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Mechanism and kinetics of hydrochloric acid initiated ε-caprolactam polymerization

1. The role of stereoelectronic control and acid catalysis*

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Summary

A mechanistic scheme is suggested for lactam polymerization initiated by hydrochloric acid on the basis of the general mechanism put forward earlier by Bertalan et al. According to this mechanism during the polymerization conditions are created which can initiate further polymerizations resulting in a characteristic inflection type kinetic curve. Experimental results can be well interpreted qualitatively on the basis of this mechanism, and therefore it can serve as a starting point also for a quantitative kinetic model.

Introduction

Our mechanistic scheme for the cationic polymerization of lactams generated by various initiators has been succesfully applied to amine salt initiated polymerization[1], to hydrolytic polymerization[2], and even to explain certain features of HCl initiated lactam polymerization[3]. This mechanism permitted, with the aid of computer assisted parameter estimation, to discuss in a quantitative manner the kinetics of amine salt initiated[1] and hydrolytic polymerization[2]. By this method a set of parameters (equilibrium and rate constants) became available which gave good agreement of experimental and calculated values. HCl initiated polymerization, however, has a number of special features making the mechanistic picture more complex resulting in a very high number of reactions which have to be considered in its kinetic treatment. This required additional experiments and a refinemy of our earlier mechanistic proposals.

These developments are presented in this paper with special emphasis on stereoelectronic control and the general mechanism of acid catalysis.

RESULTS and DISCUSSION

The mechanism of polymerization

HCl initiated caprolactam (CL) polymerization can be envisaged as shown in Scheme 1.

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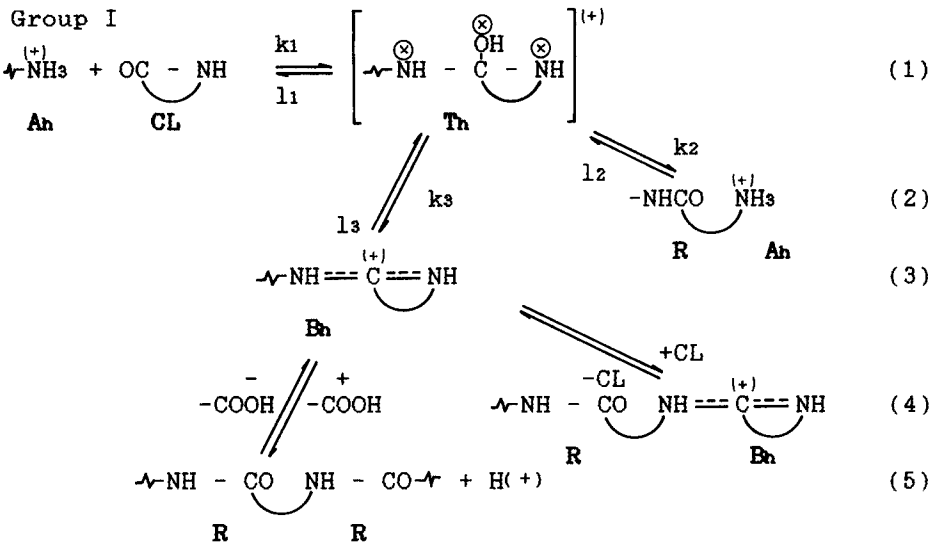
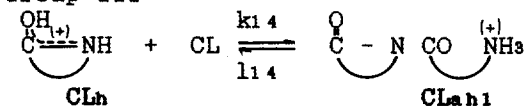
Scheme 1 Mechanism for ∈-caprolactam polymerization initiated by HCl



⊗ sites of protonation

Group III



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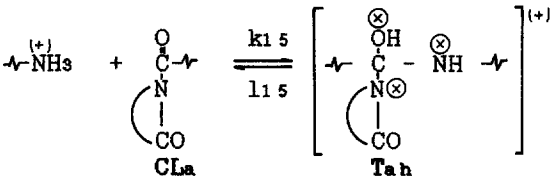

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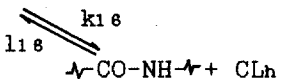

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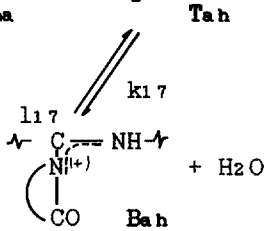

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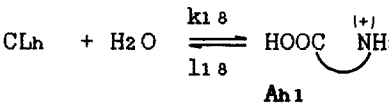

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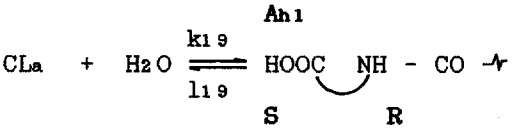

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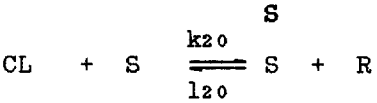

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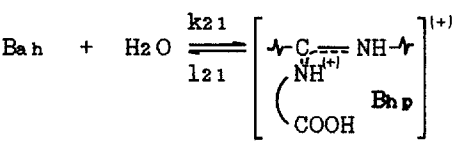

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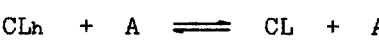
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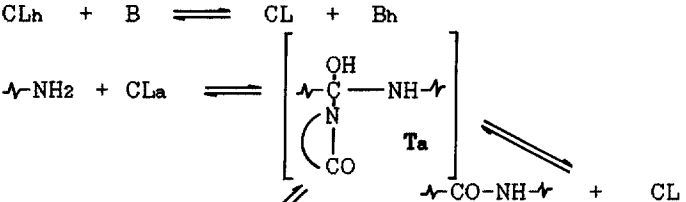

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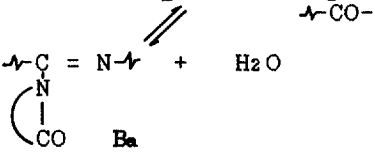

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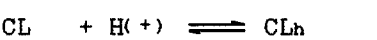
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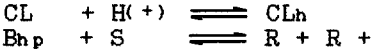
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Among this reactions depicted some are specific for HCl-s type (group III), while conditions may arise for polymerizations initiated by other types of agents such as amine salts (group I), initiators acting through hydrolysis (group II) and also for those generated by other functional groups. (Notation was selected as to confirm with our earlier paper[1].)
This complex scheme can be brought into good agreement with experimental results shown in Figs.1a,b,c, which demonstrate correlations with time of conversion, total basicity (amino and amidine groups), as well as of the concentrations of amidine and carboxyl groups and sometimes of caprolactam hydrochloride (CL_h) and acylamide groups (CL_a) in CL polymerization initiated by CL_h.

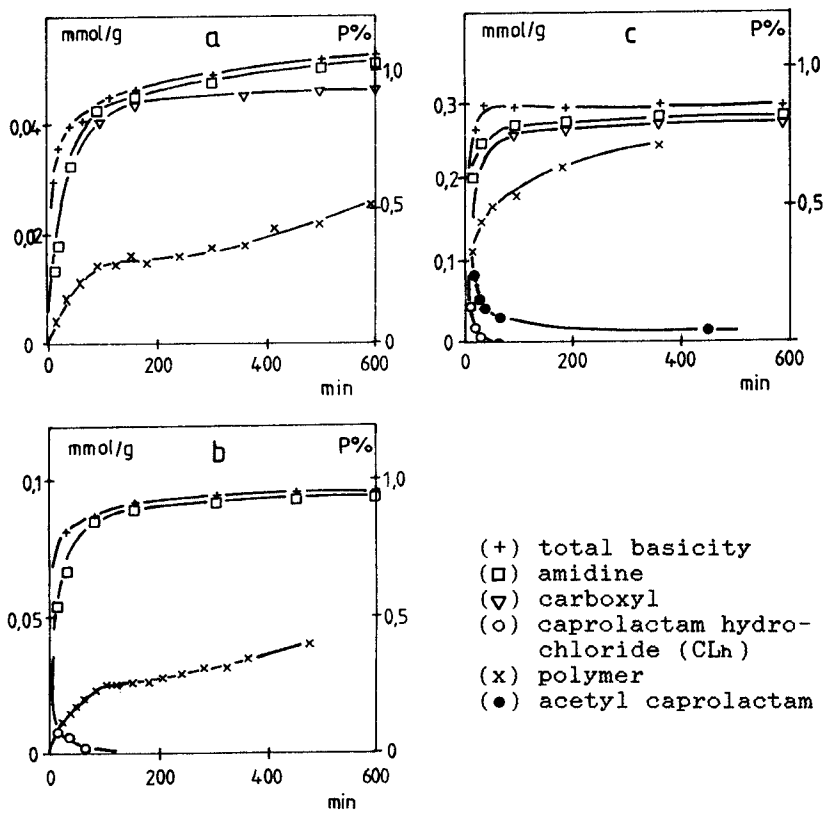


Figure 1 Conversion and functional groups vs.time in ∈-caprolactam polymerization initiated by HCl at 256 °C; Concentration of initiator: a.,0.005mol/molCL; b.,0.01mol/molCL; c.,0.035mol/molCL

In the initiation reaction CL_h reacts in a fast process with CL (reaction III/14) to give ∈-aminocaproyl-caprolactam-hydrochloride (CL_{ah1}) whereby amine hydrochloride (A_h) and acylamide (CL_a) groups are produced. This is reflected by

fast emergence of basic groups as is apparent from Figs.1a,b,c as well as the appearence of CL_a groups (see Fig.1c). Groups A_h may react with CL_a (reaction III/15) as a consequence of which the tetrahedral intermediate can give rise to either an amide linkage and CL_h (reaction 16) or to an acylamidine hydrochloride (B_{ah}) and water (W) (reaction 17). Reaction of A_h with CL in turn (reaction I/1) leads in a similar two-way reaction either to ring opening (reaction 2) or to the formation of amidine hydrochloride (B_h) and water (reaction 3). The effect of the above reactions is manifested in a high rate of polymerization and in a fast rise in the concentration of amidine groups (cf.Figs.1a,b,c). Formation of water entails a fast attack against hydrolysis sensitive groups present in the system, such as CL_h (reaction 18), CL_a (reaction 19) and B_{ah} (reaction 21) to generate in a fast reaction carboxyl groups (S). Indeed in Figs.1a,b,c it can be seen that the formation of amidine groups is accompanied by an analogous formation of carboxyl groups. Transformation of active chain propagating centers, i.e. of A_h to amidine groups (reaction 3 and 17), and of the rapid decline in the concentration of CL_h and CL_a groups (Fig.1c) results in a decrease of polymerization rate and thereby the first stage of polymerization is terminated. This happens at low initial CL_h concentrations (CL_{ho}) at low conversion (Fig.1a), while at high CL_{ho} at higher conversion (Fig.1c).

In the second stage further slow transformation of CL is effected by acidolysis due to the presence of a large concentration of S having, however a low initiating power (reaction 20). In this stage of polymerization, apart from fast hydrolytic reactions the slow hydrolysis of CL also takes place (reaction 6), which becomes important first of all when CL_{ho} is low. This is reflected by an increase of the concentration of basic groups in excess of that of CL_{ho} (Fig.1a). All this can establish the conditions of hydrolytic polymerization (group II). Under favorable kinetic conditions, i.e. when CL_{ho} is small, the first stage is followed by an acceleration of polymerization producing an inflection type kinetic curve (Figs.1a and 1b). With increasing CL_{ho} values this inflection gradually disappears to give way to normal kinetics (Fig.1c).

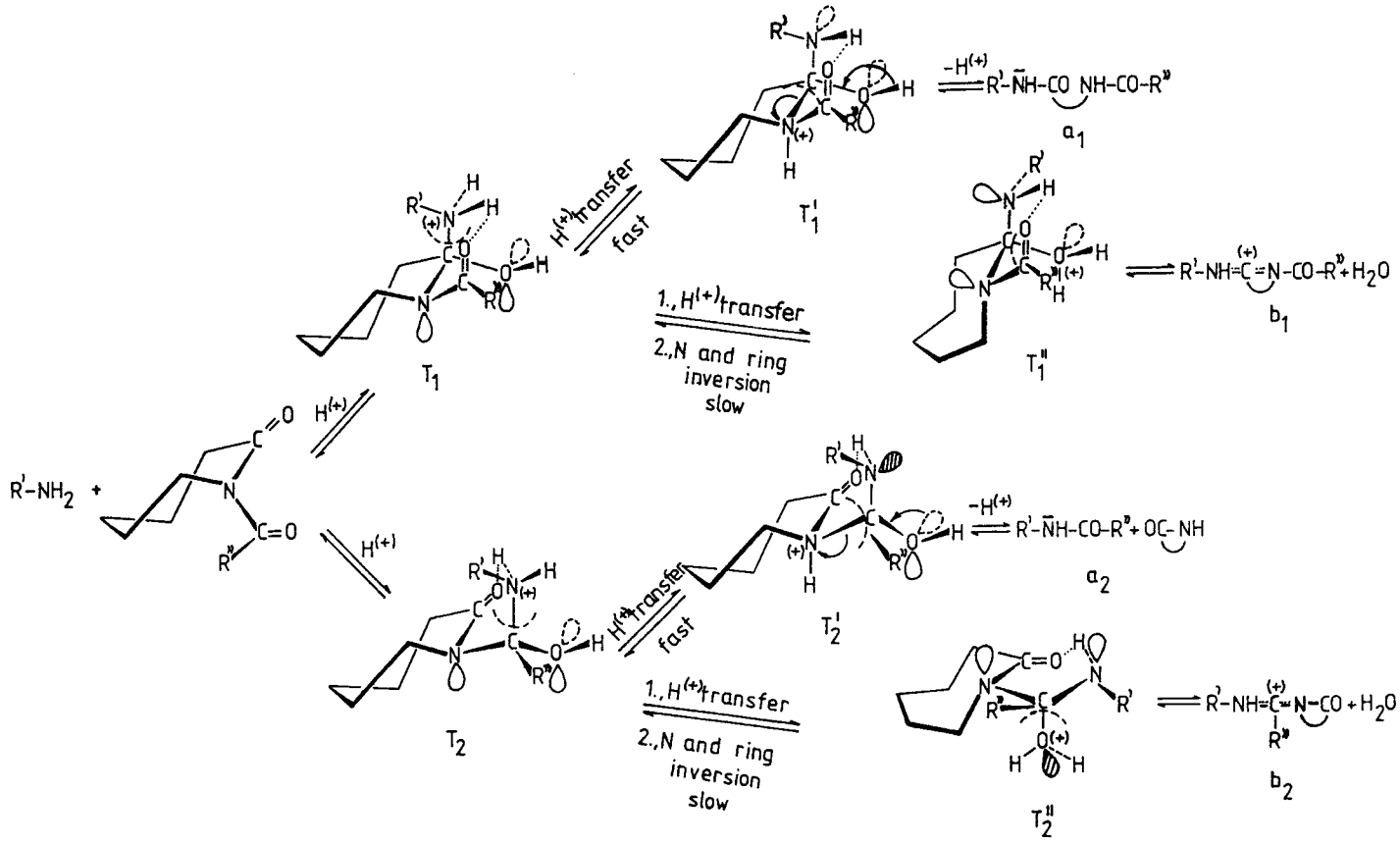
The fact that conditions for certain reactions are established in definite periods of polymerization, otherwise their kinetic probability is small, permits to neglect some reactions.

Stereoelectronic control of two-way reactions (reactions 15-17)

Stereoelectronic control of the two-way reaction in the amine salt initiated and hydrolytic polymerization of lactams, as well as detailed analysis of concomitant conformational changes were discussed in preceding papers[1,4].

Interpretation based on the principle of stereoelectronic control of chain propagation by reaction between CL_a and A_h in lactam polymerization initiated by protonic acids is shown in Scheme 2.

Taking into account the two-way reactivity of intermediates,



Scheme 2 Stereoelectronic control in acyllactam-amine reaction

nucleophilic attack of amine group may take place at the endo-carbonyl and give T_1 or at the exo-carbonyl to provide T_2 along pathways a_1, b_1 and a_2, b_2 resp.Conformational changes leading to the corresponding product occur when the lifetime of an intermediate is sufficiently long for this[5]. This condition is given for fast proton transfer between nitrogens in reactions a_1 and a_2 in Scheme 2, while the slow processes of ring inversion and N-inversion along pathway b_1 and b_2 require a much longer lifetime of the intermediates. It can be seen that for each T an -HNH...OC- hydrogen bond can be established whereby rings of different conformation are formed.These stabilize the structures of T-s thus providing for the lifetime required for taking up those particular conformations which lead to amidine formation.
In our opinion this is one of the reasons why amidine formation is faster in polymerizations initiated by strong protonic acids than in those initiated by amine salts or in hydrolytic polymerization.
For setting up a kinetic model it is necessary to know the ratio of reactions proceeding at exo- and endo-carbonyl. Relative probability of ring opening vs. lactam elimination depends on ring size and the polymerizability of the lactam. Product analysis revealed[6] that in the polymerization of p-aminobenzoyl-caprolactam lactam elimination by reaction of the exo-carbonyl dominates over ring opening involving the endo-carbonyl (67 vs. 33%). Similar ratio (3:1) was found in the reaction of N-acetyl caprolactam and cyclohexyl amine[7]. In view of this only the two-way reaction at the exocyclic carbonyl was considered in our kinetic model (Scheme 2, reactions a_2 and b_2, cf.reactions 15-17).

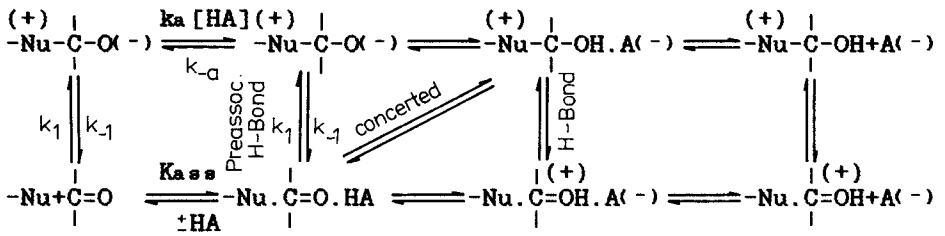
Mechanism of acid catalysis
In order to get a detailed insight into acid catalyzed cationic lactam polymerization first the site of protonation and the location of the protonation step along the reaction coordinate has to be known.
Earlier the amide nitrogen was considered as the sole protonation site[8], while recently - in an equilibrium sense -O protonation was assumed[9], although an N-protonated form could be not excluded from the mechanism as a kinetically relevant species[10]. As to the location of protonation it is generally accepted that this takes place in a fast preequilibrium at the substrate, if proton transfer precedes the rate determining step or coincides with it. This is in accord with the concept that due to the protonation first an activated monomer is formed in lactam polymerization[11].
Jencks envisaged the mechanism summarized in Scheme 3 for the acid catalyzed addition of nucleophiles onto carbonyl groups[5].
Thus according to the lifetime of the intermediate the preferred mechanism can be :
- stepwise, i.e. proceeding via one or more intermediates in several steps, or
- concerted if the lifetime of the intermediate is $<10^{-13}$ s, i.e. the vibration frequency.

Within the stepwise mechanism according to the effect of the

catalyst on the lifetime of the intermediate the reaction may proceed:

- via a stable intermediate (its lifetime is sufficient, even without acid catalysis, to form the end product, or
- via a transient intermediate. This may also involve more than one reaction pathways, namely stabilization of the intermediate by diffusion controlled proton capture or by promotion of the formation of an intermediate by hydrogen bonding (preassociation).

Scheme 3 Mechanism for general acid catalysis of the addition of a nucleophil Nu to carbonyl group [5]



Scheme 3 also comprises reaction pathway of cationic lactam polymerization, but their analysis demands further studies. On the basis of our own studies and literature data in the cationic polymerization the most of lactams an A_oT2 i.e. an acid catalyzed, oxygen protonated, bimolecular mechanism involving a tetrahedral intermediate is probable.

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