ALKALINE POLYMERIZATION OF 6-CAPROLACTAM. XLII.*
INFLUENCE OF THE NATURE OF ACTIVATOR ON THE TYPE AND CONTENT OF KETO GROUPS AND ACTIVATOR RESIDUES

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The fragments containing keto groups which occurred in the hydrolyzates of anionic polycaprolactam were identified and determined by thin-layer chromatography. The occurrence of three types of ketones together with different amine fragments corresponded to the types of activators used and to the accepted mechanism of activation and side reactions.

Nawrath[1] found 1,11-diamino-6-undecanone in a hydrolysate of polycaprolactam prepared by non-activated anionic polymerization, whereas in the hydrolysate of polymer prepared with N-acetylcaprolactam as activator there were found 1,11-diamino-6-undecanone and 1-amino-6-heptanone. Similarly, 6-aminohexanophenone units were identified in polymers prepared with N-benzoylcaprolactam as activator[2]. Therefore, it has been assumed that, depending on the kind of activator used, different α-carbon atoms and different acylating groups may enter the Claisen condensation[3] in all possible combinations giving rise to various N-acyl-3-oxoamide structures[4]. The acid hydrolysis of these structures or of structures formed by their further conversion can yield generally three types of ketones — the symmetrical ketone R.CO.R, monoamino ketone $R.CO.(CH_2)_5NH_2$, and 1,11-diamino-6-undecanone (Scheme 1).

X = ~~NH(CH$_2$)$_5$— or activator residue R

SCHEME 1

The purpose of this work has been to prove the existence of assumed ketones in the hydrolysates of anionic polycaprolactam prepared in the presence of the basic types of activators and to design an analytical test for estimation of the type of activator used in the anionic polymerization[2].

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The assumptions were proved with polymerizates prepared with fifteen activators at equimolar concentrations of sodium caprolactam and activator (43·5 μmol per g of the polymerization mixture) at 175°C (30 min). The hydrolysates were worked out according to the quantitative method described previously[2] to give benzamido derivatives of free amines and then 2,4-dinitrophenylhydrazones of ketones and benzamido ketones, respectively. During this procedure all fragments with carboxyl groups, including 6-aminocaproic acid, are removed. Evaluation of infrared spectra of the mixtures of benzamido ketones and their hydrazones by a comparison with the authentic compounds did not give unambiguous results. Therefore, the mixtures of 2,4-dinitrophenylhydrazones were separated by thin-layer chromatography using various solvent systems and some of them provided more reproducible R_F-values and better isolation than the chloroform–ether system previously used[2]. The system dichloromethane–ether (dry and ethanol-free) 19 : 1 v/v was most convenient (Table I). The volatile symmetrical ketones R.CO.R, as dipropyl ketone in our case, partially escape during polymerization and they also volatilize entirely during the benzoylation procedure. They were determined as 2,4-dinitrophenylhydrazones in the volatile fraction trapped during polymerization or in the non-thickened aqueous extract of the polymerizate. The high-boiling ketones (dibenzyl ketone, b.p. $> 300°C$) appeared in the extract as well as in the mixture of hydrazones.

The results of the qualitative tests are presented in Table II. According to the given assumption, the symmetrical ketone occurs only in the polymerizates prepared under activation of N-acylcaprolactams having a hydrogen atom at the α-carbon atom of their exocyclic acyl, as well as in the polymerizates after activation with acylating agents yielding N-acylcaprolactams by the reaction with caprolactam or caprolactam anion (diacylamines, esters, ketenes, *etc.*). If N-acylcaprolactam or the corresponding acylating agents have no acidic hydrogen atom at the α-carbon atom, only amino

TABLE I

Thin-Layer Chromatographic R_F-Data of 2,4-Dinitrophenylhydrazones of Authentic Ketones

Layer of 0·1 mm Kieselgel G, developed ascendently. Values of R_F for 1,11-dibenzamido-6-undecanone (under *A*), 1-benzamido-6-nonanone (*B*), 6-benzamidohexanophenone (*C*), dipropyl ketone (*D*).

Solvent	*A*	*B*	*C*	*D*
Tetrachloromethane	0	0	0	0·04
Tetrachloromethane–dichloromethane 1 : 1	0	0	0	0·38
1,1,2,2-Tetrachloroethane	0	0·02	0·63	0·66
Dichloromethane	0	0·18	0·19	0·88[a]
Dichloromethane–diethyl ether[b] 19 : 1	0·05	0·44	0·46	0·91
Dichloromethane–diethyl ether[c] 19 : 1	0·08	0·49[d]	0·52	0·92
Dichloromethane–ethanol 99 : 1	0·22	0·24	0·24	—

[a] R_F of formaldehyde, acetaldehyde, and acetone hydrazones were 0·57; [b] ether not dried; [c] absolute ether; [d] R_F 0·41 found for 1-benzamido-7-phenyl-6-heptanone.

TABLE II

Fragments from Polycaprolactam Prepared with Different Activators

Y = $(CH_2)_5.NH.CO.C_6H_5$. Testing by thin-layer chromatography. The chromatograms were developed ascendently with CH_2Cl_2–ether (19 : 1 v/v). Positive test: + weak, ++ medium, +++ strong.

Activator	YCOY	YCOR	RCOR [a]	R	C_6H_5CONHR'	R'
N-Butyrylcaprolactam	+++	+++	++	$CH_2CH_2CH_3$	–	–
N,N-Dibutyryl-ethylamine	+++	++	++	$CH_2CH_2CH_3$	++	CH_2CH_3
Ethyl butyrate	+++	+++	++	$CH_2CH_2CH_3$	–	–
N-Phenylacetyl-caprolactam	+++	+++	++[b]	$CH_2C_6H_5$	–	–
N-Benzoylcaprolactam	+++	+++	–	C_6H_5	–	–
N,N-Dibenzoyl-ethylamine	+++	+++	–	C_6H_5	++	CH_2CH_3
Ethyl benzoate	+++	+++	–	C_6H_5	–	–
N,N-Diphenylbenzamide	+++	+	–	C_6H_5	(+)[c]	–
N-(Phenylcarbamoyl)caprolactam	+++	–	–	–	++	C_6H_5
N-(Butylcarbamoyl)caprolactam	+++	–	–	–	++	$(CH_2)_3CH_3$
N,N'-Diphenylurea	+++	–	–	–	++	C_6H_5
N-Phenyl-2-ethyl-3-oxohexanamide	+++	+	+	$CH_2CH_2CH_3$	++	C_6H_5
N-Phenyl-2,2,4-trimethyl-3-oxopentanamide	++	+	+	$CH(CH_3)_2$	++[d]	C_6H_5
2,2,4,4-Tetramethyl-1,3-cyclobutanedione	+++	+++	+	$CH(CH_3)_2$	–	–
2,2-Dimethyl-3-isopropylidene-3-propanolide	+++	+++	+	$CH(CH_3)_2$	–	–
Without activator	+++	–	–	–	–	–

[a] Silufol plates developed with CH_2Cl_2–ether (99 : 1) or dichloromethane. [b] Determined in the hydrolyzate, weak in the mixture of solvents. [c] Diphenylamine was detected in the methanolic extract of the polymerizate by gas–liquid chromatography. [d] Detection on 0·5 × 250 × 50 mm layer with luminescent indicator (Kieselgel GF_{254}, Merck).

ketones are formed by hydrolysis. Another group of activators are isocyanate derivatives, including substituted ureas and urethans, which yield primarily N-carbamoylcaprolactam as a growth centrum. These compounds give rise only to the diamino ketone units in the polymerizate, because the alkylcarbamoyl group of N-carbamoylcaprolactams cannot take part in the Claisen condensation. 1,11-Diamino-6-undecanone structures are formed only by the condensation of N-acylcaprolactam or diacylamine groups of the growing chains in this case, similarly as it is in the non-activated polymerization or as it should be in activation by compounds without carbonyl group, as phosphates[5], triazine derivatives[6], dilactim ethers[7], *etc.*

Further distinction inside the activator types was achieved by tracing of alkylamine residues of activators. They occur either free in the polymerizate or incorporated in the polymer as neutral end groups. In the latter case, the residue acted as a regulator of the molecular weight and was determined as benzamide in the benzamido ketone mixture prior to the treatment with dinitrophenylhydrazine.

N-Phenyl-2,2,4-trimethyl-3-oxopentanamide gave both asymmetrical and symmetrical amino ketones in accordance with findings of Bäder and Amann[8], assuming the cleavage of N,2,2-trisubstituted oxoamide into ketene and amide, on the one hand, and ketone and isocyanate, on the other. Both amino and diamino ketones were unexpectedly found with N-phenyl-2-ethyl-3-oxohexanamide as a representative of N,2-disubstituted 3-oxoamides. Besides the described isocyanate cleavage[9] also the competitive acylation takes place in this case, which became more apparent because the formation of 1,11-diamino-6-undecanone moieties is suppressed obviously owing to the lower basicity of the polymerization system since the very beginning.

The last two examples are isomeric diketenes derived from isobutyric acid, *i.e.* dione and lactone forms. They may be considered the acylating agents and both act in a similar way, as follows also from the quantitative results (Table III). Higher concentration of the asymmetric ketone may be ascribed to the actually doubled initial concentration of activator (diketene can acylate twice).

The number of ketone-containing moieties per macromolecule (Table III, the last column) is typical of the type of the activator used, it should not vary too much with the polymerization temperature and time. This quantity has a decreasing tendency in the following sequence of activator types: N-acylcaprolactams > diacylalkylamines > > N-carbamoyllactams. Some activators could provide the gradual metering of growth centres throughout the polymerization period and influence the ratio of polymerization and condensation reactions in this way. The low number of keto groups per chain indicates that this may be the case of ethyl benzoate and diphenylurea. On the contrary, the ratio of 1,11-diamino-6-undecanone to the total of amino ketones ranges between 0·80 and 0·95 for most activators.

With higher polymerization temperature and prolonged polymerizations periods the concentration of 1,11-diamino-6-undecanone will grow, provided that some strong base is present in the system. This increase will be caused by the disproportio-

TABLE III

Characteristics of Polymerizate Prepared with Different Activators

Polymerization for 30 min at 175°C with equimolar concentrations of the activator and sodium caprolactam (43·4—43·7 μmol per g of the polymerization mixture); p fraction of the water-insoluble polymer in the polymerizate, $\bar{N}$ average number of macromolecular chains determined viscometrically, c_m and c_d the concentrations of amino ketone $R.CO.(CH_2)_5NH_2$ and 1,11-diamino-6-undecanone in the polymerizate (μmol/g).

Activator	p	$\bar{N}$	c_m	c_d	$\frac{c_d}{c_m + c_d}$	$\frac{c_m + c_d}{p\bar{N}}$
N-Benzoylcaprolactam	0·979	35·76	1·35	30·4	0·96	0·91
N-Butyrylcaprolactam	0·965	35·27	1·44	29·6	0·95	0·91
N-Phenylacetyl-caprolactam	0·929	19·64	3·20	12·2	0·79	0·84
N,N-Diphenylbenzamide	0·956	17·45	0·67	11·4	0·94	0·72
N,N-Dibenzoyl-ethylamine	0·973	76·24	2·20	22·7	0·91	0·34
N,N-Dibutyryl-ethylamine	0·975	72·01	1·94	21·4	0·92	0·33
Ethyl benzoate	0·902	51·74	1·36	6·48	0·83	0·17
Ethyl butyrate	0·934	51·97	1·53	9·88	0·87	0·23
N-(Phenylcarbamoyl)caprolactam	0·970	40·10	—	8·59	1·0	0·22
N-(Butylcarbamoyl)caprolactam	0·971	39·91	—	8·03	1·0	0·21
N,N′-Diphenylurea[a]	0·948	65·96	—	3·36	1·0	0·05
N-Phenyl-2-ethyl-3-oxohexanamide[b]	0·962	44·87	4·13	3·52	0·46	0·18
N-Phenyl-2,2,4-trimethyl-3-oxopentanamide	0·969	35·03	1·20[c]	5·82[d]	0·83	0·21
2,2,4,4-Tetramethyl-1,3-cyclobutanedione	0·956	—[e]	7·23[c]	16·60[d]	0·70	—
2,2-Dimethyl-3-isopropylidene-3-propanolide	0·959	—[e]	8·03[c]	16·38[d]	0·67	—

[a,b] Initial concentration of activator: [a] 46·2 μmol/g, [b] 46·4 μmol/g. [c] Measurement and calculation as for 1-benzamido-6-nonanone. [d] Measured with a spectrophotometer Cary 1115 (*cf.*[2]). [e] Polymer insoluble in part.

nation reaction between amide and amide anions, followed by condensation of the diacylamine groups into structures with diaminoundecanone moieties. Consequently, the concentration of the individual amino ketones in the polymerizate may provide an additional information about the extent of disproportionation and condensation reactions.

EXPERIMENTAL

Activators and Model Compounds

Activators derived from caprolactam have been characterized previously: N-benzoylcaprolactam[10], N-butyrylcaprolactam[11], N-phenylacetylcaprolactam[12], N-(butylcarbamoyl)caprolactam[1], N-(phenylcarbamoyl)caprolactam[13]. N-Phenyl-2-ethyl-3-oxohexanamide, m.p. 80 to 83·5°C (cyclohexane), N-phenyl-2,2,4-trimethyl-3-oxopentanamide, m.p. 94–94·5°C, and 2,2-dimethyl-3-isopropylidene-3-propanolide, b.p. 120–122°C/150 Torr were received from Bukač[9,14]. 2,2,4,4-Tetramethyl-1,3-cyclobutanedione (Fluka), m.p. 115–116°C (heptane). The other activators were prepared by common methods.

Ketone, amino ketone, benzamido ketones, and their 2,4-dinitrophenylhydrazones, which are used as standards in thin-layer chromatography, have been described[2]; 2,4-dinitrophenylhydrazone of diisopropyl ketone was received from Bukač[14]. Authentic amides were prepared by common methods.

Polymerization

The purification and drying of caprolactam, the preparation of sodium caprolactam as well as the polymerization apparatus were described earlier[15]. The polymerization procedure[16] *A* was used with argon as an inert atmosphere, which was freed from traces of oxygen on a copper catalyst and dried with potassium hydroxide and molecular sieve 5A. The content of water-extractables was determined by the method described in ref.[17]. To determine the presence of free ketones as 2,4-dinitrophenylhydrazones in the water extract, the extraction was carried out under reflux. The dry polymers were used for viscometric measurements in tricresol at 25°C (concentration 0·4 g per 100 ml of solution). The intrinsic viscosity was calculated from a single measurement using the value 0·4 for the Huggins constant; the average degree of polymerization was calculated from the equation $\bar{P}_n = 116{\cdot}8[\eta]^{1{\cdot}115}$ (ref.[16]).

Thin-Layer Chromatography

The hydrolysis of polymerizates (1 g of fillings), benzoylation of the hydrolyzates, and conversion of benzamido ketones into 2,4-dinitrophenylhydrazones were carried out as described earlier[2]. For the qualitative testing, a mixture of isolated 2,4-dinitrophenylhydrazones was dissolved in 1–2 ml of carbonyl-free dichloromethane, and about 1·5 μl aliquots of the solution were put on a chromatographic layer, either 0·1 × 75 × 35 mm layer of Kieselgel G (Merck) on a glass plate or Silufol UV 254 sheet (silicagel with a starch binder on the aluminium foil; Kavalier). Thin-layer chromatography of the mixture of isolated benzamides after benzoylation of the hydrolysate was carried out identically; the chlorination method was used for the detection of spots. Benzanilide, N-ethyl, N-butyl, and N,N-diphenylbenzamides served as standards. The solutions used for chromatography tests were directly employed for measuring of infrared spectra. The amino ketones in the hydrolysates of the polymerizates were determined quantitatively by ultra-

violet spectrophotometry after the separation of their 2,4-dinitrophenylhydrazones[2], using $\varepsilon = 18200$ and 17800 $mol^{-1}\,l\,cm^{-1}$ for the hydrazones of 1-benzamido-6 nonanone and 1-benzamido-7-phenyl-6-heptanone, respectively.

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