

THE KINETICS AND MECHANISM OF POLYMERIZATION OF N-METHYL-, N-BUTYL- AND N-BENZYL-CAPRYLLACTAM INITIATED WITH HYDROGEN CHLORIDE*

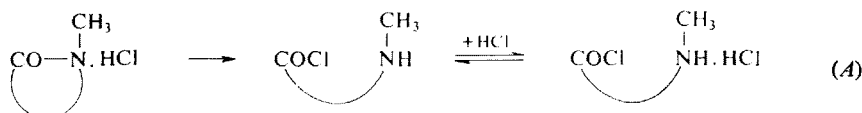
B. MASAR and J. ŠEBENDA

*Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, 162 06 Prague 6*

Received January 4th, 1974

The polymerization of N-alkyl-8-octanelactams (N-alkylcapryllactams) at 150–200°C is a first order reaction with respect to monomer and hydrogen chloride; both the activation energy and the frequency factor decrease with increasing size of the substituent. The polymerization initiated with butyryl chloride proceeds ten times slower than with hydrogen chloride or an equimolar mixture of butyryl chloride and dibutylamine hydrochloride. The main monomer fraction is incorporated into the polymer by a sequence of two reactions, namely, cleavage of N-alkyllactam with hydrogen chloride to N-alkyl-8-amino-octanoyl chloride followed by its bimolecular condensation. However, the participation of sec-amine hydrochloride catalyzed polyaddition of lactams to the carbonyl chloride group cannot be excluded so far.

Of the initiators of the polymerization of N-methyl-8-octanelactam (*I*), hydrogen chloride or lactam hydrochloride¹ is the most effective. The effect of hydrogen chloride in the cationic polymerization of the above lactam consists in the deacylating cleavage of the amide bond with formation of N-methyl-8-amino-octanoyl chloride hydrochloride²



N-methyl-8-amino-octanoyl chloride is a very unstable compound, the intermolecular addition of which (nucleophilic attack of the —COCl group by the amino group) represents a polycondensation growth reaction². The deacylating cleavage was studied also on model N,N-disubstituted amides^{2,3}. The thermolysis of N,N-dihexylbutyramide gives rise to butyryl chloride and dihexylamine hydrochloride in a 60% yield. The deacylating cleavage proceeds very quickly already at a temperature above 70°C and is followed by side reactions². The same holds for the polymerization of lactam *I* when the initiation reaction takes place at the very beginning. The concentration of the functional groups —COCl and >NH.HCl is practically constant up to a 50% conversion; after this, the concentration of —COCl reaches an unpronounced maximum and decreases².

* Part III in the series Polymerization of N-Substituted Lactams; Part II: This Journal 39, 2581 (1974).

An alternative growth reaction in the cationic polymerization initiated with hydrogen chloride is transacylation between the acyl chloride group and lactam *I* (ref.^{1,2}). The noncatalyzed addition of lactam to the end $-\text{COCl}$ group cannot be the main growth reaction, but the cocatalytic effect of other groups present there cannot be ruled out.

It has been an objective of this work to extend the knowledge of the mechanism of cationic polymerization by investigating the polymerization kinetics of *N*-alkyl-capryllactams initiated on the one hand with hydrogen chloride and on the other with carboxylic acid chloride in a mixture with cocatalysts. Kinetic measurements were supplemented by a study of changes in the molecular weight during polymerization.

EXPERIMENTAL

Monomers and Initiators

Lactam *I* (ref.¹) water content according to Fischer 0.001%. The density measured in glass dilatometers ($\beta = 1.87 \cdot 10^{-5}$), at 150–260°C follows the relationship $d = 1.035 - 7.78 \cdot 10^{-4} T$.

N-Benzyl-8-octanelactam (II) was prepared by alkylation⁴ of sodium 8-octanelactam with benzyl chloride. To a suspension of sodium 8-octanelactam obtained from 30 g (0.21 mol) of 8-octanelactam and an equimolar amount of sodium hydride in 800 ml of benzene, 33.3 g (0.26 mol) of benzyl chloride was added at 60–80°C, and reaction mixture was heated to boil for 20 h; the strong alkali content dropped to 15% of the original amount. After neutralization with acetic acid and extraction with water the raw product was dried and crystallized from light petroleum; m.p. 47.2–47.8°C. Fractional crystallization of the monomer of the mother liquor yielded further fractions; the total yield was 33 g (68% theor.). For $\text{C}_{15}\text{H}_{21}\text{NO}$ (231.3) calculated: 6.05% N; found: 6.13% N.

N-butyl-8-octanelactam (III) was prepared similarly to lactam *II* by alkylation of sodium 8-octanelactam (0.71 mol) with butyl bromide (1.06 mol) in 3000 ml of benzene; a 10% excess of sodium hydride was used in the preparation of the sodium salt. After heating at 80°C for 55 h the reaction mixture was neutralized with acetic acid, and 100 g of the product, b.p. 172 to 174°C/3 Torr, was obtained by vacuum distillation. During the subsequent rectification on a rotating column, the medium fraction was collected (72 g) containing 2.5% of 8-octanelactam. The initial lactam was removed at 160°C by preparative gas chromatography on a Perkin-Elmer F-21 apparatus with a 3 m column and poly(ethylene adipate) as the stationary phase; lactam *III* was dried on a molecular sieve and redistilled. The total content of impurities according to GLC was 0.14% (of which 0.06% of 8-octanelactam). For $\text{C}_{12}\text{H}_{23}\text{NO}$ (197.3) calculated: 73.04% C, 11.75% H, 7.10% N; found: 73.07% C, 11.79% H, 7.03% N. For the temperature range from 160 to 190°C it holds density $d = 0.987 - 7.45 \cdot 10^{-4} T$.

N-Methyl-8-octanelactam hydrochloride (IV) was prepared according to ref.¹. *N*-benzyl-8-octanelactam hydrochloride was prepared similarly to hydrochloride *IV* (ref.¹), washed with ether and dried at 25°/25 Torr for 15 min; m.p. 88–94°C; the product contained 14% of free lactam. For $\text{C}_{15}\text{H}_{22}\text{ClNO}$ (267.7) calculated: 3.73 meq. HCl/g; found by conductometric titration: 3.20 meq. HCl/g. *N*-butyl-8-octanelactam hydrochloride, recrystallized from ethereal hydrogen chloride¹, m.p. 84–84.5°C. For $\text{C}_{12}\text{H}_{23}\text{ClNO}$ (233.7) calculated: 61.65% C, 10.35% H, 6.04% N, 4.28 meq. HCl/g; found: 61.79% C, 10.45% H, 6.05% N, 4.26 meq. HCl/g (conductometrically).

The other initiators and materials used were of the same quality as in earlier papers^{1,2}.

Polymerization

The preparation of reaction mixtures and polymerization were carried out in an oxygen-free nitrogen atmosphere containing 3–4 p.p.m. of water. The experiments in dilatometers (or in ampoules, if indicated) were carried out as described in ref.¹ The initiators were dissolved in lactams at 50°C with the exception of dibutylamine hydrochloride which was dissolved at 90°C during 15 min. At 200°C the polymerization of lactam *I* initiated with hydrogen chloride proceeded already so quickly that the contraction of the reaction mixture before the position of the meniscus becomes stabilized at the beginning of the dilatometric experiment had to be taken into account. The necessary correction was determined by parallel polymerizations completed at the moment of stabilization of the surface level. Extrapolation of the linear dependence for the first order equation to zero conversion gave the kinetic onset of polymerization (1.5 min after immersion of the dilatometer).

Analytical Procedures

The monomer content *m* (%) in the product from lactam *II* was determined by sublimation at 150°C and 0.3–0.5 Torr to constant weight. The monomer content in the unextracted reaction

TABLE I

Polymerization of N-Alkyl-8-octanelactams Initiated with HCl

Rate constants *k'* cf. Eq. (1).

| <i>T</i> °C | [HCl] ₀ mmol/kg | <i>k'</i> · 10 ³ kg mol ⁻¹ s ⁻¹ | <i>T</i> °C | [HCl] ₀ mmol/kg | <i>k'</i> · 10 ³ kg mol ⁻¹ s ⁻¹ |
|-------------------------|-------------------------------|---|----------------|-------------------------------|---|
| N-Methyl-8-octanelactam | | | | | |
| 155 | 32.0 | 0.212 | 170 | 158.6 | 1.02 |
| 155 | 48.1 | 0.210 | 185 | 30.0 ^a | 2.45 |
| 155 | 95.4 | 0.220 | 185 | 47.0 | 2.50 |
| 155 | 129.7 | 0.208 | 185 | 61.6 | 2.95 |
| 170 | 16.0 | 0.84 | 185 | 137.4 | 2.82 |
| 170 | 34.1 | 0.89 | 200 | 34.5 | 8.6 |
| 170 | 69.0 | 1.01 | 200 | 78.5 | 8.9 |
| 170 | 76.6 | 0.91 | 200 | 130.8 | 8.3 |
| N-Butyl-8-octanelactam | | | | | |
| 170 | 24.2 | 0.53 | 180.3 | 85.4 | 1.01 |
| 180.3 | 24.2 | 1.08 | 190.5 | 24.2 | 2.23 |
| 180.3 | 47.7 | 0.97 | 198.3 | 24.2 | 2.43 |
| N-Benzyl-8-octanelactam | | | | | |
| 155 | 41.8 | 0.167 | 185 | 41.8 | 1.23 |
| 170 | 41.8 | 0.52 | | | |

^a With addition of 31.5 mmol of N,N-diethylacetamide/kg, the same value of *k'* was obtained.

product of lactam *I* or *III* was determined by gas chromatography as described earlier¹ (lactam *III* at 165°C). 0.1M Sodium propoxide or 0.1M-HCl (in propanol) were used for conductometric titrations of products in anhydrous propanol. Blank tests were determined from 3–5 titrations of standard compounds (potassium hydrogen phthalate, potassium hydrogen carbonate, benzoic, oxalic and hydrochloric acid) and their mixtures if strong and weak acidities were determined simultaneously. Intrinsic viscosity was determined in propanol or a 1% propanolic acetic acid; molecular weight was calculated by using expressions derived earlier¹.

The polymerization products are transparent. The crystallization of extracted samples of lactam *I* at 25°C sets in after rather a long time (weeks, months).

RESULTS AND DISCUSSION

Kinetic of Polymerization Initiated with Hydrogen Chloride

Experimental data satisfy the equation

$$\ln[M]_0/[M] = k'[HCl]_0 t = kt \quad (1)$$

up to a conversion of 50–90% (Table I, Fig. 1). Unlike the cationic polymerization of 6-caprolactam^{5,6}, the polymerization of N-alkyllactams proceeds without anomalies. With increasing size of the substituent both the activation energy (E_a) and the preexponential factor (A) decrease:

| Substituent: | methyl | butyl | benzyl |
|--|---------------------|---------------------|------------------|
| E_a , kcal mol ⁻¹ : | 32.7 | 28.0 | 25.8 |
| A , kg mol ⁻¹ s ⁻¹ : | $1.1 \cdot 10^{13}$ | $3.5 \cdot 10^{10}$ | $2.7 \cdot 10^9$ |

It may be stated that in the polymerization of lactam *I* its equilibrium content does not exceed 0.15% (Table II). This result justifies the assumption of the irreversibility of the acidolytic cleavage of lactam *I* which was used as a basis for the discussion of changes in the concentration of products of the deacylating cleavage during the polymerization initiated with hydrogen chloride². It cannot be ruled out that the equilibrium content of the monomer is even lower, as it has not been verified that in given experiments the actual final conversion value had been achieved.

The equilibrium concentration in the polymerization of N-methyl-7-heptanelactam (N-methylenantholactam) is much higher⁷ (19% at 260°C), as the eight-membered ring is much more readily formed than the nine-membered one.

Effect of Amine and Lactam Salts on the Polymerization Initiated with Acyl Chloride

Chlorides of carboxylic acids range second after hydrogen chloride as the most effective polymerization initiators of lactam *I* (ref.¹). A question arises to what extent

does the addition of N-alkyllactam to the acyl chloride group participate in the polymerization initiated with hydrogen chloride:

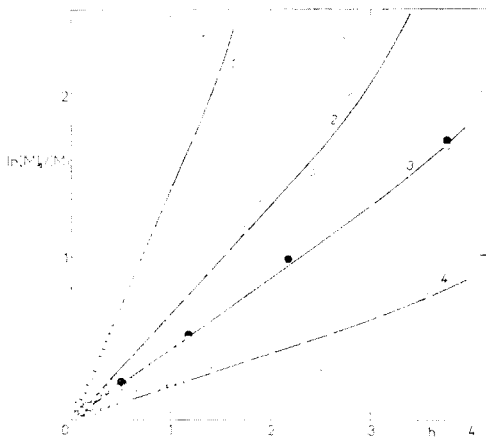
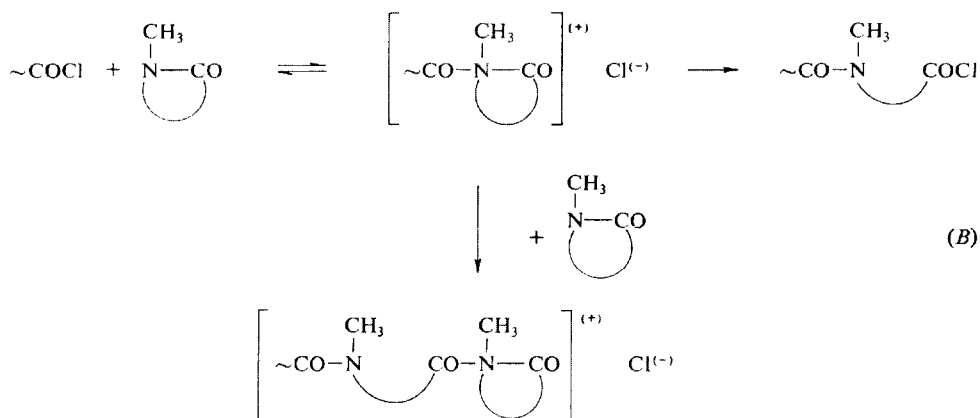


FIG. 1

Polymerization of Lactam I in a Dilatometer at 185°C

HCl Concentration, mmol/kg: 1 137; 2 62; 3 52 and 4 30; parallel experiments in an ampoule (●) with 52 mmol HCl/g.

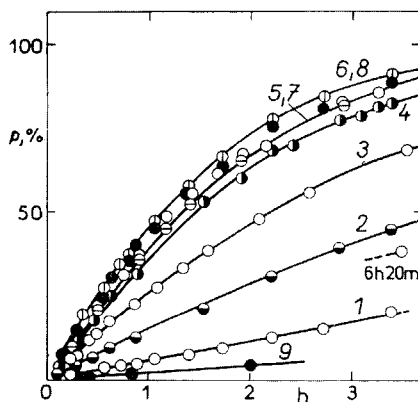


FIG. 2

Polymerization of Lactam I at 185°C Initiated with Butyryl Chloride (29 mmol/kg)

Concentration of added dibutylamine hydrochloride, mmol/kg: 1 0; 2 7.0; 3 13.9; 4 25.8; 5 32.3 (◻); 6 46.6 (●); 7 63.1 (○) and 8 90.4 (◻); triethylamine hydrochloride course 9 (●) in presence of 39.5 mmol/kg.

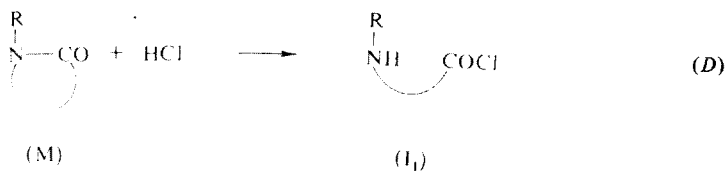
-amine hydrochloride *via* side reactions, for instance by alkylation of amine with amide^{2,8,9}, and they may be situated in the middle of the chain or at its end:



Kinetic experiments carried out so far show that only *sec*-amine hydrochloride has an accelerating effect in the polymerization initiated with acyl chloride; this effect can be explained by an immediate establishment of equilibrium (C). The initiation system consisting of equimolar amounts of acyl chloride and *sec*-amine hydrochloride has the same activity as hydrogen chloride. The system involved in both cases is the same.

Growth Reaction

The concentration of functional groups is determined by a set of reactions (I_n indicates the linear particle $\text{H}[-\text{N}(\text{CH}_2)_7\text{CO}-]_n\text{Cl}$



If the initiation activity of an equimolar mixture of butyryl chloride and dibutylamine hydrochloride (Fig. 3) is equal to that of hydrogen chloride, it means that the condensation reaction (C), and consequently similar polycondensation reactions (E)...(F)

and (G) proceed at a high speed. The condensation is assumed to take place owing to the reaction of the —COCl group with the free amino group, and not with the ammonium cation.

The polymerization rate is determined by the rate of the deacylating cleavage of the lactam (D) as the slowest process of the set of reactions described above, which is in accord with the observed first order kinetics with respect to N-alkyllactam.

With butyryl chloride as initiator the course of polymerization can only in the very beginning be approximated by first order kinetics with respect to monomer, but with increasing amount of sec-amine hydrochloride added the agreement becomes improved, as has been verified by the transformation of kinetic curves given in Fig. 2. In the polymerization initiated with butyryl chloride ($[\text{C}_3\text{H}_7\text{COCl}]_0 = \text{const.}$) with various amounts of dibutylamine hydrochloride (cf. Figs 2 and 3), the polymerization rate in the region above the equimolar ratio $[\text{>NH} \cdot \text{HCl}]_0 / [\text{—COCl}]_0$ increases slower with further additions of hydrochloride than in the region below this ratio. Although an increase in the excess of amine hydrochloride shifts the equilibrium (C)

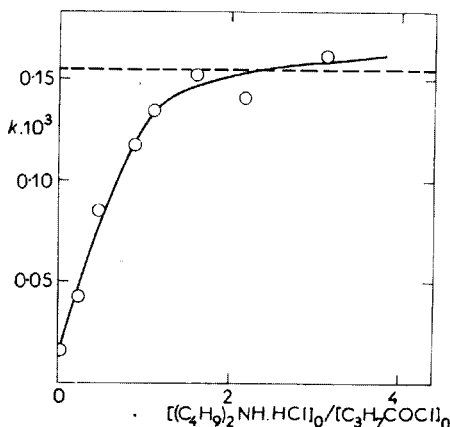


FIG. 3

Polymerization of Lactam I at 185°C Initiated with Butyryl Chloride at Constant Concentration 29 mmol/kg with Added Dibutylamine Hydrochloride

Data on the first order rate constant k (s^{-1}) were derived from experiments shown in Fig. 2; ---- polymerization initiated with hydrogen chloride in a concentration $[\text{HCl}]_0 = 2[\text{C}_3\text{H}_7\text{COCl}]_0 = 58$ mmol/kg, calculated from Eq. (1).

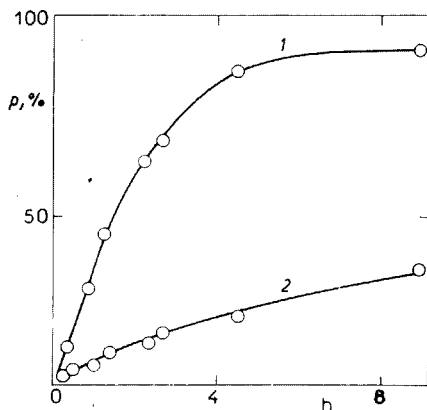


FIG. 4

Polymerization of Lactam I at 200°C Initiated with Butyryl Chloride (1) and an Equimolar Mixture of Butyryl Chloride and Tributylamine (2)

Concentration of initiators 64 mmol/kg.

further to the right in favour of the formation of hydrogen chloride, which in turn increases the rate of deacylating cleavage as the kinetically decisive polymerization step, the increase in the HCl concentration is still smaller. The concentration of hydrogen chloride cannot exceed the limiting value $[\text{HCl}]_{\text{max}} = 2[\text{C}_3\text{H}_7\text{COCl}]_0$, as follows from the stoichiometry of the reaction (C).

Besides polymer formation due to polycondensation, growth *via* the polyaddition reaction (B) also takes place. Only 10% of the polymer is formed by noncatalyzed polyaddition (Fig. 3) which consequently should be regarded as only a minor important growth reaction.

The accelerating effect of the addition of the $>\text{NH} \cdot \text{HCl}$ groups in the polymerization initiated with butyryl chloride has been explained by the reaction (C) which leads to the formation of hydrogen chloride or lactam hydrochloride. The initiation reaction itself consists in the acidolytic cleavage of lactam with formation of N-alkyl-8-aminoctanoyl chloride. The finding that in the initiation with both hydrogen chloride and an equimolar mixture of acyl chloride and sec-amine hydrochloride,

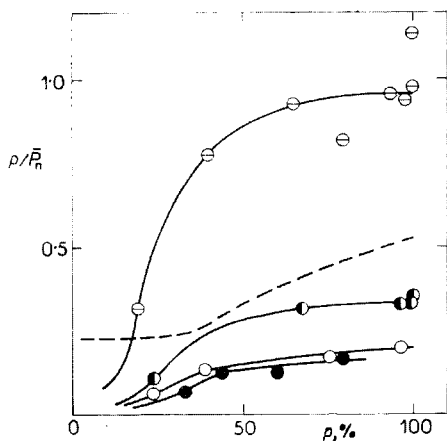


FIG. 5

Number of Macromolecules (per 100 molecules of monomer, p/\bar{P}_n) in the Course of Polymerization of Lactam I in an Ampoule

Polymerization temperature ($^{\circ}\text{C}$), hydrogen chloride concentration (mmol/kg): ● 155, 62; ○ 170, 69; ⊖ 170, 282; ⊙ 200, 70; ---- number of macromolecules in the case ⊙ calculated from the total concentration of the amino groups ($155 \cdot 2 \cdot [\text{>NH} \cdot \text{HCl}]$).

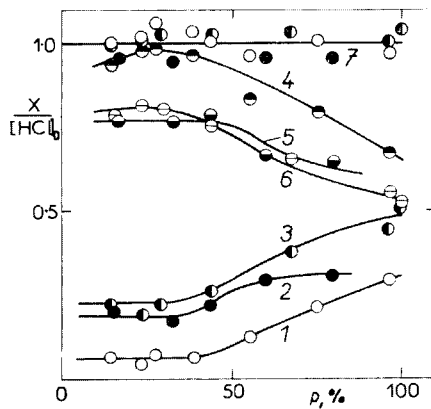


FIG. 6

Acid Groups in the Polymerization of Lactam I

Ratio of the concentrations of acid groups $[X]$ and initial initiator concentration: 1–3 $[\text{>NH} \cdot \text{HCl}]$, 4–6 strong acidity, 7 total acidity. Reaction conditions (temperature $^{\circ}\text{C}$, initial concentration HCl mmol/kg): ○ ● 155, 62; ● ● 170, 69; ⊖ ● 200, 70.

TABLE II
Monomer Content in the Product at the End of Polymerization of Lactam I

| $[\text{HCl}]_0$ mmol/kg | T °C | t^a min | Monomer % |
|-----------------------------|-----------|--------------|--------------|
| 282.0 | 170 | 1 200 | 0.08 |
| 137.4 | 185 | 510 | 0.08 |
| 70.5 | 200 | 1 440 | 0.05 |
| 29.2 | 260 | 120 | 0.15 |

^a The time includes polymerization and subsequent thermostating during which there are no more volume changes of the product.

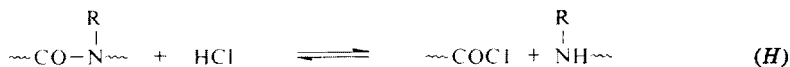
the same acidolytic equilibrium (or pseudoequilibrium, taking into account side reactions²) is established at the beginning of polymerization, gives a proof of the high rate of condensation of the —COCl and sec-amine groups, and corroborates the concepts outlined above. It cannot be excluded, however, that amine hydrochloride catalyzes the polyaddition reaction (B). The total participation of polyaddition (both noncatalyzed and catalyzed) in the cationic polymerization of N-substituted lactams cannot be determined exactly and it cannot be ruled out that both mechanisms — polycondensation (E) ... (F), (G) and polyaddition of lactam to —COCl group take part in the cationic polymerization of N-substituted lactams.

Molecular Weight in the Polymerization Initiated with Hydrogen Chloride

The dependence of the degree of polymerization on conversion is more complex than in the cationic polymerization of unsubstituted 6-caprolactam^{6,10}. The number of macromolecules, p/\bar{P}_n , increases before the polymerization halftime faster than at its beginning and at its end (Fig. 5).

The data on the total concentration of the terminal $\text{>NH} \cdot \text{HCl}$ groups can be employed only for a rough estimation of the molecular weight. The viscometrically determined number of particles in the first half of polymerization is much lower than the same quantity calculated from the content of the $\text{>NH} \cdot \text{HCl}$ groups (Fig. 5). Consequently, a large number of the end groups is present in the low-molecular weight fraction. The dependences of the endgroup content in the polymerizate (Fig. 6) coincide with what has been found earlier for the initiation with 5 mol. % HCl (ref.²). In the first half of polymerization their concentration is constant, in the second half it increases. This increase obviously takes place in the macromolecular fraction. This is probably also connected with departures from first order kinetics at conversions higher than 50% (Fig. 1).

The endgroup content in the macromolecular fraction due to the chain cleavage



does not increase linearly, but with a higher power of conversion, as is demonstrated by the exponential form of the dependence of the number of particles up to 20–35% conversion (Fig. 5). The slowing down of the increase in the total number of macromolecules toward the end of polymerization is related to the fact that the chain number is eventually determined by the equilibrium (H). To a smaller extent the increase in the molecular weight toward the end of polymerization can be assigned at the expense of side condensation reactions of the end groups^{2,11,12}.

REFERENCES

1. Masař B., Šebenda J.: *This Journal* 39, 110 (1974).
2. Masař B., Šebenda J.: *This Journal* 39, 2581 (1974).
3. Vinogradova S. V., Vasněv V. A., Komarova L. I., Koršak V. V.: *Izv. Akad. Nauk USSR, Ser. Chim.* 1970, 2590.
4. Ernest I., Heřmánek S.: *Preparative Reactions in Organic Chemistry, IV.*, p. 240. Published by Nakladatelství ČSAV, Prague 1959.
5. Doubravský S., Geleji F.: *Makromol. Chem.* 105, 261 (1967).
6. Stea G., Gechele G. B., Mariani L., Manescalchi F.: *J. Appl. Polymer. Sci.* 12, 2697 (1968).
7. Muromova S. R., Strepichejev A. A., Rogovin Z. A.: *Vysokomolekul. Soedin.* 5, 1096 (1963).
8. Klamann D.: *Monatsh.* 84, 925 (1953).
9. Klamann D., Schaffer E.: *Monatsh.* 87, 1294 (1954).
10. Doubravský S., Geleji F.: *Makromol. Chem.* 110, 246 (1967).
11. Lieber E., Cashman A. F.: *US Pat.* 2 470 504 (1949); *Chem. Abstr.* 43, 5586 (1949).
12. Braz G. I., Voznesenskaja N. N., Jakubovič A. J.: *Ž. Org. Chim.* 9, 114 (1973).

Translated by L. Kopecká.