) using ${}_0k_3 = 1.0$ and $k_3 = 21$. (Δ) Calculated from Wiloth's system.

As in Figure 7, the drawn curve represents the values of dx/dt observed in series A and B, respectively. Crosses are the values calculated from equation (3a) and the triangles those calculated after Wiloth's system of reactions using:

$$(dx/dt)_{PA} = A + B + C + D$$

where the symbols A to D represent the following contributions to lactam conversion:

$A = 0.06[xc - 0.55(c - u_1)]$ Pa uncatalyzed
$B = 20c[xc - 0.55(c - u_1)]$ PA catalyzed
$C = 0.63[xu_1 - 0.55u_2]$ $[\mathrm{PA}]_{\mathrm{ACA}}$
$D = 0.8[xzc^2 - 0.55c^2z]$ BI

It is seen that for conversion times longer than 2–3 hr., neither of the two descriptions can be said to represent the experiments better or worse than the other. However, despite the introduction by Wiloth of the special reaction $[\mathrm{PA}]_{\mathrm{ACA}}$, whose contribution to lactam conversion is only essential at the start of the process (and falls off to only about 2% of the total after 4 hr.), Wiloth's values of dx/dt tend to remain too low at small conversion times.

Consideration of the experimental data on the amino caproic acid concentration (the only independent information available) also fails to bring out a formal preference for either Wiloth's or our system as can most conveniently be shown from the following example.

In series B the ACA concentration u_1 is maximum after $t = 3.5$ hr. ($x = 7.9$, $w = 0.527$, $c = 0.060$, $u_1 = 0.0022$; *cf.* Table I). Hence, du_1/dt should be zero, and production and consumption of ACA should be in balance. This works out as follows:

	ACA production (RO)	Wiloth	Present paper
RP uncatalyzed	$8.10^{-4}(xw - 400u_1)$	0.003	0.003
catalyzed	$0.17c(xw - 400u_1)$		0.034
	$0.21c(xw - 400u_1)$	0.041	
		0.044	0.037
	ACA consumption		
PA uncatalyzed	$0.06(xu_1 - 0.55u_2)$	−0.001	
	$1.0(xu - 0.55u_2)$		−0.016
catalyzed	$0.20c(xu - 0.55u_2)$	−0.019	
	$0.21c(xu - 0.55u_2)$		−0.020
$[\mathrm{PA})_{\mathrm{ACA}}$ uncatalyzed	$0.63(xu - 0.55u_2)$	−0.010	
		−0.030	−0.036

It is seen that the contribution of Wiloth's $[\mathrm{PA}]_{\mathrm{ACA}}$ term to ACA consumption is of comparable magnitude as that of the uncatalyzed PA reaction in our scheme. In conclusion, the two schemes seem to be almost equally capable of describing the experiments.

Though Wiloth's assumption of the special $[\mathrm{PA}]_{\mathrm{ACA}}$ reaction is an entirely reasonable one, it can neither be proven nor disproven from the present data. Wiloth was driven to this assumption on the motive that a significant contribution of uncatalyzed PA is improbable on experimental ground (*e.g.*, polymerization is very slow in anhydrous systems in which, besides CL, only carboxylgroups or amino groups are present). We prefer, however, not to introduce a new reaction type (the special addition of CL onto ACA) if no further knowledge about the activity of the ionizable groups in the systems of different kind and about the form in which these endgroups react is available. On these grounds, a detailed interpretation of the formal mathematical description of the consumption of CL proportional to $({}_0k_3 + k_3c)xc$ seems somewhat speculative, as this equation perhaps describes by its first factor also the change in activity or rate constant of the endgroups.

The BI reaction mathematically introduced by Wiloth[10f] to investigate its possible influence on lactam conversion compensates, in Wiloth's scheme, for the too small conversion associated with his small rate constant of uncatalyzed polyaddition. In our opinion, the BI reaction seems to be an improbable process. It requires a tetramolecular interaction, or a termolecular one at least, if ionic complex formation between COOH and NH_2 groups is assumed.

In view of these arguments and the nature of the system investigated, we feel that, other information lacking, the simpler scheme as presented in the present paper should be given preference.

The authors wish to acknowledge frequent useful discussions with Dr. A. J. Staverman and co-workers (Delft).

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Synopsis

Kinetic runs were performed at two temperatures with ε-caprolactam–water mixtures containing from 5 to 10 mole-% of water. The concentrations of unconverted lactam x and endgroups c were determined, and in some cases also the concentration of aminocaproic acid u_1 and the quantity of cyclic oligomers formed. The concentration of water w and that of the amide groups in linear molecules were calculated from the boundary conditions. In the evaluation of the kinetics of the reaction, which run towards an equilibrium state, values of the equilibrium constants from previous determinations were used. The course of c can be satisfactorily fitted in with the picture of hydrolysis of the lactam, followed by polycondensation. The former starts off as an uncatalyzed reaction between lactam and water but is soon dominated by hydrolysis catalyzed by endgroups. The quantity of lactam thus converted appears to be only a small fraction of the total lactam conversion. If it is assumed that the bulk of lactam disappears through a reaction with rate proportional to xc^2, satisfactory fit with the experiments is obtained. This reaction is interpreted as an endgroup catalyzed polyaddition, *i.e.*, an addition of lactam onto an endgroup of a linear molecule catalyzed by another endgroup. From the determinations of aminocaproic acid concentration u_1, confirmatory evidence can also be derived that conversion of this linear monomer is for the major part due to an endgroup catalyzed reaction with lactam of a rate proportional to xu_1c and with a rate constant of the same magnitude as that pertaining in the general polyaddition reaction. It is argued that the existence of polyaddition also requires transamidation reactions between linear molecules in which one chain with its endgroup reacts with an amide group of a second chain under formation of two other chains of different lengths. This reaction will tend to produce random chain lengths and will thus accelerate the attainment of a normal Flory-Schulz MW distribution in the reaction product. The rate of formation of cyclic oligomers during polymerization is also in line with the assumption that these substances are mainly produced by a transamidation reaction of a chain endgroup with an amide group of the same chain, rather than by cyclic condensation of a chain of the required length. A survey of rate constants is given. There is general agreement with those given by Wiloth.

Résumé

On a exécuté des séries de mesures cinétiques a deux temperatures avec des mélanges de ε-caprolactame avec de l'eau contenant de 5 à 10 mol. pourcent d'eau. On a déterminé la concentration de la lactame x et celle des groupes terminaux c. En certaines séries on a aussi déterminé la concentration de l'acide aminocaproique u_1 et la quantité des oligomères cycliques formée. Les concentrations de l'eau libre w et des groupements amides qui se trouvent dans les molécules linéaires, furent calculées des conditions limites. Dans l'évaluation de la cinétique des reactions, qui mènent à une équilibre, les valeurs des constantes d'équilibre connues d'un travail précédent furent employées. Le cours de c pendant la réaction se trouve en accord avec l'hydrolyse de la lactame suivie par polycondensation. La première commence comme une réaction non-catalysée entre lactame et eau, qui est bientôt dominée par l'hydrolyse catalysée par un groupe terminal. La quantité de la lactame transformée par l'hydrolyse apparait de ne présenter qu'une fraction très petite de sa transformation totale. Si celle-ci est attribuée à une autre reaction qui se poursuit avec une vélocité proportionelle a xc^2, on se trouve en accord satisfaisant avec les données expérimentales. Cette réaction est interpretée comme une polyaddition catalysée par groupes terminaux, c. a d. l'addition de la lactame à un groupe terminal catalysée par un autre groupe terminal. En confirmation, on déduit des mesures de la concentration u_1 de l'acide aminocaproique que ce monomère lineaire est en majeur partie transformé par une reaction avec la lactame, catalysée par un groupe terminal, qui s'accomplit avec une vélocitée proportionelle à xu_1c et dont la constante de vitesse est du même grandeur que celle trouvée pour la polyaddition générale.

Zusammenfassung

An ϵ-Caprolactam-Wasser Gemischen mit 5 bis 10 Mol-Prozent Wasser wurden kinetische Messungen bei zwei Temperaturen durchgeführt. Die Konzentrationen des nicht umgewandelten Lactams x und der Endgruppen c wurden bestimmt und in einigen Fällen auch die Konzentration u_1 der Aminocapronsäure sowie die Menge der gebildeten zyklischen Oligomeren. Die Konzentration des Wassers w und die der Amidgruppen in linearen Molekülen wurde aus den Grenzbedingungen berechnet. Bei der Auswertung der Kinetik der Vorgänge, die zu einem Gleichgewicht führen, wurden die aus einer früheren Arbeit bekannten Gleichgewichtskonstanten benützt. Der Gang von c ist in Übereinstimmung mit einer Hydrolyse des Lactams gefolgt durch Polykondensation. Erstere beginnt als unkatalysierte Reaktion zwischen Lactam und Wasser, wird aber bald dominiert von einer durch Endgruppen katalysierten Hydrolyse. Die Menge des Lactams welche durch diesen Vorgang verbraucht wird erscheint als eine kleine Fraktion des totalen Lactamumsatzes. Die Annahme, dass die Hauptmenge des Lactamumsatzes durch eine andere Reaktion mit einer Geschwindigkeit proportional xc^2 erfolgt, liefert eine befriedigende Übereinstimmung mit den experimentellen Daten. Diese Reaktion wird gedeutet als eine durch Endgruppen katalysierte Polyaddition, d.h. eine Addition des Lactams an eine Kettenendgruppe, katalysiert durch eine andere Endgruppe. Aus Bestimmungen des Verlaufs der Konzentration u_1 der Aminocapronsäure geht bestätigend hervor dass der Umsatz dieses linearen Monomeren hauptsächlich erfolgt durch eine Reaktion mit dem Lactam welche durch Endgruppen katalysiert wird und mit einer Geschwindigkeit proportional xu_1c und mit einer Geschwindigkeitskonstante der selben Grösse als die der generellen Polyadditionsreaktion verläuft. Das Auftreten der Polyadditionsreaktion weist darauf hin dasz auch Transamidierung zwischen linearen Molekülen auftreten wird, wobei die Endgruppe einer Kette reagiert mit einer Amidgruppe in einer anderen Kette unter Bildung zwei neuer Ketten. Diese Reaktion wird die Ausbildung einer MW Distribution nach Flory-Schulz beschleunigen. Die Bildungsgeschwindigkeit der zyklischen Oligomeren weist ebenfalls darauf hin dass diese Substanzen nicht in erster Linie durch zyklische Selbstkondensation von Ketten entsprechender Länge sondern hauptsächlich durch eine Transamidierungsreaktion zwischen einem Kettenende mit einer Amidgruppe derselben Kette gebildet werden. Ein Vergleich der ermittelten Geschwindigkeitskonstanten mit den von Wiloth angegebenen zeigt im Allgemeinen gute Übereinstimmung.