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ANIONIC POLYMERIZATION OF 6-CAPROLACTAM—LVIII

THE RELATIVE RATES OF ELEMENTARY REACTIONS IN THE ACTIVATED ANIONIC POLYMERIZATION OF ε-CAPROLACTAM IN TETRAHYDROFURAN*

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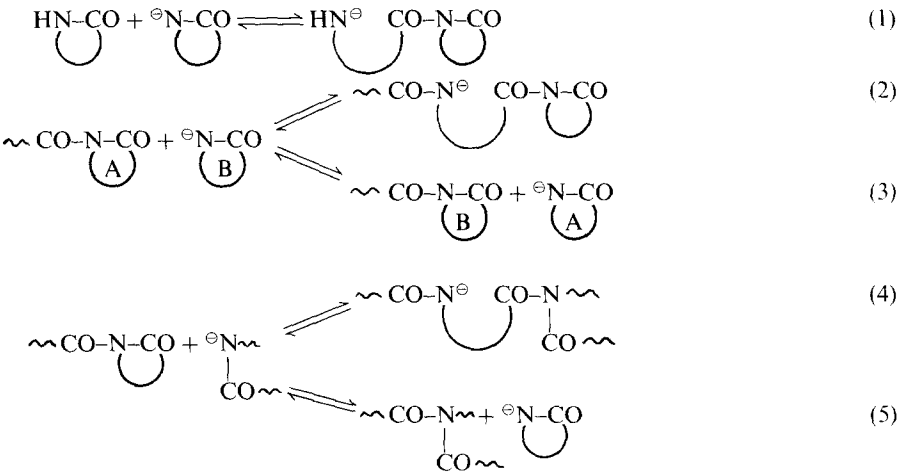
Abstract—In the reaction between the potassium salt of ε-caprolactam and *N*-propionyl-ε-caprolactam or *N*-benzoyl-ε-caprolactam in tetrahydrofuran at 25°, the consumption of both reactants and the formation of structures giving ketones by hydrolysis were investigated. Analysis of the data allowed determination of the relative rates of polymerization, of the acylation of amide groups of a linear monomer unit and of the condensation of diacylamino groups.

INTRODUCTION

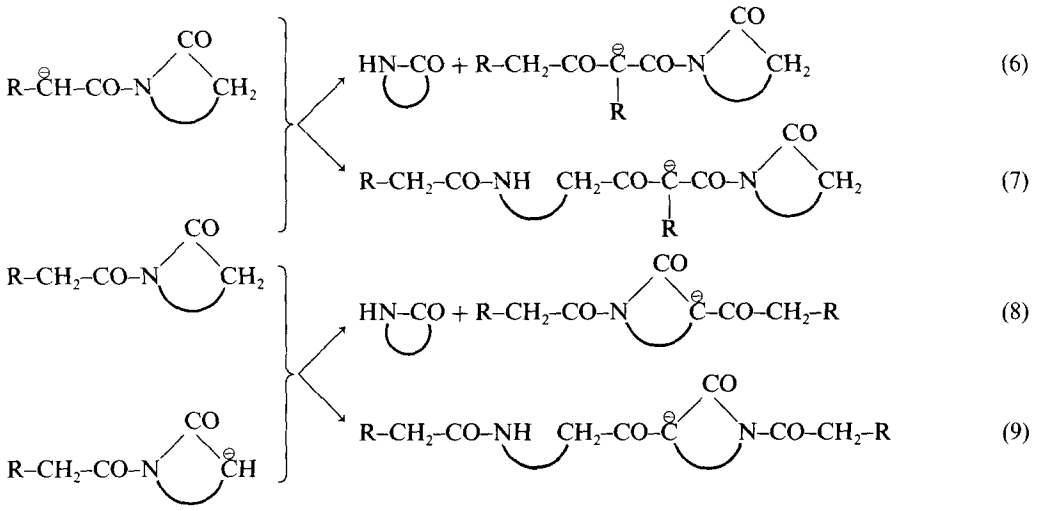
According to recent views [1], a number of parallel and consecutive reactions (some of them reversible) occur under the conditions for the anionic polymerization of lactams. In the initial stage, the situation is not much simpler, as at least two types of acylation must be taken into account.

The acylation reactions at the nitrogen atom (1–5) are classified as initiation (1), polymerization (2) and exchange (3–5) reactions, depending on the type of the acyl group which participates in the reaction, i.e. the lactam acyl or the cyclic or exocyclic acyl of *N*-acyllactam (for simplicity, lactam salts are shown without cations as N-anions):



Acylation on the carbon atom next to the carbonyl group of acyllactam (6–9) gives rise to structures which on hydrolysis yield ketones. Acylation of two possible C-anions of acyllactam with the cyclic or noncyclic acyl of acyllactam then gives rise to four types of ketone precursors (for simplicity, mesomeric anions are shown as C-anions without cations):

*Part LVII: *Chemický Prům.* **35**, 361 (1985).



The initiation reaction 1 is very slow compared with the propagation reaction 2 and the exchange reactions 3–5 [2, 3] and becomes important only in the nonactivated polymerization or in the polymerization of very reactive four-membered lactams [4]. Thus, in the polymerization of five- to seven-membered lactams at low temperatures, the initiation reaction 1 can be neglected.

According to the reported data for five- to seven-membered lactams, the exchange reaction 3 is five to ten times faster than the polymerization [5, 6]. Hence, the acylation of N-anions with the exocyclic acyl of acyllactam (reactions 3,5) is much faster than with the cyclic acyl with ring-opening (2,4). It may be assumed therefore that a similar situation will arise in the acylation of mesomeric C-anions of acyllactams, so that the condensation reactions 6 and 8 should be faster than reactions 7 and 9. Under specific conditions, acylation of the C-anion may also occur in the neighbourhood of nitrogen or on the oxygen atom of the enolate form of acyllactam [8].

The sparse data on some of these reactions during the initial stages of polymerization do not allow comparison of the rates of the individual reactions, because they were obtained under different conditions. To obtain comparable values, the system *N*-acyl-ε-caprolactam–potassium salt of ε-caprolactam was investigated under conditions enabling the acylation reactions to be studied both on the nitrogen and on the carbon atom.

EXPERIMENTAL

Materials

N-propionyl-ε-caprolactam and *N*-benzoyl-ε-caprolactam were prepared from ε-caprolactam, acid chloride and triethyl amine in ether [9]; purity ≥ 99.9% (GLC), content of acid impurities determined titrimetrically ≤0.1%. The potassium salt of ε-caprolactam was prepared in an amount needed for the particular reaction from potassium t.-butoxide and ε-caprolactam [10]. THF, after predrying and distillation with Na metal, was repeatedly distilled with $LiAlH_4$ in the presence of triphenylmethane under Ar (moisture content by coulometric titration according to Fischer was 8–10 ppm).

Kinetic measurements

N-propionyl-ε-caprolactam or a defined solution of *N*-benzoyl-ε-caprolactam in THF was added to a solution of the potassium salt of ε-caprolactam in a 15 ml thermostated cell with a syringe in an atmosphere of dry Ar. In the case of *N*-benzoyl-ε-caprolactam, the reaction is heterogeneous virtually from the start; each sample used in the determination of ketone precursors was therefore prepared separately from THF solutions of the components and the whole product was used for further processing. In the other cases, samples were withdrawn by syringes and introduced into a solution of the internal standard (8-octanolactam, benzophenone or fluorene) for chromatographic determination; this solution contained acetic acid or 10% H_2SO_4 imbibed in solid Na_2SO_4 in an excess needed for acidifying the reaction mixture. ε-Caprolactam released by acidifying and *N*-acyl-ε-caprolactam were determined by gas chromatography in stainless-steel columns (1 m, i.d. 2 mm) packed with 10% Carbowax 20M on Chromosorb W-HMDS 80–100 mesh (column temperature 170–190°, N_2 as carrier gas 30–50 cm^3/min) or HPLC on the reverse phase-glass columns (15 cm, i.d. 3.2 mm) packed with Separon Six C 18, 5 μm (Laboratory Instruments, Prague); methanol–water (70:30, v/v), 0.2 ml/min as the mobile phase; u.v. monitor Cecil 2112 was used at 220 or 254 nm.

Determination of β-keto compounds

The reaction was stopped with conc. HCl in excess (*ca* 20 μl) in a sample which was withdrawn or prepared separately in an ampoule, THF was evaporated *in vacuo*, 1 ml of 1 M HCl was added, the ampoule was flushed with Ar and sealed. Hydrolysis, benzoylation and HPLC and GLC analyses of the ketones were performed as for pure β-keto compounds [8].

Content of readily hydrolyzable (imide) groups

A sample of the reaction mixture [w (g)] was withdrawn into 0.05 M HCl in excess [2–3 ml, H_0 (mmol)] and transferred by means of 3 ml acetone and 3 ml water into a conductometric titration cell. 0.05 M NaOH [3–4 ml, B (mmol)] in excess was added and the closed vessel was heated to 50° for 60 min. The excess of NaOH was titrated with 0.05 M HCl [H consumption (mmol)] with a conductometric indication by means of a Digital-meter DIGI LF 6104E bridge (WTW Weilheim, FRG). The amount of imide groups I (mmol/g) = $(w \times KL_0 + B - H_0 - H)/w$, where KL_0 is the initial concentration of the potassium salt of ε-caprolactam (mmol/g).

Separation and characterization of products by GPC

The reaction of equimolar amounts of *N*-propionyl-ε-caprolactam and the potassium salt of ε-caprolactam (0.41 mol/l) at 25° in THF was stopped with acetic acid at *ca* 50% conversion of acyllactam, the precipitate was removed by filtration, and the THF solution was repeatedly injected for gel chromatographic separation into five columns (1.2 m long, i.d. 9 mm) packed with styrene–divinylbenzene gel (exclusion limit ~2000) and connected in series; a Waters R403 differential refractometer was used as detector, THF was the mobile phase. The individual fractions were collected, evaporated and dried in vacuum 13 Pa for several days; the oily residues were characterized by mass spectra and used in the determination of specific response (injected with a known amount of polystyrene as the internal standard). Since the individual fractions stripped the starting compounds, the contents of ε-caprolactam and *N*-propionyl-ε-caprolactam in these fractions were determined by gas chromatography (cf. above), and the specific responses were corrected. The samples taken during the reaction and acidified with acetic acid were chromatographed similarly after filtration and addition of the polystyrene standard, and the chromatogram was evaluated by means of specific responses. The mass spectra of oligomers were recorded with a GS–MS LKB 9000 (70 eV) spectrometer.

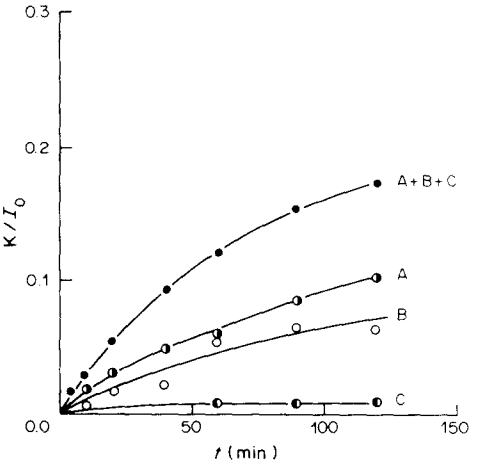


Fig. 1. Formation of precursors of 3-oxopentane (A), 1-amino-6-oxooctane (B) and 1,11-diamino-6-oxoundecane (C) in the reaction of *N*-propionyl-ε-caprolactam (0.081 mol/l) with potassium salt of ε-caprolactam (0.078 mol/l) in THF at 25°. K/I_0—amount of precursor related to the initial amount of *N*-propionyl-ε-caprolactam (mol/mol).

RESULTS AND DISCUSSION

Choice of reaction conditions

Under the usual polymerization conditions, i.e. at low concentration of catalytic components, the extent of side reactions compared with the polymerization is so small that the ratio of elementary reactions cannot be determined. In order to suppress the polymerization and to stress the condensation, the reactions were studied at an equimolar ratio of acyllactam and potassium salt of lactam. In more polar media the reactions under study proceed too quickly [11]; for this reason, THF was used as the reaction medium, because it makes possible a convenient investigation of the reactions and dissolves sufficient of the potassium salt of ε-caprolactam.

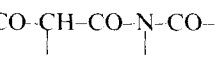
Formation of ketone precursors

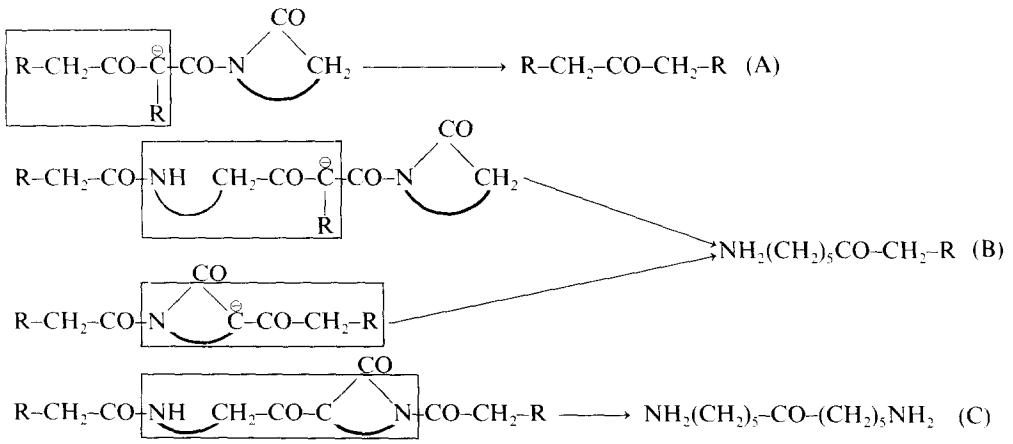
In the reaction of *N*-propionyl-ε-caprolactam, reactions 6–9 give rise to four types of structures, the hydrolysis of which yields three ketones A–C (3-oxopentane, 1-amino-6-oxooctane and 1,11-diamino-6-oxoundecane):

The precursor most quickly formed is that of ketone A; the precursor of ketone C is formed more slowly by an order of magnitude (Fig. 1). Hence, the acylation of C-anions of acyllactam with the exocyclic acyl (propionyl) is much faster than acylation with the cyclic acyl accompanied by ring-opening, similarly to the acylation on the nitrogen atom [5, 6].

With *N*-benzoyl-ε-caprolactam, the extent of condensation reactions is much smaller than with *N*-propionyl-ε-caprolactam (Fig. 2), especially since the first propagation step (reaction 2) is much faster. Moreover, condensation with the participation of two exocyclic acyls (reaction 6), which for *N*-propionyl-ε-caprolactam is the source of more than one half of the ketone precursors, also cannot take place.

In condensations 6–9, two acyllactam molecules are consumed while giving rise to the group





(for the case under investigation, R = CH_3).

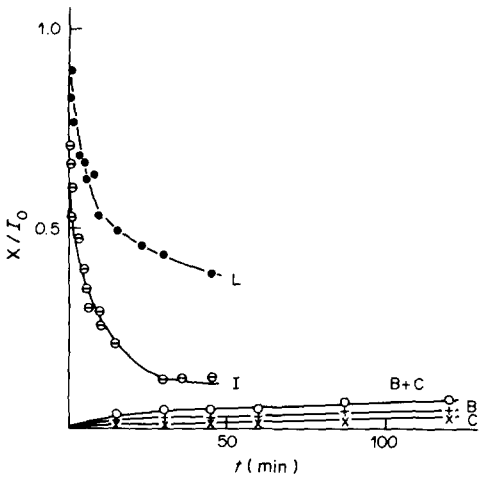


Fig. 2. Reaction of *N*-benzoyl-ε-caprolactam (I) with potassium salt of ε-caprolactam (KL) in THF at 25°. Initial concentrations: $I_0 = KL_0 = 0.055$ mol/l; amounts of I, total lactam L and forming precursors of 1-amino-6-phenyl-6-oxohexane (B) and 1,11-diamino-6-oxoundecane (C) are related to the initial amount of I.

which undergoes hydrolysis at the same rate as *N*-acyllactam [8]. Thus, the consumption of readily hydrolyzable groups of the diacyl amine type (DA) equals the increase in the amount of ketones (K) formed by the hydrolysis of the precursors A–C, so that $K = -DA$ (Fig. 3).

In agreement with the mechanism of formation of ketone precursors by bimolecular reactions 6–9, the rate of their formation is proportional to the square of acyllactam concentration (k_2 was found to be 7.2×10^{-4} l/mol sec for an equimolar amount of *N*-propionyl-ε-caprolactam and the potassium salt of ε-caprolactam at 25°). However, the acyllactam concentration decreases not only by reactions 6–9, but also by polymerization 2 and by exchange reactions 4 and 5 which are not second-order with respect to acyllactam. On the other hand, the lactam concentration increases by some of the reactions just mentioned (reactions 5, 6, 8), so that the acyllactam concentration decreases much more quickly than that of lactam (Fig. 4). For this reason, the acyllactam consumption by condensation reactions cannot be expressed by means of a simple relation for the bimolecular reaction.

Acylation of amide groups of the polymer and polymerization

Changes in the acyllactam and lactam concentrations by polymerization (2) and by acylation reactions on amide groups of the polymer (reactions 4 and 5) can be calculated from the determined concentrations of *N*-acyllactam and lactam by introducing the following corrections for the extent of condensation reactions 6–9. The formation of one ketone precursor

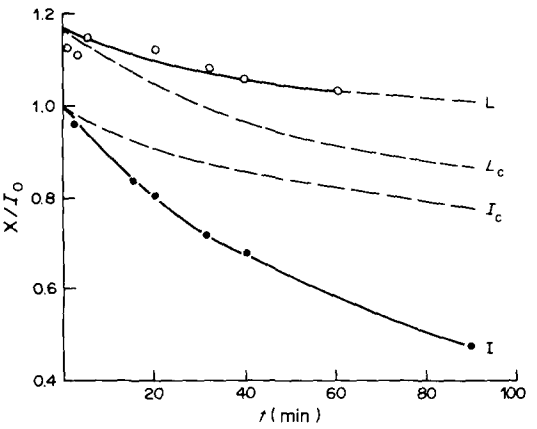


Fig. 4. Reaction between *N*-propionyl-ε-caprolactam (I) and potassium salt of ε-caprolactam (KL) in THF (25°); $I_0 = KL_0 = 0.079$ mol/l; amounts of I, total lactam L (KL and lactam formed from I) and the corrected I_c and L_c values are related to the initial amounts of the components.

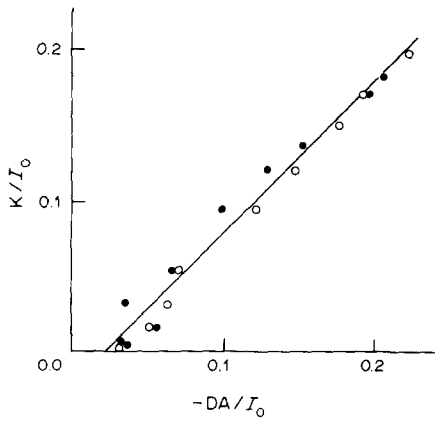


Fig. 3. Correlation of the decrease of readily hydrolyzable groups of the diacyl amine type (-DA) and of the increase in all ketones (K) formed from the precursors in the reaction between *N*-propionyl-ε-caprolactam (I) and potassium salt of ε-caprolactam (KL) in THF (25°) related to the initial concentration I_0; $I_0 = KL_0 = 0.078$ mol/l.

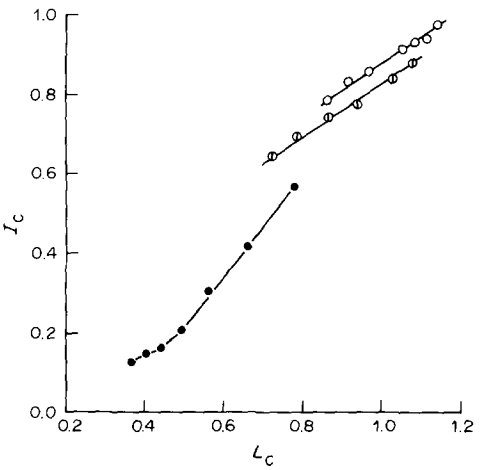


Fig. 5. Dependence of the corrected amount of ε-caprolactam (L_c) on the corrected amount of *N*-acyl-ε-caprolactam (I_c) in the reaction between equimolar amounts of potassium salt of ε-caprolactam and *N*-propionyl-ε-caprolactam (○—0.079, ◑—0.170 mol/l) or *N*-benzoyl-ε-caprolactam (●—0.055 mol/l).

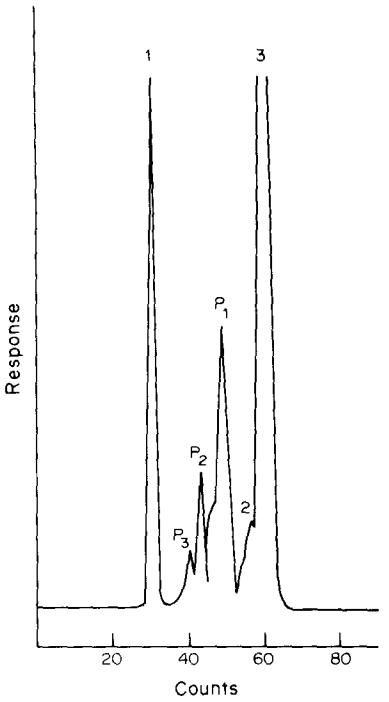


Fig. 6. Gel permeation chromatogram of the reaction products for *N*-propionyl-ε-caprolactam with potassium salt of ε-caprolactam (products soluble in THF after acidifying the reaction mixture): 1—polystyrene standard, P_1, P_2, P_3-oligomers; 2—dipropionyl-ε-caprolactam; 3—starting compounds.

consumes two molecules of *N*-acyllactam, so that double the determined sum of ketones (K) must be added to the determined concentration of *N*-acyllactam (I). The corrected concentration of *N*-acyllactam (I_c) is thus given by $I_c = I + 2K$.

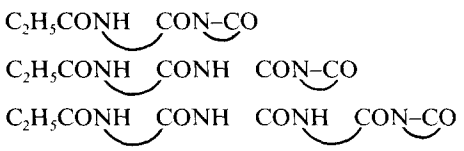
Similarly, the corrected lactam concentration (L_c) is calculated so that the fraction of lactam formed by reactions 6 and 8 is subtracted from the determined lactam concentration (L). The extent of reaction 6 equals the content of ketone A precursors; the extent of reactions 7 and 8 leading to precursor B is given predominantly by reaction 8 occurring without ring-opening, so that $L_c = L - (A + B)$.

Thus the difference ($L_0 - L_c$) gives changes in the lactam concentration brought about by reaction 2 (lactam consumption) and by acylation reaction 5. Similarly, the difference ($I_0 - I_c$) expresses the acyllactam consumption by reactions 2 and 5. The determined amounts of *N*-propionyl-ε-caprolactam and ε-caprolactam and the corrected concentrations derived therefrom are plotted in Fig. 4.

The plot of the I_c values thus corrected vs L_c (Fig. 5) shows changes in the concentrations of *N*-acyllactam and lactam in the polymerization and acylation of amide groups of the polymer, i.e. the ratio of *N*-acyllactam consumed in reactions 2, 4, 5 to lactam consumed in polymerization (2) and released in the acylation of amide groups of the polymer. For *N*-benzoyl-ε-caprolactam (with the exception of the beginning and end of the reaction), $\Delta I/\Delta L = 1.28$. This means that 1.14 mol of 1.28 mol *N*-benzoyl-ε-caprolactam react by polymerization reaction 2 and 0.14 mol acylate the amide groups of polymer, predominantly by reaction 5 (i.e. without ring opening); 0.14 mol ε-caprolactam are released in the process.

From the initial rates of the decrease of I_c and L_c, we have that $\Delta I/\Delta L$ is much higher at the beginning of the reaction. This result suggests that at the beginning of the reaction some other reactions also consume *N*-acyllactam.

In the reaction of *N*-propionyl-ε-caprolactam, $\Delta I/\Delta L$ is smaller than unity (Fig. 5). This does not rule out, however, that some of the amide groups of the polymer are acylated by reaction 5. By using GPC, fractions have been isolated from the reaction products, the mass spectrum of which indicates the presence of propionylated oligomers (Fig. 6). In fractions of oligomeric products characterized by molecular ions in the mass spectrum with $m/z = 281$, 393 and 505, denoted below as P_1, P_2 and P_3,



their propionylated derivatives were always present ($m/z = 337$, 449 and 561). The propionylated dimer appears as a shoulder on the peak of the dimer. Moreover, the peak of dipropionyl-ε-caprolactam (peak 2) is also visible. It may be estimated that in this case the ratio of polymerization (2) to acylation (5) exceeds 2.

Ratios of rates of elementary reactions

Although the investigated system of equimolar amounts of *N*-acyllactam and of the potassium salt of lactam seems simple, complications arise in an attempt to study reactions to higher conversions. The acylation ability of ketone precursors can be compared with the effect of *N*-acyllactams [8], so that these precursors may acylate the lactam anion or the amide group of the polymer while giving rise to *N*-alkyl-2-oxoamides:

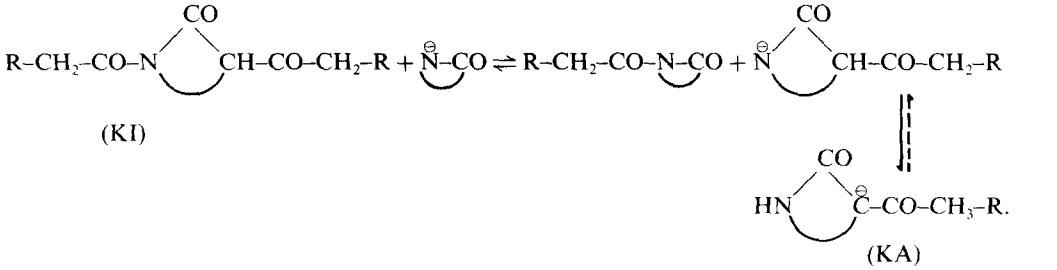


Table 1. Reaction of equimolar amounts of potassium salt of ϵ-caprolactam with *N*-benzoyl-ϵ-caprolactam (BL) or *N*-propionyl-ϵ-caprolactam (PL) in THF at 25° ($BL_0 = 0.055$ and $PL_0 = 0.081$ mol/l)

Reaction	Initial rate × 10^6 (mol/l sec)	
	PL	BL
(1–4) Formation of ketone precursors	4.7	0.4
(1) Precursors of ketone A	2.7	—
(2 + 3) Precursors of ketone B	1.8	0.1
(4) Precursors of ketone C	0.2	0.3
(5) Polymerization first step	8.9	232
(6) Acylation of polymer by PL or BL	0.3	29

The lactam is consumed, and the starting *N*-acyllactam is formed again from some ketone precursors. As compared with ϵ-caprolactam, the corresponding *N*-alkyl-2-oxoamides (KA) and the starting *N*-acyl-*N*-alkyl-2-oxoamides (KI) are by 7 and, respectively, 14 orders of magnitude more acid [8]; this is why the equilibrium between N and C anions given above is shifted in the indicated direction. Hence, due to the condensation and some further reactions, the concentration of potassium salts of both lactam and *N*-acyllactam and their dissocation are considerably reduced. Moreover, the reaction mixture becomes heterogeneous at higher conversions in the case of *N*-propionyl-ϵ-caprolactam and within a few minutes with *N*-benzoyl-ϵ-caprolactam.

Hence, it has so far been impossible to evaluate the whole course of the model reaction; therefore, only the initial rates of elementary reactions were evaluated (Table 1). Since the reacting components were used in an equimolar ratio, it was possible to evaluate formally the initial stage of elementary reactions as a second-order reaction with respect to one of the components, e.g. *N*-acyllactam, and to calculate the initial rate of the elementary reaction.

Rate constants of propagation reactions

N-propionyl-ϵ-caprolactam and the potassium salt of ϵ-caprolactam react in an equimolar amount in a series of polymerization reactions 2 giving rise only to oligomers $P_1, P_2 \ldots P_{i-1}, P_i$. Oligomers soluble in THF (P_1, P_2 and only partly soluble P_3) could be separated and determined by GPC (Fig. 6). At a low polymerization temperature, there is no need to consider the reverse reaction, so that

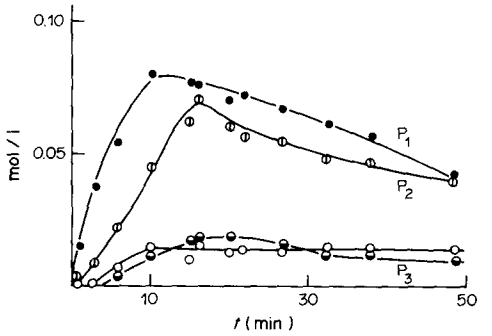


Fig. 7. Products of the reaction between *N*-propionyl-ϵ-caprolactam (I) and potassium salt of ϵ-caprolactam (KL; THF, 25°) soluble in THF after acidifying; $I_0 = KL_0 = 0.34$ mol/l; ○—dipropionyl-ϵ-caprolactam, P_1—dimer, P_2—trimer, P_3—tetramer.

Generally, the rate constants $k_1, k_2 \ldots k_i$ may be different, as found for the acidolytic polymerization [12]. For the rates of formation of P_1 and P_2 we have:

$$dP_1/dt = k_1 I L^a - k_2 P_1 L^a$$

$$dP_2/dt = k_2 P_1 L^a - k_3 P_2 L^a.$$

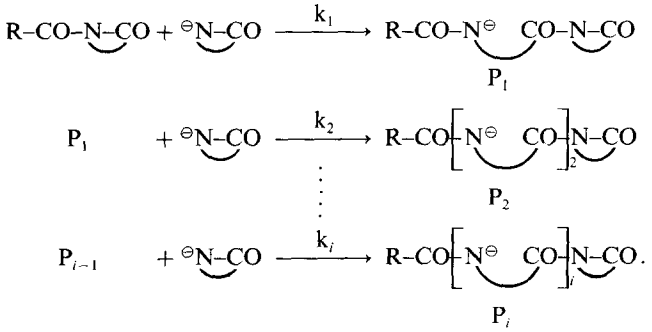
In the maximum of the concentration of P_1, $dP_1/dt = 0$, so that $k_2 = k_1 I/P_1$. Similarly, in the maximum of the concentration of P_2, $k_3 = k_2 P_1/P_2$. By substituting the corresponding P_1 and P_2 values from Fig. 7 and the value of I, we obtain $k_2 = 0.0023$ and $k_3 = 0.0027$ mol$^{0.87}$/l$^{0.87}$ sec.

For the initial rate of formation of P_1, we have:

$$(dP_1/dt)_0 = k_1 I_0 L_0^a.$$

Over the investigated concentration range, $a = 0.87$ (Ref. [11]), so that by putting $I_0 = L_0 = 0.34$ mol/l and 0.00020 mol/l sec for the initial rate of formation of P_1 (from Fig. 7) we obtain $k_1 = 0.0015$ mol$^{0.87}$/l$^{0.87}$ sec.

The concentration of P_3 in Fig. 7 represents only the soluble part of the oligomer; the maximum is shifted towards the beginning, and the values do not give a real k_4. With respect to the accuracy of determination of the concentrations of I, P_1 and P_2 (P_1, P_2 include also propionylated oligomers), it cannot be decided unambiguously whether the rate constants for the initial polymerization steps do indeed slightly increase or whether they can be regarded as constant.



If the relations derived in this study are to be applied to real polymerization systems, one should note essential differences from the model system studied: the reaction took place at low temperature in a medium with low dielectric constant (7.58 for THF at 25°), and at the beginning of the reaction all the monomer was present as a potassium salt.

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