

## THE INFLUENCE OF A CATION ON THERMAL DEGRADATION OF ANIONIC POLYMERIZATES OF $\epsilon$ -CAPROLACTAM

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The decrease of polymerization degree of anionic  $\epsilon$ -caprolactam polymerizates upon further thermal exposure depends on the initiator concentration and on the ratio of initiator-activator. The values of polymerization degree of polymerizates exposed to prolonged heating ( $\bar{P}_\infty$ ) exhibit a strong dependence on the initiator concentration. This clearly indicates a primary role of the latter in the degradation process. The effect of cation type on the relationship  $\bar{P}$  vs  $t$  is, especially in initial stages, unimportant over a broad concentration range, using alkaline salts of  $\epsilon$ -caprolactam as initiators at 250°C, the initiator-activator ratio being 0.5–3. This fact may be accounted for by a total dissociation of salts participating in disproportionation reaction at this stage. The plot of  $\bar{P}$  vs  $c_I^{-0.5}$  was found to be linear within given concentration range of catalytic components and for all initiators used (Li-, Na-, K-, and Cs-salts of  $\epsilon$ -caprolactam). The values of linearity constants correlate with ionization potentials of corresponding metals. In none of the cases an effect of activator presence on values of  $\bar{P}$  was observed. The initiation activity of the system was diminished at the ratio initiator-activator equal 3, before achieving an equilibrium concentration of polymer regardless the type of cation.

Anionic polymerizates of  $\epsilon$ -caprolactam undergo destructive changes upon heating, the degradation process being accompanied by a decrease of molecular weight<sup>1–7</sup>. Compared with the degradation of hydrolytic polymerizates<sup>8,9</sup> this decrease is substantially faster, proceeds also at lower temperatures<sup>7</sup>, and is induced by the presence of basic components of catalytic system in the polymerization mixture.

Polymerization degree  $\bar{P}$  increases in the course of anionic polymerization till an equilibrium monomer-polymer is reached. Then it goes through a maximum in the case of both activated<sup>3,6,10</sup> and non-activated polymerization<sup>5,11,12</sup>. The decreasing tendency after reaching the maximum may be regarded as a formal beginning of the degradation process although degradation proceeds practically simultaneously with polymerization. In the case of activated polymerizates the value of this maximum is higher than would correspond to the concentration of activator (a source of propagating centres), being determined by a simultaneous existence of condensation and degradation reactions in the course of polymerization<sup>10</sup>. Empirical relationships<sup>10</sup> have been established between the value of this maximum and concentration of catalytic components. The decrease in  $\bar{P}$ , whose rate is dependent on temperature, concentration, and ratio of catalytic components, is attributed to the change of number of particles caused by degradation and to changes in molecular weight distribution.

The value of  $\bar{P}$  determined from viscometric data may be influenced also by branching of macromolecules which becomes important in polymerizates with higher content of catalytic compo-

nents<sup>13</sup>. While the distribution of molecular weights is somewhat changed even after a prolonged heating<sup>5</sup>, the value of  $\bar{P}$  approaches a limiting value<sup>3,5-7</sup> after a certain time. The latter is dependent on the initial concentration of initiator and on temperature. On the other hand, the dependence of this value on activator concentration is inexpressive at higher temperatures<sup>7</sup>.

The increase of number of particles is assumed to be due to the fission of amide bonds under the influence of a strong base<sup>14</sup>. According to Šebenda and Kouřil<sup>15</sup> these fission reactions are, in fact, disproportionation reactions of amide groups induced by caprolactam anions. Also the disproportionation of amide bonds induced by anions of linear transamide groups may lead to the increase in number of particles if followed by reacylation of the newly formed branched imide structure by the caprolactam anion. The concentration of these anions may be determined, besides other factors, also by the dissociation of corresponding salts in the reaction medium and therefore by the type of cation. The mentioned disproportionation reactions lead also to the formation of imide structures. Other reactions of these groups give relatively acid products which lower the basicity of the system and thus the concentration of caprolactam and amide anions active in disproportionation reactions. Thus they are the second degradation process determining factor.

The studies performed on model systems<sup>14,16-19</sup> have shown that a whole complex of reactions is involved whose final products include also branched structures<sup>19,20</sup>.

In previous works dealing with the degradation of anionic polymerizates, exclusively sodium salt of  $\epsilon$ -caprolactam was employed as an initiator of polymerization. Only in work<sup>7</sup> the course of thermal degradation was examined on polymers prepared by thermal adiabatic polymerization of caprolactam using Li, Na, K, and Ca salts of  $\epsilon$ -caprolactam as initiators. The experimental arrangement used in the mentioned work can, however, create a misleading impression about the influence of cation, namely taking into account that polymers were prepared under different conditions (135–220°C) and the degradation carried out at 250°C. This has encouraged us to study the influence of a cation on degradation to some detail, using polymerizates prepared under isothermal conditions, the temperature being the same as that of degradation.

## EXPERIMENTAL

### The Preparation of Alkaline Salts of $\epsilon$ -Caprolactam

Sodium and potassium salts were prepared by the reaction of alkaline metal methanolate with  $\epsilon$ -caprolactam according to the method described previously<sup>21</sup>; the same method was used for the preparation of cesium salt. The purity of these salts was checked using the same method as described in the original paper<sup>21</sup> (methanol content was lower than 1% in all cases). The methanol to be determined was first transformed to formaldehyde and a coloured product of its reaction with the Schiff's agent was determined colorimetrically. Cesium salts prepared by this method were further purified by crystallisation from 5% caprolactam solution in dry pyridine and dosed in crystalline form into the polymerization mixture.

*Lithium salt of  $\epsilon$ -caprolactam.* Caprolactam (60 g of standard purity) was dissolved in 300 ml of dry toluene in a three-necked 500 ml flask fitted with a reflux condenser, magnetic stirrer

TABLE I

The Initiation Activity of Alkaline Salts of  $\epsilon$ -Caprolactam

The polymerization of caprolactam at 80°C in bulk; N-benzoylcaprolactam used as activator (A), initiator (I) — alkaline salt of caprolactam, turbidity time  $t_t$  — the polymerization time till the first visible turbidity of polymerizing mixture caused by precipitating polymer,  $p_1$  the polymer content one hour after the appearance of turbidity.

Me	$c_I$ mol.%	$c_A$ mol.%	$\text{CH}_3\text{OH}^c$ mol.%	$t_t$ s	$p_1$ %
Li <sup>a</sup>	0.254	0.254	—	1 360	5.91
Li <sup>b</sup>	0.226	0.226	3.6	1 403	5.23
Na	0.250	0.250	0.8	1 310	5.98
K	0.244	0.244	0.9	840	7.78
Cs	0.226	0.226	0.5	550	8.03

<sup>a</sup> Salt prepared from lithium hydride. <sup>b</sup> Salt prepared from lithium methanolate according to ref.<sup>21</sup>.

<sup>c</sup> Methanol content in alkaline salt of  $\epsilon$ -caprolactam prepared from lithium methanolate.

and a nitrogen supply. 1 g of LiH was added under the stream of nitrogen and the mixture was heated to 50°C while stirring. The reaction was followed by measuring the volume of hydrogen evolved. After two hours the residual lithium hydride and a first part of lithium caprolactam precipitate were removed from the reaction mixture by filtration. The excessive caprolactam was then removed by freezing and filtration. The last filtrate was left standing at room temperature, the precipitated lithium caprolactam separated by filtration through a sintered glass funnel, washed with dry ether and dried at 50°C and 0.1 Torr pressure. The purity of this salt was checked by conductometric titration; the initiation activity (Table I) of this product was higher than that of the salt prepared according to the method described previously<sup>21</sup> (3–4% methanol present).

### Polymerization

N-benzoylcaprolactam was used as activator<sup>22,23</sup>. The preparation of polymerization mixture and filling of ampoules has already been described<sup>24</sup>. The polymer content was determined from the weight loss after a four times repeated extraction of polymerizates with boiling water (after 5 minutes' boiling) using the procedure described previously<sup>10</sup>. Polymerization degree was calculated according to relationship<sup>25</sup>  $P = 133[\eta]^{1.34}$ ; intrinsic viscosity was calculated from a result of one measurement in *m*-cresol at 25°C,  $c = 0.4$  g/dl using the value of Huggins constant  $k_H = 0.34$  (ref.<sup>26</sup>).

## RESULTS AND DISCUSSION

In the case of  $\epsilon$ -caprolactam polymerizates prepared by heating an  $\epsilon$ -caprolactam–alkaline salt of  $\epsilon$ -caprolactam–activator of acyllactam type system, the degradation is a consequence of multitude of side reactions, some of them being caused by anions while the other are independent of ion presence in the system. A cation should in-

fluence the process mostly because of different dissociation of corresponding salts. This was corroborated by finding a dependence of the rate and degree of polymerizate degradation on the ionisation potential of a corresponding metal<sup>7</sup> when  $\epsilon$ -caprolactam Li-, Na-, K-, and Ca-salts, resp. were used as initiators. When interpreting the differences between polymerization and degradation of Li-polymerizates and those of other alkaline metals, the authors based their reasoning on differences of dissociation of corresponding salts, not excluding, however, a possible selective effect of cation on some side reactions, similar to that observed in the case of disproportionation of Na- and K-salts of non-substituted acylamides<sup>20</sup>. The latter reaction may be regarded as a remote analogy of disproportionation reactions proceeding in polymerizate being degraded.

From the mechanistic point of view the reacylation reaction is an analog of disproportionation. The comparison of a cation influence both in polymerization and degradation processes is, therefore, justified. The influence of cation on the rate of low temperature (80°C) anionic polymerization is somewhat apparent from Table I, which shows an order of catalytic activities of Li < Na < K < Cs being parallel with the decreasing ionisation potential of corresponding metals. This tendency is in accordance with the published data<sup>27</sup> concerning the dissociation of  $\epsilon$ -caprolactam alkaline salts (Li, Na, K). These results confirm the expected ionic character of the reaction of propagation. Even under these conditions, however, side reactions proceed together with the propagation reaction<sup>17</sup>, thus lowering the real concen-

TABLE II

Thermal Degradation of Polycaprolactam Prepared at 250°C Using the Ratio Initiator/Activator 1 : 3

The concentration of alkaline  $\epsilon$ -caprolactam salt 0.083 mol.%, N-benzoylcaprolactam 0.250 mol.%;  $t$  duration of sample thermal exposure,  $p$  polymer content.

$t$ min	Li <sup>a</sup>		K		Cs	
	$p$ , %	$\bar{P}$	$p$ , %	$\bar{P}$	$p$ , %	$\bar{P}$
5	76.9	499	80.7	494	79.6	572
15	78.6	550	—	—	84.6	597
30	79.2	545	82.2	515	83.4	596
60	79.4	486	83.2	447	83.5	562
120	81.2	443	—	445	—	482
180	—	—	85.5	408	84.0	417
240	81.3	341	84.8	361	84.6	386
1 440	81.3	222	84.2	239	85.0	252

<sup>a</sup> Concentration of lithium/caprolactam 0.079, N-benzoylcaprolactam 0.237 mol.%.

tration of catalytic components; in the case of a more pronounced selective influence of cations on the course of side reactions, the above conclusions about the propagation reacylation reaction might be questionable.

The samples used for degradation studies were prepared by isothermal polymerization at the temperature equal to that of degradation (250°C). Both processes were carried out in the same closed system. The values of polymerization degrees of polymers as functions of degradation time for individual cations and corresponding

TABLE III

The Degradation of Polycaprolactam at 250°C

The concentration of alkaline  $\epsilon$ -caprolactam salt ( $c_I$ ) and N-benzoylcaprolactam ( $c_A$ ) in mol%,  $t$  time of degradation (time measured from the immersion of reaction vessel to a thermostat; polymerization is completed within 2–6 minutes).

$t$	Li	K	Cs	$t$	Li	K	Cs
min	$c_I = 0.125, c_A = 0.250$			min	$c_I = 0.250, c_A = 0.250$		
5	717	665	765	5	683	675	750
	88.0 <sup>a</sup>	89.0 <sup>a</sup>	88.6 <sup>a</sup>				
10	685	632	717	10	608	545	609
15	657	608	686	15	524	519	557
30	587	—	619	30	404	417	425
45	542	527	—	45	360	360	—
60	524	497	537	60	342	344	347
120	456	446	443	120	296	279	261
180	389	386	391	180	223	229	216
240	344	335	352	240	203	201	196
1 440	231	233	248	1 440	170	173	167
	$c_I = 0.500, c_A = 0.250$			$c_I = 0.750^b, c_A = 0.250$			
5	555	533	549	5	465	415	447
10	421	420	427	10	331	346	344
15	327	362	369	15	261	282	279
30	244	269	267	30	186	192	205
60	197	206	205	60	150	150	156
120	160	162	156	120	—	120	120
180	—	143	138	180	110	113	112
240	140	136	132	240	108	112	110
1 440	132	126	121	1 440	107	111	103

<sup>a</sup> Polymer content in non-equilibrated polymerizates. <sup>b</sup> Lithium caprolactam concentration 0.722; cesium caprolactam 0.716; the ratio 3 : 1 catalytic components was preserved.

ratios of catalytic components are presented in Tables II and III. At the ratio initiator : activator equal to 3 : 1 (Table I) the initiation activity of a catalytic system disappears in all the cases studied (Li, K, Cs). This happens before an equilibrium content of polymer is reached, similarly as in previously studied case<sup>17</sup> of sodium caprolactam. It may thus be concluded that cations have not a selective effect on any of side reactions.

In the case of equilibrium polymerizates (Table II) the close resemblance of degradative changes of  $\bar{P}$  for all the cations studied, is striking. Differences in  $\bar{P}$  values of these polymers are, with a few exceptions, within an experimental error, especially at initial stages of degradation. These results are in contrast with those presented in ref.<sup>7</sup> where the rate as well as the extent of degradation decrease with the decreasing degree of dissociation of corresponding salts, the degradation being distinctly different namely in the case of Li-polymerizate; these differences may, however, be due to different heat treatment of samples during the polymerization.

This agreement in the case of degradation of polymers prepared in the presence of alkaline salts of  $\epsilon$ -caprolactam can be explained when assuming that these salts are completely dissociated under conditions of experiment. The justification of this assumption follows from the extrapolation of the temperature dependence of dissociation of caprolactam Na- and K-salts<sup>27</sup>. Similarly, a complete dissociation may be expected in the case of other alkaline salts, namely cesium salt of caprolactam. Although the polymerizing or degrading system is substantially different from  $\epsilon$ -caprolactam (neutralisation reactions of various anions proceed, strongly dissociated salts suppress the dissociation of  $\epsilon$ -caprolactam salts) the type of cation could not influence the concentration of caprolactam anions if the values of corresponding dissociation constants were sufficiently high.

If a complete dissociation of alkaline salts participating in disproportionation reactions is assumed then the same rate of these reactions must be admitted for all cations used. From the agreement of the degradation course ( $\bar{P}$  vs  $t$  plot) then follows that also the influence of cation on other side reactions will be unimportant at least from the point of view of the influence on the polymerization degree. The time dependence of  $\bar{P}$  is, as mentioned above, the results of disproportionation and other side reactions. The influence of cation on the course of individual types of reactions cannot thus be estimated judging from identical  $\bar{P}$  vs  $t$  plots. In the case of side reactions the individual character of cation could be pronounced as a consequence of limited dissociation of acid salts of products formed by the disappearance of propagating centres, carboxylates and carbonates being expected to have a significant influence<sup>28,29</sup>. This would show up namely in later stages of the process.

The limiting values of polymerization degree of degradation products may be used as a criterion of significance of these influences. The limiting value of polymerization degree (in our case  $\bar{P}$  of samples degraded for 24 hours) is probably the result of equilibrium establishment between condensation and fission reactions catalysed

by slightly basic products of the strong basis reaction products. The relationship between the initial concentration of initiator and the limiting value  $\bar{P}_\infty$  can be described by an empirical expression which is obeyed in all the studied cases (Li-, Na-, K-, and Cs-salts):

$$\bar{P}_\infty = kc_1^{-0.5} + A \quad (1)$$

This expression was derived previously for the case of Na-polymerizates<sup>3,5-7</sup> (Fig. 1). The values of constants  $k$  and  $A$  for individual cations are following:

Cation	Li	Na	K	Cs
$k$	7.21	7.39	7.52	8.96
$A$	28.7	28.7	18.9	-7.8

The differences, with the exception of cesium caprolactam, are relatively small. The tendency is apparent, however, which corresponds to the sequence ionisation potentials of corresponding metals. The values of  $\bar{P}_\infty$  determined for polymers prepared by non-activated anionic polymerization under similar conditions (concentration and type of initiator) are almost identical with those of corresponding polymerizates prepared in the presence of activator although the initial values of  $\bar{P}$  are higher in the latter case. It thus follows that the relations describing the disappearance of a strong base or that valid for imide groups added to the system (or formed through disproportionation reactions) will be identical under these circumstances.

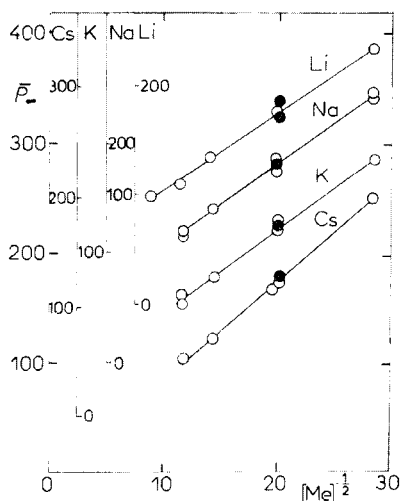


FIG. 1

The Dependence of  $P_\infty$  on Alkaline Salt of  $\epsilon$ -Caprolactam Concentration

Alkali metal (Me) concentration in gequiv.:  
 : mol of  $\epsilon$ -caprolactam; concentration of N-benzoyl- $\epsilon$ -caprolactam (mol/mol of lactam):  
 ○  $2.5 \cdot 10^{-3}$ , ● 0.

This relation will probably not be influenced by the basicity of the reaction medium. The latter will be substantially higher during polymerization and in initial stages of degradation of nonactivated polymerizates than in the case of activated polymerization. The values of  $\bar{P}_\infty$  also indicate that the assumed differences in the dissociation of corresponding alkaline salts of acid products of catalytic system disappearance can be only small.

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