

ENDGROUPS AND MOLECULAR WEIGHTS IN THE POLYMERIZATION OF LACTAMS INITIATED WITH CARBOXYLIC ACIDS UNDER ANHYDROUS CONDITIONS

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It has been found that polymers of capro-, enantho-, capryl- and lauro lactam prepared by polymerization initiated with carboxylic acids under comparatively mild conditions (230°C) contain less carboxylic groups than corresponds to the initiator consumed. The deficit in carboxylic groups increases with the polymerization time and depends also on the character of lactam and initiator. The osmometrically or viscometrically determined molecular weights approach the value calculated from the consumption of monomer and initiator, which indicates that carboxylic groups disappear rather in the polymer than by the decomposition of initiator. Although the polymerization was initiated with carboxylic acids in an anhydrous medium, all polymers contain basic groups.

Numerous relationships used for the molecular weight calculations of polyamides from viscosity measurements are based on the number average molecular weight determined from the endgroup content. The viscosity – molecular weight relationship was calibrated by means of polymers prepared by the hydrolytic polymerization or by the polymerization in an anhydrous medium with carboxylic acids or primary amines as initiators¹⁻³. It is assumed at the same time that the number of carboxylic or amino groups remains unchanged during the polymerization. However, earlier papers indicated that carboxylic groups are lost during the heating of caprolactam polymers^{4,5}. Also it has been proved recently that the heating of hydrolytic polycaprolactam to 250°C results in a decrease in the content of the amino and carboxylic groups⁶. At temperatures above 270°C the content of basic groups increases⁶, similarly to the polymerization of lauro lactam⁷. In the polymerization of caprolactam initiated with phenylacetic acid⁸ in an anhydrous medium a large decrease in the carboxylic groups was observed already at 230°C. In this case, however, the carboxylic groups were determined in the extracted product; with respect to the relatively low molecular weight of polymers a considerable amount of endgroups in the form of linear oligomers was also certainly removed by extraction.

In order to evaluate the extent of decay of the carboxylic groups the content of carboxylic groups in both the extracted and unextracted polymerization product was

studied in this work, and the fraction of incorporated initiator was followed. The correlation between the molecular weight and the endgroup content was used to support reasonings about the polymerization mechanisms^{8,9}. Changes in the endgroup concentrations indicate side reactions which may affect both the growth reaction and the resulting molecular weight and its distribution. The side reactions will depend on the structure of the initiator and lactam. Several types of carboxylic acids were therefore investigated, and the effect of the size of the lactam ring on changes in the endgroup content was verified.

EXPERIMENTAL

Chemicals. Caprolactam (6-hexanelactam) crystallized from benzene five times, enantholactam (7-heptanelactam) prepared according to ref.¹⁰, purified by oxidation with potassium permanganate followed by crystallization from cyclohexane, capryllactam (8-octanelactam) crystallized four times from a benzene-cyclohexane (1 : 1) mixture, lauroactam (12-dodecanolactam) crystallized three times (under nitrogen) from dimethoxyethane purified by calcium hydride. Caproic (hexanoic) acid was rectified, b.p. 102°/15 Torr, lauric (dodecanoic) acid, m.p. 43·5°C (water-ethanol mixture, 1 : 4), phenylacetic acid, m.p. 75·5–76·0°C (benzene). N-Caproyl-6-aminocaproic (N-hexanoyl-6-aminohexanoic) acid: sodium salt of the acid was prepared by reacting 1·03 mol of caproyl chloride with 1·00 mol of sodium 6-aminocaproate in 300 ml of aqueous 3·8M sodium hydroxide at 0°C. After dilution with 600 ml of water and 600 ml of methanol the acid was released from the reaction mixture on a Dowex 50 W ion exchanger; after evaporation of the solvents (under reduced pressure) the acid was purified by crystallization from the mixture tetrahydrofuran–light petroleum (1 : 3), m.p. 49·3°C; neutralization equivalent: 4·36 mmol/g (calculated: 4·36 mmol/g).

Polymerization. The lactam was weighed and put into the flask of the filling device (Fig. 1); for polymerizations initiated with lauric, phenylacetic or N-caproyl-6-aminocaproic acid the respective amount of acid was added and the compounds were dried at 25°C/0·2 Torr for 100 h. The completeness of drying was verified by a parallel polymerization test without initiator. Before polymerization the content of the flask was melted under nitrogen; if caproic acid was used as initiator, the necessary amount of the latter was introduced into the flask in a stream of nitrogen by means of a syringe. After stirring the polymerization mixture was poured into ampoules which were then sealed under nitrogen. The polymerization temperature was $230 \pm 0·05^\circ\text{C}$.

Analyses. The content of acid and basic groups was determined conductometrically in the starting polymerization mixture and polymerization products¹¹. Conductometric titration (in dry and aqueous pyridine¹²) did not reveal any anhydride groups in the polymerization products. The lactam and initiator content (with the exception of N-caproyl-6-aminocaproic acid) was determined in the polymerizates by gas chromatography on a Perkin-Elmer F 11 apparatus with the FID detection and with nitrogen (50 ml/min) as the carrier gas. The lactams were determined as follows: the polymerizates were extracted at 20°C for 20 h with methanol while stirring (2–5 g polymerizate/100 ml methanol); the internal standard for determination, acetanilide, was present during the extraction. After filtration, an aliquot part of the extract was analyzed on a 1 m column with 5% Carbowax 20 M on Chromosorb W at 180°C. For the determinations of caproic, lauric and phenylacetic acid the polymerizates were extracted with acetone in the same way. Lauric and caproic acid were determined in aliquot parts of the extracts on a 1 m column packed with 15% polyethylene glycol adipate on Chromosorb W; caproic

acid was determined at 120°C with valeric acid as the internal standard, lauric acid was determined at 175°C with caprylic (octanoic) acid as the internal standard. Phenylacetic acid was determined on a 1 m column packed with Porapak Q at 235°C with benzoic acid as the internal standard. In the determinations of lauric and phenylacetic acid in the polymerizates of capro- and enantho-lactam, it was necessary to remove the lactam by sublimation from neutralized extracts (20 h at 80°C/0.5 Torr); after this, the acid was released from its sodium salt with an acetone solution of dichloroacetic acid. In such cases the internal standards were added only after the sublimation. The content of N-caproyl-6-aminocaproic acid was determined by gel chromatography on an apparatus manufactured at the Institute of Macromolecular Chemistry of the Czechoslovak Academy of Sciences with five 1 m columns packed with polystyrene gel, exclusion limit 2200 units. The polymerizates (50–100 mg) were extracted with tetrahydrofuran (1 ml) at 20°C for 20 h while stirring; an aliquot part of the extract was analyzed after centrifugation.

Molecular weights of polymers. The molecular weight M_c was calculated from the lactam and initiator consumed using the relationship:

$$M_c = M_I + \frac{M_L([L]_0 - [L])}{([I]_0 - [I])}, \quad (1)$$

where M_I , M_L respectively are molecular weights of the initiator and lactam, and $[L]_0$, $[L]$, and $[I]_0$, $[I]$ respectively are concentrations of the lactam and initiator (mol/kg) at the respective times 0 and t .

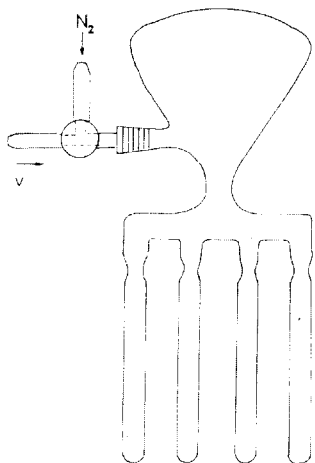


FIG. 1

Scheme of the Filling Device
V Vacuum or syringe.

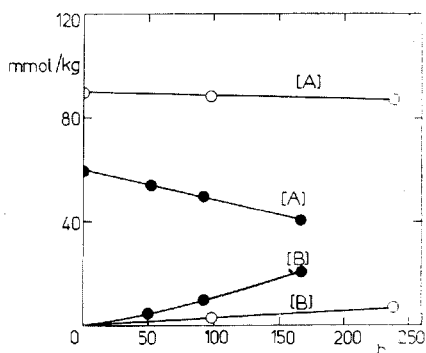


FIG. 2

Content of Carboxyl Groups [A] and Basic Groups [B] in the Polymerizate of Caprolactam in the Polymerization Initiated with Lauric (○) and Phenylacetic Acid (●) at 230°C

The content of the acid and basic groups was determined by conductometric titration¹¹ of polymers obtained from the caprolactam polymerizates by extracting them with water for 20 h (25°C); polymers of the other lactams were extracted by boiling with benzene (3 × 30 min). The various M values were calculated as follows: $M_A = 1000/[A]$ from the content of the acid groups $[A]$ (mol/kg), $M_{AB} = 1000/([A] + [B])$ from the sum of the acidic $[A]$ and basic $[B]$ groups, and $M_P = 1000/[P]$ from the concentration of the phenyl groups $[P]$ (mol/kg) in the polymer; $[P]$ was determined from the absorbancy of 2% solutions of polymer in a 50% H_2SO_4 (wt./wt.) at 258.8 nm ($\epsilon = 140$).

The M_0 values were determined by the VPO method using a Hitachi Perkin-Elmer 115 apparatus at 60°C in 2,2,3,3-tetrafluoropropanol.

The M_v values were calculated from the intrinsic viscosities of caprolactam polymers using relationships^{3,13} $P_n = 278[\eta]^{1.89}$ for polymers having $[\eta] \leq 0.2$ and $P_n = 119[\eta]^{1.34}$ for

TABLE I

Polymerization of Caprolactam Initiated with Lauric or N-Caproyl-6-aminocaproic Acid at 230°C

ΔL Conversion of caprolactam (%), $[I]_0$, and $[I]$ is the initial and final concentration of initiator (mmol/kg) respectively, $[A]$, $[B]$ and $[NH_2]$ are contents of carboxylic, basic, and primary amino groups (mmol/kg) respectively; subscripts n and e distinguish the data for unextracted and extracted samples respectively, Q is the portion of carboxylic groups in soluble oligomers (%) after subtracting the incorporated initiator, $Q = ([A]_n - [I] - [A]_e \cdot \Delta L/100)/([I]_0 - [I])$.

Time, h	ΔL	$[I]_0$	$[I]$	$[A]_n$	$[B]_n$	$[A]_e$	$[B]_e$	$[NH_2]_e$	Q
Lauric acid									
98	13.6	90	9	88	3.1	472	23.3	7.0	—
238	62.5	90	0	87	7.1	129	12.0	3.8	—
32	13.1	400	152	400	3.8	1760	8.0	—	—
64	34.5	400	64	396	5.1	968	8.1	—	—
N-caproyl-6-aminocaproic acid									
65	10.4	100	—	100	4.5	447	24.7	8.7	—
239	70.0	100	—	92	8.3	125	10.8	4.1	—
10	6.5	375	—	378	2.2	1247	7.3	—	—
12	7.7	375	187	370	2.4	1203	8.2	—	50
16	10.8	375	176	374	2.4	995	10.3	—	45
24	14.5	375	—	375	3.6	892	10.1	—	—
30	18.5	375	147	371	4.4	819	10.8	—	26
40	27.0	375	127	370	4.6	755	10.5	—	17
44	31.2	375	—	370	5.0	740	10.4	4.6	—
64	43.0	375	—	378	6.8	600	10.5	—	—
100	65.0	375	45	377	7.1	442	8.1	—	12
210	86.8	375	26	367	7.0	378	6.1	2.7	3
280	9.20	375	18	362	5.9	350	5.5	—	5

polymers having $[\eta] > 0.2$. The intrinsic viscosities were calculated from 3–4 measurements in tricresol at 25°C at concentrations of 0.3 to 0.9 g/dl.

Deamination of polymers. The participation of primary amino groups in the total content of bases in the polymer was determined from the decrease in bases during the deamination of polymers with nitrous acid¹⁴ (4 h of reaction of the sample with a 0.1M freshly prepared NaNO_2 solution in a 0.1M aqueous acetic acid at 80°C).

RESULTS AND DISCUSSION

Carboxylic Groups

In the polymerizations of lactams initiated at 230°C under anhydrous conditions with carboxylic acids the content of carboxylic groups in the polymerization products decreases (Tables I–III and Fig. 2). Under comparable concentrations of lauric acid the decrease in carboxylic groups in the polymerization of all lactams under investigation is roughly the same (Tables I–III). The velocity of this decrease (c. 1% in 100 h) is much slower than for the hydrolytic polymerizate of caprolactam which is c. 100 times faster⁶ than the results reported here); in the hydrolytic polymerizate the carboxylic groups are present as anions ($-\text{COO}^-$) or ammonium salt ($-\text{COO}.\text{NH}_3-$) which apparently are more readily decarboxylated than the free carboxylic groups ($-\text{COOH}$).

In the polymerization of caprolactam initiated with phenylacetic acid the carboxylic groups disappeared ten times faster than in the polymerizations initiated with the other acids (Fig. 2). Derivatives of phenylacetic acid are known to be thermally less stable than similar derivatives of n-alkanecarboxylic acids. The decay of carboxylic groups goes on even when there is no more free phenylacetic acid present in the reaction mixture at a concentration perceptible by the analytical method used (Table II). This means that the phenylacetamide groups in the polymer participate in the decay of the carboxylic groups.

The content of the carboxylic groups in extracted polymers in the initial stage of the polymerization is much lower than corresponds to the incorporated acid (Tables I–III), obviously as a consequence of a large amount of soluble linear oligomers (Table I). With increasing molecular weight of the polymer the portion of carboxylic groups passing into the extract decreases and their loss becomes prevalent owing to degradation reactions. This phenomenon is particularly pronounced in polycaprolactams prepared with phenylacetic acid. Such polymers always contain more phenyl than carboxylic groups; after a long polymerization time the extracted polymer contains almost all phenyl groups added at the beginning of polymerization while the content of carboxylic groups is considerably lower (Table II). The results described above indicated that the decay concerns rather the carboxylic groups in the polymers than in the non-incorporated molecules of acids.

TABLE II

Polymerization of Caprolactam Initiated with Phenylacetic Acid at 230°C
 Meaning of symbols see Table I, [P] content of phenyl groups (mmol/kg).

Time, h	ΔL	$[I]_0$	[I]	$[A]_n$	$[B]_n$	$[A]_e$	$[B]_e$	$[P]_e$
60	13.2	52	—	—	—	366	36	382
52	4.8	60	1.5	54.0	5.2	833	10	910
92	10.3	60	0	50.0	10.2	370	50	450
167	69.3	60	0	41.2	20.8	53	20	90
39	27.6	288	—	—	—	645	5	700
39	34.2	294	—	—	—	606	8	655
52	6.7	62 ^a	2.0	56.5	8.6	725	38	807
92	19.8	62 ^a	0	54.0	13.7	250	39	290
167	75.1	62 ^a	0	44.6	19.4	54	17	80

^a With 2.6 mmol/kg octylamine added.

TABLE III

Polymerization of Lactam Initiated with Lauric Acid at 230°C

Meaning of symbols see Table I, molecular weights M_c , M_A , M_{AB} calculated from the conversion of initiator and lactam (M_c), acid groups content (M_A) and from the sum of acid and basic groups (M_{AB}) are defined in the Experimental; concentration of lauric acid was in all cases not detectable by the analytical methods used.

Time, h	ΔL	$[I]_0$	$[A]_n$	$[B]_n$	$[A]_e$	$[B]_e$	$[NH_2]_e$	M_c	M_A	M_{AB}
Enantholactam										
239	82.8	72	65.5	6.6	79	7.1	4.2	11 500	12 700	11 600
Capryllactam										
20	24.4	66	62.4	3.9	235	13.9	7.0	3 800	4 250	4 000
166	96.9	66	62.8	2.9	55	3.1	1.6	14 600	18 150	17 150
Laurolactam										
20	5.7	65	61.9	0	715	2.6	2.6	1 060	1 400	1 390
48	13.1	65	63.2	0	425	1.2	—	2 200	2 350	2 340
120	25.0	65	62.6	0.4	230	1.6	1.6	3 620	4 300	4 150
238	41.9	65	60.1	0.4	140	0.8	0.8	5 540	7 100	7 050

Basic Groups

Although the polymerizations were initiated with carboxylic acids under anhydrous conditions, basic groups were formed in all cases (Tables I–III). The amount of basic groups in the case of lauro lactam was lower by an order of magnitude than in the case of the remaining lactams under study; in lauro lactam polymers, all bases were found

TABLE IV

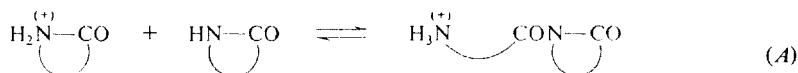
Molecular Weights of Polycaprolactams Prepared by Polymerization with n-Alkanecarboxylic Acids at 230°C

Meaning of symbols see Table I and Experimental.

Time, h	$[I]_0$	M_c	M_A	M_{AB}	M_V
Caproic acid					
60	60 ^a	—	1 820	1 790	1 400
52	66	1 200	1 410	1 350	1 200
92	66	1 500	1 540	1 480	1 400
190	66 ^b	5 600	5 900	5 400	5 250
Lauric acid					
98	90	1 840	2 120	2 020	1 850
238	90	7 000	7 800	7 100	7 500
32	400	700	570	570	700
64	400	1 160	1 030	1 020	1 200
N-Caproyl-6-aminocaproic acid					
65	100	—	2 250	2 120	2 400
239	100	—	8 000	7 400	6 700
10	375	—	800	795	600
12	375	600	840	835	650
16	375	720	1 000	990	770
24	375	—	1 120	1 100	800
30	375	980	1 220	1 200	960
40	375	1 220	1 320	1 300	1 200
44	375	—	1 350	1 330	1 340
64	375	—	1 660	1 640	1 530
100	375	2 160	2 260	2 200	2 150
210	375	2 500	2 640	2 600	2 240
280	375	2 600	2 860	2 800	2 380

^a $M_0 = 1\,350$; ^b $M_0 = 5\,500$.

to be represented by primary amino groups. Blank tests without initiator showed that these groups could be formed by traces of water only in the case of lauro lactam. The amount of bases formed in the blank tests was very low and was roughly the same for all lactams investigated in this work. Thus, in the polymerization of capro-, enantho-, and capryllactam the bases must have been formed prevailingly by side reactions. It was established, moreover, that for these poly lactams the primary amino groups represent only one part of the basic groups detected, and also that unlike poly lauro lactam one part of these primary amino groups disappears in the course of further polymerization (Tables I and III). Amino groups can also be formed by disproportionation reaction between the protonized and neutral lactam⁸:



In the cationic polymerization of lactams initiated with hydrogen chloride this reaction is immediately followed by side reactions by which the amino groups are transformed into amidine groups^{16,17}. Similar reactions can obviously proceed also in polymerizations initiated with carboxylic acids. The velocity of formation of basic groups in the polymerizations of capro-, enantho-, and capryllactam was the higher the higher the velocity of decay of carboxylic groups (Tables I–III, Fig. 2). It seems clear therefore that the formation of basic groups is at least partly related with the degradation reactions^{6,15}.

TABLE V

Molecular Weights of Polycaprolactams Prepared by Polymerization with Phenylacetic Acid at 230°C

Meaning of symbols see Table I and Experimental.

Time, h	[I] ₀	M _c	M _A	M _{AB}	M _P	M _V	M ₀
60	52	—	2 730	2 500	2 620	2 420	2 400
52	60	960	1 200	1 170	1 100	1 000	—
92	60	2 300	2 700	2 380	2 220	2 350	—
167	60	11 800	18 850	13 700	11 100	12 000	11 800
39	288	—	1 550	1 540	1 430	1 460	1 450
39	294	—	1 650	1 630	1 530	1 640	1 600
52	62 ^a	1 200	1 380	1 220	1 240	1 100	—
92	62 ^a	3 300	4 000	3 460	3 400	3 100	2 900
167	62 ^a	12 700	18 500	14 000	12 500	14 000	—

^a With 2.6 mmol/kg octylamine added.

Molecular Weights

The molecular weights of polymers, M_A , calculated from the content of the carboxylic groups in polymers were mostly higher than the theoretical values M_c (Tables III–V). The real molecular weights of caprolactam polymers determined viscometrically, M_v , or osmotically, M_0 , prove that the molecular weights M_A calculated from the content of carboxylic groups do not reflect the actual state. The M_v and M_0 values approach rather M_c , which confirms that the carboxylic groups disappear only after they had been incorporated into the polymer phase. The majority of the polymer molecules have obviously the $R_1 \sim \text{COOH}$ structure (R_1 is the neutral residue of the initiator $R_1\text{COOH}$). Besides these molecules the polymers also contain the $\text{NH}_2 \sim \text{I}$ molecules (I being the acyllactam groups), and molecules containing other basic, probably amidine groups, as well as neutral endgroups due to decarboxylation.

If the carboxylic groups disappear during the polymerization owing to the decarboxylation reaction¹⁵, the likeliest structure of the residue R is the methyl group. The concentration of the methyl groups is so low, however, that it could not be perceived by NMR. The carboxylic groups can also disappear by a reaction with formation of 3-oxoamide¹⁸ and 1,11-diacylamino-6-undecane¹⁵ units.

The real molecular weights M_v and M_0 are closest to M_{AB} (Tables IV and V) which includes macromolecules of the $R \sim \text{COOH}$ and $\text{NH}_2 \sim \text{I}$ type and does not include only those macromolecules which have lost their carboxylic group. In the polymerization initiated with n-alkanecarboxylic acids their amount can be neglected. Only with phenylacetic acid as initiator, when the deficit in the carboxylic groups is high, do the real molecular weights approach rather the M_p values (Table V).

Thus, the content of the carboxylic groups in the extracted polymer does not lead to unambiguous conclusions about the kinetics and mechanism of polymerization with carboxylic acids in an anhydrous medium. In the initial stage of polymerization the carboxylic groups present in the high polymer fraction are not equal to the incorporated initiating acid owing to the large amount of soluble linear oligomers. During the following long polymerization period the content of carboxylic groups in the polymer varies because of the degradation reactions. These changes are much pronounced in polymerizations with less stable acids, such as *e.g.* phenylacetic acid.

Hence, standard caprolactam polymers for the calibration of the viscosity-molecular weight relationship from the endgroup content can be prepared by the polymerization initiated with carboxylic acids under anhydrous conditions only at rather short polymerization times (up to 100 h at 230°C) and with n-alkanecarboxylic acids as initiators. An easier route for the preparation of such polymers over a sufficiently wide range of molecular weights is hydrolytic polymerization which proceeds faster, so that the extent of degradation reactions is smaller.

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