ALKALINE POLYMERIZATION OF 6-CAPROLACTAM. L.* THE ACTIVATION EFFECT OF N,N-DISUBSTITUTED AMIDES OF 3-OXOACIDS AND DIMERS OF SUBSTITUTED KETENES

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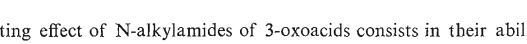
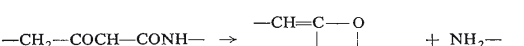
To verify the feasibility of regeneration of the growth centres *via* the substituted ketene dimer, the effect of both these dimers and N,N-disubstituted amides of 3-oxoacids on the anionic lactam polymerization was investigated. However, none of the compounds studied led to a fast polymerization of caprolactam in the presence of sodium caprolactam. On the other hand, the polymerization proceeded very fast if the caprolactam solution of the N,N-disubstituted 3-oxoamide or alkylketene dimer was first heated to 250°C and only then sodium caprolactam was added. Thus, a regeneration of the growth centres from 3-oxoamides *via* diketene seems highly unlikely.

The activating effect of N-alkylamides of 3-oxoacids consists in their ability to be thermolyzed while yielding isocyanate[1–4], ketene, or diacyl amine[3,5], which react with lactams with formation of growth centres. N-Alkylamides of 3-oxoacids could also split into amine and diketene[3,4]:



(*A*)

which could acylate the lactam while giving rise to growth centres:



(*B*)

This possibility may be verified by the determination of the activation effect of N,N-dialkylamides of 3-oxoacids which without a preceding dealkylation cannot form N-anions needed for the above splittings. Some N,N-disubstituted 3-oxoamides, *e.g.* N-tert-butylacetoacetanilide dissociate to yield isocyanates, probably after a preceding dealkylation[4], so that they also could activate the anionic polymerization of lactams. However, some data found sporadically in the literature indicate

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that N,N-disubstituted 3-oxoamides are inactive[1,5], and we therefore decided to investigate the problem in more detail.

EXPERIMENTAL

The dimers of ethyl-, butyl- and hexadecylketenes were prepared from the respective acid chlorides according to ref.[6].

N,N,2-Trisubstituted 3-oxohexanamides were prepared by the addition of amines to the dimer of ethylketene similarly to ref.[1] N,2-Diethyl-N-(tert-butyl)-3-oxohexanamide, b.p. 103—104°C : : 1 Torr, n_D^{25} 1·4538; for $C_{14}H_{27}NO_2$ (241·1), calculated: 69·66% C, 11·27% H, 5·80% N; found: 69·40% C, 11·24% H, 5·74% N. N-(2-Ethyl-3-oxohexanoyl) piperidine, b.p. 175°C/15 Torr, n_D^{25} 1·4780; for $C_{13}H_{23}NO_2$ (225·3) calculated: 69·30% C, 10·29% H, 6·22% N; found: 69·49% C, 10·18% H, 6·40% N. N,N-2-Triethyl-3-oxohexanamide according to ref.[1], (*cf.* ref.[7]). N,N-Dimethyl--2-ethyl-3-oxohexanamide, b.p. 110°C/7 Torr n_D^{25}, 1·4569; calculated: 7·62% N; found: 7·56% N; (*cf.* ref.[8]).

Polymerization

Procedure 1: The polymerization experiments were carried out in an apparatus described previously[1] with the difference that the resulting polymerization mixture was not polymerized adiabatically, but at a constant bath temperature. In one of both containers a solution of sodium caprolactam in caprolactam was prepared and kept at 100°C, while the other container was used for a solution of N,N-disubstituted 3-oxohexanamide in caprolactam kept at 250°C for 15 min. After this time both solutions were mixed and heated in a thermostat maintained at 175 ± 0·3°C and 200 ± 0·3°C. The results are summarized in Table I. A similar procedure was used for polymerizations in the presence of alkylketene dimers after a preliminary heating of the dimer solution in caprolactam followed by mixing with the solution of sodium caprolactam in caprolactam; the results are given in Table II.

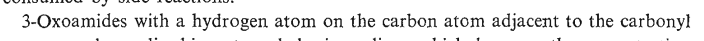
Procedure 2: After dissolution of the activator (0·3 mol. %) in a 0·3—0·6 mol. % solution of sodium caprolactam in caprolactam the solution was heated to the polymerization temperature. In contrast with the results obtained by procedure 1 (Tables I and II), no polymerization occurred under the given conditions, not even in the case of an increase in temperature from 175 to 200°C or a twofold increase in the sodium salt concentration. In the case of aldoketene dimers the polymerization did not occur also if an equimolar amount of aniline was added.

RESULTS AND DISCUSSION

Since already small amounts of the activators considerably accelerate the anionic polymerization, of lactams an acceleration of polymerization in the presence of N,N-dialkyl-3-oxoamides could indicate a decomposition with formation of active compounds. As follows from the results given in the experimental part, none of the 3-oxoamides under investigation which had been added to the sodium caprolactam solution in caprolactam caused the expected fast polymerization even at 200°C, when the non-activated polymerization due merely to sodium caprolactam should already have taken place. Baeder and Amann[5] explain the inactivity of N,N-disubstituted 3-oxoamides by their relatively high thermal stability.

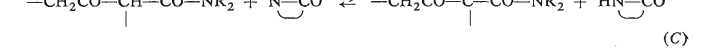
It is surprising, however, that the polymerization did not occur even in the presence of the N,N-disubstituted 3-oxoamide containing one tert-butyl residue on the nitrogen atom, since these compounds are known to split with formation of isocyanate after the splitting-off of isobutene[4]. This result suggests that in the presence of a strong base either other reactions take place, or the growth centres or lactam anions are consumed by side reactions.

3-Oxoamides with a hydrogen atom on the carbon atom adjacent to the carbonyl group may be enolized in a strongly basic medium, which decreases the concentration of the lactam anions:



(C)

The enolate anion can then split to give amine and diketene[3]:



(D)

TABLE I

Anionic Polymerization of Caprolactam in the Presence of 3-Oxoamides $C_3H_7COCH(C_2H_5)$. . $CONR^1R^2$ after a Preceding Heating of the Solution of 3-Oxoamide in Caprolactam to 250°C for 15 min

I Initiator (sodium caprolactam), A 3-oxoamide.

R^1	R^2	I (mol. %)	A (mol. %)	T °C	Time, min: total	Time, min: solidification	Yield %
C_2H_5	$C(CH_3)_3$	0·310	0·312	175	30	7	92·0
C_2H_5	$C(CH_3)_3$	0·615	0·338	175	30	2	95·6
C_2H_5	$C(CH_3)_3$	0·580	0·375	200	30	2	91·5
C_2H_5	C_2H_5	0·307	0·310	175	60	—[a]	30·5
C_2H_5	C_2H_5	0·497	0·500	175	30	15	48·0
C_2H_5	C_2H_5	0·308	0·290	200	30	7	73·1
CH_3	CH_3	0·300	0·300	175	60	—[a]	3·0
$-(CH_2)_5-$[b]		0·300	0·300	175	60	—[a]	9·6

[a] No solidification took place during the given polymerization time. [b] N-(2-ethyl-3-oxohexanoyl)-piperidine.

TABLE II

Polymerization of Caprolactam in the Presence of Ketene Dimers R—CH=C(—CO)—O and 0·5% of Sodium Caprolactam after a Preceding Heating of the Ketene Dimer Solution in Caprolactam

A Ketene dimer.

R	A mol. %	Heating °C	Heating min	Polymerization °C	Polymerization min	Polymerization solidification, min	Polymer %
C_2H_5[a]	0·3	250	10	200	30	5	82
C_2H_5	0·3	200	60	200	30	7	72
C_2H_5[a]	0·3	150	10	200	30	—[b]	—
$C_{16}H_{33}$[a]	0·3	200	60	200	60	7	92
$C_{16}H_{33}$	0·3	200	60	200	30	3	91
$C_{16}H_{33}$	0·3	200	60	175	60	30	44
$C_{16}H_{33}$	0·3	200	15	200	30	10	81
$C_{16}H_{33}$	0·3	180	20	200	60	—[b]	0
$C_{16}H_{33}$	0·3	180	60	200	30	30	41
$C_{16}H_{33}$	0·5	200	60	200	30	10	32
$C_{16}H_{33}$	0·15	200	60	200	30	—[b]	12
n-C_4H_9	0·3	200	60	200	30	8	68

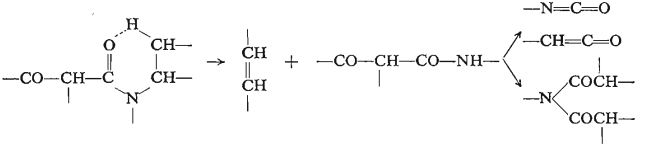
[a] Sodium caprolactam from NaH. [b] No solidification took place during the given polymerization time.

Since the enolic forms of the alkylketene dimers are strong acids (pK for the dimer of methylketene is 2·8, ref.[9]), the formation of the ketene dimers very strongly decreases the concentration of the catalytically active lactam anions. This is why even in the system sodium caprolactam–ethylketene dimer no polymerization took place, despite the fact that the ketene dimer is an acylating agent and should therefore activate the anionic polymerization. In a basic medium, diketene may also be consumed by polymerization[9]; moreover, the polymeric products thus formed and containing ketone and ester groups may consume an additional fraction of strong base by condensation reactions. The decay of activity of the ethylketene dimer, irrespective of the cause, (that is, acidity or the polymerization with subsequent reactions outlined above), is so fast that not even its addition to the amine can take place. As a result, the anionic polymerization of caprolactam activated with the ethylketene dimer did not take place even in the presence of aniline when under other circumstances 3-oxoanilide, an effective activator[1], would have been formed.

However, in the absence of strong bases at least some of N,N-disubstituted 3-oxoamides should undergo thermolysis with formation of isocyanates[4] which after the

addition of sodium caprolactam should lead to a fast anionic polymerization. To verify this assumption, sodium caprolactam was dissolved in a caprolactam solution of 3-oxoamide which prior to it was heated to 250°C. In this arrangement, the compounds formed by thermolysis may first react with caprolactam while giving rise to the growth centres on which the polymerization sets in after the addition of sodium caprolactam. Under these conditions, all 2-ethyl-3-oxohexanamides investigated here activated the anionic polymerization (Table I), which suggests that in the presence of strong bases the thermolysis proceeds either differently from that in a neutral medium, or is immediately followed by other reactions during which the active components are destroyed (growth centres and/or lactam anions).

The activating effect of N,N-disubstituted 3-oxoamides may be explained by the fact that their thermolysis involves an eliminating dealkylation with formation of an N-monosubstituted 3-oxoamide (*cf.* ref.[4]) which then activates the polymerization by the known procedure[3,10]:



(*E*)

From the viewpoint of this mechanism it is easy to understand that the highest activating effect is exhibited by 3-oxoamide which has a tert-butyl residue on its nitrogen atom; this compound is easiest to dealkylate, since it also yields most readily the cyclic structure needed for the eliminating dealkylation. This possibility is already much smaller for the N,N-diethyl derivative, as well as for the corresponding piperidide, and almost none for the dimethyl derivative. The activating effect decreases accordingly in the order of activators given above (Table I).

The activating effect of N,N-disubstituted 3-oxoamides could also be explained by assuming that the alkylketene dimer formed by reaction (*A*) (ref.[4]) ketoacylates the lactam with formation of N-acyl-3-oxoamide growth centres according to reaction (*B*). This hypothesis is supported by the fact that anionic polymerization did take place if the solution of diketene in caprolactam had been heated before the addition of a strong base (Table II).

However, with respect to the importance of the influence of the N-substituents on the activating effect of 3-oxoamides it may be inferred that of both mechanisms under consideration the dealkylating elimination (*E*) plays the predominant role.

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