Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Šebenda, JAN(1972) 'Lactam Polymerization', Journal of Macromolecular Science, Part A, 6: 6, 1145 — 1199

To link to this Article: DOI: 10.1080/10601327208056889

URL: http://dx.doi.org/10.1080/10601327208056889

J. MACROMOL. SCI.—CHEM., A6(6), pp. 1145-1199 (1972)

Lactam Polymerization

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ABSTRACT

After a survey of the present knowledge of the reaction mechanism of initiation and chain growth in the cationic, anionic, as well as hydrolytic polymerization, a detailed discussion is given of side reactions accompanying all types of lactam polymerizations. The side reactions play an important role in the anionic and cationic polymerizations and lead both to the decay of active species and to the formation of irregular structures inside the polymer molecules.

INTRODUCTION

During the past decade a great number of new lactams and lactam polymers has been synthetized including optically active ones [1-36]. Although not all of the new lactams could be polymerized until now, great progress has been achieved with respect to the architecture and properties of the polymers as well as the elucidation of the various reaction mechanisms of lactam polymerization. The principles of the known types of polymerization were revealed at the end of the fifties [37-75] but, during more recent years, great progress has been attained in the detailed knowledge of the reaction scheme.

Studies of the cationic and anionic polymerization have revealed that the polymerization is in most cases accompanied by side reactions destroying the active species and introducing irregular structures into the polymer.

At the present time many attempts are directed toward the synthesis of strictly regular polymers in order to achieve a maximum of the desired particular property. For a successful synthesis of such perfect materials (e.g., synthetic analogs of natural polymers, biopolymers) we have to select optimum polymerization conditions which yield the most regular polymer.

Almost any kind of lactam polymerization involves chemical activation of the monomer and/or the growing end, and these highly reactive species give rise to side reactions interfering with the propagation reaction. The nature and extent of side reactions depend on the kind of initiation as well as on the structure of the monomer unit.

REACTION MECHANISMS OF INITIATION AND PROPAGATION

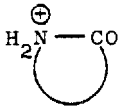
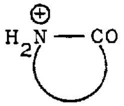
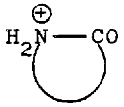
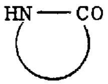
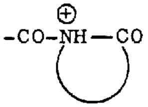
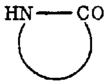
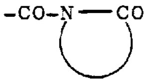
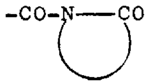
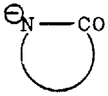
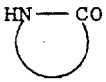
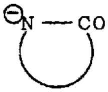
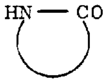
It follows from the nature of the amide bond which is being cleaved during polymerization that polymerization of lactams having a hydrogen atom at the amide nitrogen can proceed through transacylation reactions in which the acylating species can be represented by neutral lactam, protonated lactam, N-acylated lactam, protonated N-acylated lactam, and the carboxyl group. The nucleophile can be the amino group, lactam, lactam anion, and the carboxylate anion (Table 1).

It follows from Table 1 that lactam polymerizations can involve a variety of growing species to which monomer or activated monomer is added. Obviously, not all of these active species can coexist simultaneously. On the other hand, more than one type of propagation reaction can be expected to proceed with a given initiator. The same types of reactions involving polymer amide groups (activated or unactivated) lead to scission or exchange reactions.

Depending on the nature of the initiating species and on the polymerization conditions, one of the many possible reactions usually predominates.

Polymerizations starting under substantially anhydrous conditions can be initiated either with strong bases capable of producing lactam anions (anionic polymerization) or strong acids which do not split off water under polymerization conditions (cationic polymerization). The term hydrolytic polymerization has been reserved for polymerizations initiated with water or water-releasing substances.

TABLE 1. Initiation and Propagation Reactions

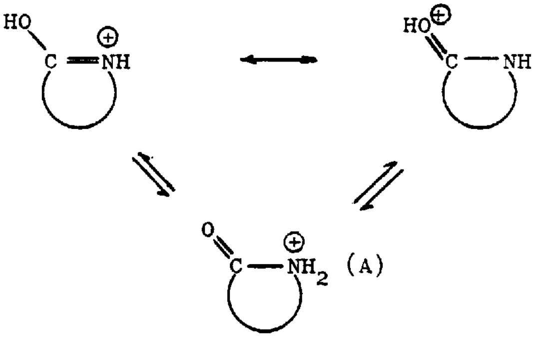
Acylating species	Nucleophile	Mechanism
	NH_2—	Hydrolytic, cationic
	$^{\ominus}$O-CO-	Hydrolytic
		Cationic
		Cationic
	NH_2—	Cationic, anionic
		Anionic
		Anionic
	NH_2-	Hydrolytic

N-Substituted lactams cannot form all of the species listed in Table 1 and, therefore, they will be treated separately.

Cationic Polymerization

Under anhydrous conditions, polymerization can be initiated with acids which do not form anhydrides under the polymerization conditions, as well as with salts of such acids with amines or amides [72, 73]. Because the monomer cation is involved in the initiation and propagation reactions, the polymerization is usually designated as cationic.

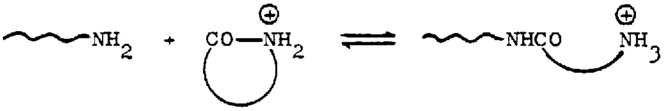
Protonation of amides occurs preferentially at the oxygen atom but a small fraction of N-protonated amide is assumed to be present in the tautomer equilibrium [76] (Eq. 1). The amidium cation (A) has an increased acylating ability because of the lack of resonance stabilization and reacts with the nucleophiles present in the polymerization medium. In the polymerization initiated with lactam salts of strong acids, the strongest nucleophile present is the monomer. Acylation of the latter with the amidium cation yields aminoacyllactam [76-79] (Eq. 2). Now the strongest nucleophile is represented by the primary amine group, and acylation of the latter by protonated lactam results in the incorporation of one monomer



(1)

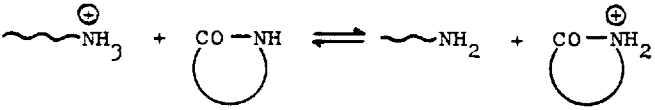
(2)

unit into the polymer [80] with preservation of the growth center (Eq. 3) and regeneration of protonated lactam through the equilibrium



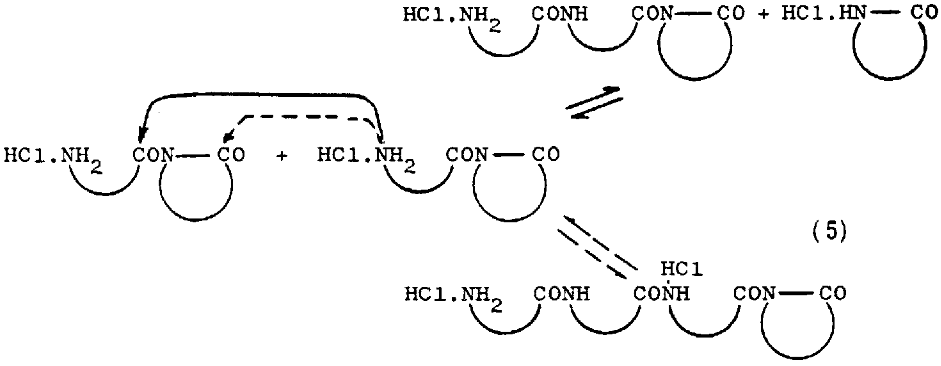
(3)

shown in Eq. (4). The equilibrium concentrations of amine and imide



(4)

groups are attained quickly, and the reverse initiation reaction, i.e., aminolysis of acyllactam, has been found to proceed very rapidly [73, 78-83]. Therefore, Doubravszky and Geleji concluded [81, 82, 84-86], that bimolecular aminolysis of aminoacyllactam molecules contributes to the propagation reaction (Eq. 5). Reaction (5) destroys



(5)

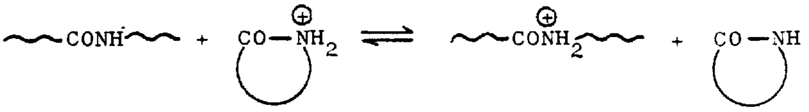
the equilibrium (2) and regenerates the strongly acidic amide salt (e.g., lactam hydrochloride). New aminoacyllactam molecules are formed by reaction (2), and in this way the sequence of reactions (2) and (5) contributes to the total lactam consumption [81, 82, 84-87], provided that at least one lactam molecule is involved in the initiation reaction (2). The corresponding N-(oligo-ω-aminoacyl)-lactams formed in reaction (3) or in the sequence of reactions (2) and

(5) were identified in cationic polymers of caprolactam [77, 80, 88] and caprylolactam [89].

The same kind of reactions occurs in polymerizations initiated with salts of tertiary amines [90]. The only difference arises from the effect of the strongly basic tertiary amine on the equilibria (2) and (4), decreasing the concentration of the active species, i.e., amidium ions, and amine and imide groups.

In polymerizations initiated with salts of primary and secondary amines [91-93], the chain growth proceeds predominantly via addition of protonated lactam to the amine group (Eq. 3). The rate of incorporation of the initiating amine is proportional to its basicity. The initial concentration of amidium cations increases with decreasing basicity of the amine, and the contribution of reactions (2) and (5) to the over-all lactam consumption is increased.

With increasing conversion, the concentration of protonated lactam is decreased in favor of protonated polymer amide groups (Eq. 6) which take part both in the initiation reaction (2) (with lactam molecules) and in exchange reactions (with polymer molecules).

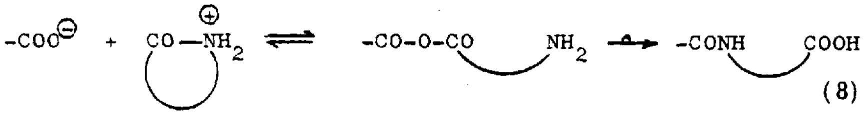


(6)

Polymerizations of caprolactam initiated under anhydrous conditions with carboxylic acids of medium and low acidity proceeded with an induction period [49, 93, 94]. The length of the induction period and the maximum rate of polymerization were determined by the pK_a value of the initiating acid [94, 95]. It appears that in polymerizations with acids of different pK_a more than one reaction mechanism can be operative. Among the nucleophiles present in the equilibrium of Eq. (7), either the amide group or the anion derived from

(7)

the initiating acid can be acylated. Acylation of the lactam amide group in reaction (2) produces aminoacyllactam which may grow by reactions (3) and (5). In the initiation with weak acids, e.g., caproic or stearic acid, acylation of the anion can lead to anhydride formation with subsequent rearrangement [75] (Eq. 8). Besides, carboxylic



(8)

acids are known to yield anhydride and water at elevated temperature [96] (Eq. 9). In the subsequent hydrolysis (Eq. 10), a low

$$2\text{—COOH} \rightleftharpoons H_2O + \text{—CO—O—CO—} \qquad (9)$$

$$\text{—CONH—} + H_2O \rightleftharpoons \text{—COOH} + NH_2\text{—} \qquad (10)$$

$$(\text{—CO})_2O + NH_2\text{—} \rightleftharpoons \text{—CONH—} + \text{—COOH} \qquad (11)$$

concentration of amine groups can be established at which slow propagation proceeds by reaction (3).

The induction period observed in polymerizations with carboxylic acids corroborates the latter mechanism. On the other hand, the induction period can be due to the changing composition of the polymerizing mixture (i.e., formation of transamide) which affects the degree of dissociation of the active species.

For a given lactam, the relative rates of acylation of the lactam and of the anion derived from the initiating acid depend on the structure and basicity of both nucleophiles. With increasing acidity of the initiating acid, the nucleophilicity of the corresponding anion decreases and acylation at the amide group becomes more important. Incorporation of the initiating acid (RCOOH) by reactions (8)-(11) will decrease and an increasing fraction of the latter will remain in the polymerizing mixture. Finally, an equilibrium will be established (Eq. 12) which

$$\text{RCONH}\sim\sim + \sim\sim\text{COOH} \rightleftharpoons \text{RCOOH} + \sim\sim\text{CONH}\sim\sim\sim \qquad (12)$$

determines the acidity of the polymerizing medium. Hence, increased acidity of the initiating acid results in increased acidity of the medium during polymerization. This in turn increases the rate of the initiation and polymerization reactions, as well as the proportion of the various initiation and propagation reactions.

In polymerizations with very strong acids, the corresponding anion (e.g., Cl^-) is not acylated at all because of its low basicity and, therefore, the initiating acid is not incorporated into the polymer. In this case the strongest nucleophile is the lactam amide group which undergoes acylation and polymerization via reactions (2), (3), and (5) predominates. On the other hand, unsubstituted aliphatic carboxylic acids yield anions of higher nucleophilicity and these anions compete with lactam molecules for the acylating amidium ion in reaction (8). In addition, water formed in reaction (9) can initiate a hydrolytic polymerization with a high $COOH/NH_2$ ratio. As a matter of fact, small amounts of amine groups could be detected in polymers prepared with carboxylic acid but, for the present time, it cannot be decided whether the amine groups originated from reaction (2) or reaction (10).

Polymerizations initiated with strongly complexing compounds should also be considered as cationic [77, 97, 98] (e.g., $ZnBr_2$, $CrCl_3$), for they are known to coordinate lactam molecules. Coordination increases the acylating ability of the lactam which can initiate a cationic polymerization at elevated temperatures. Alternatively, polymerization can be initiated by the acid resulting from deprotonation of the amide group [98].

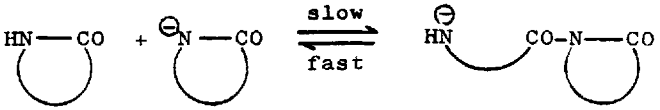
Anionic Polymerization

Strong bases capable of forming the free lactam anion (Eq. 13) may initiate an anionic polymerization, provided that substances

(13)

reacting with the growth centers are substantially absent. Suitable bases include metal hydrides, amides, and organometallic compounds. Lactam anions can also be generated in the reaction mixture by electrolysis of neutral salts. In this case, however, polymerization ceased very soon after the interruption of electrolysis [99].

The initiation process involves a ring-opening transamidation (disproportionation) (Eq. 14). The primary amine anion is immediately neutralized by an amide proton to regenerate the lactam

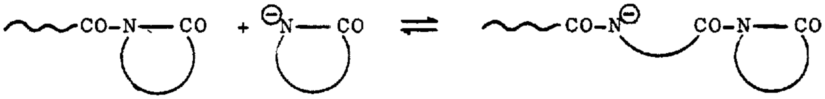


(14)

anion (or polymer amide anion) and to form an aminoacyllactam [63-68, 100, 101] (Eq. 15).

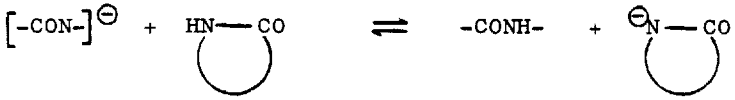
(15)

The actual propagation center is the cyclic amide linkage of the N-acylated terminal lactam ring. Acylation of the amide nitrogen increases the electron deficiency of the amide linkage, and this increases the reactivity of the ring amide carbonyl toward attack by the nucleophilic lactam anion [63-68] (Eq. 16). The subsequent



(16)

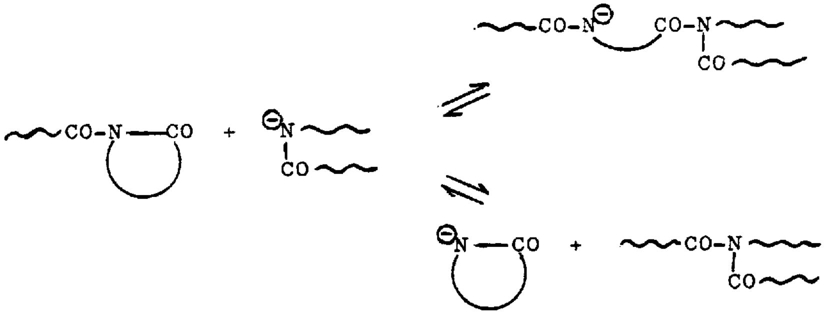
proton exchange with the monomer is very much faster [102] than the addition reaction (16) and leads to an equilibrium between lactam and polymer-amide anions (Eq. 17).



(17)

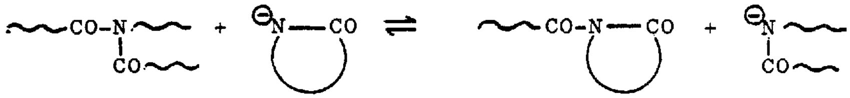
As soon as polymer amide anions are formed in the propagation reaction (16) they undergo acylation by the acyllactam groups either with ring opening (Eq. 18) or with formation of lactam anions (Eq. 19). Reaction (19) represents depolymerization whereas reaction (18), when followed by acylation of a lactam anion (Eq. 20) results in the incorporation of one lactam unit and represents the second path of propagation. Thus any kind of imide group (i.e., acyllactam and diacyl amine) takes part in the propagation.

The polymer amide groups and the corresponding anions are also involved in the disproportionation reactions producing imide groups (Eqs. 21 and 22). However, the number of polymer molecules is increased only in such disproportionation reactions in which at least one lactam anion is involved, whereas reactions (22) do not alter the number of polymer chains unless followed by reaction (20).



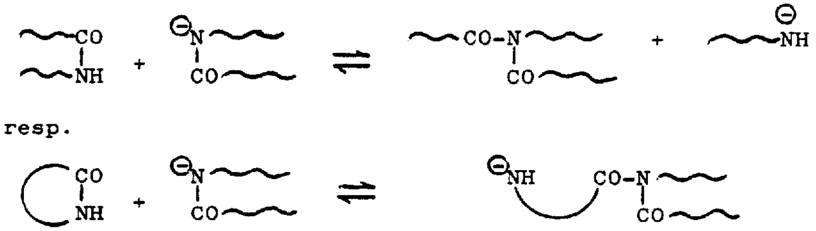
(18)

(19)



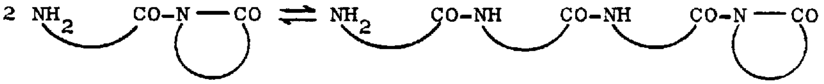
(20)

(21)



(22)

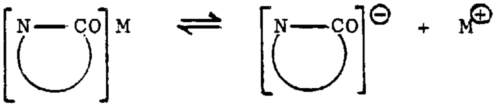
The acylation reaction (16) is much faster [103, 104] than the initiation reactions (14), (21), and (22) and, therefore, induction periods are observed in polymerizations initiated with lactam anions [68, 105]. Contrary to the cationic polymerization, the contribution of the initiation reactions (14) and (21) and the subsequent bimolecular aminolysis (Eq. 23) to the total lactam conversion is negligible



(23)

in the anionic polymerization. The aminolysis (23) may only contribute to the increase of the molecular weight [101, 106-108] which is very steep at the beginning of polymerization.

The rate of polymerization depends on the concentrations of the acyllactam and diacylamine groups as well as of the activated monomer (lactam anion). The concentration of the latter is determined by the equilibrium (17) and by the dissociation of the lactam salt [105] (Eq. 24).

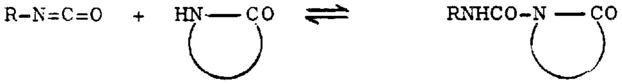


(24)

The dissociation of lactam salts depends on the nature of the counterion and, for alkali metal salts, the rates of the initiation and propagation reactions increase in the order [109-111]: Li < Na < K < Cs. Lactamates of some complex-forming cations almost do not dissociate at all. Therefore, chromium lactamate alone is incapable of initiating the polymerization of caprolactam [112], and anionic polymerization in the presence of lactamates of some complex-forming cations proceeds at reasonable speed only when an additional dissociating lactam salt is present [112-115].

Instead of forming the propagation centers in the slow initiation reactions, the electronegatively substituted lactam can be added as such at the beginning of polymerization (e.g., as N-acyllactam) or formed in situ by fast reactions with suitable precursors, e.g., with acid chlorides, anhydrides, and isocyanates [67, 116-127] (Eqs. 25 and 26). The initiating activity of such substances, usually designated as activators or cocatalysts, has to be comparable to that of the acyllactam growth center.

(25)



(26)

The rate of addition of the first lactam anion depends on the structure of the activator residue in the initiating center [124]. Bulky acyl groups, e.g., in pivaloylcaprolactam, decrease the rate mainly by sterical hindrance. Highly electronegative substituents like the benzoyl [103, 124] group increase the rate of addition of the first lactam anion (Fig. 1).

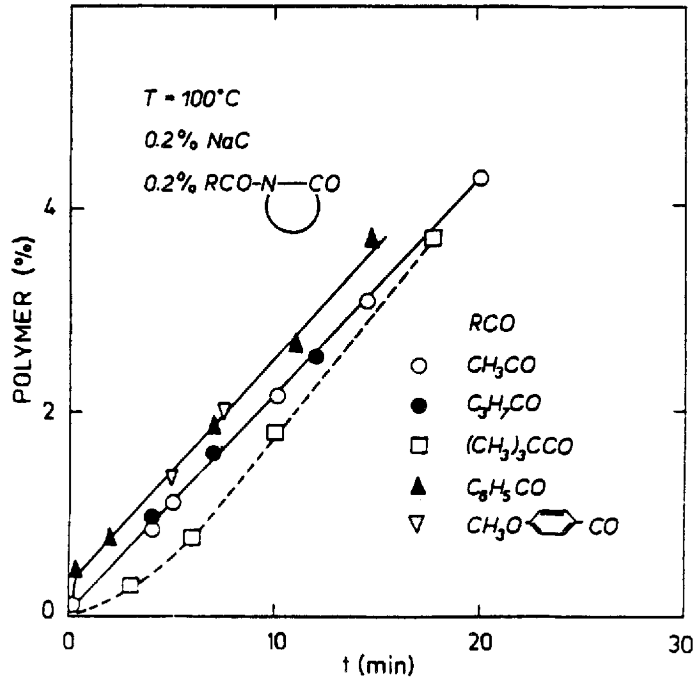


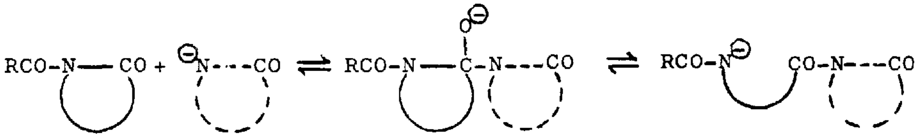
FIG. 1. Anionic polymerization of caprolactam with various acyllactams at 100°C. Concentration of sodium caprolactam and acyllactam, 0.2 mole % [124].

However, the activator can determine not only the rate of addition of the first lactam unit, but it may affect the whole course of polymerization. In the first addition the activator residue is incorporated at the end of the polymer molecule (R—NH~~~~) and these structures may influence the basicity during the polymerization. For example, N-(p-nitrophenyl)carbamoylcaprolactam produces stronger acidic urea groups than those derived from N-phenylcarbamoylcaprolactam.

Therefore, polymerization with the former proceeds more slowly because of the decreased concentration of lactam anions [123].

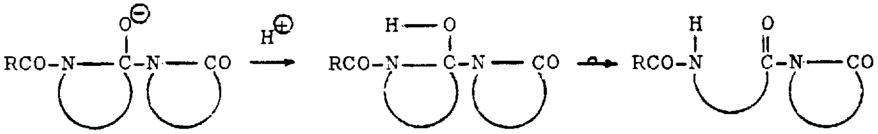
If only the indicated reactions proceeded, then the polymerization products should reveal the characteristic features of living polymers. However, as will be shown below, side reactions may consume both active species, i.e., imide groups and strong base.

Different views have been put forward on the detailed mechanism of ring opening. Most probably the nucleophilic attack of the lactam anion at the cyclic carbonyl group of an N-acylated lactam results in the intermediate symmetric mesomeric anion which then rearranges with ring opening [128, 129]. In this process one lactam molecule is incorporated into the polymer (Eq. 27). It is the lactam molecule which was the terminal unit which is incorporated into the polymer, while the former lactam anion becomes the endstanding N-acylated lactam. This sequence of lactam units was proved by using different lactams as lactam anion and as N-acyllactam growth center [104].



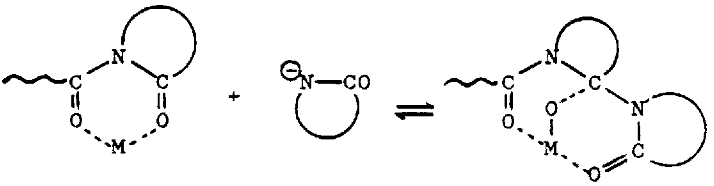
(27)

On the other hand, Champetier and Sekiguchi [130, 131] suggested that the intermediate anion is first neutralized by a proton from a lactam or polymer amide group and then the neutral molecule rearranges with opening of the penultimate ring (Eq. 28).



(28)

It has also been suggested that the acylating ability of the acyllactam is increased by coordination of the cation to the imide carbonyl groups [70, 130-132]. The incorporation of one lactam unit was assumed to proceed through addition of a lactam anion, followed by protonation and rearrangement (Eqs. 29 and 30). Although reactions (28)-(30) cannot be excluded, namely with complexing cations, preference is given to reaction (27).



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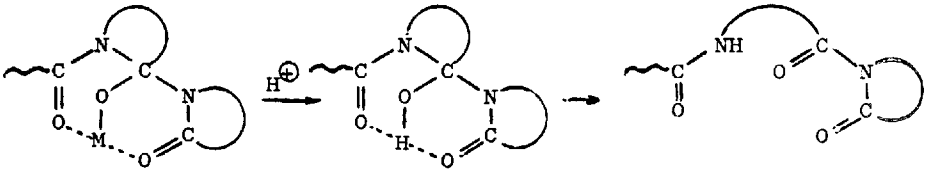
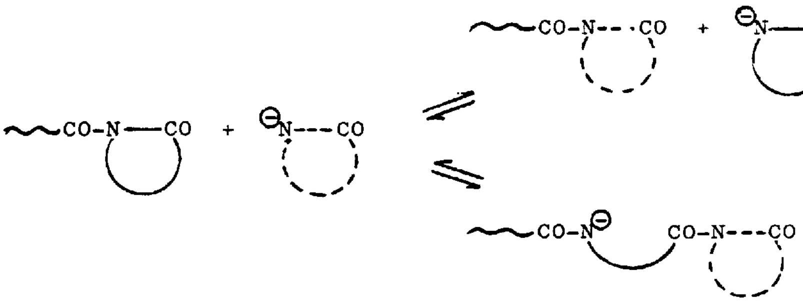


(30)

In the homogenous copolymerization of lactams [133-138], the equilibrium composition of the copolymer is controlled thermodynamically. On the other hand the nonequilibrium composition of the copolymer formed at the beginning of polymerization is controlled kinetically. In this case the relative rates of incorporation of the copolymerizing lactams are not necessarily determined by the rate of reactions in which the lactam ring is cleaved. Vofsi et al. [139] were able to show that in the anionic copolymerization of pyrrolidone and caprolactam the acyl-exchange reaction (31) occurs faster than the propagation reaction (16). As a result, the



(31)

(16)

composition of the copolymer is determined by the transacylation equilibrium (31), the position of which depends on the concentration and acidity of both lactams as well as on the nucleophilicities of their anions [139]. In this way the relatively low copolymerization activity observed for caprolactam [140, 141] is easily explained.

Hydrolytic Polymerization

In the water-initiated polymerization the hydrolysis-condensation equilibria involving monomer and polymer amide groups (Eqs. 32 and 33) determine the concentration of the amine and carboxyl groups

(32)

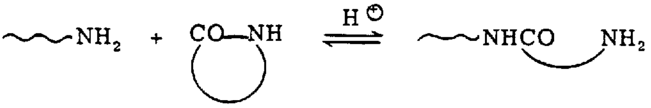
$$-CONH- + H_2O \rightleftharpoons -COOH + NH_2- \qquad (33)$$

taking part in the propagation reactions and, finally, determine the molecular weight of the polymer [37, 38, 42, 51, 52, 54, 55, 142-148]. The same equilibria are being established in polymerizations initiated with amino acids or salts of carboxylic acids with primary or secondary amines.

Kinetic as well as chemical evidence proved that in the hydrolytic polymerization of caprolactam the hydrolysis of monomeric lactam (Eq. 32) and subsequent condensation of the amino acid (Eq. 34)

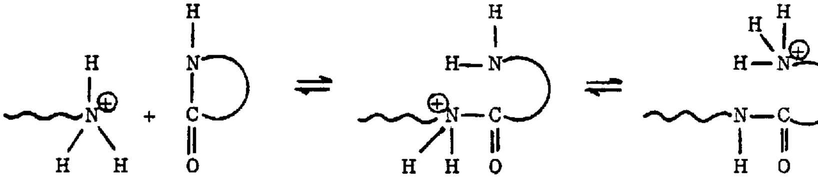
$$\sim\sim COOH + NH_2(CH_2)_5COOH \rightleftharpoons H_2O + \sim\sim CONH(CH_2)_5COOH \qquad (34)$$

constitute only a few per cent of the total lactam consumption [43, 149]. The predominating propagation reaction consists in stepwise addition of lactam molecules to the end groups [43, 61]. Hermans and associates have given an unambiguous proof that the main chain growth reaction consists in the acid catalyzed addition at the amine group [41] (Eq. 35). However, different paths are found in the literature for the detailed mechanism of this reaction.



(35)

Although the addition of N-protonized lactam at the neutral amine group (Eq. 3) seems to be most compatible with general rules of organic chemistry [41, 47, 48], some authors assumed that propagation proceeds through addition of neutral lactam to the ammonium ion [74, 79, 80, 95] (Eq. 36), or by addition of lactam to the undissociated salt [150] (Eq. 37).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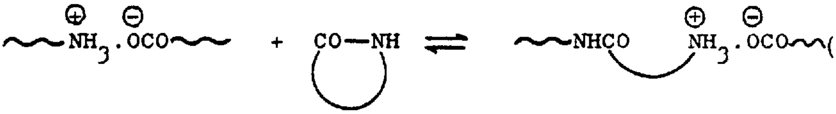
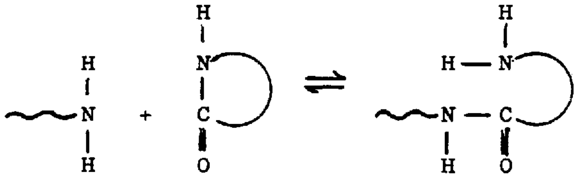

(37)

The main reason why some authors prefer reaction (36) or reaction (37) is the fact that the equilibrium (4) is shifted to the left side. Therefore, a two-step mechanism has been suggested for the addition of the lactam unit at the ammonium group [151]: after a proton exchange between the ammonium group and lactam (Eq. 4), the free amine group is acylated with the protonized lactam (Eq. 3).

If the acid-catalyzed addition at the amino group proceeded via reaction (36), then the uncatalyzed reaction (Eq. 38) should proceed


(38)

even faster because of the increased nucleophilic character of the free amino group as compared to that of the ammonium ion. However, the polymerization initiated with primary amines is known to proceed very slowly [49, 94], and with respect to the low nucleophilicity of the ammonium group, reaction (36) or reaction (37) should proceed even slower. On the other hand, reaction (3) is very fast because of the strong acylating activity of the protonated lactam towards the strong nucleophile (amine). Moreover, the indicated reaction path (Eq. 3) proceeds in a very favorable way because during the incorporation of the lactam unit, the protonated amide yields a protonated amino group (either in one step or in two successive steps). Hence, the major fraction of lactam should polymerize via reaction (3) with such initiators as water, amino acids, or with salts of primary and secondary amines with carboxylic acids. Reaction (3) certainly contributes significantly to the cationic polymerization initiated with Brønsted and Lewis acids as well as with salts of amines and amides with inorganic acids.

The large variation of the reaction constants during polymerization has been explained by the changing dielectric constant [47, 48]. In the course of polymerization the dielectric constant decreases from 15.1 to 5.2 and, as a result, the degree of ionization is decreased drastically from $\alpha = 0.78$ to $\alpha < 0.001$. Reaction constants of stepwise addition of lactam to end groups corrected for the changing degree of ionization described the polymerization much more satisfactorily than the uncorrected ones [47, 48]. It follows from this treatment that the catalyzed reaction is decisive in hydrolytic polymerization with equimolar concentration of amine and carboxyl groups. The uncatalyzed reaction, on the other hand, becomes important at a very high ratio of $NH_2/COOH$ when no carboxyl groups are available for catalysis, i.e., protonation of lactam is suppressed. The dielectric constant of the medium also depends on the water content and, therefore, the ionization of end groups will increase with increasing water content.

The changing composition not only influences the ionization of end groups but also changes the activity of reactants. Giori and Hayes [144, 145] found that the acitivity of water is lower in caprolactam than in the resulting polymer. In addition, the activity of water in the equilibrium polymer increases with increasing water content. Therefore, the equilibrium constants of polycondensation corrected for the water activity coefficient describe the polycondensation equilibrium much better than the apparent equilibrium constants related to the concentration only.

Polymerization of N-Substituted Lactams

The decreased tendency of N-substituted lactams to undergo polymerization is due to both enthalpic and entropic effects. In the small and medium lactams up to the eight-membered ring, the change in configuration from cis to trans occurring during the polymerization of the unsubstituted lactams is largely lost in N-substituted lactams. The difference in resonance stabilization between the cis- and transamide bond is about 1.4 kcal/mole [152], and this value corresponds very well to the difference between the heats of polymerization of the unsubstituted and the N-methylated lactams (Table 2). In addition, N-substitution seems to make the polymerization entropy more negative than substitution at the carbon atoms.

TABLE 2. Heats of Polymerization from Heats of Combustion [153]

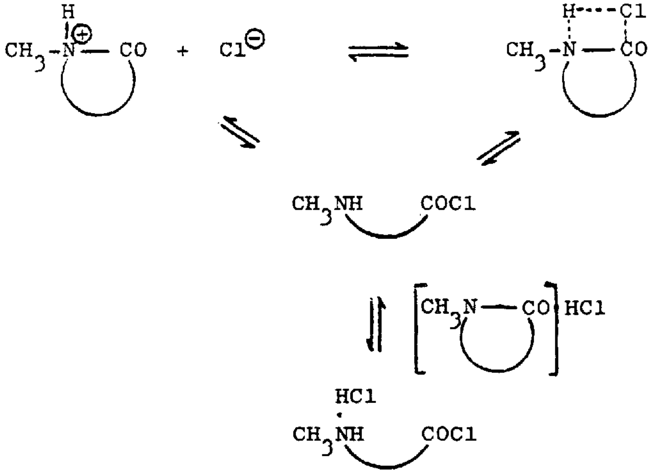
	ΔH_p (kcal/mole)		$\Delta H_s - \Delta H_u$
Lactam	Unsubstituted	N-Methylated	(kcal/mole)
Caprolactam	3.8	2.3	1.5
Enantholactam	5.3	3.9	1.4

For these reasons only the more strained four-, eight-, and nine-membered N-substituted lactams have been polymerized thus far [7, 9, 18, 31]. The highly strained 2,2-dimethyl quinuclidone, i.e., a bridgehead lactam, is very unstable and undergoes polymerization at room teperature [29].

Not all initiators capable of polymerizing unsubstituted lactams are able to initiate the polymerization of N-substituted lactams. Since neither the lactam anion nor its N-acylated derivative can be formed, anionic polymerization could not be initiated by strong bases. Only a very slow polymerization can be initiated with primary or secondary amines [9, 31], because no protonation can occur by the lactam amide hydrogen. The highest initiating effect for N-substituted lactams was observed with carboxylic and inorganic acids [9, 31].

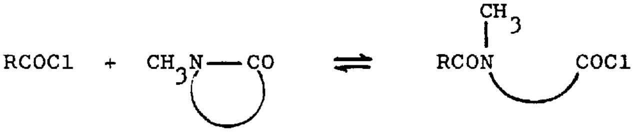
The polymerization with hydrogen chloride starts with the formation of highly reactive intermediates. Whereas unsubstituted lactams undergo disproportionation (Eq. 2) with the formation of aminoacyl lactam, with N-substituted lactams this reaction cannot occur because of the lack of hydrogen at the amide group. The only nucleophile which may be converted into an activated intermediate is the anion of the acid, i.e., the chloride ion. Acylation of the Cl^- anion with the protonated lactam yields the chloride of the corresponding carboxylic acid (Eq. 39). The formation of carboxylic acid chlorides has been confirmed both in model reactions of dialkylamine hydrochloride and in the polymerization product [31].

With acyl chlorides alone [31], the polymerization proceeded at least 20 times slower than with hydrogen chloride so that the prevailing growth reaction cannot consist in the acylation of the lactam by the



(39)

acyl chloride (Eq. 40). Also, the hydrochloride of dibutyl amine initiated only a slow polymerization [31], so that the contribution of catalyzed aminolysis (Eq. 41) is only of minor importance. On the



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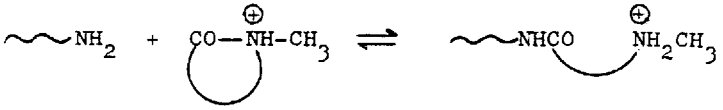
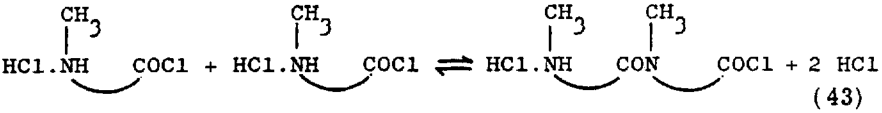


(41)

other hand, the initiating effect of acyl chlorides was increased substantially by the addition of secondary amine hydrochloride (Fig. 2). These facts indicate that both the amine and the acid chloride are involved in the chain growth reaction which consists most probably of the polycondensation of the amino acid chloride (and its hydrochloride) (Eqs. 42 and 43). The regenerated hydrogen chloride or lactam hydrochloride then produces additional amino acid chloride molecules through reaction (39). This mechanism is very similar to the cationic polymerization of unsubstituted lactams in which the fast formation of reactive intermediates and their subsequent

(42)



(43)

bimolecular addition (or condensation) represents the predominating propagation reaction.

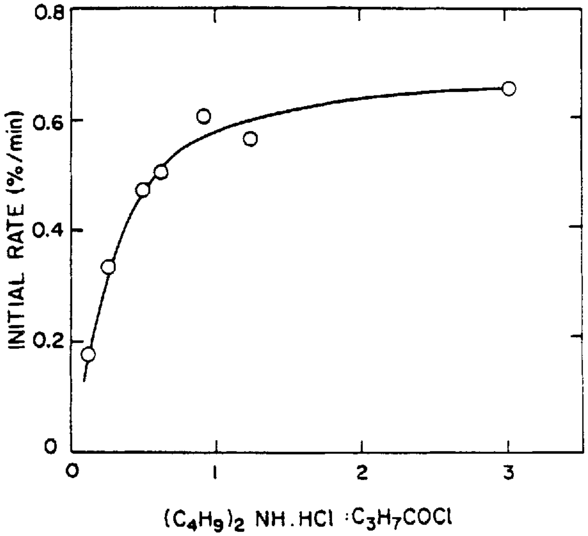


FIG. 2. Polymerization of N-methylcaprylolactam at 185° C with constant concentration of butyryl chloride (0.46 mole %) and varying concentration of dibutyl amine hydrochloride [31].

The hydrolytic polymerization of N-substituted lactams (e.g., with water, amino acids, or salts of carboxylic acids with primary and secondary amines [9, 18]) can be assumed to proceed by the same mechanism as the polymerization of unsubstituted lactams, i.e., the acid-catalyzed addition to the amine group (Eq. 41).

SIDE REACTIONS AND IRREGULAR STRUCTURES

The activation of growth centers and monomer is accompanied by a corresponding increase in the tendency to undergoing side reactions. The faster the polymerization reaction, the more reactive are the active species. The diacyl amine (imide) structures involved in anionic as well as in cationic polymerizations represent highly reactive species giving rise to a series of side reactions.

Cationic Polymerization

Polymerization initiated with small amounts of caprolactam hydrochloride [85] as well as with benzyl amine hydrochloride [92] showed a similar course (Fig. 3). With both initiators the polymerization slowed down long before reaching monomer-polymer equilibrium.

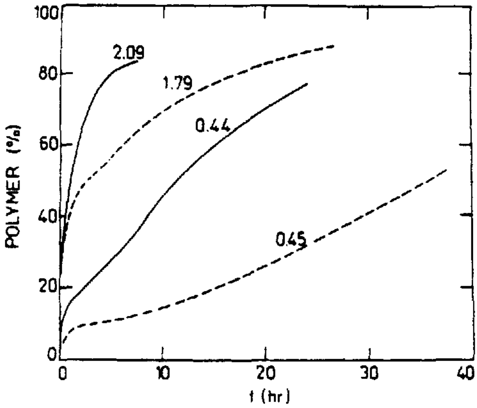
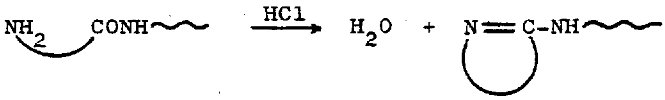


FIG. 3. Cationic polymerization of caprolactam at 256°C with caprolactam hydrochloride (- -) (Ref. 85) or benzylamine hydrochloride (——) (Ref. 92); concentrations in mole %.

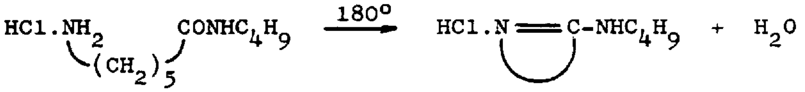
The fast decline of the rate of polymerization suggests that deactivation of the catalytic species might be due to the same kind of reactions.

Schlack and associates found that primary amine groups were substantially absent in cationic caprolactam polymers prepared with amine hydrochloride and that the basic groups were represented by amidine groups [154-159]. It has been suggested that amidine groups are formed by cyclization of terminal monomer units (Eq. 44).



(44)

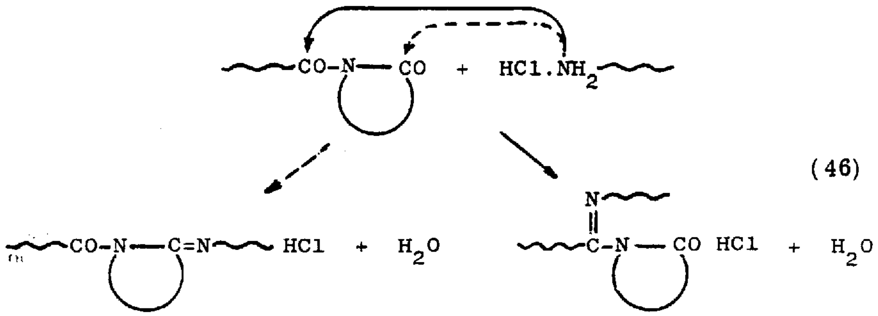
This cyclization was verified in the corresponding model reaction [154, 156, 158] (Eq. 45). The same amidine was formed also from



(45)

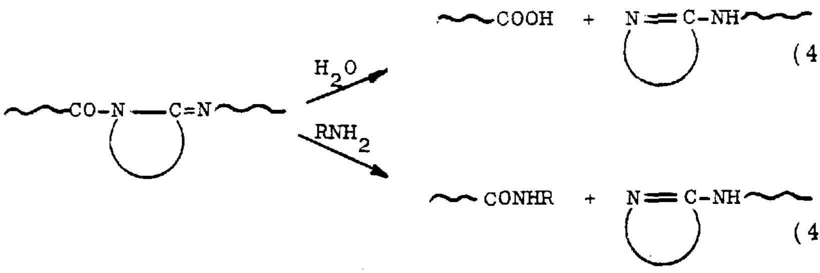
butylamine hydrochloride and caprolactam [160], and cyclization of the terminal amine group was also confirmed for linear oligomers [151]. The assumption of preferential formation of semicyclic amidine groups in caprolactam polymers was supported by the fact that amidine groups were not detected in cationic polymers of capryl- and laurinolactam which cannot yield stable cycles [155, 158].

However, it must be taken into account that amine hydrochlorides yield amidines much faster with imides than with amides [161, 162]. The same reaction might also occur in the cationic polymerization between the terminal amine groups and one of the acyllactam carbonyl groups (Eq. 46). Subsequent hydrolysis (Eq. 47) or aminolysis (Eq. 48) then yields semicyclic amidine groups. In polymerizations



(46)

initiated with amine hydrochloride, the acidity of the medium and the content of imide groups formed in reaction (2) will be much lower



(47)

(48)

than in polymerizations with caprolactam hydrochloride. Hence, the slower decay of catalytic activity with the former catalyst (Fig. 3) could be due both to the decreased rate of reaction (46) as well as of reaction (44).

The strongly basic amidine groups not only cannot add lactam molecules, but they also decrease the effective concentration of lactam cations and thus considerably slow down the polymerization reactions (2), (3), and (5). As a matter of fact, the hydrochloride of the amidine carboxylic acid, $HCl.N{=}C{-}NH(CH_2)_5COOH$, initiated a slow polymerization only [158].

The high concentration of amine and imide groups attained at the very beginning of polymerization [82] indicates that the initiation reaction (2) is very fast (Fig. 4). Therefore, at any moment of polymerization, nearly equilibrium concentrations of amine and imide groups, corresponding to the instantaneous concentration of amide hydrochloride, will be maintained. A comparison of Figs. 4 and 5 indicates that the concentrations of active species (amine and

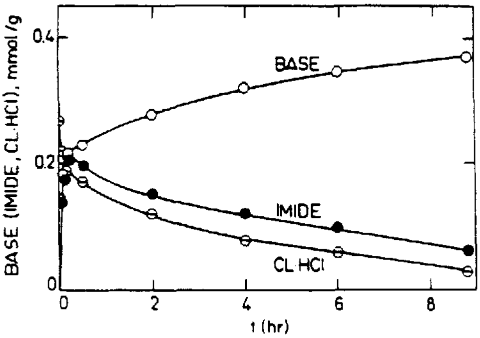


FIG. 4. Concentration of active species during cationic polymerization of caprolactam. Initial concentration of caprolactam hydrochloride, 0.405 mmole/g; temperature, 194°C [82].

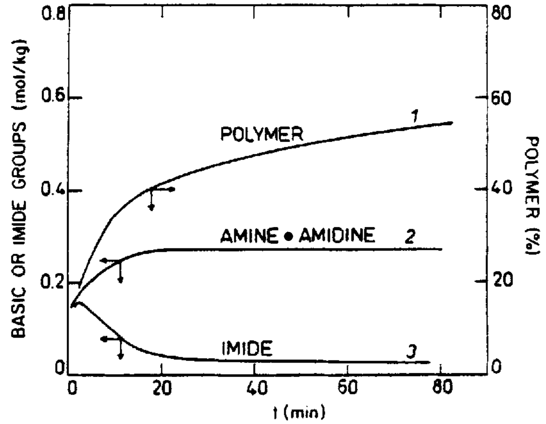
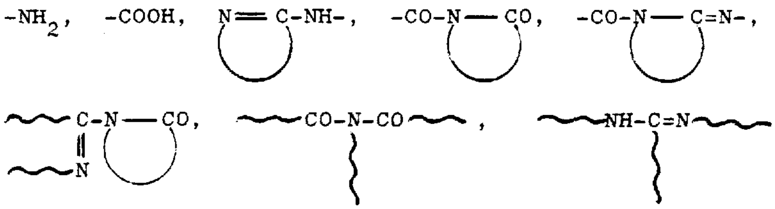


FIG. 5. Course of polymerization and concentration of active species in cationic caprolactam polymerization. Concentration of caprolactam hydrochloride: 2.64 mole % (Curve 1) and 3.05 mole % (Curves 2 and 3); data from Refs. 82 and 85. Temperature: 256°C.

imide groups as well as lactam hydrochloride) and the rate of polymerization are changing simultaneously during the polymerization so that any kinetics has to be evaluated in terms of the changing composition of the active species.

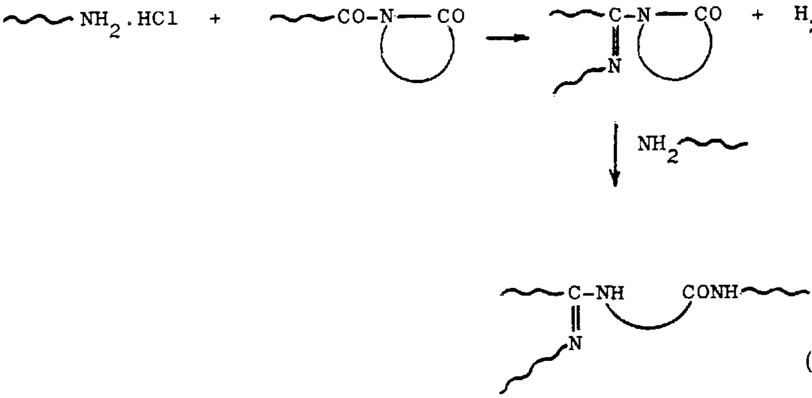
Until now the role of water formed in reactions (44) and (46) has not been discussed satisfactorily. It has been assumed that water participates in the later (slower) stages of polymerization by initiating a hydrolytic polymerization [158, 163] although carboxyl groups are said to be substantially absent in cationic polymers [73, 79]. However, with respect to the presence of imide and acyl amidine groups, formation of carboxyl groups is possible and, in the slow period of polymerization, chain growth involving carboxyl and amine groups should be operative. Small amounts of amine groups can be admitted to be maintained by the low residual acidity of the carboxyl groups and of the amide hydrochloride which could be detected in cationic polymers even after long periods of polymerization [87].

The structure of macromolecules present during polymerization may be deduced from the combination of the possible end groups, as well as from the corresponding cyclic and noncyclic irregular structures inside the polymer molecule:



During the cationic polymerization of caprolactam, molecules of different activity are present: from very active molecules growing at the amine and acyl lactam ends to molecules growing only very slowly or molecules incapable of propagation unless they are activated again by reaction (2).

The broad molecular weight distribution of cationic caprolactam polymers [163] is certainly due to the fact that the initiation reaction proceeds as long as amide hydrochloride is present and, therefore, new chains are being formed during the fast polymerization period. The progressive broadening during the slow period and the presence of two maxima on the differential curve has been explained by the superimposition of two polymerization mechanisms, namely hydrolytic polymerization at the amine group and aminolysis of acyl lactam [163]. In addition, we have to bear in mind that formation of amidine groups involving the exocyclic carbonyl and subsequent aminolysis (Eq. 49) results in branching. Amidine



(49)

formation proceeds slower than polymerization, so that the indicated branching should occur mainly between polymer molecules, resulting in a bimodal molecular weight distribution.

Anionic Polymerization

Both active species taking part in the propagation reactions (16), (18), and (20), i.e., lactam anions and imide groups, are very reactive, and detailed studies of the anionic polymerization of caprolactam revealed that the catalytic activity is not constant [67, 71, 104, 129, 164-169]. In some cases the changes in catalytic activity are so violent that the active species decay before polymerization equilibrium can be achieved (Fig. 6) [167-169]. It has been ascertained that all anionic polymers contain less imide groups [165-167] than corresponds to the starting amount of activator (Table 3), the content of strong bases decreasing in the same way [120, 167, 169-171]. That is why a considerable effort has been devoted to the elucidation of

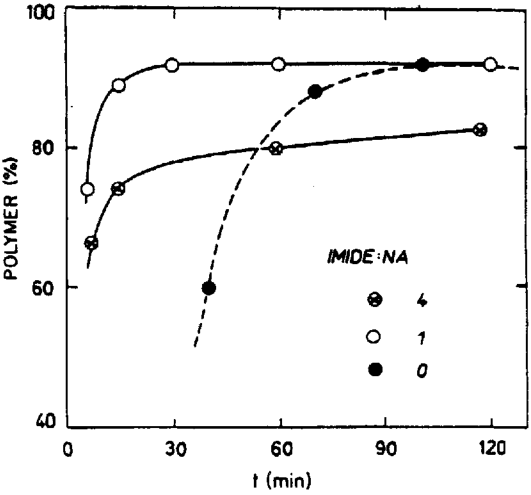


FIG. 6. Anionic polymerization of caprolactam at 210°C. Concentration of butyrylcaprolactam: 0.036 mmole/g(○, ⊗) and 0 (●); concentration of sodium caprolactam 0.036 (●, ○) and 0.009 mmole/g (⊗) (data from Refs. 168 and 169).

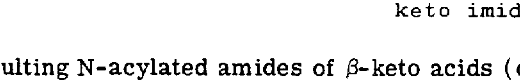
TABLE 3. Decay of Imide Groups in Anionic Caprolactam Polymerization[a]

T (°C)	t (min)	I_0	Na_0	ΔI
80	2	0.762	0.152	0.122
80	2	0.627	0.157	0.138
80	20	0.762	0.152	0.242
100	2	0.773	0.039	0.093
100	2	0.770	0.077	0.150

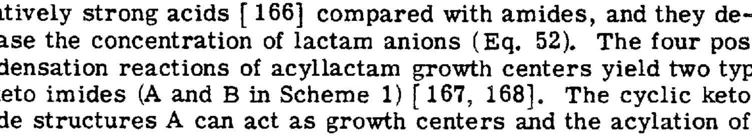
[a] Initial concentrations of sodium caprolactam (Na_0) and imide groups (I_0) in mole/kg.

side reactions responsible for the decay of the catalytic components [71, 100, 104, 164-170, 172-184].

It has been shown that in a strongly alkaline medium the imide groups undergo a Claisen-type condensation, provided that the α-carbon atom has at least one hydrogen [128, 166] (Eqs. 50 and 51).

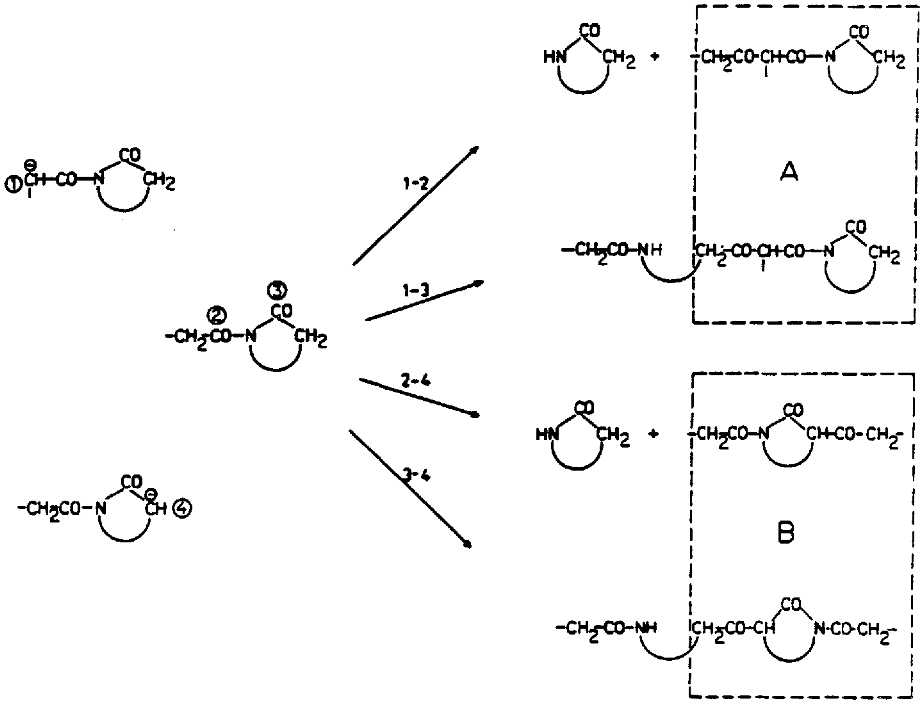


$$-\mathrm{CO}\underset{|}{\mathrm{N}}\mathrm{COCH_2}- \;+\; \mathrm{B}^{\ominus} \rightleftharpoons -\mathrm{CO}\underset{|}{\mathrm{N}}\mathrm{CO}\overset{\ominus}{\mathrm{C}}\mathrm{H}- \qquad (50)$$

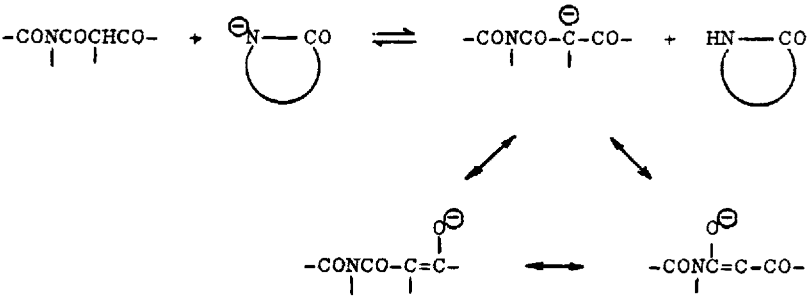


$$-\mathrm{CO}\underset{|}{\mathrm{N}}\mathrm{CO}\overset{\ominus}{\mathrm{C}}\mathrm{H}- \;+\; -\mathrm{CO}\underset{|}{\mathrm{N}}\mathrm{CO}- \rightleftharpoons \underset{\text{keto imide}}{-\mathrm{CO}\underset{|}{\mathrm{N}}\mathrm{CO}\underset{|}{\mathrm{C}}\mathrm{HCO}-} \;+\; {}^{\ominus}\underset{|}{\mathrm{N}}\mathrm{-CO}- \qquad (51)$$

The resulting N-acylated amides of β-keto acids (denoted as keto imides), containing one hydrogen atom in the α-position, are relatively strong acids [166] compared with amides, and they decrease the concentration of lactam anions (Eq. 52). The four possible condensation reactions of acyllactam growth centers yield two types of keto imides (A and B in Scheme 1) [167, 168]. The cyclic keto imide structures A can act as growth centers and the acylation of lactam anions (Eq. 53) results in the formation of a β-keto amide structure inside the polymer molecule. The cyclic keto imides B



SCHEME 1. Condensation of acyllactam growth centers in anionic polymerization.



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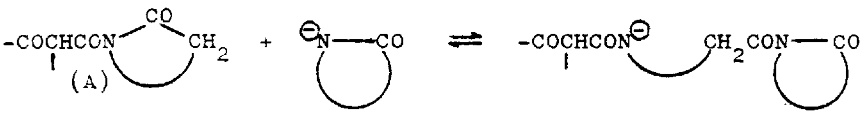
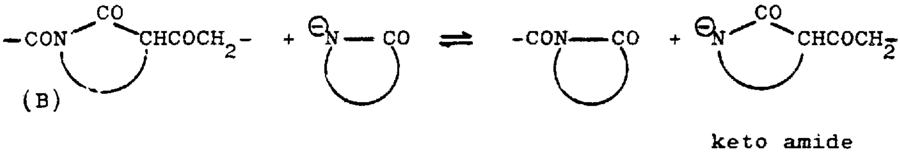
as well as the linear ones can yield active end groups through acylation of lactam anions with the formation of growth centers and



(53)

keto amides (Eqs. 54 and 55). Thus the sequence of condensation and acylation reactions (50)-(55) results in the conversion of one imide group into one keto amide structure.



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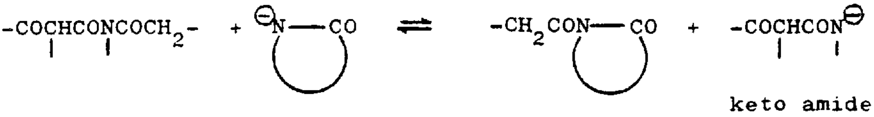
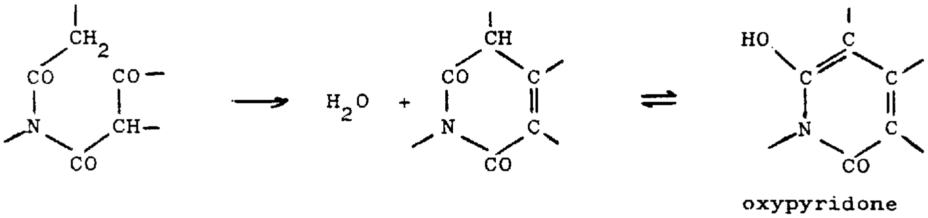


(55)

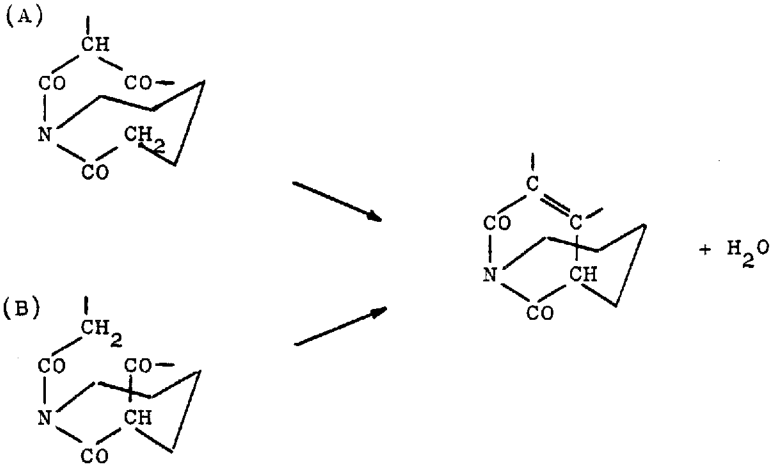
The acidity of keto amides having one α-hydrogen atom is much higher than that of the monomer or polymer amide groups. Therefore the formation of keto amides not only decreases the concentration of imide groups (growth centers) but also lowers the concentration of lactam anions.

As derivatives of β-keto acids, the keto imides as well as keto amides contain highly reactive $\rangle C{=}O$, $-CH_2-$ or $-\underset{|}{C}H-$ groups yielding a great number of condensation possibilities. Intramolecular condensation of keto imides was assumed to yield oxypyridone [128] (Eq. 56). The corresponding condensation of cyclic keto imides A



(56)

and B (Eq. 57) is very improbable in small and medium lactams because of the high strain imposed by the bridgehead nitrogen atom, and only condensation of open chain keto imides (56) can be expected to occur.

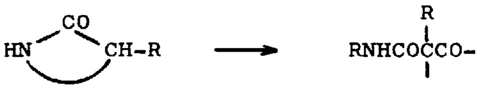


(57)

Keto imides and keto amides seem to be the key intermediates in the side reactions leading to the decay of imide groups and lactam anions. In this connection a great effort has been devoted to the investigation of the formation and behavior of keto amides at elevated temperature and in the presence of strong base [166, 167, 172-177, 180, 183, 185, 186]. The α-substituted keto amides represent low molecular analogs of structures formed in the polymerization of lactams with a methylene group next to the carbonyl (Eq. 58) whereas

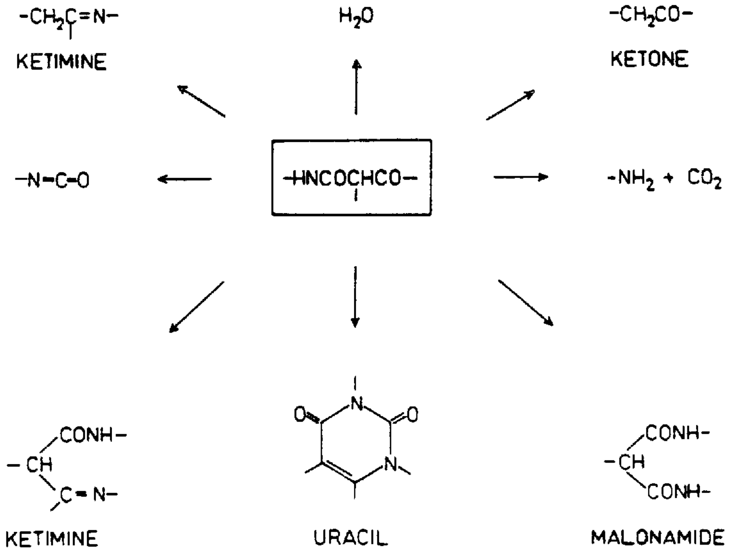
(58)

the α,α-disubstituted keto amides are expected to be formed in the anionic polymerization of α-monosubstituted lactams (Eq. 59).



(59)

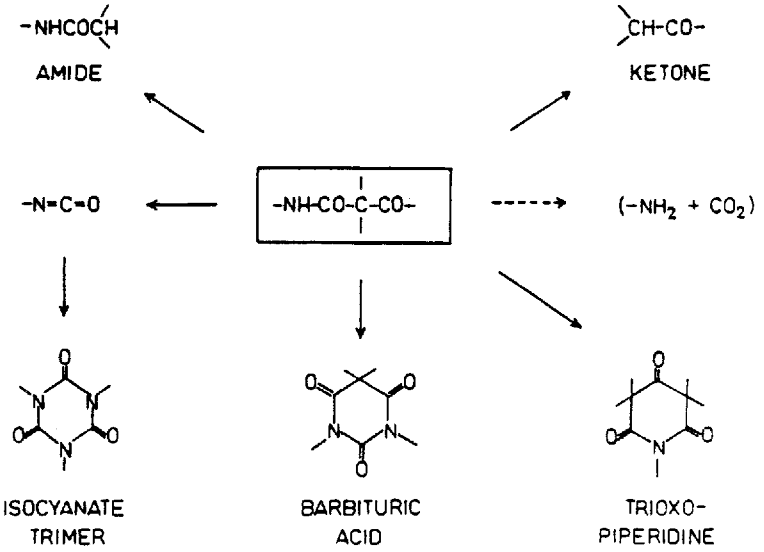
The main reaction products formed from α-monosubstituted [173, 177, 185, 186] and α,α-disubstituted [172, 175, 176] keto amides are summarized in Schemes 2 and 3. The most important reaction is the formation of isocyanate. The formation of



SCHEME 2. Products formed from α-substituted keto amide at elevated temperature in the presence of strong base.

barbituric acid, trioxopiperidine, uracil, and malonamide can be explained as a consequence of addition or carbamoylation reactions of isocyanate [173, 176, 177]. It has to be emphasized that the relative amounts of the aforementioned irregular structures strongly depend on the basicity and polarity of the medium [176].

Irrespective of the fact that the anionic polymerization is started under anhydrous conditions, water is being formed from the beginning of polymerization at elevated temperature and interferes with the initiation and propagation reactions. The base-catalyzed hydrolysis of imide groups is very fast and consumes both lactam anions and imide (Eq. 60). Hydrolysis of keto imides [166] or keto amides [187] yields both carbon dioxide and

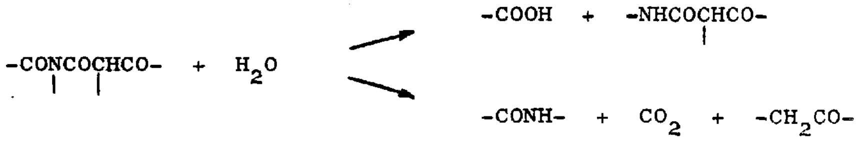


SCHEME 3. Products formed from α,α-disubstituted keto amide.

carboxylic acid (Eqs. 61 and 62). In the presence of strong base, carboxylate and carbonate are formed and the concentration of lactam anions is decreased (Eqs. 63 and 64).

$$\underset{|}{-\mathrm{CONCO}-} + H_2O + {}^{\ominus}\mathrm{N}\text{—}\mathrm{CO} \longrightarrow -\mathrm{COO}^{\ominus} + -\mathrm{NHCO}- + \mathrm{HN}\text{—}\mathrm{CO}$$

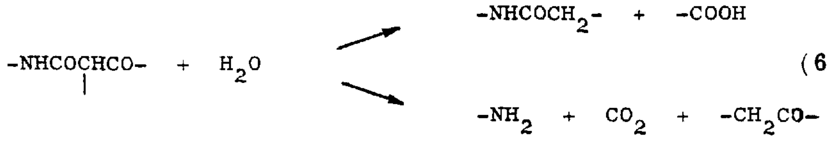
(60)



$$-\mathrm{CO}\underset{|}{\mathrm{N}}\mathrm{CO}\underset{|}{\mathrm{C}}\mathrm{HCO}- + H_2O \begin{cases} \nearrow -\mathrm{COOH} + -\mathrm{NHCO}\underset{|}{\mathrm{C}}\mathrm{HCO}- \\ \searrow -\mathrm{CONH}- + CO_2 + -CH_2CO- \end{cases}$$

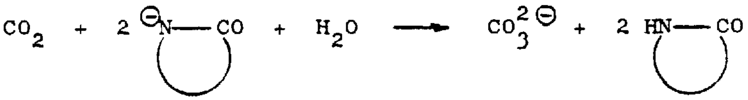
(61)

It is reasonable to assume that the reactions observed with low molecular weight analogs also occur during the polymerization of lactams having one or two hydrogen atoms in the α-position to



(62)

(63)



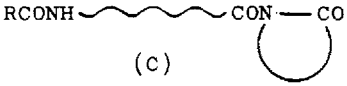
(64)

the carbonyl. As a matter of fact, the expected ketone, i.e., diaminoundecanone, has been detected in anionic caprolactam polymers, together with small amounts of a monoamino ketone resulting from condensation of the activator [180, 183]. The formation of sodium carbonate and carboxylate as well as carbon dioxide was also ascertained during the anionic polymerization of caprolactam [167, 170, 179, 182].

It has to be pointed out that at temperatures around 200° most of the side reactions proceed very rapidly. Even after short reaction periods, most of the initial sodium caprolactam was converted into carbonate and carboxylate and characteristic values of end groups, keto units, and molecular weight were attained [168, 169, 183] (Figs. 7 and 8). At temperatures above 200° the major fraction of keto groups is formed at the beginning of polymerization (Fig. 8) and every polymer molecule contains approximately one keto structure on the average. As long as lactam anions are present, the slow disproportionation reactions (14), (21), and (22) increase the number of polymer molecules. Due to the very fast side reactions the content of keto structures increases by condensation so that the prevailing fraction of macromolecules formed during this period contains two basic groups per molecule [170].

The great variety of irregular structures which can be present either inside or at the ends of the polymer molecules, together with the regular end groups (i.e., acyllactam, activator residue, and amine group) give rise to a variety of types of macromolecules.

The regular molecules formed in activated anionic polymerization are terminated by an acyllactam group and an activator residue:



(c)

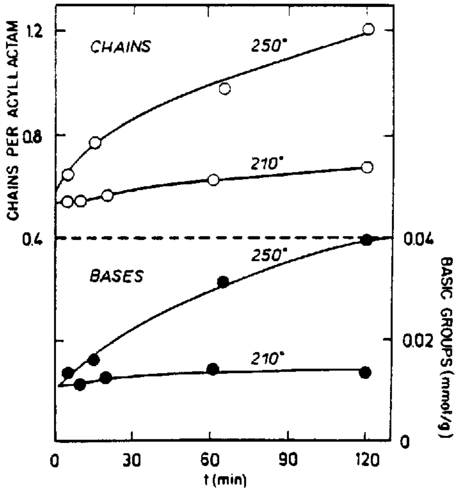
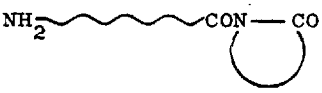


FIG. 7. Number of polymer molecules and basic groups during anionic caprolactam polymerization [168] with equimolar concentration of sodium caprolactam and butyrylcaprolactam (0.036 mmole/g).

and the corresponding oligomers of Type C were identified in anionic caprolactam polymers [188]. In polymerizations initiated only with lactam anions, the regular polymer chains are terminated by an amine and acyllactam group:



Those polymer molecules containing acyllactam or other imide groups are able to propagate by reactions (16), (18), and (20), whereas the remaining polymer molecules are incapable of growing. However, such dead polymer molecules can again be activated.

As long as lactam and polymer amide anions are present, the slow disproportionation reactions produce imide groups acting as growth centers. Additional growth centers can also be formed from some irregular structures. The most important source of both active species is the keto amide anion. At elevated temperature the N-anion dissociates (Eq. 65) into isocyanate which is an effective

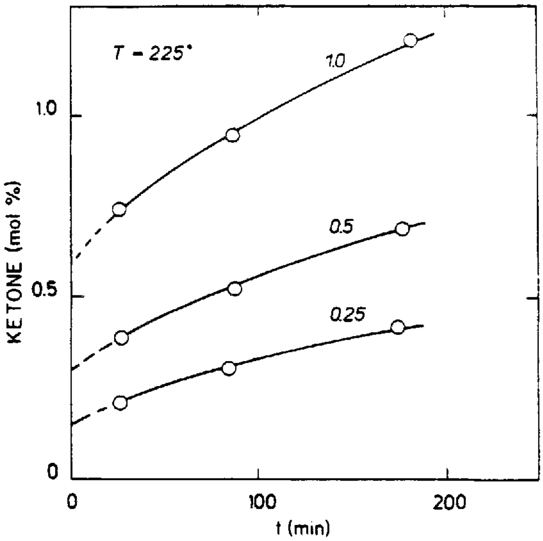
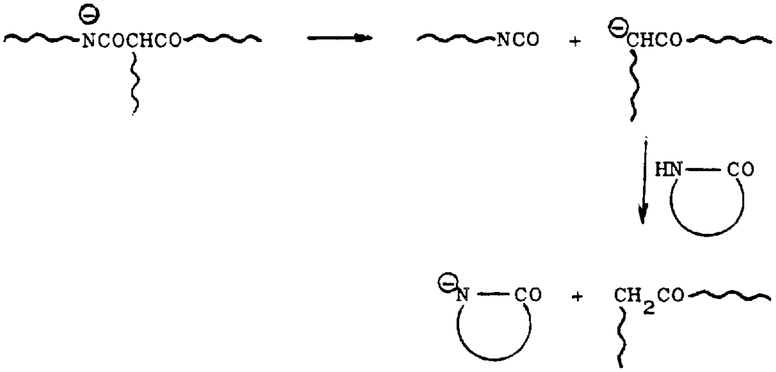


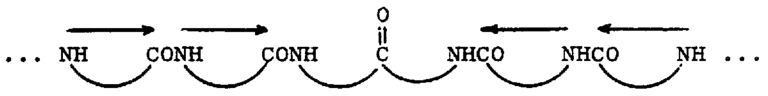
FIG. 8. Content of keto units in anionic caprolactam polymers [183]. Polymerization at 225°C with equimolar amounts of sodium caprolactam and benzoylcaprolactam; concentration in mole %.

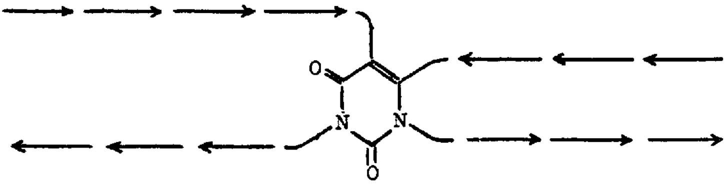


(65)

activator. In the subsequent neutralization, lactam or polymer amide anions are regenerated. This scheme of regeneration of active species is supported by the fact that sodium salts of keto amides are effective anionic catalysts [174].

The direction of the monomer units is uniform only in regular linear molecules. In branched polymer molecules or in linear molecules containing a keto group, the direction of monomer units is altered at the irregular unit as shown. The formation of insoluble polymer with polyfunctional activators [71] indicates that condensation reactions changing the direction of monomer units occurred.





Branching in anionic caprolactam polýmers is evidenced both by the molecular weight distribution [189] and by the fact that, on the average, more than two end groups are present per polymer molecule [168, 190].

The sterically unhindered acyllactam growth centers (e.g., butyrylcaprolactam or benzoylpyrrolidone) are incorporated completely into the growing polymer chains even at the very beginning of polymerization [69]. However, the number of polymer molecules formed at the very beginning of polymerization is lower than the initial number of activator molecules because the very fast side reactions decrease the number of polymer molecules (Fig. 7). Therefore, the initial number of macromolecules depends in a complicated manner on the initial concentration of both activator and lactam anions [168, 191, 192] (Fig. 9).

It has been found [169] that at temperatures around 200° the imide groups and the strong base disappeared at a ratio 2.5:1. It follows from this stoichiometry that a high catalytic activity can be maintained for longer periods only with an activator:initiator ratio less than 2.5. However, even with a higher excess of activator the catalytically active base does not disappear completely and a low concentration of active base is present for very long periods [169]. This residual basicity is due mainly to the presence of carbonate and carboxylate.

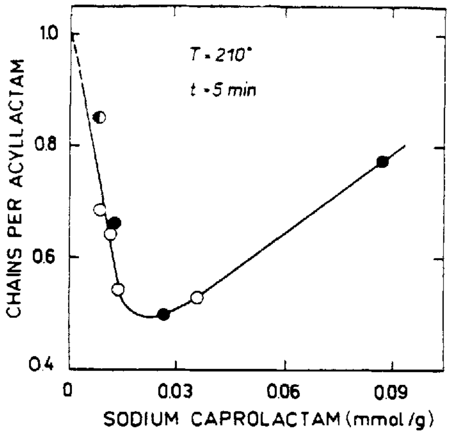
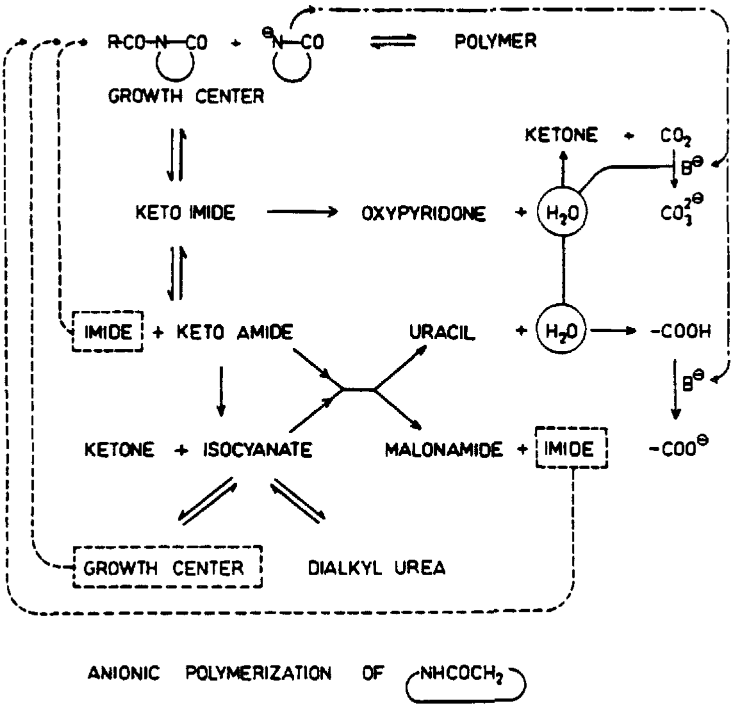


FIG. 9. Number of polymer molecules formed per activator molecule in anionic caprolactam polymerization [168]. Polymerization, 5 min at 210° C; concentration of acyllactam, 0.088 (◐), 0.026 (●), and 0.036 mmole/g (○).

The side reactions discussed so far are summarized in Scheme 4. It follows from this scheme that the anionic lactam polymerization involves a complex set of reversible and irreversible as well as consecutive reactions in which the active species disappear and are regenerated again in several reaction paths. Mastering the kinetics of all reactions is extremely difficult and, therefore, the course of polymerization could be described only by simplified [193] or empirical [194] equations which are valid in a narrow range of reaction conditions. The main problem consists in the fact that the actual concentrations of imide groups and lactam anions change drastically from the very beginning of polymerization and they are very different from their initial concentrations. The instantaneous concentration of active base at the given polymerization temperature has been estimated indirectly [169] from the rate of formation of new polymer molecules by the disproportionation reactions requiring lactam and polymer amide anions. It turned out that only a small fraction of the initial active base is present at the end of polymerization (Table 4).

Hydrolytic Polymerization

Hydrolytic polymerization seems to proceed under the smoothest conditions because the growing species are much less activated than



SCHEME 4. Side reactions occurring during anionic polymerization of lactams HNCOCH_2.

TABLE 4. Decay of Strong Base in Anionic Caprolactam Polymerization[a]

Sodium caprolactam (mole %)	Time (min)	Effective base (%) 210°C	250°C
0.4	10	21	5.7
0.4	20	14	2.4
0.4	30	8	1.5
0.4	50	4	0.8
0.4	100	3	0.5
0.1	30	1.1	0.5
0.1	50	0.9	0.3
0.1	100	0.6	0.1

[a] Initial concentration of butyrylcaprolactam: 0.4 mole %; effective concentration of base in per cent of initial sodium caprolactam [169].

in cationic or anionic polymerizations. However, even in hydrolytic polymerization the formation of irregular structures and cross-linked polymer has been observed.

Reimschuessel and Dege recently found that deamination and decarboxylation of hydrolytic polycaprolactam occurred even in essentially oxygen-free atmosphere [195]. Above 270°C the decarboxylation proceeded about ten times faster than the formation of ammonia and the loss of carbon dioxide even exceeded the initial content of carboxyl groups. Whereas the content of carboxyl groups decreased, the concentration of amine groups increased above 250°C (Fig. 10) and the polymers contained unequivalent amounts of carboxyl and amine groups. Therefore, end group determinations cannot be used for molecular weight determinations of hydrolytic caprolactam polymers prepared at (or heated above) 250°C.

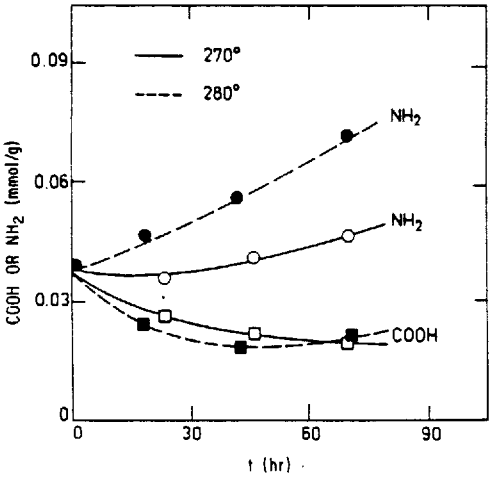
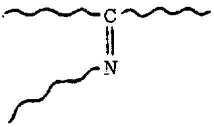


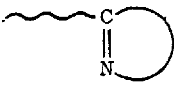
FIG. 10. Carboxyl and amine groups in hydrolytic polycaprolactam [195].

The degradation reactions are not necessarily accompanied by viscosity changes. Although a significant amount of ammonia and carbon dioxide was formed during prolonged heating at 260°C, the viscosity of the polymer remained fairly constant because the degradation reactions were compensated by condensation reactions. At temperatures exceeding 270°C the degradation reactions decreasing the molecular weight predominate [195].

For polymers of laurinolactam, on the other hand, the content of basic groups increased much slower than for caprolactam polymers and the content of carboxylic groups even remained constant over a long period [196]. This different behavior of nylon 6 and 12 at elevated temperatures could be due to the different length of the monomer unit, as well as to the very different equilibrium monomer content in both polymers because the monomer seems to take part in the thermal decomposition of caprolactam polymers [195].

Irrespective of the different reaction mechanisms proposed for the deamination and decarboxylation of caprolactam polymers, these reactions finally yield keto and secondary amine groups incorporated into the polymer chain [195, 197]: $-NH(CH_2)_5CO(CH_2)_5NH-$ and $-CO(CH_2)_5NH(CH_2)_5CO-$. Hydrolysis of such thermally degraded caprolactam polymers yielded 1,11-diamino-6-undecanone and a small amount of di-(6-carboxypentyl)amine [197]. A part of the keto structures may react with amine groups to yield the Schiff base which is present either as a branching unit or as a semicyclic end group:





Secondary reactions involving the Schiff base structures lead to cross-linking [195, 197] and to structures giving a positive reaction with Ehrlich's reagent [198].

Kamerbeek et al. proved that the formation of di-(5-carboxypentyl) amine units in side reactions and incorporation of the trifunctional units inside the polymer chains is insufficient to cause cross-linking. Addition of this secondary amine to polycaprolactam and subsequent heating did not lead to fast gelation. On the other hand, addition of 1,11-diamino-6-undecanone caused gelling [197]. Trifunctional groups of $^{A}_{A}\!\!>\!\!-B$ type alone cannot cross-link A—B type polymers unless complementary $^{B}_{B}\!\!>\!\!-A$ type units or at least diamines (B—B) are present. At high temperatures the trifunctional secondary amine units are formed much faster than the diamine structures and, therefore, the addition or formation of the latter is decisive for cross-linking.

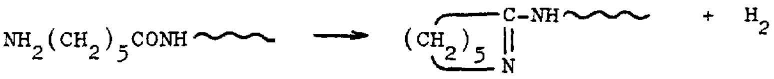
Most susceptible to deamination are hydrolytic polymers of β-lactams (acetidinones) containing at least one hydrogen atom at the α-carbon. Beta-elimination of ammonia occurred at temperatures around 200° C, leading to terminal vinyl groups [5]. As a consequence the polymer cannot grow at this end any more and high molecular weights cannot be achieved.

Vinyl as well as nitrile groups were also identified in caprolactam [197] and in laurinolactam polymers [196]. It has been assumed that vinyl groups are formed by the scission of the polyamide chain (Eq. 66) and the amide groups formed yield nitrile groups by dehydration [196, 197]. Water, besides ammonia and carbon dioxide,

$$\sim\!\sim\!\sim CONH{-}CH_2{-}CH_2\sim\!\sim\!\sim \longrightarrow \sim\!\sim\!\sim CONH_2 + CH_2{=}CH\sim\!\sim \qquad (66)$$

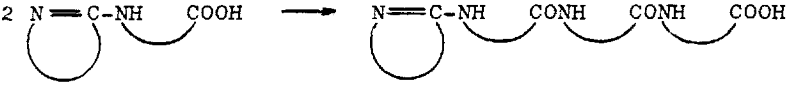
had been identified among the products of the thermal decomposition of polycaprolactam [195, 197]. In a closed system water will cleave the polymer amide groups, decreasing the molecular weight and producing additional amino and carboxylic groups.

Primary amine groups may undergo cyclization with the formation of semicyclic amidine groups at the end of the chain [199-201] (Eq. 67).



(67)

Semicyclic amidine groups are known to undergo a ring-opening polyaddition with carboxyl groups [188] (Eq. 68). This is why amidine



(68)

groups could not be detected safely in hydrolytic polymers prepared in the melt. In the solid state, on the other hand, the bimolecular opening of the semicyclic amidine by a carboxyl group is greatly suppressed and, after heating a hydrolytic polycaprolactam below its melting point, the amidine groups represented 40% of all basic groups [158]. In cationic polymers in which carboxyl groups are substantially absent amidine formation occurs easily even at high temperatures and almost all basic groups are present as amidine groups [158]. Therefore, the equivalence of basic and carboxyl groups is no evidence that side reactions did not occur and that the polymer does not contain any foreign structures. Amidine formation was observed only in caprolactam polymers but not in polymers of capryl- and laurinolactam [158], because of the unfavorable ring size.

End groups are also lost at moderate temperatures and even during extended periods of storage at room temperature [202]. Most probably, contact with oxygen and water during the processing, machining, and extraction may produce weak structures, e.g., hydroperoxides, which slowly decompose and change the content of acidic and basic groups and to a certain extent also the viscosity of the polymer.

Certain side reactions are obviously inherent to each type of lactam polymer. Hydrolytic polymers can be regarded as uniform and stable polymers neither in the melt nor in the solid state because the end groups undergo irreversible changes.

One of the cleanest methods of obtaining polycaprolactam consists in the solid state polymerization of crystalline aminocaproic acid yielding a highly oriented polymer [203]. Under selected conditions, even high molecular weight polycaproamide with intrinsic viscosities up to 1.0 dl/g may be obtained [204] by solid state polycondensation of crystalline aminocaproic acid immersed in liquid media.

CYCLIC AND LINEAR OLIGOMERS

Lactam polymerizations are equilibrium processes which lie well toward the polymer side for all rings except the five- and six-membered as well as highly substituted seven-membered rings. Besides the linear high-molecular weight polymer and monomeric lactam, cyclic as well as linear oligomers are also present in the equilibrium polymerization product.

Oligomers can be defined as homologous compounds of low molecular weight (up to about 1000) which, contrary to high molecular weight polymers, differ in their physical properties sufficiently to allow their separation into individual compounds. This definition implies that some properties of oligomers (e.g., melting point, solubility, rotation, x-ray pattern) are different from those of high polymers and, therefore, the oligomers have to be regarded as foreign substances in high polymers as far as such properties are concerned.

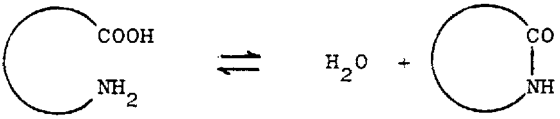
From the point of view of structural unity, the cyclic oligomers have to be considered as particles of a different structure although their chemical composition and sequence of monomer units is the same as in linear polymers. As a consequence of the cyclic structure and the absence of end groups, cyclic oligomers behave differently from the linear oligomers and high molecular polymer. The melting temperature of the lower cyclic oligomers is much higher than that of the linear oligomers (Table 5). From the hexamer upward the melting temperatures of the cyclic oligomers slowly approach those

TABLE 5. Melting Points of Linear [205, 206] and Cyclic [207] Caprolactam Oligomers

n	$\mathrm{H[HN(CH_2)_5CO]_nOH}$	$\mathrm{[HN(CH_2)_5CO]_n}$
2	201	348
3	202	244
4	201	256
5	205	254
6	205	259
7	208	
21	212	

of the linear polymer [208], most probably due to decreasing intramolecular hydrogen bonding. The high extent of intramolecular hydrogen bonding in cyclic oligomers is also reflected in the very low Mark-Houwink parameter (a = 0.22) which indicates that they behave as rigid spheres in solution [209].

The cyclic components can be formed by cyclization of the linear oligomer (Eq. 69) or by intramolecular transacylation between an end group and an amide group. (Eq. 70), as well as through the corresponding bimolecular reactions [210, 211] (Eqs. 71 and 72). Similar reactions could be written for any of the known transacylation mechanisms.



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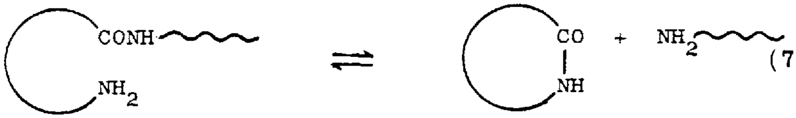

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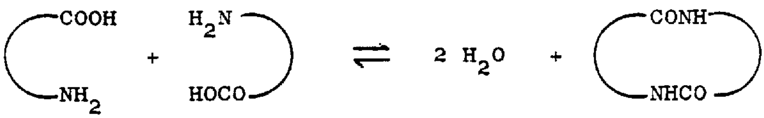
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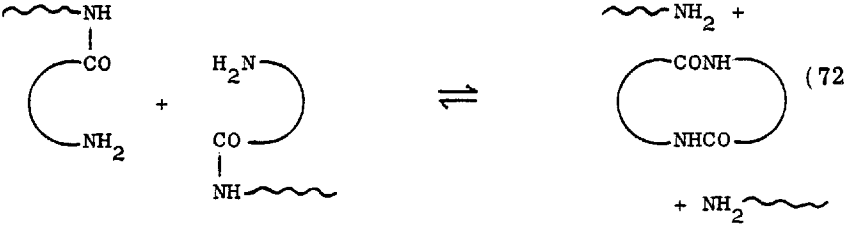
(72)

As a result, the equilibrium concentration of each cyclic compound is given by the corresponding cyclization constant and the concentration of end groups (or active groups).

Semlyen and Walker [212] applied the Jacobson-Stockmayer cyclization theory and the rotational isomeric state model of the linear polymer [213] for the calculation of the concentration of macrocyclic oligomers. Assuming that the heat of polymerization equals zero, fairly high amounts of very large rings were predicted to be present at equilibrium. The calculated and experimental curves are almost parallel (Fig. 11). However, the calculated values are too high, irrespective of the fact that the experimental values can be too low because of incomplete extraction of the oligomers. It appears that the assumption of $\Delta H_p = 0$ is not valid, at least for the lower cyclic oligomers. For example, the heat of polymerization of the 13-membered laurinolactam was estimated to be 1.4-3.1 kcal/mole [196, 214] and although intramolecular hydrogen bonding decreases the heat of polymerization of the cyclic caprolactam dimer, it still should be different from zero. In addition, the cyclization constant will depend not only on the ring size and bond angles, but also on the number of amide groups present in the cyclic compound (Fig. 11).

Although cyclic oligomers have not yet been identified in polymerization products of some lactams, e.g., four-membered lactams, pyrrolidone, and piperidone, the formation of large rings may be expected to occur during the polymerization of almost any polymerizable lactam. The equilibrium fraction of cyclic oligomers in the low molecular weight fraction depends on the ring size and substitution of the lactam, and may be even higher than 30% of the extractables (Table 6). The monomer and a fraction of low molecular cyclic

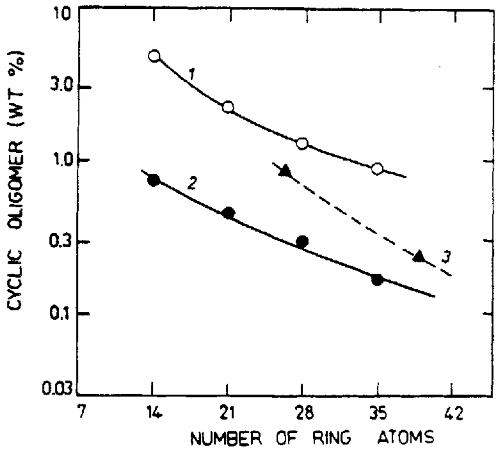

FIG. 11. Equilibrium content of cyclic oligomers. Caprolactam polymers: calculated [212] (Curve 1) and determined in the extractables [216, 217] (Curve 2). For laurinolactam polymers determined in the extractables [217] (Curve 3).

TABLE 6. Content of Monomer and Extractable Oligomers in Equilibrium Polymers at 250° C

Lactam	Extractables (%)	Monomer (%)	Oligomers (%)	Ref.
Caprolactam	10.2	8.1	2.1	215
α-Methyl	15.6	10.3	5.3	135
β-Methyl	27.8	19.2	8.6	136
δ-Methyl	25.5	22.4	3.1	136
ϵ-Methyl	18.5	12.0	6.5	134

oligomers can be removed from the polymerization product by extraction. The higher cyclics, however, still remain in the extracted polymer, and molecular weights calculated from the content of end groups may be estimated too high for the low molecular weight polymers.

The content of the individual linear oligomers in equilibrium polymer corresponds to the molecular weight distribution, and the fraction of linear oligomers decreases with increasing molecular weight of the polymer. In high molecular weight caprolactam or laurinolactam polymers the weight fraction of linear oligomers is 10 times smaller than the fraction of cyclic oligomers [216-218]. In low molecular polymerization products, however, the fraction of linear oligomers is not negligible and may account for the deviation of some properties of such polymers. Due to the high content of end groups, the spectra or optical rotation of linear oligomers can differ from those of the high polymer. In addition, the behavior of cyclic and linear oligomers in solution differs remarkably from that of linear polymers. The low value of the Mark-Houwink parameter for linear caprolactam oligomers ($a = 0.53$) indicates that linear oligomers are too short to achieve the shape of a random coil [219].

CONCLUSIONS

Any kind of lactam polymerization proceeds through transacylation reactions in which intramolecular activation of the monomer or polymer amide group plays an important role. In anionic and cationic polymerizations, activated monomer and activated growth centers of increased reactivity are involved in the propagation reactions. The highly reactive imide group, amide anion, or amidium cation give rise to fast side reactions which consume the active species. As a result, the initially very fast polymerization is slowed down and, sometimes, even stops before monomer-polymer equilibrium is attained.

The nature and extent of side reactions is dependent on the concentration and character of initiator, temperature, and, above all, on the structure of the lactam. In the anionic polymerization the sequence of side reactions starts with condensation reactions at the carbon atom next to the carbonyl group. Hence, the α,α-disubstituted lactams are not expected to undergo such side reactions. Contrary to the living anionic polymers derived from vinyl or olefin monomers, living lactam polymers do not maintain a constant number of polymer molecules. As long as lactam anions are present, the number of chains should increase due to the initiation reaction until the equilibrium between amine and imide groups is attained.

In the anionic polymerization of lactams having at least one α-hydrogen, the strongly basic lactam or polymer amide anions introduce a series of side reactions that result in compounds which decrease the basicity and thus drastically slow down the polymerization.

Similarly, the strongly acidic compounds initiating a cationic polymerization produce strongly basic amidine groups which not only are inactive as growth centers but also bind the strong acid and thus decrease the rate of polymerization.

Side reactions destroying the reactive species constitute a very important part of anionic and cationic polymerization and may seriously interfere with the chain growth. In cationic polymerization, side reactions even change the proportion of the individual propagation reactions.

In addition, side reactions give rise to irregular structures inside and at the ends of macromolecules. Bifunctional irregular units may change the direction of the sequence of monomer units and tri- and tetrafunctional groups are sites of branching and cross-linking.

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Accepted by editor September 20, 1971
Received for publication October 28, 1971