

POLYMERIZATION OF N-METHYLCAPRYLLACTAM WITH ACIDS, WATER, AMINES, AMINE SALTS AND ACID CHLORIDES

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During the polymerization of N-methylcapryllactam the initiation activity of the compounds investigated decreases as follows: anhydrous hydrogen chloride > carboxylic acid chlorides > > aliphatic amine hydrochlorides > 85% phosphoric acid > carboxylic acids \approx amino acids \approx \approx water. Hexamethylenediamine was practically inactive as catalyst, which suggests that the noncatalyzed aminolysis of N-methylcapryllactam and probably also of unsubstituted lactams proceeds only very slowly. From end group determination, a relationship $[\eta] = 2.34 \cdot 10^{-4} M_n^{0.78}$ (in propyl alcohol) or $[\eta] = 2.92 \cdot 10^{-4} M_n^{0.78}$ (in propyl alcohol containing 1% of acetic acid) has been derived for unfractionated polymers.

It is known¹ that substitution at the nitrogen atom reduces the polymerizability of lactams much more than substitution at the carbon atoms of the ring. The main reason consists in the fact that N-substitution removes the *cis*-character of the amide group in the lactam, which in turn reduces the heat of polymerization by approximately 1.4 kcal/mol, *i.e.* by the difference in the enthalpies of the *cis*- and *trans*-conformation of the amide bond². This is why only N-substituted lactams derived from more strained rings can be polymerized. So far, only the polymerizability of the four-³ and eight-membered¹ N-substituted lactams has been confirmed, while no such proof exists for the five- to seven-membered rings. The data on the reaction mechanism of the polymerization of N-substituted lactams are very scarce and it has been suggested that their polymerization proceeds by the same mechanism as that of unsubstituted lactams^{1,3}. Owing to the absence of the hydrogen atom on the nitrogen atom, as well as for steric and structural reasons it may be expected that the initiation, polymerization, and side reactions proceed differently or in a different ratio than in the case of lactams with an unsubstituted amide group.

It has been the objective of this paper to verify the activity of a number of initiators which may aid to determine the main types of reactions occurring during the polymerization of N-substituted lactams. For this purpose, we chose N-methylcapryllactam (1-methyl-1-aza-2-cyclononane), for which one may expect both a sufficient polymerization rate and a high equilibrium conversion.

EXPERIMENTAL

Compounds Used

N-Methylcapryllactam (I) was obtained similarly to N-methylcaprolactam⁴. A solution of 1080 g (7.65 mol) of capryllactam and 1057 g (8.38 mol) of dimethyl sulphate in 2500 ml of benzene was refluxed 46 h. On decomposition of the reaction mixture with a concentrated solution of potassium carbonate, 845 g (71%) of 2-methoxy-1-aza-1-cyclononene (b.p. 82–86°C/0.5 Torr) and 30 g of I were obtained by distillation. A benzene solution of the lactim ether was boiled (15 h) in the presence of dimethyl sulphate (1%), and I was collected as the fraction distilling at 106–109°C/2 Torr during the subsequent rectification; the total yield of I was 52% (related to the starting lactam). According to gas chromatography, the product was free from the starting lactam and contained less than 0.001% of water (by coulometric titration). For C₉H₁₇NO (155.2), calculated: 69.63% C, 11.04% H, 9.02% N; found: 69.81% C, 11.25% H, 9.14% N.

N-Methylcapryllactam hydrochloride (II) was obtained by introducing 9 g of anhydrous hydrogen chloride into a solution of 5 g of I in 130 ml of anhydrous ether at 0°C. On evaporation of the solution to 90 ml at 100 Torr and cooling to –30°C crystalline II precipitated. After filtration, washing with dry ether and drying at 25°C/0.5 Torr, 3.42 g (56%) of II, m.p. 101–102°C was obtained. For C₉H₁₈NOCl (191.7), calculated: 56.39% C, 9.46% H, 7.30% N, 18.50% Cl; found: 56.58% C, 9.61% H, 7.08% N, 18.59% Cl (by titration with mercuric chloride).

N-Methyl-8-aminooctanoic acid (III): a mixture of 0.40 g of I in 10 ml of concentrated hydrochloric acid was heated to boil under a reflux for 26 h. On evaporation of water and the excess of hydrogen chloride at a pressure of 20 Torr the product was dissolved in 50 ml of water and hydrogen chloride was removed on a column with 20 ml of strongly basic anion-exchanger Dowex-1. After elution of III with 100 ml of 25% aqueous acetic acid, the eluate was evaporated to dryness, the dry residue was twice recrystallized from acetone–water–ethanol (6 : 3 : 1); yield of III 0.20 g (45%), m.p. 138.5–139.2°C. For C₉H₁₉NO₂ (173.3), calculated: 62.39% C, 11.05% H, 8.08% N; found: 62.08% C, 11.15% H, 7.97% N.

Hydrochlorides of caprolactam, butyl amine, dibutyl amine and triethyl amine were prepared similarly to II and (with the exception of caprolactam hydrochloride) were recrystallized from acetone or acetone–ethanol. 8-Capryllactam, m.p. 73–4°C (produced by BASF, Hoechst), phosphoric acid reagent grade, 85%, stearic acid, m.p. 70–71°C (acetone). The other compounds used were purified prior to use by distillation, sublimation, or crystallization.

Polymerization

The reaction mixture of 2–3 g of I and a chosen amount of initiator was degassed (at –78°C) in an ampoule or a dilatometer and on sealing of the reaction vessel (nitrogen atmosphere, moisture 3–4 p.p.m.) was heated to a chosen temperature (Tables I, II). During dilatometric measurements the temperature was maintained constant within ±0.03°C and the volume was read off with an accuracy of ±0.0005 cm³ at an overall contraction of 0.05–0.1 cm³. Parallel experiments carried out in ampoules confirmed that the polymer content throughout the polymerization process is proportional to the contraction. The ratio of the volumes of the gaseous and liquid phases in dilatometers was 0.1–0.3 and in the ampoules it was approximately unity.

Analytical Procedures

The concentrations of the monomer in the polymerization product were usually determined by GLC of the solution (0.6–1 μl) of 50 mg of the polymerizate in 2.5 ml of a propanolic solu-

tion of N-methylcaprolactam (0.5%) and sec-butyl amine (0.1%) (Perkin-Elmer F-11 apparatus with a flame ionization detector, 1 m column with 10% of poly (ethylene adipate) on Chromosorb W, injection temperature 230°C); at 155°C the retention times of N-methylcaprolactam (internal standard) and monomer were respectively 7 and 15.5 min (response constant $0.934 \pm \pm 0.006$). The mean error of monomer determination from three measurements was 2.5%. The concentration of the polymer, $p = 100(M_0 - M)/M_0$, where M_0 and M are the initial and actual concentrations of the monomer respectively.

The polymer content of some samples was determined by distillation or extraction. By heating 0.2 g of the sample to 155°C/0.2 Torr a constant weight was attained within five hours, but according to gas chromatographic data the sample still contained about 1% of the monomer. During the extraction of the reaction products with water (8–12 h at 80–90°C with 4 . 100 ml water/g of product) a fraction of the oligomers is also extracted, and the polymer content is lower by 0.5–7% compared with p calculated from GLC data. The extracted polymers were dried at 50°C/10–20 Torr 12 h and then at 100°C/1 Torr for 24 h.

The content of acids and bases was determined by conductometric titration in 10–15 ml of propanol-water (95 : 5); the weighed amounts were chosen so as to make the consumption of 0.1M-HCl or NaOH (aq.) 0.015–0.025 ml.

Reduced viscosities of 0.2–1.5% polymer solutions or solutions of the polymerization products in propanol (or in propanol with 1% of acetic acid) were measured at 25°C in Ubbelohde's viscometer (capillary 0.7 mm); the solutions were thermostated 20 min/50°C before measure-

TABLE I

Hydrolytic Polymers Prepared at 250°C

t Time (in h), p polymer yield (in %) determined by extraction with water, [A] concentration of acids and [B] concentration of bases in the extracted product; $[H_2O]_0$, [A] and [B] in mmol/kg.

$[H_2O]_0$	t	p	[A]	[B]	$[\eta]^a$	$[\eta]^b$	k_H^b
26.1	270	38.4	48.5	55.5	0.492	—	—
38.6 ^c	250	90.7	31.5	34.5	0.741	0.912 ^e	0.33
40.0	270	60.2	45	68.5	0.515	—	—
53.4	270	71.4	52.5	61	0.500	—	—
64.8	170	61.8 ^d	76 ^e	73 ^e	0.542	—	—
65.2	270	80.5	58.5	65	0.458	0.588 ^e	0.35
71.1	140	69.1 ^d	68 ^e	94 ^e	0.405	—	—
98.4	270	90.1	55	77	0.405	0.525	0.32
133.1	270	95.5	69	91	0.372	—	—
196.8	270	95.5	85	113	0.305	0.377	0.34
263.7	270	95.4	123	139	0.261	0.322	0.34
332.7	270	93.3	157	155	0.222	0.284	0.32
						0.268 ^e	

^a In propyl alcohol. ^b In propanol with 1% of acetic acid. ^c 270°C. ^d Determined by GLC (the experiments were not used to calculate the relationship $[\eta] - M_n$). ^e Determined in unextracted polymerizate.

ments. It was found that low amounts of the monomer do not affect the flow time. Polymer solutions density at concentration of 4 mg/cm^3 (0.814 g/cm^3) could be employed over the whole range of concentrations investigated here.

RESULTS AND DISCUSSION

Relationship between molecular weight and intrinsic viscosity. The knowledge of the molecular weight is important for the evaluation of the participation of the individual initiators and for the elucidation of the mechanism of their action. Owing to the expected relatively low molecular weights osmometry could not be used. Therefore, the relationship between intrinsic viscosity and molecular weight was determined from the concentrations of the end groups of hydrolytic polymers for which it may be assumed that each macromolecule has at its end one amino and one carboxy group. From the data for unfractionated polymers (Table I) the values of the constants K and α of Mark-Houwink's equation were calculated: $K = 2.34 \cdot 10^{-4}$ and $\alpha = 0.78$ for measurements in propyl alcohol and $K = 2.92 \cdot 10^{-4}$, $\alpha = 0.78$ for measurements in propyl alcohol containing acetic acid (1%). The increase in K due to the addition of acetic acid may be assigned to an increase in the volume of a partly drained coil by protonization of the amide groups.

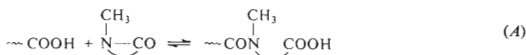
In the region of intrinsic viscosities below 0.6 the Huggins constant increases in propanol with decreasing molecular weight owing to increasing association of the end groups similarly to other polyamides^{5,6} (Table I). The presence of acetic acid depresses the association, so that the Huggins constant is independent of molecular weight also in the region of lower viscosities⁵ ($k_H = 0.34$).

Initiation with Carboxylic Acids and Hydrolytic Polymerization

Not only water, but also amino acids or salts of amines and carboxylic acids can be classified as hydrolytic initiators. In the case of initiation with water the growth centres arise by hydrolysis which is slower than polymerization and, therefore, the polymerization proceeds with an induction period (Fig. 1). Also the initiation with 6-aminocaproic acid exhibits a short induction period, because a part of the amino acid probably undergoes cyclization to yield caprolactam and water before the first lactam molecule is added. In the case of the polymerization initiated with N-methylaminooctanoic acid there is no induction period, since cyclization to form a nine-membered ring is very difficult and consequently cannot compete with the polymerization reaction.

While the polymerization of caprolactam initiated with amino acids⁷ is faster than that initiated with carboxylic acids⁸, the situation in the polymerization of N-methylcapryllactam is just the opposite (Fig. 1). In contrast with caprolactam, where the main growth reaction is an acid catalyzed aminolysis of the lactam⁹, the main

growth reaction during the polymerization of N-methylcapryllactam is the acidolysis of lactam



It seems remarkable that the initiation with carboxylic acids gives rise to polymers which besides carboxylic groups also contain a large amount of basic groups (Table II), so that the macromolecules are not terminated in a uniform way. Also hydrolytic polymers which should contain an equimolar amount of amino and carboxy groups often contain more basic than acidic groups (Table I). Apparently, at very long reaction times (at 250°C) degradation reactions become operative, which lead to a decrease in the content of the carboxy groups and to an increase in the content of the basic groups. Similar changes were observed for hydrolytic polycaprolactam¹⁰ heated to 270°C for long periods. Owing to the possible degradation, no unambiguous conclusions can be drawn from a comparison between the initial concentration of initiator, molecular weight and the content of the functional groups of the polymer. The degradation reactions are suggested by the fact that even in unextracted reaction products the content of acids does not correspond to the initial content of initiator (Table II). The comparison is further complicated by the fact that during the extraction of polymers also a considerable number of end groups may escape in the form of oligomers, particularly in the case of low-molecular weight polymers (Table I). The viscosity molecular weight of a polymer obtained with stearic acid (23000) is much higher than 1/A (13600). Apart from an incomplete incorporation of the initiator, this difference may be due to the condensation of macromolecules or to a different molecular weight distribution compared to the hydrolytic polymers. Also for polymers obtained with 6-aminocaproic acid the molecular weight calculated from the intrinsic viscosity is higher than that calculated from the content of the amino and carboxy groups.

Cationic Polymerization

Hydrochlorides of lactams and amines are typical cationic initiators of the lactam polymerization. The initiation reaction of unsubstituted lactams consists in the formation of N-(ω-aminoacyl)lactam^{11,12}; the growth then proceeds both by bimolecular aminolysis of the acyllactam group¹² and by acid catalyzed addition of lactam (or protonized lactam) onto the amino group¹¹⁻¹³. In the case of N-substituted lactams no acyllactams can be formed, and the only nucleophile capable of acylation with protonized lactam is the anion of the initiating acid



A study of this reaction is the subject of a forthcoming paper¹⁴ from which it follows that the main growth reaction during the initiation with hydrogen chloride is the bimolecular condensation of the amine and carbonylchloride group. The chain growth by the addition of lactam to acyl chloride^{15,16} (Fig. 2) is slower. The acid catalyzed addition of lactam to the amino group is very slow (Fig. 2 curve δ); in contrast with the polymerization of unsubstituted lactams it is not important in the polymerization of N-substituted lactams initiated with hydrogen chloride.

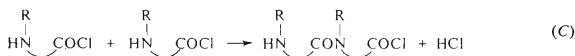


TABLE II

Polymerization with Various Initiators at 250°C

t Time (in h), $p = 100(M_0 - M)/M_0$, where M is the chromatographically determined monomer content, $[\eta]$ intrinsic viscosity (in dl/g), \bar{P}_n number average degree of polymerization, $[A]$ and $[B]$ content of acids or bases in unextracted polymer product; $[I]_0$, $[A]$ and $[B]$ in mmol/kg.

Initiator	$[I]_0$	t	p	$[\eta]^a$	\bar{P}_n	$[A]$	$[B]$
Phosphoric acid 85%	44.0	120	99.9	—	—	—	—
Phosphoric acid 85%	64.5	140	99.8	0.453	104	164	0
Stearic acid	58.1	140	67.5	0.596	148	74	48
Stearic acid	67.2	170	72.5	0.507	120	79	29
Phenylacetic acid	63.3	156	71.1	0.386	85	57	25
Benzoic acid	62.7	156	70.9	0.419	94	72	18
6-Aminocaproic acid	58.1	140	61.1	0.397	88	56	73
6-Aminocaproic acid	75.9	170	67.5	0.518	124	79	75
8-Methylaminoctanoic acid	64.4	181	76.5	0.521	125	31	65
N-Methylcapryllactam hydrochloride ^b	62.1	6	100.0	1.682	559	64	0
N-Methylcapryllactam hydrochloride	70.5	20.5	100.0	0.163	28	54	99
Caprolactam hydrochloride ^b	64.3	6	100.0	1.031	299	74	0
Caprolactam hydrochloride	56.7	140	100.0	0.095	14	113	61
Hexamethylenediamine	31.6	140	2.9	—	—	5	91
None	0	150	2.5	—	—	—	—
Butylamine hydrochloride ^b	63.6	113	86.5	0.386	85	—	—
Dibutylamine hydrochloride ^b	63.3	113	93.5	0.501	118	—	—
Triethylamine hydrochloride ^b	62.5	10	18.0	1.540	499	—	—
Butyryl chloride ^b	60.6	13.5	99.8	0.679	175	—	—
Benzoyl chloride ^b	64.1	10	100.0	0.635	160	—	—
Aluminium bromide	34.0	140	100.0	0.059	8	176	160
Triphenylmethylsodium + N-Methylaniline	87.0	23	0.0	—	—	—	—

^a In propyl alcohol. ^b Temperature 200°C.

TABLE III

Acid Catalyzed Aminolysis as Growth Reaction During the Polymerization of Caprolactam (C) and N-Methylcapryllactam (N)

ρ maximum polymerization rate (% conversion/h).

Initiator ^a	Temperature, °C	ρ_C	ρ_N
Primary amine hydrochloride	200	55	3.9
Water	250	32	0.65
ω -Amino acids	250	44	0.55–0.65
Phosphoric acid (85%)	250	56	4
Carboxylic acids of the aliphatic series ^b	250	1–3	0.8

^a $[I]_0 = 64 \text{ mmol/kg}$, ^b acidolysis.

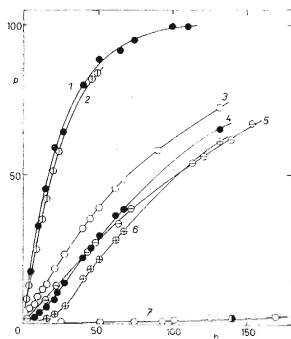


FIG. 1

Polymerization at 250°C

Initiator (mol.%): 1 85% phosphoric acid (0.7), 2 caproic acid (3.6), 3 stearic acid (1.05), 4 6-aminocaproic acid (1.2), 5 N-methyl-8-aminooctanoic acid (1.0), 6 water (1.0), 7 hexamethylenediamine (0.5; ●) and without initiator (○); polymer yield (in %) determined by extraction with water.

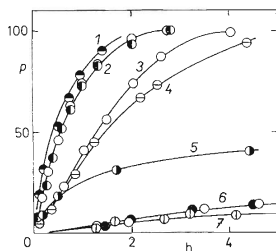


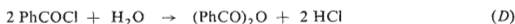
FIG. 2

Polymerization at 200°C

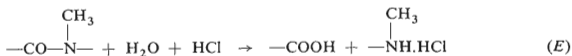
Initiator (mol.%): 1 benzoyl chloride (2.0) + water (0.5), 2 caprolactam hydrochloride (1.0; ○) and N-methyl-8-capryllactam hydrochloride (1.0; ●), 3 benzoyl chloride (2.0), 4 butyryl chloride (0.95), 5 N-methyl-8-capryllactam hydrochloride (1.0) + water (0.6), 6 butylamine hydrochloride (1.0; ●) and di-butylamine hydrochloride (1.0; ○), 7. triethylamine hydrochloride (1.0; ⊙). Meaning of ρ as in Fig. 1.

At higher temperatures (250°C) with hydrochlorides of lactams as initiators the molecular weight decreases much below a value corresponding to $1/[I]_0$ after rather long reaction periods; the concentration of the acidic or basic groups exceeds the initial concentration of initiator, so that consecutive reactions obviously become already operative (Table II).

The polymerization initiated with chlorides of acids is markedly accelerated by the addition of water ($[-COCl] > [-H_2O]$). In this case, the $-COCl$ group is hydrolyzed with formation of hydrogen chloride, which is a more active initiator than acyl chloride (Fig. 2). The increase in the polymerization rate due to the addition of water with benzoyl chloride as initiator (Fig. 2, curves 1 and 3) corresponds to the formation of 2 mol HCl per 1 mol of added water:



However, the addition of water slows down the polymerization initiated with N-methylcapryllactam hydrochloride (Fig. 2). The hydrolysis of the lactam or polymer amide group gives rise to strongly basic amino groups which considerably reduce the concentration of hydrogen chloride (lactam hydrochloride):



The polymerization activity of the end groups thus formed is incomparably lower (Table II, Figs 1 and 2).

On the average, one macromolecule is formed per one molecule of initiator by the polymerization with hydrochlorides of primary or secondary amines. On the other hand, much fewer chains are formed in the case of triethylamine hydrochloride (Table II), since the tertiary amine cannot act as the growth centre and the initiation with hydrogen chloride (or with lactam hydrochloride I) is very slow because of the very small dissociation of amine hydrochloride (Fig. 2, curve 7).

Other Initiators

85% Phosphoric acid is an effective initiator and the polymerization is of the first order with respect to monomer. For equimolar water and phosphoric acid concentrations (177 mmol/kg) it was found that at 230–280°C

$$-d[M]/dt = k_p[\text{H}_3\text{PO}_4]^a [\text{H}_2\text{O}]^b [M] = k[M], \quad (I)$$

where

$$k = 1 \cdot 10^7 \exp(-27000/RT) (\text{s}^{-1}).$$

Aluminium bromide is also a very effective initiator, while with hexamethylenediamine the polymerization proceeded as slowly as without initiator (Table II, Fig. 1). Thus, noncatalyzed aminolysis is not important in the polymerization of both substituted and unsubstituted lactams (for caprolactam, the catalytic effect of the amide proton is operative⁸). For N-substituted lactam, not even the acid catalyzed aminolysis is an important reaction, or is not a growth reaction at all, as has been found in the case of initiation with amino acids. This also follows from a comparison of the activity of other initiators in the polymerization of N-methylcapryllactam and caprolactam^{8,17-19} (Table III).

Basic compounds of the triphenylmethylsodium type are inactive (Table II), since there is no nucleophilic attack from the part of the anion on the carbonyl group.

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