

KINETICS AND MECHANISM OF ϵ -CAPROLACTONE ANIONIC
POLYMERIZATION UNDER THE INFLUENCE OF AMINES

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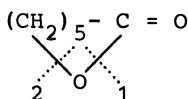
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Abstract - The identity of the ϵ -caprolactone products from polymerization under the influence of amines has been studied, and conclusion about alkyl oxygen fission of the lactone ring at polymerization has been made. The main kinetic features of polymerization and molecular-weight distribution change on forming poly- ϵ -caprolactone are discussed. On the basis of these data, polymerization mechanisms for lactones under the influence of amines are proposed.

INTRODUCTION

In recent years lactones polymerization processes by amines have been intensively investigated. This interest is caused first of all by the fact that lactones and poly lactones appear to be very effective modifiers in the cure of epoxy oligomers by amines (Refs. 1-3). It has been shown in a number of publications (Refs. 4-7) that lactones in the presence of amines can polymerize forming polyesters with reactive end groups, which is of practical interest. Unfortunately, the kinetics and mechanism of the lactones polymerization processes by amines, are not clear enough up to now and the few published results in this field are either contradictory or not correct (Refs. 8&9). The review and analysis of this literature has been given (Ref. 10).

The lactone ring opening by nucleophilic reagents can proceed with the fission of both acyloxygen (1) and alkyloxygen (2)



(1)

i.e. a lactone can act both as acylating and alkylating agent. Just because of the double reactivity of lactones the problem of the character of lactone ring opening appears to be the most important one for understanding the mechanism of polymerization processes.

This problem has been thoroughly studied in a number of investigations (Refs. 5-14). Some results concerning the lactone ring fission by a series of nucleophilic reagents are summarized in Table 1. The results have been quoted from the work of Yamashita et al. (Ref. 11).

As shown in the Table, the type of ring opening depends to a great extent on reagent nucleophilicity as well as on peculiarities of lactone structure. Thus, fission of the β -propiolactone ring goes through the acyloxygen bond, with strong nucleophilic reagents such as alkaline metals alcoholates. Whereas decomposition of α,α -bischloromethyl- β -propiolactone goes on mainly through the alkyloxygen bond under similar conditions.

The direction of the ring opening can be varied by changing the temperature or the polarity of the reaction medium. For example, if the medium polarity or temperature increases in the reaction between β -propiolactone and lithium ethylate the ring opening through alkyloxygen bonds becomes predominant.

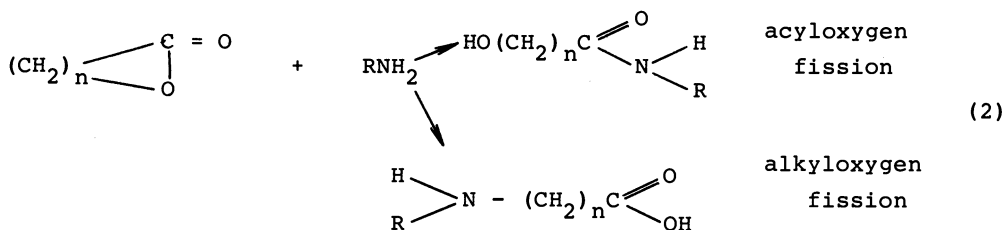
TABLE 1. Ring opening of β -lactones by anionic catalysts (Ref. 8)

β -Lactone	Catalyst	Reaction product	
		Alkyloxygen fission	Acyloxygen fission
β -Propio- lactone	NaOAc	+	?
	NaOEt	(+)	+
	LiOEt	-	+
	Mg(OEt) ₂	-	+
	Al(OEt) ₃	-	+
α, α -Bis- chloromethyl- β -propio- lactone	NaOEt	+	(+)
	LiOEt	+	(+)
	Mg(OEt) ₂	-	+
	Al(OEt) ₃	-	+

+ the main product; (+) a small quantity of the product;
- its absence.

Note, that the reaction products identification, which leads to the conclusion about the fission mechanism, should be conducted very carefully.

Really, two possible primary products (aminoacid and aminoalcohol) can be expected from the reaction of lactone and amine:



Identification of both acid and amide groups in the reaction products has led Gresham and coworkers (Ref. 8) to the conclusion that both fission mechanisms occur in this case. Later, we shall see this conclusion to be a mistake.

In the present report our work on the detailed examination of kinetics and mechanism of ϵ -caprolactone anionic polymerization will be discussed. The investigations were carried out recently at the Institute of Chemical Physics, Academy of Sciences of the USSR.

ϵ -Caprolactone (ϵ -CL) and aniline were the main chemicals used. Methods applied to reagent purification and to the investigation of the polymerization kinetics and molecular structure of forming polymers have been already described (Refs. 12-17). Kinetic investigations were carried out at 150 - 220°C.

The following questions will be considered below:

1. The structure of reaction products of ϵ -CL with aniline and the fission mechanism of ϵ -CL.
2. The main kinetic features and mechanism of the process.
3. Changes of the molecular-weight distribution of poly-CL during the formation process.

THE STRUCTURE OF REACTION PRODUCTS OF ε-CAPROLACTONE WITH ANILINE

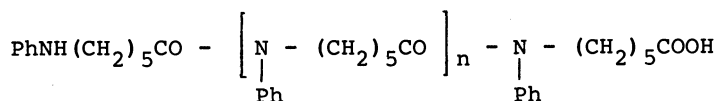
The identity of the polymerization products of ε-CL with aniline was studied by infrared and ultraviolet spectroscopic methods, gel permeation chromatography (GPC) and chemical analysis of functional groups using the potentiometric titration which allows the differentiation of primary, secondary and tertiary amine groups, and amide groups. Polymerization products with and without acid and alkali additives and reprecipitated polymers were investigated. This approach allowed us to examine the nature of the reaction products formed, more reliably and effectively.

The main results of this investigation can be formulated in the following way.

The native polymers contain amine and carboxylic groups including ionized forms. Carboxylate anions transform to carboxyl groups after acidifying the polymer solution with hydrogen chloride; ammonium transforms to free amine group after alkali is added. Besides, amide groups appear in the monomer-aniline mixture when their ratio is smaller than 10 : 1. Data on quantitative analysis of functional groups and molecular weights of the products formed at different initial ratios lactone-aniline are given in Table 2.

It can be seen that aniline is converted to tertiary amine groups at ratios lactone:aniline > 10 : 1, carboxylic groups formed simultaneously have a concentration twice that of the initial aniline, and the products containing amide groups are absent. Molecular weights of the polymers determined by the GPC method correspond completely to the values obtained when counting every molecule of the forming polymer to contain one amine group and two carboxylic groups, i.e. polyester with two end carboxylic groups is formed under these conditions. A fraction containing amide groups is easily reprecipitated from the native polymer solution in acetone, using heptane.

It has been established by the GPC method (Ref. 15) that in this case the reaction products contain oligoamides of linear and cyclic structure



n = 0, 1, 2

(3)

and

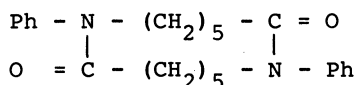


TABLE 2. Functional analysis data and molecular weights of products from the reaction of ε-CL with aniline

Lactone: aniline mole ratio	Amine groups*					Carboxyl groups*	Amide groups*	\bar{M}_n	
	[A] ₁₀	[A] ₁	[A] ₂	[A] ₃	∑[A] _i			calc.	expt.
3.68	1.89	0.04	0.14	0.98	1.16	2.35	0.73	-	500
4.9	1.52	0.08	0.17	0.97	1.22	2.14	0.28	-	700
10.0	0.81	0.00	0.00	0.80	0.81	1.59	0.00	1260	1230
13	0.63	0.00	0.00	0.63	0.63	1.30	0.00	1530	1760
80	0.11	0.00	0.00	0.10	0.10	0.24	0.00	8350	8670

* Functional groups content is given in 10⁻³ g.equiv/g. A₁, A₂, A₃, ∑A_i are concentrations of primary, secondary, and tertiary amine groups and their sums, correspondingly.

It is obvious that indicated products can be obtained only as a result of the polycondensation of the amino acid formed at the very beginning, or by the polymerization of N-phenylcaprolactam formed from the amino acid, i.e. they are products of the amino acid secondary transformation. The character of the kinetic curves of the reaction products accumulating (Fig. 1), and the kinetics of lactone and aniline consumption in the 1:1 ratio (Fig. 2) are in full agreement with this conclusion.

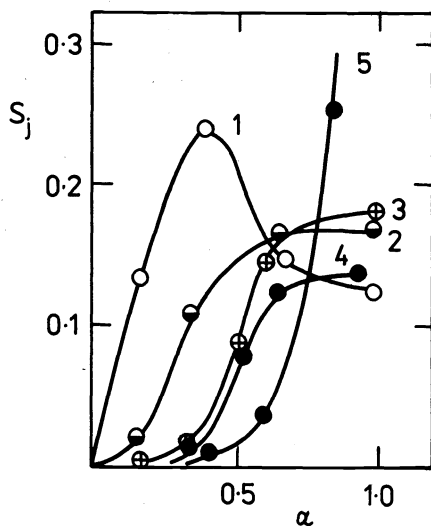


Fig. 1. The change of individual oligomers (S_j) part in reaction mixture at $[M]_0/[A]_0 = 3:1$ at 180°C : (1) dimeric cycle + amino diacids, (2) polyamides of the structure (scheme 3) at $n = 0$; (3) $n = 1$; (4) $n = 2$; (5) ϵ -CL oligomers.

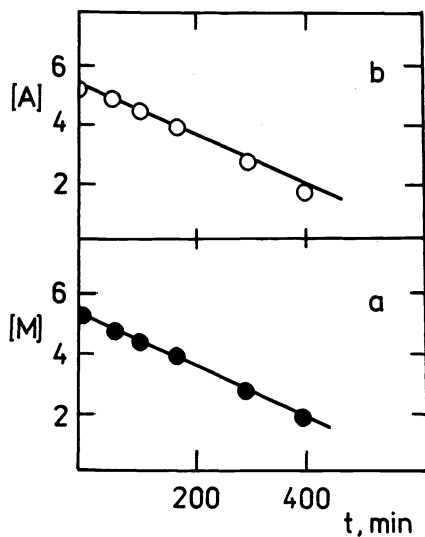


Fig. 2. Kinetic curves of ϵ -CL (a) and aniline (b) consumption at $[M]_0/[A]_0 = 1:1$ at 180°C .

As shown in Fig. 2, both components are consumed strictly equimolecularly, linear and cyclic oligoamides being formed.

Thus, the discovery of amide groups without proof of their origins cannot be the basis for conclusions about the fission mechanism.

THE MAIN KINETIC FEATURES OF THE PROCESS

Figure 3 shows a typical form of kinetic curves obtained by the gas-liquid chromatographic method. The S-type character of the kinetic curves of the lactone and aniline consumption attracts our attention. The consumption time of aniline is commensurable with the whole polymerization process time. The initial polymerization rate increases linearly with increasing lactone and aniline concentration. The polymerization proceeds to the full consumption of the monomer, the additional portion resumes the reaction but without the induction period. The molecular weight of the forming polymer increases in this case. On the one hand, these facts testify to the "living" character of the investigated reaction system, on the other hand, they allow us to suppose not only slow initiation of active centres, but also the possibility of autocatalytic character of their appearance and propagation. They also allow us to suppose that the autocatalysis is connected with the accumulation of carboxylic groups in the system at the formation of amino acid in the initiation act, which is in equilibrium with its ionized form. Really, the addition of such proton acids such as acetic, trifluoroacetic and hydrochloric acids reduce or completely suppress the induction period, and they increase the polymerization rates (depending on the concentration) (Fig. 4).

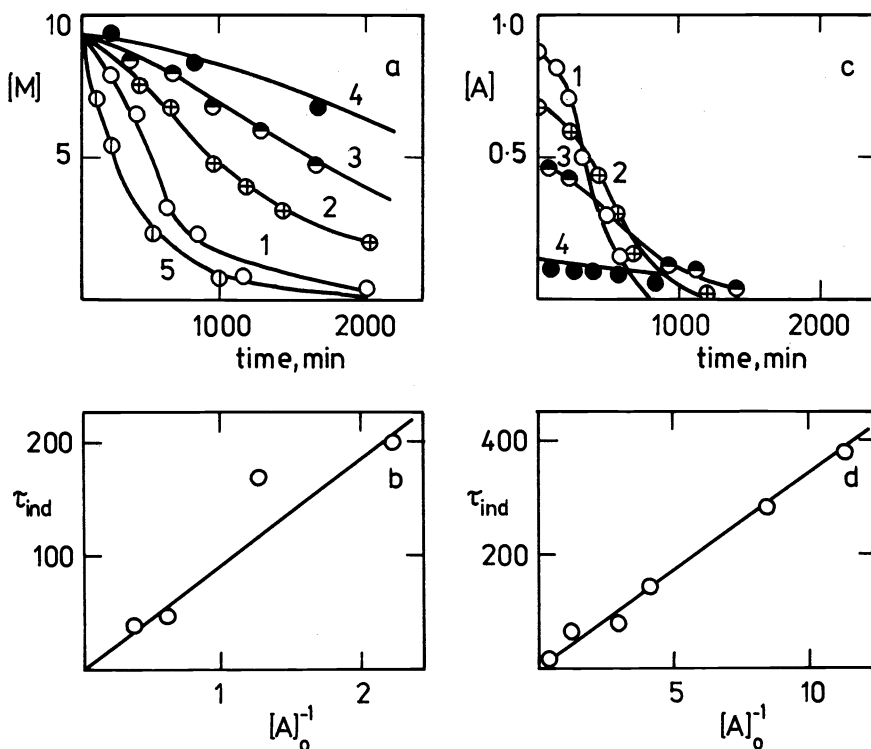


Fig. 3. Kinetic curves of ϵ -CL (a) and aniline (b) consumption at 180°C; $[A]_0$, mol/l: 0.86 (1); 0.68 (2); 0.45 (3); 0.12 (4); 1.68 (5). The dependence of induction period τ_{ind} (min) of kinetic curves on $1/A$ (l/mol) for CL (c) and aniline (d).

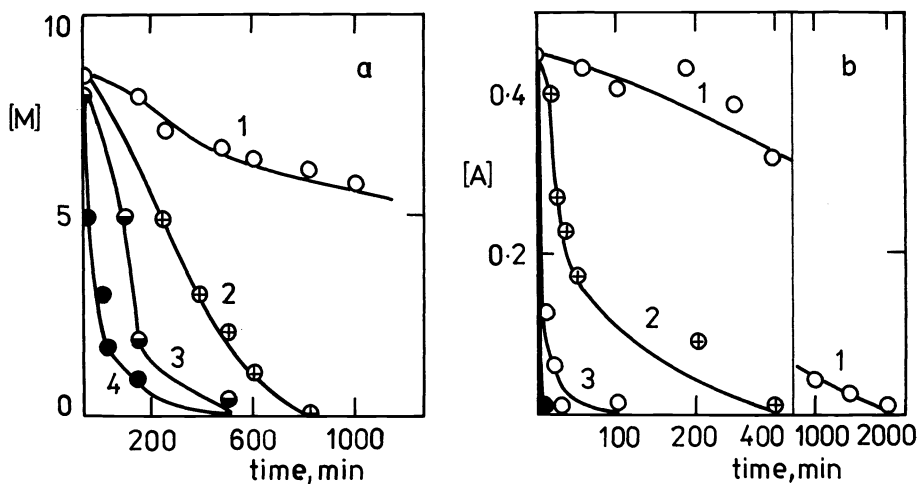
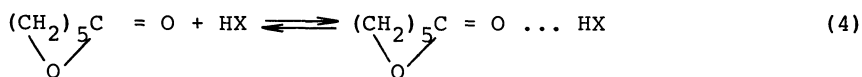


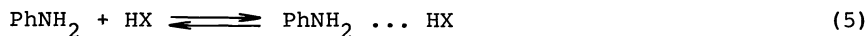
Fig. 4. Kinetic curves of ϵ -CL (a) and aniline (b) consumption at 180°C and $[A]_0 = 0.45$ mol/l without acid additives (1) and with additives of acetic acid, mol/l: 0.11 (2); 0.25 (3); 0.47 (4).

Note, that the lactone polymerization by the action of acids according to the cationic mechanism (when aniline is absent) is by 2 - 3 orders slower, i.e. the cationic process contributes only negligibly to the observed effect of acid additives.

The initial polymerization rate increases linearly with the concentration of acid additives up to the ratio acid:aniline = 1:1. Further increase of acid leads to a drop in the polymerization rate. On account of these facts, we can suppose that the catalysis of the reactions of initiation and propagation of active centres lies in lactone cycle activation to the nucleophilic attack by the formation of donor-acceptor complexes with hydrogen bond formation



On the other hand, the pronounced polymerization rate dependence on the acid concentration testifies the fact that aniline molecules are bound to acid in a complex

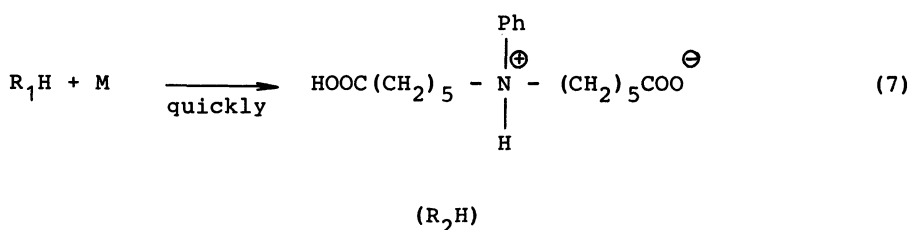
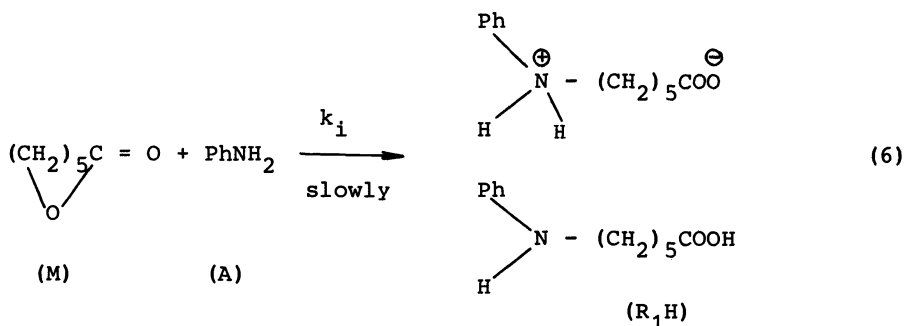


In this complex, the amine is unreactive and the acid is also unreactive.

It was examined by special tests. Aniline hydrochloride dissociating at reaction temperatures causes rapid quantitative lactone polymerization, whereas aniline acetate, which does not dissociate under similar conditions, cannot initiate the lactone polymerization.

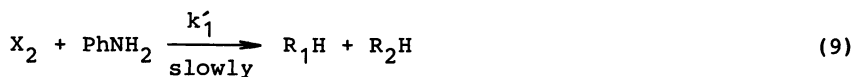
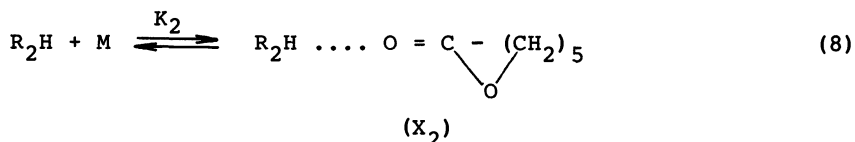
Taking into account the fact that the initial rate of lactone consumption at high lactone concentration ($>10 : 1$) exceeds the initial aniline

consumption rate by a factor of two (Fig. 3), and the fact that the intermediate secondary amine groups are undetectable, as well as the data expounded in the previous section, the initiation mechanism of lactone polymerization process can be presented as the following reaction sequence



k_i is the rate constant limiting initiation stage of the non-catalytic reaction.

Analogous reactions go on also with the monomer activated by the forming carboxylic group (autocatalytic initiation reaction):



K_2 is the equilibrium constant; k'_1 is the rate constant of the catalytic initiation reaction.

The true active propagating centre is the zwitterion with the RH_2 structure (scheme 7).

Treatment of the kinetic scheme indicated for initiation stage leads to the expression (11)

$$\ln \frac{[\text{A}]_0}{[\text{A}]} - k_i \int_0^t [\text{M}] dt = k_i'' \int_0^t [\text{M}] ([\text{A}]_0 - [\text{A}]) dt$$

$$k_i'' = k_i' K_2 \tag{11}$$

which describes our experimental data quite satisfactorily (Fig. 5).

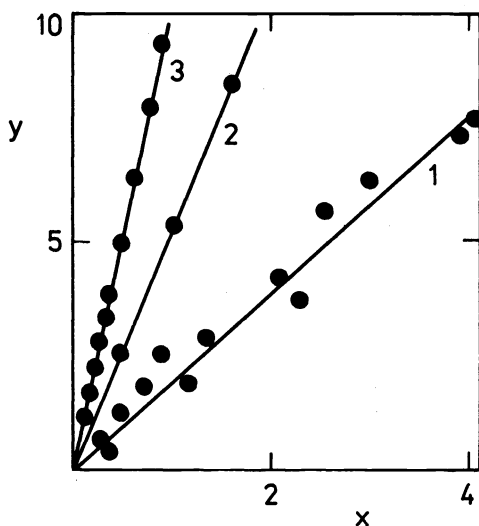


Fig. 5. Experimental kinetic dependence in coordinates of equation (10) at 180°C (1); 200°C (2); 220°C (3).

$$x = \int_0^t [M]([A]_0 - [A]) dt; \quad y = \ln([A]_0/[A]) - k_1 \int_0^t [M] dt$$

Calculated values of kinetic parameters for non-catalytic (k_1) and catalytic (k_1'') reactions of initiation stage are given in Table 3.

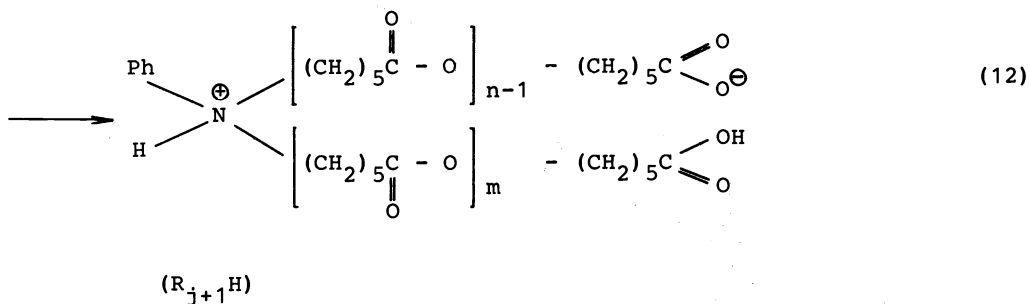
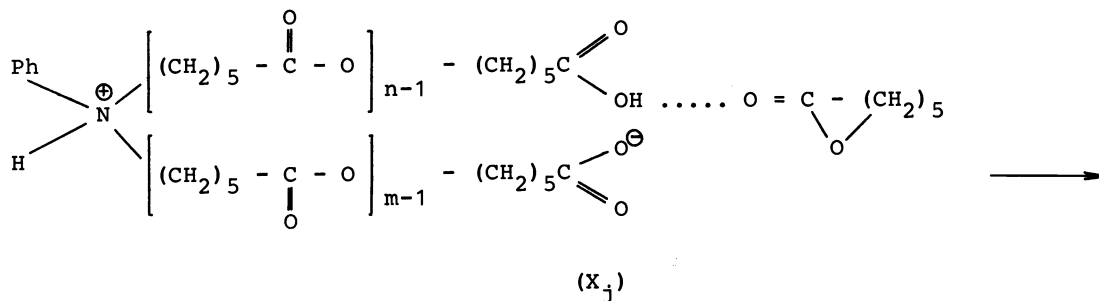
TABLE 3. Kinetic parameters of initiation stage, k_1 ($l \text{ mol}^{-1} \text{ s}$) and k_1'' ($l^2 \text{ mol}^{-2} \text{ s}$)

Rate constants	180°C	200°C	220°C	k_0	$E_a, \text{kJ mol}^{-1}$
$k_1 \times 10^5$	0.043	0.18	0.65	5×10^9	131.5
$k_1'' \times 10^5$	1.9	4.3	7.9	7×10^2	69.0

k_0 is the preexponent multiplier, E_a is the activation energy

As one ought to expect, the activation energy of the initiation autocatalytic reaction appears to be considerably lower than the non-catalytic one.

The chain propagation stage includes non-catalytic and catalytic reactions. From the kinetic point of view, the first reaction can be ignored. As the kinetic analysis has shown, the catalytic reaction of the chain propagation goes on by internal nucleophilic attack of carboxylate anion on monomer bound in a complex:



Schematically the reaction of chain propagation can be written as follows:



k_p is the constant of the chain propagation rate; K is the equilibrium constant of the complex formation reaction.

Kinetic treatment of this scheme considering initiation reaction (schemes 6 - 10) leads to the expression:

$$\ln \frac{[\text{M}]_0}{[\text{M}]} - 2k_1'' \int_0^t B \, dt = 2k_p' \int_0^t ([\text{A}]_0 - [\text{A}]) \, dt
 \tag{14}$$

where

$$\begin{array}{l}
 B = [\text{A}]([\text{A}]_0 - [\text{A}]) \\
 k_p' = k_p K
 \end{array}$$

This equation describes satisfactorily the experimental data (Fig. 6).

The values of kinetic parameters determined by this equation are given in Table 4.

TABLE 4. Kinetic parameters of chain propagation reaction

Rate constant	180°C	200°C	220°C	k ₀ , l mol ⁻¹ s	E _a , kJ mol ⁻¹
k _p ', l mol ⁻¹ s	0.325	0.415	0.600	1.2x10 ²	27.2

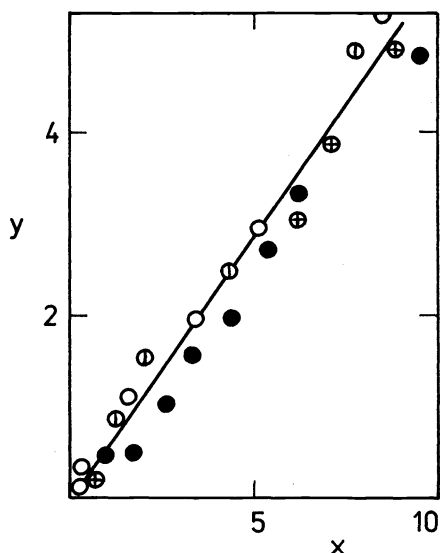


Fig. 6 Kinetic experimental dependence in coordinates of equation (14) at $[A]_0 = 0.29$ (●); 0.45 (○); 0.86 (⊕); 0.12 (⊗) mol/l at 180°C .

$$x \equiv \int_0^t ([A]_0 - [A]) dt, \quad y \equiv \ln([M]_0/[M]) - 2k_1'' \int_0^t \text{Bdt.}$$

As has already been mentioned, the side transformation reactions of initially forming amino acid into linear and cyclic oligoamides become an important factor in the ratios lactone:aniline = 10:1. With respect to the mechanism of lactone polymerization process under the influence of amines, the side reactions must be suppressed under the following circumstances:

- (1) when lactone concentration increases, due to the competitive reaction of amino acid with monomer, leading to amino diacid (scheme 7);
- (2) when acid is added, due to the binding of free amine groups into donor-acceptor complexes;
- (3) when an excess amine is added, due to the binding of amine groups into an unreactive complex with free carboxylic groups.

These conclusions have been completely confirmed by the experiment.

The conclusions made in this section about the mechanism and kinetic parameters of the reactions studied could be examined independently by the investigation of the molecular-weight characteristics of polymers being produced. The results obtained for conditions when the role of side reactions of the created linear and cyclic oligomers can be neglected are given below.

KINETIC OF THE MOLECULAR-WEIGHT DISTRIBUTION CHANGE OF
 POLY- ϵ -CAPROLACTONE IN THE PROCESS OF ITS FORMATION

The kinetics of ϵ -caprolactone polymerization has been characterized by changes in polymerization degrees of forming polymer, \bar{P}_N (number average) and \bar{P}_W (weight average), representing changes in its molecular weight distribution; the following expressions have been obtained:

$$\bar{P}_N = 2 + \frac{k'_p \int_0^t [M] ([A]_0 - [A]) dt}{[A]_0 - [A]} \quad (15)$$

$$\bar{P}_W = \frac{3k'_p \int_0^t [M] ([A]_0 - [A]) dt + 4k'_p{}^2 \int_0^t [M] \int_0^t [M] ([A]_0 - [A]) dt dt}{2([A]_0 - [A]) + k'_p \int_0^t [M] ([A]_0 - [A]) dt} \quad (16)$$

The values \bar{P}_N , \bar{P}_W and \bar{P}_W/\bar{P}_N were calculated from Eqs. (15) and (16) using constants values found during the polymerization process. Calculated dependences of such parameters as function of monomer conversion or time are given in Figs. 7 and 8 (full lines).

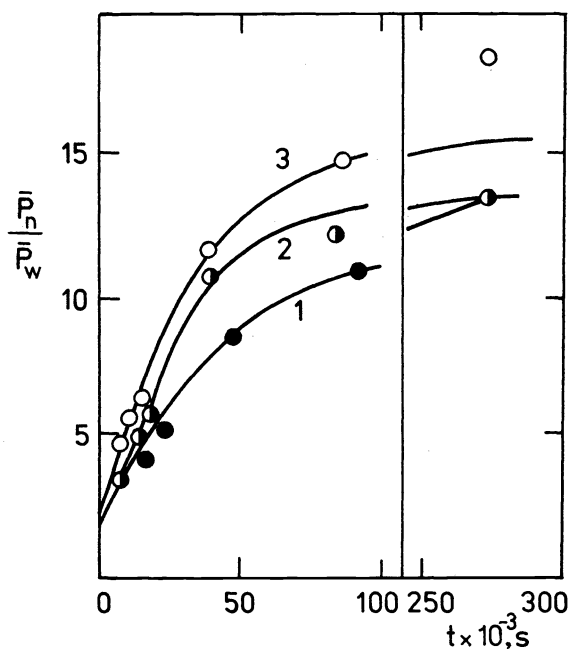


Fig. 7. The dependence of number average (1,2) and weight average (3) polymerization degrees in the course of polymerization calculated from GPC data (dots) and calculated from the equations (15) and (16) (full lines); (1) 180°C and (2,3) 200°C.

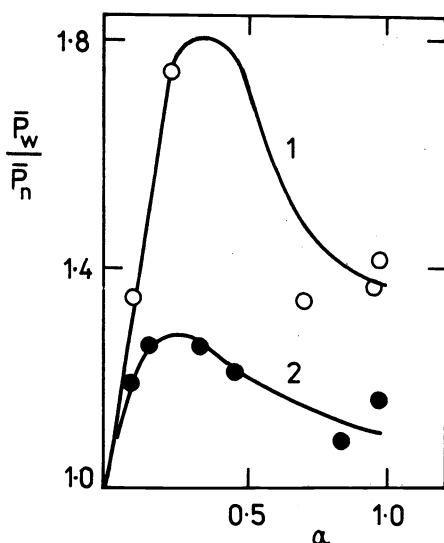


Fig. 8. \bar{P}_w/\bar{P}_n dependence on the conversion of CL at 180°C and 200°C (2) calculated from the GPC data (dots) and from Eqs. (15) and (16) (full lines). $[M]_0 = 8.6$ and $[A]_0 = 0.86$ mol/l.

The results of experimental investigation of the same parameters are given here. As can be seen from the Figures, the calculated and experimental dependences quantitatively coincide (excluding reaction end stages for $T = 200^\circ\text{C}$). The increase of weight average of polymerization degree and polymer polydispersity is observed. The latter tend to the value $\bar{P}_w/\bar{P}_n = 2$ at a very long heating of native polymer at 200°C . These facts show the lactone polymerization process under investigating conditions to be accompanied by a very slow exchange reaction going on according to a mechanism of chain transfer reaction with rupture (Ref. 18). This reaction does not practically take place at or below 180°C .

Note, that polymer polydispersity is characterized by the pronounced dependence on the conversion, the maximum coincides with position of the full consumption of aniline, i.e. with the end of the initiation process. This fact confirms once more the conclusion that the initiation process of the investigated reaction is slow.

Finally, we ought to pay attention to the fact that absolute polydispersity values are higher at lower polymerization temperatures. It becomes clear if we consider the temperature dependence of the initiation reactions rate constants and chain propagations (Tables 2 and 3). Initiation reaction rates increase faster with temperature than the reaction rate of the chain propagation, i.e. the relative rate of the initiation reaction increases with increasing temperature. Thus, the investigation of the molecular-weight characteristics of forming polymers fully confirms the proposed mechanism of ϵ -CL polymerization by amines described here.

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