ALKALINE POLYMERIZATION OF 6-CAPROLACTAM. XXXVIII.* DETERMINATION OF KETO GROUPS IN ANIONIC POLYCAPROLACTAM

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A method has been worked out for determination of keto groups and structures yielding keto groups on hydrolysis in polycaprolactam prepared by the anionic polymerization. The products of total hydrolysis of the polymer are benzoylated, the mixture of benzoylated amino and diamino ketones is separated from the benzoylaminocaproic acid and converted to 2,4-dinitrophenylhydrazones, which are separated by thin layer chromatography and determined photometrically.

Former studies on side reactions in anionic polymerization of lactams[1,2] indicated that keto carbonyls were incorporated into polymers as N-acyl-β-oxoamide and β-oxoamide structures. At elevated temperatures, these structures may undergo a complicated series of side reactions producing a number of irregular structures incorporated into the polymer[2]. One type of these structures comprises derivatives of ketones which may be isolated from polycaprolactam hydrolyzate as Schiff bases of amino ketones[3].

For a better understanding of the side reactions in the anionic polymerization of caprolactam, determination of the ketones in polymers seems to be necessary. This paper evaluates some methods of determination of carbonyl groups from the viewpoint of their applicability to this problem and gives the suitable analytical procedure.

EXPERIMENTAL

All melting points were determined by means of the Boetius apparatus and are not corrected.

Compounds

1,11-Diamino-6-undecanone was prepared[4] as an intramolecular ketimine 2-(5-aminopentyl)-4,5,6,7-tetrahydro-3*H*-azepine (*Ia*) from 60 g of caprolactam and 65 g of calcium oxide in the yield of 14·6 g (30%); b.p. 78·5—79·0°C/0·25 Torr, n_D^{20} 1·4973 (reported[4] b.p. 102—103°C/0·3 Torr). Other ketimines were prepared from the corresponding alkyl magnesium halides and O-methylcaprolactim[5]: 2-Methyl-4,5,6,7-tetrahydro-3*H*-azepine (*Ib*), b.p. 44—46°C/22 Torr, n_D^{20} 1·4905, 2-phenyl-4,5,6,7-tetrahydro-3*H*-azepine (*Ic*), b.p. 134—135·5°C/16 Torr, n_D^{20} 1·5642, 2-propyl-4,5,6,7-tetrahydro-3*H*-azepine (*Id*), b.p. 69—70·5°C/9—10 Torr, n_D^{20} 1·4672, and

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2-benzyl-4,5,6,7-tetrahydro-3*H*-azepine (*Ie*), b.p. 122°C/1·5 Torr, n_D^{20} 1·5480. The aqueous solutions of amino ketone hydrochlorides, prepared from the ketimines and an equivalent amount of diluted hydrochloric acid, were agitated with about 10% excess of benzoyl chloride (on the amino ketone) and the fourfold excess of 2M-NaOH at room temperature. The surveys of the prepared benzamido ketones *IIa—e* and their 2,4-dinitrophenylhydrazones *IIIa—e* are given in Table I. Polycaprolactam samples (1—3) were prepared by polymerization of 10 g caprolactam with sodium caprolactam (43·5 mmol/kg) and N-benzoylcaprolactam (43·5 mmol/kg) under various conditions: 1 — 100°C, 5 min; 2 — 175°C, 5 min; 3 — 280°C, 200 min. The preparation and purification of monomer and catalyst components as well as apparatuses and procedures were described elsewhere[6].

Photometric Determination of Amino Ketones

The polymerizate (1 g) was heated in 4 ml of diluted hydrochloric acid (1 : 1) for 15 h at 150°C or 45 h at 120°C in evacuated and sealed ampoules, which were previously flushed with nitrogen. The mixture was diluted with 50 ml of water and cooled to 20°C. To the agitated solution 7—8 ml of 2M-NaOH, 1·2 ml of benzoyl chloride (p.a. redistilled), and 17—19 ml of 2M-NaOH were added gradually. The benzoylation was completed after one hour of stirring and cooling. The alkaline reaction mixture was extracted with five 25 ml portions of chloroform. The extract was evaporated *in vacuo*, dried at room temperature (0·6 Torr) for 18 hours and dissolved in 2 ml of ethanol.* The solution was treated at room temperature for 18 hours with 10 ml of a 0·2% solution of 2,4-dinitrophenylhydrazine (recrystallized from methanol*) in 2M-HCl and then it was extracted with five 10 ml portions of chloroform.* The extract was concentrated *in vacuo* and diluted with chloroform* to 2—10 ml. Aliquots (about 80 and 60 μl) of the solution were put on a thin layer as strips 23 × 2—3 mm. The amounts of solution applied were determined by differential weighing of the micropipette. Chromatographic layers (thickness 0·5 mm) were prepared from Kieselgel G (Merck) on plates 25 × 5 cm and were stored over solid potassium hydroxide. The chromatograms were developed in ascending chloroform up to a 160—185 mm distance of the front. The bands of the individual hydrazones were scrapped into columns (30 × × 5 mm with a cotton wool filter in the stem) and eluted with 4—6 ml of ethanol. The eluates were diluted to a chosen volume, according to the amount of hydrazone, at 20°C and their optical density was measured with a spectrophotometer Unicam SP 100 at the corresponding λ_{max}. The calibration plot (Fig. 1) was determined by performing the procedure with hydrolyzates

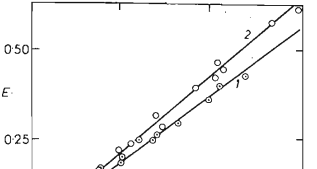


FIG. 1

Calibration of Photometric Determination of Amino Ketones in Polycaprolactam Hydrolyzates

1 Ia, *2 Ic*; the straight lines represent smoothing of experimental values by the least square method.

* Carbonyl-free solvent.

of the mixtures of authentic benzamidoketones *IIa* and *IIc* with 1 g of caprolactam. The individual steps of the procedure were calibrated similarly. The analytical yields of *Ia* and *Ic* from the complete procedure were calculated from the apparent and actual extinction coefficients and were 82·4 and 84·4%, respectively.

RESULTS AND DISCUSSION

Evaluation of Different Methods

Determination of keto carbonyls directly in the polymer would be of great advantage. Their concentration may be assumed to be of the same order of magnitude as the concentration of catalyst components, *i.e.* below 1 mol. %, based on monomer. However, the direct spectrometric method cannot be used in the presence of a large excess of amide groups.

Small amounts of keto groups were determined spectrophotometrically in copolymers of styrene with propiolactone after conversion into 2,4-dinitrophenylhydrazones and reprecipitation[7]. We tried to convert keto groups in the polymer into 2,4-dinitrophenylhydrazones, in 96% sulphuric acid as a solvent, and to determine the concentration of hydrazones in the reprecipitated polymer by spectrometry. However, the quantitative conversion of keto groups into hydrazones was not achieved.

To avoid these complications, we turned our attention to the determination of keto groups in the hydrolyzate of polymers (or polymerizates). After total hydrolysis in the presence of excess of mineral acid, β-dicarbonyl structures are assumed to undergo exclusively keto forming splitting with evolution of carbon dioxide. For the determination of the total content of ketones in hydrolyzates we tried the procedure of Lappin and Clark[8], modified by Jordan and Veatch[9]. We found, similarly to Holzbecher[10], with different model ketones, that the extinction coefficients strongly depend on the ketone structure. The differencies are caused mainly by the influence of substituents on the ketone–hydrazone equilibrium in the homogeneous solution. Especially ketones with hydrophilic functions, as amino ketones and oxoacids, were converted into hydrazones only in a small fraction.

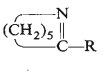
It is obvious that the individual ketones can be determined only after their isolation from hydrolyzates. Nawrath[3] found 1,11-diamino-6-undecanone and 1-amino-6-heptanone among the products of the total hydrolysis of anionic polycaprolactam. Generally, the hydrolyzate of a polymerizate, prepared with N-acylcaprolactam $R.CO.\overline{N(CH_2)_5CO}$ as activator, may contain also the ketone R.CO.R (which was not a part of the polymer) besides amino ketones $R.CO(CH_2)_5NH_2$ and 1,11-diamino-6-undecanone. The ketone R.CO.R can be formed only if the radical R has a dissociable hydrogen at the α-carbon atom.

Amino ketones were isolated as cyclic ketimines *I* by extraction of the alkalized hydrolyzate by different solvents, similarly as Nawrath[3] had isolated 2-(5-amino-

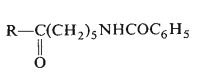
pentyl)-4,5,6,7-tetrahydro-3*H*-azepine (*Ia*) and 2-methyl-4,5,6,7-tetrahydro-3*H*-azepine (*Ib*). They were converted into benzamido ketones *II* immediately after their isolation, because they are unstable in a form of cyclic ketimines as well as of ammonium salts. The salts are easily oxidized and turn dark in air; ketimines polymerize on standing to viscous oils and may split ammonium or water, creating vinyl or nitrile groups[3]. Benzamido derivatives were separated by absorption chromatography on a silicagel column. However, even repeated extraction with various solvents (ether, benzene and chloroform) did not lead to the quantitative extraction of ketimines. Therefore, the straight benzoylation of the hydrolyzate was used, with subsequent extraction of benzamido ketones with chloroform from the alkaline aqueous solution. For this purpose the partition coefficients were estimated for chloroform – 0·1M-NaOH: 6-benzamidocaproic acid 0·003, 1,11-dibenzamido-6-undecanone (*IIa*) 16·9, 6-benzamidohexanophenone (*IIc*) 15·0. Several extractions with chloroform were supposed to be quantitative. The chromatographic fractions of benzamido ketones were contaminated by benzoic acid from excessive benzoyl chloride in the benzoylation and the separation was not satisfactory. When the fraction of benzamido ketones had been converted into 2,4-dinitrophenylhydrazones *III* prior to the column chromatography, the separation was better but the hydrazones were partially hydrolyzed in the column. Better results were obtained at the separation of *III* by thin layer chromatography providing a possibility to work with smaller amounts under milde condition.

Photometric Determination of Amino Ketones Separated by Chromatography

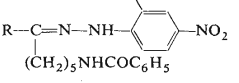
The procedure of analysis is described in details in the experimental part. Calibrations of individual steps and the analytical yields of steps were determined with authentic hydrazones *IIIa* and *IIIc*, pure benzamides *IIa* and *IIc* and by means of hydrolyses of mixtures containing *IIa*, *IIc*, and caprolactam. The results are summarized in Table II. The calibration plot for the whole procedure is in Fig. 1. The yields of single steps are satisfactorily reproducible. The standard deviations of the apparent extinction coefficients determine the accuracy of analyses of both amino ketones.



Ia–e



IIa–e



IIIa–e

Ia, R = $(CH_2)_5NH_2$
Ib, *IIb*, *IIIb*, R = CH_3
Ic, *IIc*, *IIIc*, R = C_6H_5

Id, *IId*, *IIId*, R = $CH_2CH_2CH_3$
Ie, *IIe*, *IIIe*, R = $CH_2C_6H_5$
IIa, *IIIa*, R = $(CH_2)_5NHCOC_6H_5$

The absorption maximum of solutions of *IIIa* in ethanol (λ_{max} 365 nm) is situated similarly to those of other 2,4-dinitrohydrazones of aliphatic ketones. The maximum of *IIIc* is shifted to 378 nm, apparently because of the extended π-electron system of the chromophor. The spectra of chromatographic fractions are identical with the spectra of authentic hydrazones. The separation power of distilled chloroform (pure grade) in thin layer chromatography fluctuated considerably. The R_F values are affected by ethanol, present in chloroform as stabilizer (about 1%). The plates run in ethanol-free chloroform had low R_F values of *IIIc* and, especially, of *IIIa*. The R_F values of hydrazones of simple aldehydes (impurities) were lower, too, even when chloroform saturated with water was used. Distilled chloroform without further treatment was used for isolations giving the following bands and ranges of R_F values: 0·08—0·20 (*IIIa*), 0·25—0·55 (*IIIc*), one

TABLE I

Benzamido Ketones *II* and their 2,4-Dinitrophenylhydrazones *III*

Compound (yield, %)	M.p., °C (solvent)	λ_{max}, nm (ε)	Formula (mol. w.)	Calculated/Found		
				% C	% H	% N
II	126—127	—	$C_{25}H_{32}N_2O_3$	73·50	7·90	6·89
(77)	(benzene)		(408·5)	73·52	8·04	7·04
IIb	55—56	—	$C_{14}H_{19}NO_2$	72·07	8·21	6·00
(68·5)	(benzene–cyclohexane)		(233·3)	71·98	8·24	6·22
IIc	96	—	$C_{19}H_{21}NO_2$	77·26	7·17	4·79
(97)	(benzene)		(295·4)	77·22	7·26	4·73
IId	63—64	—	$C_{16}H_{23}NO_2$	73·53	8·87	5·36
(90)	(heptane–cyclohexane)		(261·4)	73·60	8·82	5·37
IIe	68·5—69·5	—	$C_{20}H_{23}NO_2$	77·63	7·49	4·53
(67)	(heptane–cyclohexane)		(309·4)	77·63	7·55	4·68
IIIa	94—98	365	$C_{31}H_{36}N_6O_6$	63·25	6·17	14·28
(90)	(benzene–methanol)	(21 986)	(588·6)	63·09	6·15	14·53
IIIb	123—124	358	$C_{20}H_{23}N_5O_5$	58·10	5·61	16·93
(90)	(methanol)	(21 017)	(413·4)	58·38	5·80	17·07
IIIc	139·5—141·0	378	$C_{25}H_{25}N_5O_5$			14·73
(90)	(benzene)	(25 569)	(475·5)	—	—	14·78
IIId	137—139	363	$C_{22}H_{27}N_5O_5$	59·85	6·16	15·86
(53)	(methanol)	(22 100)	(441·5)	59·66	6·08	16·43
IIIe	140—141	360	$C_{26}H_{27}N_5O_5$			14·31
(< 5)	(benzene–methanol)	(21 630)	(489·5)	—	—	14·21

to four weak bands 0·11—0·45 (A_1-A_4); a weak band at the start line 0·0—0·05 (B); hydrazones of formaldehyde and benzaldehyde 0·60—0·90 (C_1-C_3). The bands A_1-A_4 and B appeared also in chromatograms of the chloroform extract of a 2,4-dinitrophenylhydrazine solution in 2M-HCl. The intensity of these bands fluctuated according to the excess of the reagent used. These compounds may be considered as oxidation products of hydrazine and their appearance did not affect the determinations of *Ia* and *Ic*. Ketones, other than that corresponding to *Ia* and *Ic*, were not found in the products. However, some compounds could be removed during the analytical procedure (especially ketones carrying acid functions, *e.g.* carboxyl groups), or their hydrazones may be hidden in the bands A_1-A_4, B, or C_1-C_3.

Examples of determination of *Ia* and *Ic* in hydrolyzates of three different polymerizates are presented in Table III. The results illustrate the region of concentration for

TABLE II

Calibration of Individual Steps in the Photometric Determination of Amino Ketones *Ia* and *Ic*
n Number of measurements, ε_a the mean value of apparent extinction coefficient in mol^{-1} l cm^{-1} calculated by the least square method, *Q* loss during the calibrated step in %.

Step[a]	*Ia*			*Ic*		
	n	ε_a	*Q*	*n*	ε_a	*Q*
Thin layer chromatography separation and elution	9	22 133	0·0	8	22 922	10·4
Reaction with 2,4-dinitrophenylhydrazine and 2nd extraction	9	21 393	3·3	8	22 164	3·3
Hydrolysis, benzoylation and 1st extraction	12	18 548[b]	13·1	12	21 026[c]	5·0

[a]The procedure starts with this step and continues as in the complete analytical process. [b,c]The standard deviations are [b]270 and [c]240.

TABLE III

Photometric Determination of Amino Ketones *Ia* and *Ic* in Polycaprolactam
The single determinations of amino ketone in mmol per kg of polymerizate are given.

Sample	*Ia*	*Ic*
1	0 0 0 0	0·5 0·5 0·6 0·6
2	1·4 1·4 1·4 1·4 1·1 1·6	22·2 22·0 21·7 21·4 21·2 20·7
3	2·7 2·9 2·6 2·7	90·8 89·3 90·4 90·8

which the method is suitable. The mean deviation of two parallel determinations of *Ia* in one hydrolyzate was ±0·9 mmol of *Ia* per kg of polymerizate in the concentration region 11 – 110 mmol/kg for a series of 31 polymerizates. Similarly to the determination of *Ic* in the mixture with *Ia*, the other monoamino ketones can be determined occurring in the hydrolyzate of polymers prepared with other activators than N-benzoylcaprolactam. For this purpose 1-benzamido-6-heptanone (*IIb*), 1-benzamido-6-nonanone (*IId*) and 1-benzamido-7-phenyl-6-heptanone (*IIe*), and their 2,4-dinitrophenylhydrazones *IIIb*, *IIId*, *IIIe* can be used as standards.

It was found that the manner of preparation of samples for hydrolysis and the conditions of storage of polymers affected the determination of amino ketones in non-extracted polycaprolactam. A part of ketimine *Ia* as well as *Ic* may be present in some polymerizates in the free form and it might volatilize. In addition, a part of structures derived from *Ia* may be present as amino end groups which may react with oxygen. Therefore, the polymer should be hydrolyzed as soon as possible after preparation and it might not be disintegrated into fine particles, *e.g.* filings, but into the rough chips only.

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REFERENCES

1. Šebenda J.: This Journal *31*, 1501 (1966).
2. Bukač Z., Šebenda J.: This Journal *32*, 3537 (1967).
3. Nawrath G.: Preprints of Scientific Communications, P. 335. International Symposium on Macromolecular Chemistry, Prague 1965.
4. Nawrath G.: Angew. Chem. *72*, 1002 (1960).
5. Dudek V., Li Kvan O.: This Journal *30*, 2472 (1965).
6. Čefelín P., Šebenda J.: This Journal *26*, 3028 (1961).
7. Yamashita Y., Umehara K., Ito K., Tsuda T.: J. Polymer Sci. *B 4*, 241 (1966).
8. Lappin G. R., Clark L. C.: Anal. Chem. *23*, 541 (1951).
9. Jordan D. E., Veatch F. C.: Anal. Chem. *36*, 120 (1964).
10. Holzbecher Z.: This Journal *32*, 4393 (1967).

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