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Some Remarks on the Cationic Polymerization of Caprolactam

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Synopsis

The cationic polymerization of caprolactam under anhydrous conditions above the polymer melting point with caprolactam hydrochloride as initiator is examined. Analytical and polymerization results under different conditions and with the addition of several substances are compared with the existing theories and discussed.

In addition to the so-called hydrolytic polymerization of caprolactam (CL), which has found wide industrial applications, the anionic anhydrous process, the mechanism of which has only recently been elucidated, has also found limited industrial applications.

On the other hand, the anhydrous cationic polymerization, first disclosed in 1959 by Kruissink and Van der Want[1] and subsequently studied in greater detail by Reinisch and Jaeger,[2] Rothe et al.,[3] Doubravszky and Geleji[4] and Schlack,[5] has not shown promise for industrial application.

Various materials have been suggested as initiators, including HCl,[1-4] HBr,[6] *p*-toluensulfonic acid,[1,2] β-naphthalenesulfonic acid,[3] $HClO_4$,[1] H_2SO_4 and H_3PO_4,[3] the monoamide of sulfuric acid,[1] hydrochlorides of different amines such as hexamethylendiamine[1] and cyclohexylamine,[2] and salts of acidic nature, such as NH_4Cl, NH_4BF_4, and $(NH_4)_2SO_4$.[1]

There has been emphasis only on the HCl-catalyzed polymerization, but the mechanism has not been completely elucidated. The present work was carried out in order to obtain more information about this mechanism.

EXPERIMENTAL

Materials

Caprolactam (Montecatini Edison) was further purified by crystallization from acetone, followed by drying at 60°C for 48 hr under 20 mm Hg. The water content was determined by the Karl Fischer method.

Caprolactam hydrochloride was prepared by bubbling anhydrous gaseous HCl in an anhydrous solution of CL in diethyl ether and was subsequently crystallized from acetone, mp 157–158.5°C.

Polymerizations

Reactants were charged in Pyrex glass ampoules (17 mm diameter) which were charged under nitrogen as already described[7] and subsequently sealed under vacuum. Polymerizations were effected in an oil bath regulated at ±1.5°C.

Conversion

Conversion was determined by grinding 5 g of polymer and subjecting it to Soxhlet extraction for 16 hr with methanol. After drying at 85°C under vacuum for 8–10 hr and weighing, it was assumed that the insoluble material was polymer. The extracting methanol was then evaporated and the residue extracted with diethyl ether. It was then assumed that the ether-soluble material consisted of monomer and insoluble oligomers.[8]

Relative Viscosity

The relative viscosity of 1 g of dried polymer, the residue from methanol extraction, which was dissolved in 100 ml of 95.6% H_2SO_4 at 20 ± 0.1°C was measured.

Polymerization of *p*-Aminobenzoylcaprolactam Hydrochloride

The polymerization was carried out at 250°C for 30 min under water pump vacuum in a Pyrex glass ampoule, 17 mm in diameter, equipped with a cooling trap for collecting the volatile products. After cooling, the contents of the trap were analyzed and identified as caprolactam hydrochloride by thin layer chromatography and infrared spectroscopy. The contents of the ampoule were ground to powder and subjected to Soxhlet extraction with methanol. The residue was characterized by infrared spectroscopy and intrinsic viscometry in 95.6% sulfuric acid at 20 ± 0.1°C in Ostwald viscometers.

Potentiometric Titrations

Potentiometric titrations were performed in trifluoroethanol as solvent. Basic and acid groups were determined with 0.02*N* aqueous HCl or NaOH solutions. Glass/calomel electrodes with an agar–agar KNO_3 bridge were used.

In the presence of free basic groups the initial potential was found in the range −40 to −120 mV and the neutralization point occurred at −180 to −200 mV. In the presence of strong acid groups, the initial potential was found in the range −280 to −240 mV; the neutralization point was at −180 to −200 mV.

The neutralization point for weak acidity was found at +10 to −10 mV.

We found that under these conditions the hydrochlorides of aminic terminal groups in the polyamides were not detectable.

Chlorides were determined in the same solution with 0.02*N* aqueous $AgNO_3$ solution and glass/Ag electrodes.

RESULTS AND DISCUSSION

Plots of conversion and viscosity of the resulting polymer versus time are given in Figures 1–3, for different temperatures and catalyst concentrations. This behavior is similar to that previously observed by other authors[1–3,9] who also used the dilatometric technique, however without any conclusive evidence due to the complexity of the reaction mechanism. The cationic polymerization shows a definitely slower rate than the hydro-

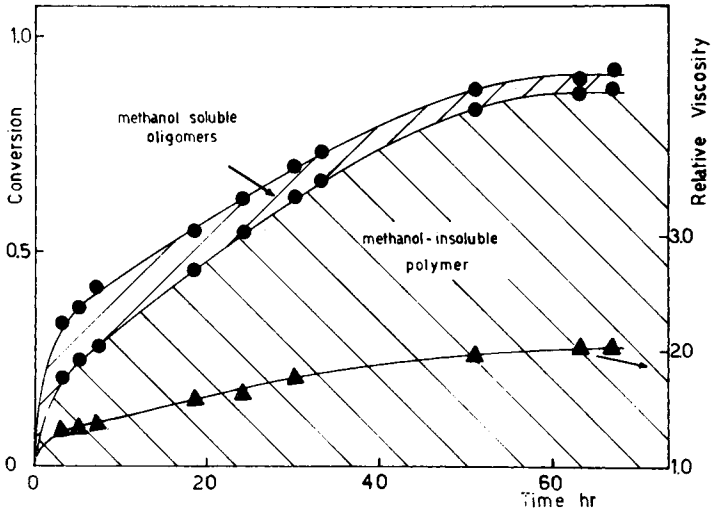


Fig. 1. Conversion and polymer viscosity vs. time for the polymerization of caprolactam initiated by caprolactam hydrochloride (1×10^{-2} mol/mol CL) at 250°C. Total conversion is expressed by the sum of methanol-insoluble polymer and methanol-soluble oligomers.

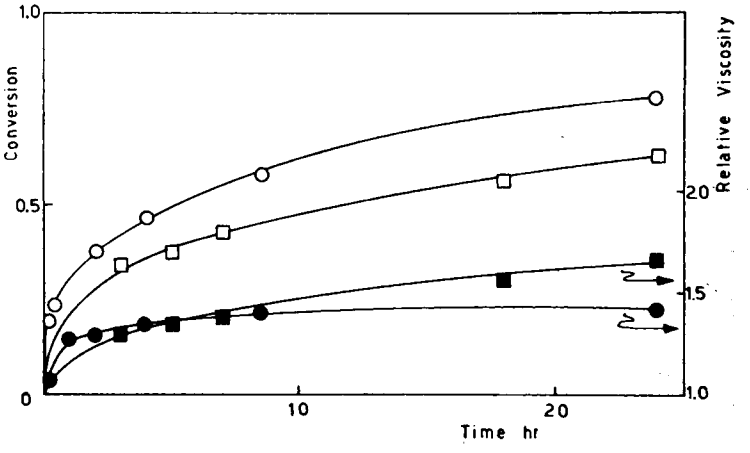


Fig. 2. Conversion (○, □) (methanol-insoluble polymer) and viscosity (●,■) vs. time at 250°C for two different initiator concentrations: (○) 2.5×10^{-2} mol/mol CL; (□) 1×10^{-2} mol/mol CL.

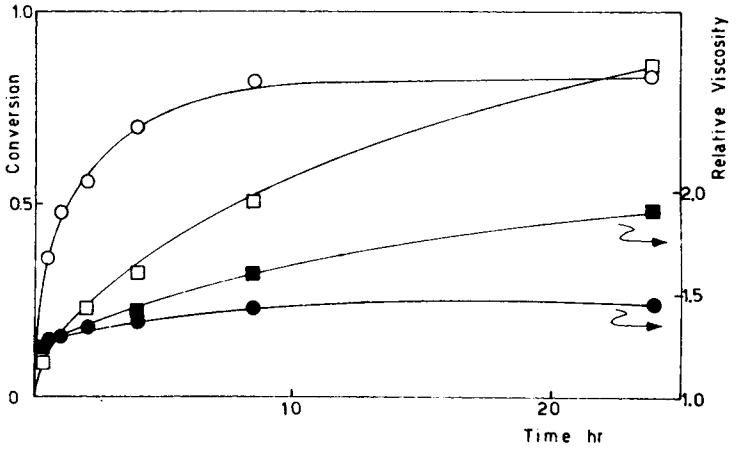
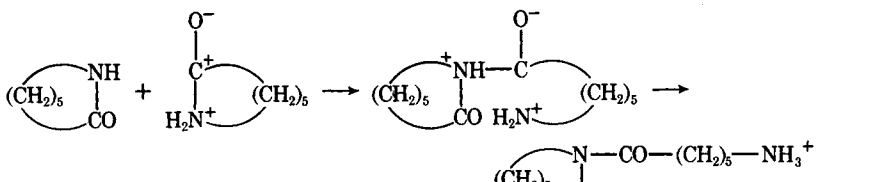


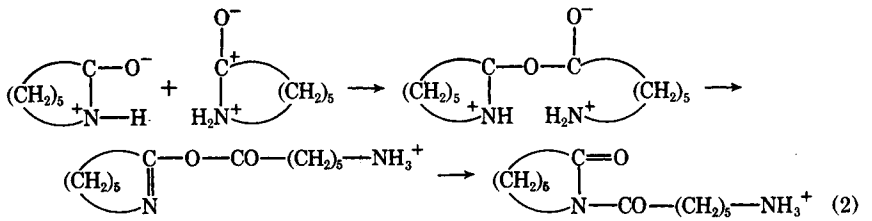
Fig. 3. Conversion (○,□) (methanol-insoluble polymer) and viscosity (●,■) vs. time at 275°C for two different initiator concentrations: (○) 2.5 × 10^{-2} mol/mol CL; (□) 1 × 10^{-2} mol/mol CL.

lytic and anionic processes at the same temperature and catalyst concentration. At the beginning of the polymerization the rate of conversion is relatively faster,[1] but it is very rapidly followed by a plateau in the conversion–time plot; this is especially evident if lower amounts of initiator are present. This behavior is shown in Figures 2 and 3 for runs with initiator concentrations of 1 × 10^{-2} and 2.5 × 10^{-3} mol/mol CL.

The first stage of the reaction is undoubtedly the formation of aminocaproyl caprolactam hydrochloride [eqs. (1) and (2)].



(1)

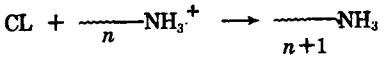


(2)

The formation of ϵ-aminocaproyl caprolactam was first hypothesized by Van der Want and Kruissink[1] and subsequently confirmed by Reinisch and Jaeger by both titration and infrared data[2] and by comparison with the synthesized product.[3]

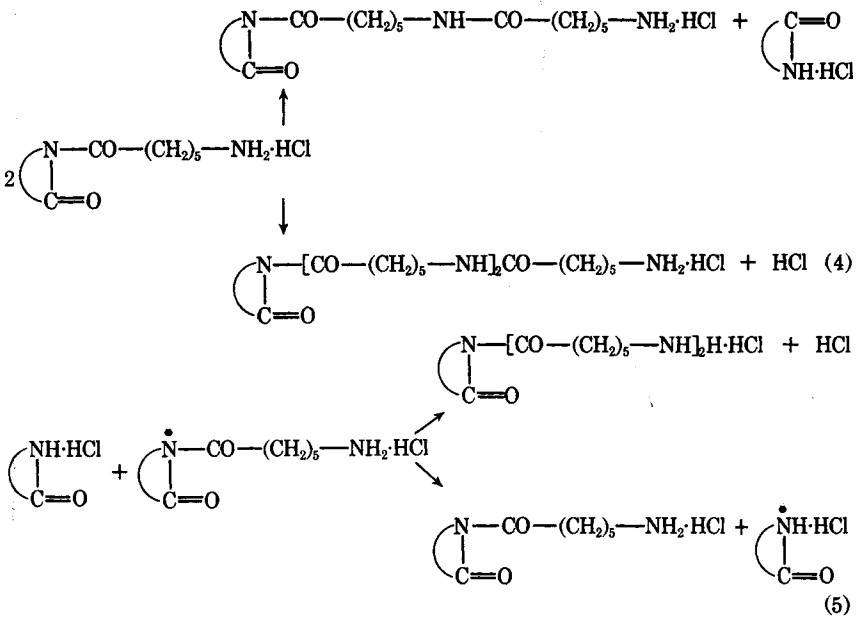
The nature of the propagation stage, on the other hand, has not been yet

clarified. Van der Want and Kruissink[1] and Burnett et al.[10] suggested the opening of the lactam cycle by the ammonium ion [eq. (3)].



(3)

However, Doubravszky and Geleji[4] have recently suggested a propagation mechanism involving an ammonium ion and an imidic group [eqs. (4) and (5)].

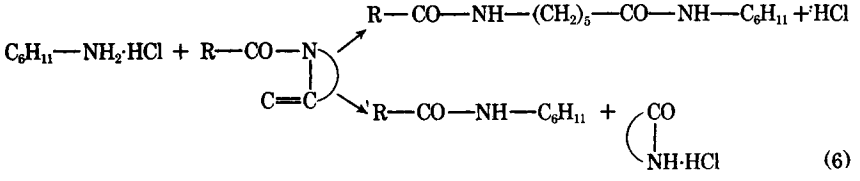


(4)

(5)

In support of this, Doubravszky and Geleji noted that the rate of polymerization of anhydrous HCl-catalyzed polymerization increased on addition of imide groups (acetyl caprolactam); moreover, the presence of strong acidity was detectable during the whole course of the reaction.

As a further support, Reinisch and Jaeger[11] have shown that the reaction between amines and hemicyclic imides (acyl caprolactam) is in accord with the mechanisn of Doubrovszky and Geleji [eq. (6)].



(6)

However, whatever the propagation mechanism, the formation of the plateau and the fast decay of the reaction rate suggest the existence of an alternative process which causes inactivation of the polymerization. This could be explained with the formation of amidine groups as chain ter-

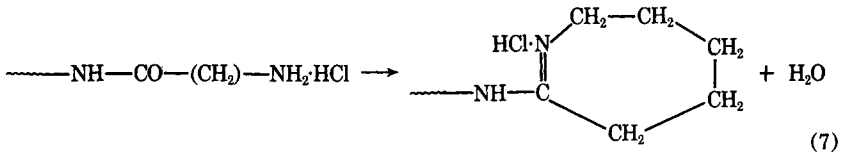
TABLE I
Titration of the Reaction Product of HCl-Catalyzed Polymerization of Caprolactam[a]

HCl, mol/mol CL	Temperature, °C	H_2O, ppm[b]	Time, min	Strong acidity, meq-%	Weak acidity meq-%	Weak acidity Theoretical, meq-%[c]	Free base, meq-%
0.04	250	<50	5	10.3	19.8	33.57	
			10	4.3	31.5		
			15	2.6	27.2		
			20	1.7	32.9		
			30	1.1	31.5		
			60	0.7	32.9		
			130	0.5	33.9		
			240	0.5	33.0		
0.04	275	600	5	3.8	14.3	23.67	
			15	0.5	14.3		
			30	0.5	21		
			120	0.5	22		
			510	0.5	21		
			1440	0.5	21		

0.025	250	<50	5	5.8	22		
			15	2.2	17.7		
			30	0.7	17.2		
			60	0.5	19.4	21.31	
			120	0.5	20		
			240	0.5	19.0		
			510	0.5	19.9		
			1440	0.5	19.5		
0.01	275	600	5	1.7	6.7		
			15	0.6	6.6		
			30	0.5	6.6	8.7	
			120	0.5	7.5		
			510	0.5	7.4		
			1440	0.5	6.1		
0.01	250		1800		7.98		0.95
			3060		7.30		0.87
0.02	250		1800		15.6		0.45
			3060		15.1		0.5

[a] Chloride values omitted since they equal the theoretical value in all cases.
[b] H_2O by Karl Fischer titration.
[c] Theoretical for added HCl.

minals, as postulated by Schlack,[5] with the concomitant evolution of water [eq. (7)].



(7)

The strongly basic amidine group (comparable to quaternary ammonium salts[12]) strongly bonds the hydrochloric acid catalyst, thus preventing further polymerization.

We have tried to clarify the polymerization mechanism by potentiometric titration of the reaction mixture. The data we obtained, which are given in Table I, are not comparable with the ones previously obtained,[1-3] where indicators were used. It is seen from Table I that, at the beginning of the polymerization, strong acidity (probably due to unreacted caprolactam hydrochloride) is detectable. This acidity rapidly decreases with polymerization time; however, it never completely disappears, except after a very long time, when traces of weak bases are found. Weak acidity, on the other hand appears at the beginning of the polymerization; it does not vary with time, within experimental error, and its value is very near to the amount of added HCl. This can be possibly explained by considering that all the previously discussed propagation mechanisms lead to formation of chains that bear terminal imido groups. It is known[2,13] that these groups hydrolyze with particular ease to give carboxyl groups and it is likely, therefore, that the former are hydrolyzed to weak acids even during the titration. The initial fast decrease in strong acidity is certainly to be attributed to the formation of aminocaproyl caprolactam hydrochloride. However, the persistence of traces of strong acidity is not attributable to ammonium ions (which are considered propagating centers by both mechanisms), as they are neutral under our titration conditions. It can be explained by an incomplete transformation of caprolactam hydrochloride to the initiator, if the propagation mechanism of Kruissink and Van der Want is valid; alternatively, a continuous re-formation of strong acidity (caprolactam hydrochloride), according to the propagation mechanism of Doubravszky and Geleji, can be considered. The presence of traces of free bases after a very long reaction time could be explained by hydrolysis of some cyclic amides due to the water evolved during amidine formation.

Confirmation that the propagation mechanism, at least in the first reaction stage, follows the Doubravszky and Geleji hypothesis, was obtained as follows. We synthesized *p*-aminobenzoyl caprolactam hydrochloride according to Rothe[14] and heated it in glass ampoules, under vacuum at ca. 250°C for 1 hr., the volatile products being collected in a trap. In the ampoule we obtained a polymeric mass, soluble only in concentrated sulfuric acid, with an intrinsic viscosity in this solvent of 0.6 at 20°C. The product decomposed at ca. 360°C without softening. Its

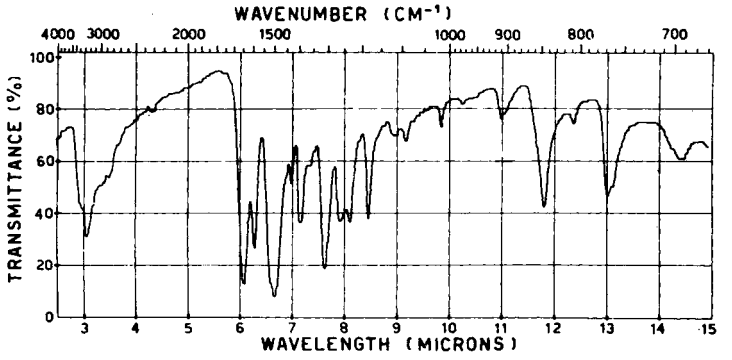
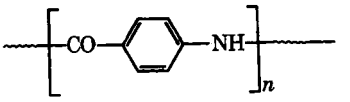


Fig. 4. Infrared spectrum of polymer from *p*-aminobenzoyl caprolactam hydrochloride.

infrared spectrum (Fig. 4) agrees with the constitution of a polymer having the structure I.[15]



I

The evolved product was identified as caprolactam hydrochloride by thin-layer chromatography and confirmed by infrared analysis. This shows that reaction takes place in agreement to the mechanism suggested by Doubravszky and Geleji. If the mechanism proposed by Kruissink and Van der Want were valid, no polymer would have been obtained.

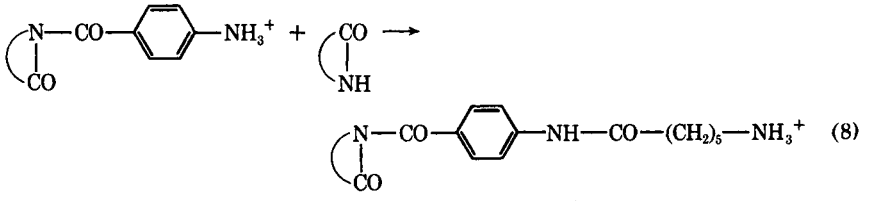
We have also carried out polymerizations with *p*-aminobenzoyl caprolactam hydrochloride (1×10^{-2} mol/mol CL) at 250°C as initiator. As far as the reaction rate is concerned, the results given in Table II show a behavior similar to that with HCl. It is remarkable that, on starting with a neutral material (under our titration conditions) strong acidity developed

TABLE II
Titration of the Reaction Products of the Polymerization of Caprolactam at 250°C Initiated by *p*-Aminobenzoyl Caprolactam Hydrochloride[a]

Time, min.	Conversion, %[b]	Relative viscosity	Titration, meq-%	
			Strong acidity	Weak acidity
10	10.2	—	1.2	6.5
20	16.5	—	0.8	5.7
30	17	1.24	0.3	6.2
60	19.1	1.26	0.1	7.1
120	24.6	1.20	0.0	7.8
240	27.6	1.32	0.0	7.8
420	35.1	1.33	0.0	8.5

[a] *p*-Aminobenzoyl caprolactam hydrochloride, 0.01 mol/mol CL; 0.6 meq-%.
[b] Methanol-insoluble polymer plus methanol-soluble oligomers.

during polymerization and subsequently disappeared, paralleling the behavior in Table I. Formation of strong acidity can only be explained with formation of caprolactam hydrochloride according to Doubravszky and Geleji. The above results seem to be in apparent contrast with the results of Rothe,[14] who, by reacting *p*-aminobenzoyl caprolactam at 190°C with caprolactam obtained (II), among other reaction products (where, however aromatic amines were absent),



(8)

II

indicating a reaction mechanism as proposed by Kruissink and Van der Want. This discrepancy could possibly be explained by the differences in experimental conditions.

The mechanism was investigated further by a few polymerizations in which equimolar amounts of various substances were added of the caprolactam hydrochloride catalyst (1×10^{-2} mol/mol CL) (Fig. 5). It is seen that, if water was added, a much faster process develops; this may be due to prevention of amidine formation. (Amidines have not been found in hydrolytic caprolactam polymerization, but only in the strictly anhydrous cationic polymerization.[16] It must be remembered that, due to the instability of imide groups in the presence of water, in this case only a propa-

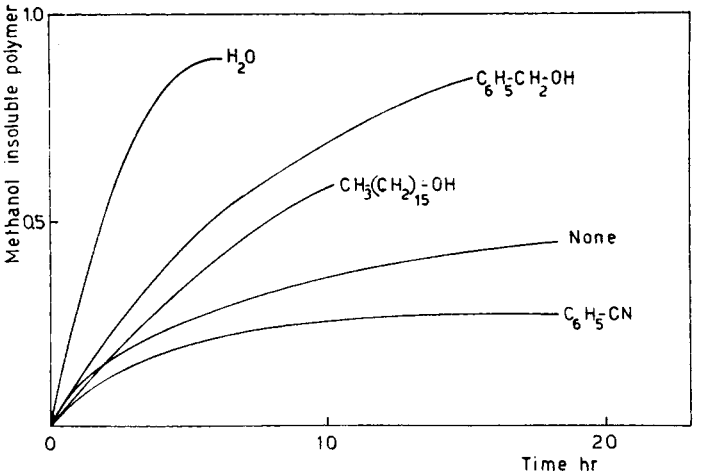


Fig. 5. Methanol-insoluble polymer vs. time in the polymerization of caprolactam at 250°C with caprolactam hydrochloride (1×10^{-2} mol/mol CL plus 1×10^{-2} mol/mol of various substances as indicated and water 2.5×10^{-2} mol/mol CL.

gation mechanism involving ammonium ions (Kruissink and Van der Want) should exist.

Acceleration effects were also obtained by the addition of alcohols which possibly, under the polymerization conditions, etherified, liberating water. On the other hand, retardation was obtained by addition of basic materials, such as benzonitrile; these may act, as amidines, possibly by capturing HCl.

It could be suggested, therefore, that the cationic polymerization of caprolactam initiated above the polymer melting point by small amounts of anhydrous hydrochloric acids, starts with the formation of ϵ-aminocaproyl caprolactam followed by a propagation mechanism involving ammonium ions and imide groups, according to Doubravszky and Geleji. The propagation is then blocked, or at least strongly retarded by amidine formation, which absorbs hydrochloric acid with simultaneous water evolution. The polymerization seems then to proceed by simple ammonium ion propagation, at least as the main mechanism, as in the classical hydrolytic process.

Work on the molecular weight distribution of the polymer is in progress and will be published later.

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References

1. G. M. Van der Want and Ch. A. Kruissink, *J. Polym. Sci.*, **35**, 119 (1959).
2. G. Reinisch and W. Jaeger, *Faserforsch. Textiltech.*, **13**, 79 (1962); *ibid.*, **13**, 161 (1962).
3. M. Rothe, G. Reinisch, W. Jaeger, and I. Schopov, *Makromol. Chem.*, **54**, 183 (1962).
4. S. Doubravszky and F. Geleji, paper presented at International Symposium on Macromolecular Chemistry, Prague 1965.
5. P. Schlack, paper presented at Intern. Chemiefaser-Symposium, Reutlingen-Stuttgart, Germany, 1965.
6. M. Rothe, *Makromol. Chem.*, **67**, 90 (1963).
7. G. B. Gechele and G. Stea, *Europ. Polym. J.*, **1**, 91 (1965).
8. F. Wiloth, *Makromol. Chem.*, **27**, 37 (1958).
9. S. Doubravszky and F. Geleji, *Makromol. Chem.*, **105**, 261 (1967).
10. G. M. Burnett, J. N. Hay, and A. J. MacArthur, paper presented at Symposium on the Chemistry of Polymerization Process, London, 1965; *Polymerization of Caprolactam. I. Initiation by Amines* Soc. Chem. Ind. Monograph No. 20, London, 1966.
11. G. Reinisch and W. Jaeger, *Faserforsch. Textiltech.*, **16**, 583 (1965).
12. H. A. Staab, *Einfuhrung in die theoretische organische Chemie*, Verlag Chemie, Weinheim, 1959, p. 638.
13. J. Sebenda and B. Mikulova, *Coll. Czechoslov. Chem. Commun.*, **29**, 738 (1964).
14. M. Rothe, H. Boenisch, and D. Essig, *Makromol. Chem.*, **91**, 24 (1966).
15. N. Yoda and Y. Matsubara, *J. Polym. Sci. A*, **2**, 253 (1964).
16. G. Falkenstein, Doktorarbeit, Technische Hochschule, Stuttgart, 1965.

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