MECHANISM OF CATIONIC LACTAM POLYMERIZATION

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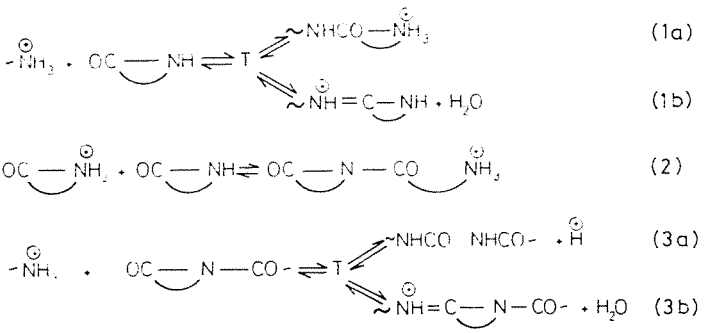
Abstract

The authors suggested a new mechanism for the interpretation of cationic lactam polymerization according to which in the chain propagation reaction, through the appropriate intermediates, compounds belonging to various polymer homologous series are formed and additional polymerization processes are superimposed onto the original ones. On the basis of the new mechanism a kinetic model has been developed by the computer simulation of which rate and equilibrium constants could be determined. The latter enabled, a good quantitative description of polymerization.

Large amounts of polyamides are produced by lactam polymerization, the polymerization mechanism is, however, not fully cleared up yet.

The chain propagation reaction of cation polymerization initiated by the salts of amines with carbonic or protic acids has been described earlier by reaction (1a) and in case of protic acid initiators by reaction (2) (3a) and (1a) resp., (without formation of T) [1].



where

T = tetrahedral intermediate

$\cup = -(CH_2)_n-$, $n=5$ caprolactam

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However, the characteristic polymerization kinetics and other experimental results could not be explained on the basis of this mechanism in the case of some types of initiators.

Thin-layer chromatographic studies of oligoamides produced by different cationic initiators proved that—in contrast to earlier assumptions—in the course of polymerization, polymer homologues containing amidine groups were also formed. Based on this, a new reaction mechanism providing an explanation for experimental results was suggested [2, 3, 4].

According to this mechanism, in the acid-catalyzed reactions between the nucleophilic chain propagation centre and the carbonyl group containing monomer (reaction 1a—1b) or acylamide group (reaction 3a—3b) a tetrahedral intermediate (*T*) is formed in a first step. Depending on the reaction conditions, this intermediate leads to the formation of the next member of the homologous series or to the formation of amidine group and water [2—6]. The produced water—depending on the hydrolysability of the compounds formed in the polymerization—yields new functional groups generating additional polymerization depending on the kinetic conditions. The characteristic inflection-type kinetic curves are the result of the superposition of polymerization generated by the initiator and by the functional groups in the course of polymerization. In the polymerization induced by different initiators the *C*-terminal carboxyl groups and *N*-terminal groups, including the amidine groups, have been followed by a method elaborated at our Department [4—7]. The change of functional groups during polymerization shows good agreement with the reaction mechanism suggested [4, 8, 9, 10]. With the computer simulation of the kinetic model based on this mechanism, we were able to determine rate and equilibrium constants. Conversions and concentration changes of functional groups calculated using these constants have been found to be in good agreement with experimental data. This mechanism provides an unambiguous description not only of our own measurements, but also of those found in the literature, and their interpretation is more reasonable, as well [9, 10].

The two-directional chain propagation reactions proceeding through a tetrahedral intermediate and the ratio of the products of these reactions can be well explained in terms of the stereoelectron control theory suggested by Deslongchamps, at the same time the ratios obtained by kinetic calculations for the two reactions are also in accordance [10]. While to fulfil the conditions of stereoelectron control for ring opening reactions only a proton transfer has to occur on the intermediate, in contrast to the amidine formation requires also a change in ring conformation and N-inversion in addition to the proton transfer [10]. It is in accordance with the kinetic fact that the rate constant of the ring opening reaction is higher by about one order of magnitude compared to that of amidine production within the temperature range measured [10].

It could be proved that the mechanism of the polymerization of lactams having greater ring size than caprolactam (e.g. capryllactam, lauryllactam) is similar, howerer, the ratio of the rate constants of the two-directional reactions is of different value in the polymerization of each lactam [7].

It is to be mentioned that this mechanism has been presented at the symposium entitled "Ring opening polymerization" of the American Chemical Society in 1977.

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