POLYMERIZABLE LACTAMS

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INTRODUCTION

Since 1940, as I am told, Japanese chemists have been working in the field of Polyamide 6 and today Japan is the largest producer of polycaprolactam filaments and fibres in the world. When, nearly 43 years ago, I entered the artificial fibres industry with the aim of making silky filaments of cellulose acetate, Japanese silk was our ideal. Later on, the combination of silk with acetate yielded textiles of a very high aesthetic value. Thirty-seven years ago I tried, for the first time, to make a dyeable synthetic fibre containing amino groups and in this the chemical constitution of fibroin basically served as a model. Nobody, however, believed in a real success those days. So this premature work was merely regarded as a personal hobby.

By the end of the thirties lactams did not play any role in industrial chemistry and they did not seem to offer many interesting problems in the domain of scientific research as a class. This situation has been changed completely by two inventions originated practically at the same time. W. Reppe and his coworkers found a relatively cheap synthesis of α-pyrrolidone, starting from acetylene and formaldehyde via butyrolactone. They were able to show that the *N*-vinylated lactam was easily convertible into a very useful water soluble vinyl polymer. At the same time in the Berlin plant "Aceta" of the former IG-Farbenindustrie AG caprolactam and its higher ring homologues were found to be polymerizable.

It was W. H. Carothers who in his famous work on ring formation and polymerization for the first time made an extensive and critical investigation on the transformation of cyclic monomers with more than four ring atoms, especially those containing ester and acetal groups, into linear polymers. Typical compounds with oxygen as the hetero atom which proved to be polymerizable in the presence of appropriate catalysts were the six-membered esters trimethylene carbonate, ethylene oxalate, δ-valerolactone and the seven-membered heterocycles ε-caprolactone and tetramethylene formal.

POLYMERIZATION OF CAPROLACTAM

In the series of polymerizable heterocyclic compounds with exocyclic amide groups, Carothers[1] first mentioned the anhydrides of *N*-carboxy-α-amino-carboxylic acids, detected by H. Leuchs[2], but himself did no experimental work on this (later on) important field. In his comprehensive and now regarded as classical study of 1931 with the simple title "Polymerization"

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he pointed out that the lactams of γ-amino-butyric acid and of δ-amino-valeric acid, i.e. α-pyrrolidone and α-piperidone were completely stable substances, the indifferent piperidone being quite a contrast to the easily polymerizable oxygen isologue. In view of this striking difference Carothers accepted it as a fact without much hesitation, when he found together with G. J. Berchet[3], that the seven-membered ϵ-caprolactam was not polymerizable either, not even in the presence of catalysts. Unfortunately it is not known which substances the two Americans did try as possible reaction initiators, so we don't know why their experiments in 1931 failed.

It was, however, not this statement of Carothers and Berchet which finally led to the polymerization of caprolactam. When the critical experiments were carried out, we had only an abstract of Carothers paper, without any remark on the stability of the lactam. The real starting point was an observation made by us when we polycondensed the *N*-methoxy-carboxy-ϵ-aminocaproic acid prepared by acylation of the raw aminocaproic acid with methylchloroformate (*Figure 1*). This reaction led, probably with

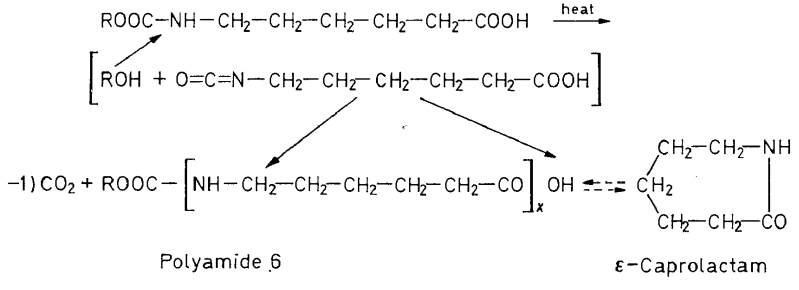


Figure 1. Polycondensation of urethane-*N*-ϵ-caproic acid

ϵ-isocyanatocaproic acid as an intermediate, directly to spinnable Nylon 6 together with a significant amount of caprolactam as an interfering by-product. Since the yield of lactam was not constant and varied with changing reaction conditions such as temperature and pressure we thought that an equilibrium had been set up with a possible isocyanate participation. Hence we concluded that caprolactam should be polymerizable at least in the presence of an appropriate initiator. The first such experiment in which ϵ-aminocaproic acid hydrochloride was used as a transamination catalyst, first as a source for a small amount of water to provide for the end-groups, and finally as a chain-length regulator, yielded a Polyamide 6, which, without further purification, could be spun to a highly elastic filament with a tenacity of 4·3 g/den after cold drawing (cf. *Figure 2*).

Instead of aminocaproic acid hydrochloride other hydrochlorides of amide-forming amines could be used. In this case the number of free carboxyl groups was drastically reduced or practically eliminated. This resulted in excellent melt-spinning properties. After extraction of the monomer and the low oligomers the regeneration of low-molecular substances went on much slower up to the equilibrium for a given temperature of the melt and for a sufficient low water content. As it was known from a study of aminocaproic acid derivatives, this recovery of monomeric lactam is predominantly

W. H. CAROTHERS
(Transformation of cyclic monomers into linear polymers, 1930–31)

By the courtesy of E.I. du Pont de Nemours and Co.

O. WALLACH
Nobel prize winner, 1910
(Synthesis of caprolactam from cyclohexanone, 1900)

By the courtesy of Chemische Berichte

the consequence of a combined ring-formation and splitting at the carboxyl end of the polymer chain. Besides the amine hydrochlorides anhydrous hydrogen chloride also was capable of initiating the polymerization of caprolactam. For reasons unknown at that time the hydrogen chloride initiated reaction did not yield good polymers and was therefore of no interest for commercial purposes.

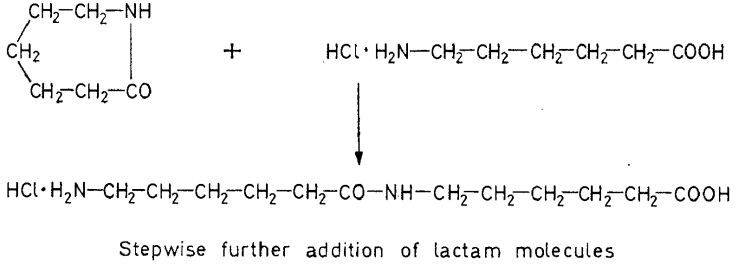


Figure 2. Polymerization of ϵ-caprolactam initiation with ϵ-aminocaproic acid hydrochloride (1938)

The polymerization with hydrochlorides of amino compounds has been adopted for a small scale fibre production only. As some corrosion occurred and the uptake of traces of iron could deteriorate the spinning characteristics of the polymer and even more the stability of the fibrous material, this otherwise very effective method had to be abandoned as well.

Since then for the commercial production of fibres the polymerization initiated by small amounts of water or water forming substances such as aminocaproic acid became the normal procedure and so it is today. As a rule the average chain length is regulated just as is usual in the manufacture of Nylon 66 by amide-forming carboxylic acids—mainly acetic acid which may eventually be replaced by a less volatile substance such as sebacic acid.

The acylation of course means a sequestering of amino groups and consequently a loss in affinity towards dyestuffs especially those with acidic groups. This disadvantage may, however, be overcome by replacing the acids by amide forming amines as molecular weight regulators. Especially useful are primary–tertiary diamines in which the tertiary nitrogen is a member of a heterocyclic saturated ring such as 6-morpholino-hexylamine-1.

Mechanism of caprolactam polymerization

In the first period of development during the war nobody had time enough to investigate the reaction mechanism by time-consuming analytical and kinetic methods. As to the mechanism most observations seemed to be in agreement with a stepwise addition of lactam molecules to ionized amino groups with of course some polycondensation. Our formulation of 1939† is reproduced in *Figure 3* from a summary report on polyamides. This mechanism was criticized on the basis that the formation of the polymer even in the presence of only traces of water was not a polymerization in a strict sense, but a latent polycondensation with all lactam molecules being first

† P. Schlack: Report to IG-Farbenindustrie AG, 1939

Caprolactampolymerisation
"Es wurde angenommen, daß sich ein Gleichgewicht folgender Art herausbildet:

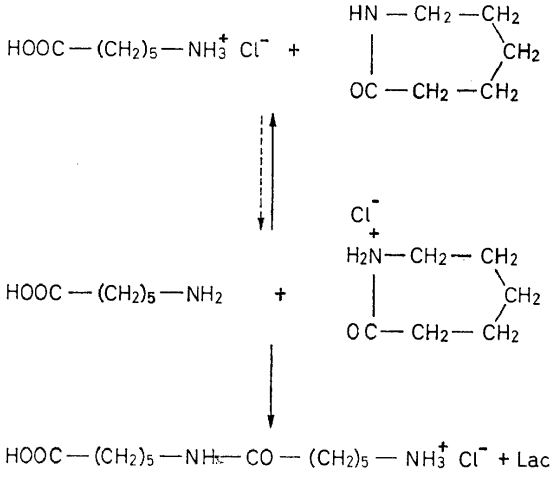


Figure 3. Die nach diesem Schema gebildeten "Dipeptide" können dann die Rolle der ursprunglichen Aminocapronsäure übernehmen, bis schließlich ein hochpolymeres Produkt erreicht ist und die Reaktion zum Stillstand kommt."

converted into aminocaproic acid by hydrolysis. Since dry hydrogen chloride also did initiate the polymerization though not to the fibre forming state, the ability of caprolactam to undergo polymerization had to be accepted basically. This cationic process seemed to be somewhat analogous to the anionic polymerization of caprolactam.

Anionic polymerization

The anionic process was first carried out by using sodium amide and potassium t-butyrate as initiators, the caprolactam being freed from traces of water by azeotropic distillation with decahydronaphthalene. But this method was not regarded as promising. Shortly after the first discussion between Du Pont and IG-Farben, R. M. Joyce and D. M. Ritter[4] in Wilmington discovered the same reaction and observed the superior reaction rate of this anionic polymerization. They used metallic sodium as the initiator.

In Germany the anionic polymerization was further developed during the war time by E. Hubert and A. Hamann but it was not possible to make this process available for the commercial production of a fibre-grade polyamide. Polymer quality remained inferior. The colour was not satisfactory due to some side reactions such as the one leading to β-dicarbonyl groups and the reproducibility was not good either. A fundamental disadvantage was the instability of melt viscosity after the rapid polymerization due to an abnormal chain-length distribution. Only years after the war an improved method which overcomes this severe difficulty was discovered.

As to the mechanism of the anionic polymerization it was clear that in this case the reaction took quite a different course in comparison with the normal cationic hydrolytic procedures. In view of an old paper of Titherley, who observed the formation of imide structures by treating amides with metallic

sodium, we regarded the formation of *N*-amino-caproyl-caprolactam as the first and slow proceeding step (cf. *Figure 4*). The second, but very fast step, is the polymerization by intermolecular aminolysis, yielding to Polyamide 6. This explanation of 1939 is still essentially true today. The answer to the question, whether the aminoacyl-lactam in one step provides only one

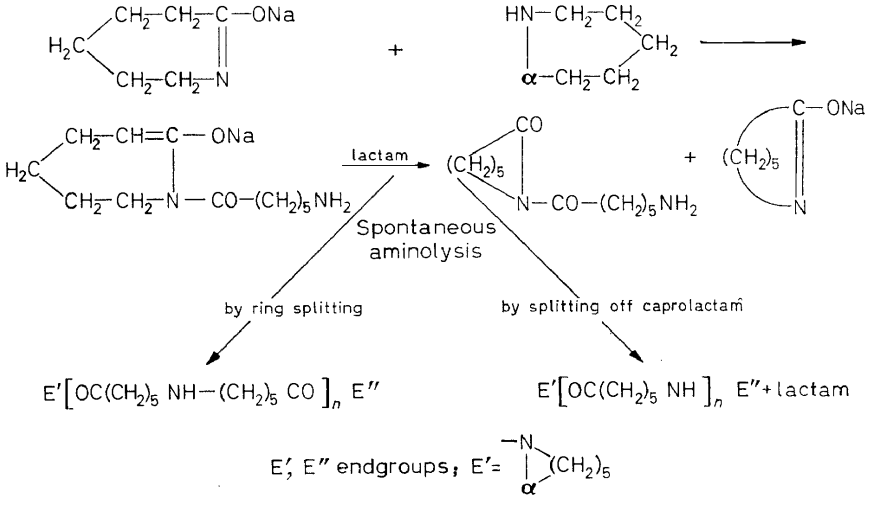


Figure 4. Polymerization of caprolactam with sodium lactamate (1939)

aminocaproyl residue for the polymer formation besides one mole of regenerated caprolactam or if in addition a ring-splitting takes place with the intermediate formation of an active "dipeptide" residue has not been given yet. In this case, two aminocaproyl rests would be incorporated into the growing polymer chain in one reaction step.

Cationic polymerization

Some years after the war at different places an active and careful scientific research started with a view to elucidating the mechanism of the lactam polymerization. New lactams were found to be polymerizable and prejudices were corrected. In view of the technical procedure the hydrolytic initiation of polymerization seemed to be of foremost importance. The kinetics of this reaction have been carefully studied by numerous workers; among others D. Heikens, P. H. Hermans, T. G. Majury, A. Matthes, S. Smith, A. J. Staverman and, in particular, F. Wiloth. These workers established essentially that the reaction may actually be considered as a stepwise addition of caprolactam to the amino groups, which has in fact to be regarded as an acylation. The addition takes place at the amino groups of aminocaproic acid added *a priori* or formed in the melt, and further on at the terminal amino groups of the precondensates. The carboxylic groups, resp. the carboxyions of this system act as catalysts. Besides this, to a minor extent a simple polycondensation of the previously formed linear oligomers containing amino and carboxylic end groups in the ratio 1:1 can occur. In

any case this refutes the often raised objection that the reaction is a cryptopolycondensation. A strong argument stressed by P. H. Hermans against it is that the rate of the reaction for the lactam conversion is far too high for such a mechanism.

The only serious deficiency of the practical process is that the reaction does not come to an end in the case of caprolactam but leads to an equilibrium, depending on the temperature. Polyamide 6 has therefore to be freed from monomer and low-molecular cyclic oligomers by water extraction before spinning. However, I want to draw your attention to the fact that the higher lactams behave much more favourably in this respect.

The cationic polymerization of caprolactam initiated by salts of amino compounds and strong acids such as hydrogen chloride without addition of water, actually the reaction which started the development of Nylon 6, was investigated some years ago by G. M. van der Want and Ch. A. Kruissink and also by F. Wiloth, although its technical importance could not have been deduced, as far as I know.

The kinetic measurements are in agreement with the assumed stepwise addition of lactam molecules to the ionized amino groups. In the case of caprolactam, however, the reaction proceeds relatively slowly in contrast to the next higher homologue, the C_7 lactam. The difference is, at least partly, due to a complication, which shall be discussed afterwards.

The so-called anhydrous cationic polymerization of caprolactam in the presence of a strong acid only proceeds in a complicated manner and as a consequence is of no use for a large scale industrial production. The substances that may act as strong acids are hydrogen halides especially or substances splitting off hydrogen halides. This reaction is of academic interest, however. G. M. van der Want and Ch. A. Kruissink supposed that the polymers in this case are free from carboxylic groups and carry acyllactam endgroups, but they could not say anything definite about the reaction mechanism. M. Rothe and coworkers[5] later found that primarily the salt of a dimer of caprolactam, the already mentioned *N*-ε-aminocaproyl-caprolactam, is formed. They succeeded in isolating this reactive intermediate as tetraphenyl borate and could identify it by comparison with a synthetic product. The formation of this salt is due to the acylating effect of the amidium cation, on the non-ionized caprolactam. The acylating effect of amidium ions is covered in the older literature in many examples. The *N*-aminocaproyl-caprolactam hydrochloride reacts like any hydrochloride of a primary non-aromatic base with an excess of caprolactam, so that it can be further acylated stepwise with lactam, the ammonium salt endgroups being preserved or transferred, respectively. The reaction proceeds slowly and non-uniformly unless the addition of water converts it to the hydrolytic type. As we will see later, the formulation in *Figure 5* needs some addition.

Upon examining the basic endgroups of a polycaprolactam made with the help of a hydrochloride of a primary amino compound such as butylamine hydrochloride, you will find that they do not consist exclusively of primary amino groups. A considerable amount of them resist the action of nitrous acid and hence cannot be desaminated. This anomaly had been observed for the first time before the war. We supposed that semicyclic

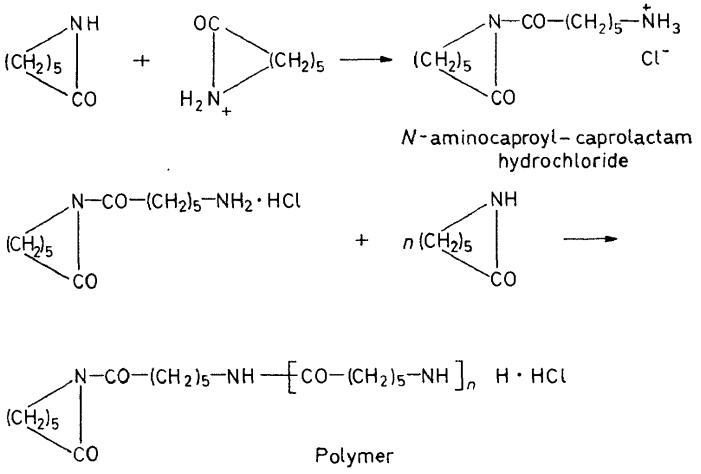


Figure 5. Caprolactam polymerization with hydrogen chloride

amidine groups had been formed but the phenomenon was not published then and was definitely elucidated only two years ago (*Figure 6*). Model tests confirmed the possibility of such a cyclization of terminal amino caproyl residues forming the ring by a condensation with the last

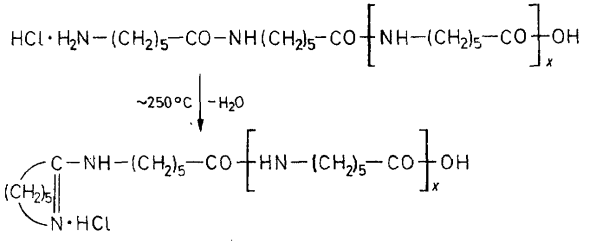


Figure 6. Amidine formation at the basic chain-end of Polyamide 6 in the melt (polymerization of caprolactam with ϵ-amino caproic acid as initiator)

carbonamide group, followed by the elimination of one mole of water. This water formation is a remarkable fact. Hence it is not possible to carry out a cationic polymerization of dry caprolactam with amine hydrochlorides as initiators without disturbing the mechanism by side reactions due to this newly formed water. Therefore besides the ionic addition polymerization polycondensation will occur to some extent also.

The presence of these amidine endgroups has been proved in some instances by splitting off the amidine residue by means of hydroxylamine. The amide oxime corresponding to caprolactam is split by aminolysis as shown in *Figure 7*. It may be identified by the well-known colour test with ferric chloride. Unfortunately this test is not useful for a quantitative determination because of the insufficient stability of the amide oxime. In this case only the indirect titration method after desamination is available as yet. The same reaction proceeds when Nylon 6 is treated with caprolactam

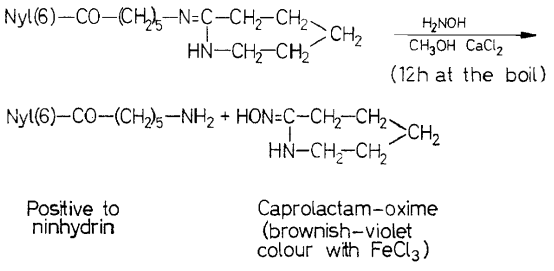


Figure 7. Amidine endgroups in Nylon 6 amidoxime test

methylether till we have a negative ninhydrin test so that practically all amino groups are converted into amidine groups. The material is tested then by the hydroxylamine method (*Figure 8*).

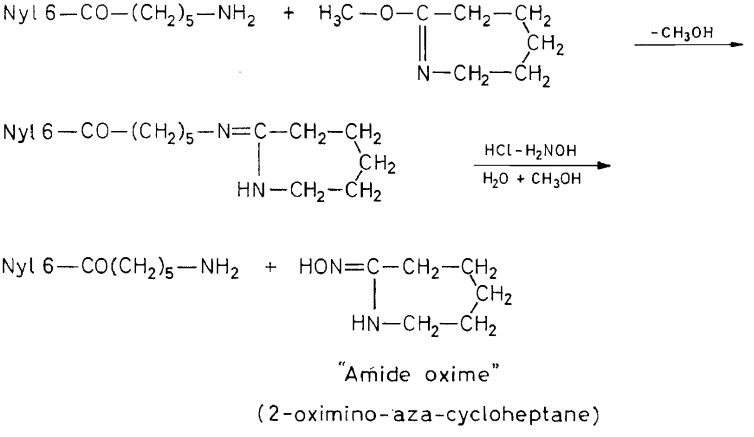


Figure 8. Amidination of Nylon 6 (fabric), hydroxylamine test

It may be mentioned here that the formation of cyclic amidines is characteristic for Nylon 6 while with other commercial polyamides such endgroups could not be detected, this not so even with Nylon 7. It is also interesting to note that some amidine groups can be found after thermosetting of "Perlon" respective Nylon 6 tissues groups which were not present before that treatment. By heating for two hours at about 190°, i.e. below the melting point, the effect is quite remarkable (*Table 1*).

Table 1. Development of amidine groups by heating Polyamide 6 below the melting point in the absence of O_2 (2 h; 195°C)

Material	*Base equivalent*	*Ninhydrin test*
(1) Untreated	$3{\cdot}5 \times 10^{-5}$	+++
(2) Heat treated	$2{\cdot}1 \times 10^{-5}$	++
(3) Heat treated and desaminated	$0{\cdot}97 \times 10^{-5}$†	—

† Amidine content in relation to (1) = 27 mole %; in relation to (2) = 46 mole %.

Such semicyclic amidine endgroups are to be found not only in caprolactam polymers made with amine salts as initiators but also in the low molecular weight products originated by cationic polymerization with anhydrous acids, such as hydrogen chloride only. Since amidinium salt groups are also formed here to a certain extent by the elimination of water, the "anhydrous" ionic polymerization cannot be said to be the unique reaction mechanism either.

Obviously the polymer then contains two different cyclic endgroups: imido endgroups and amidine endgroups, both of which can be identified with hydroxylamine and ferric salts as hydroxamic acid and as amidoxime groups, respectively. It is still a matter of discussion, whether the normal hydrolytically initiated polymerization is proceeding also via primarily formed amidino compounds as it has been supposed a long time ago and as was newly proposed again independently by J. Körösi and Z. Csurös, J. Körösi and coworkers at the Prague symposium last year[6]. It is however a fact, established already in 1939, that compounds containing both carboxy groups and seven-membered semicyclic amidine groups are converted rapidly to high molecular polyamides in the heat. This reaction is practically a disproportionation of these two reactive groups resulting in a new carbonamide link (*Figure 9*).

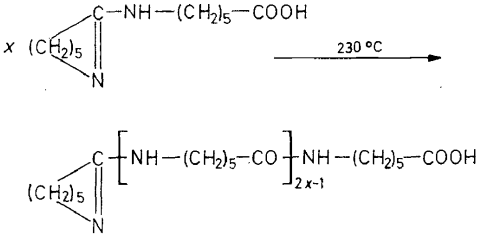


Figure 9. Polymerization by disproportionation (Netherland patent 60 069 (1939/47) IG Farbenindustrie, P. Schlack)

Anionic high-speed polymerization

The anionic high-speed polymerization is becoming the centre of interest more and more. A report on this subject will be given later in this lecture. As already mentioned the simple anionic reaction is supposed to proceed via aminocaproyl-caprolactam as the intermediate, which turns spontaneously into the polymer depending only upon the rate of its formation. According to this explanation and neglecting side reactions the polymer has to show acyllactam endgroups which, indeed, have been detected repeatedly by different workers. The split off caprolactam could be identified by means of chromatography. The conversion into the polymer may on one hand be considered an aminolytic process, and on the other hand it may be considered to have been brought about by the addition of lactamate ions to the carbonyl of the imide groups: presumably both these reactions overlap.

An important progress was due to industrial research on the five-membered butyrolactam. American workers had found that α-pyrrolidone might be

polymerized to a fibre-forming polyamide of high molecular weight just as caprolactum, but only by the anionic process. Until this discovery, the substance was considered definitely non-polymerizable. Examining the course of the reaction, the team found out that this polymer formation, proceeding rather rapidly by itself, could be accelerated considerably by adding substances which acylate the lactam at the nitrogen under the reaction conditions, or better still by adding *N*-acyl derivatives of pyrrolidone at the start. The first U.S. patent on this discovery was published in 1956. In the next year Professor Wichterle and co-workers in Prague found, that the anionic polymerization of caprolactam is accelerated by *N*-acylated lactams or generally with *N*-substituted imides[7].

Considering that the normal hydrolytically initiated polymerization of caprolactam takes several hours, that the so-called "high-speed polymerization" by the addition of lactamates or lactamate forming agents at temperatures of about 250°C still takes some minutes, but that the anionic polymerization in the presence of such cocatalysts, takes place in seconds, one cannot but admire the extraordinary progress that has been achieved by careful and critical research.

The ionic polymerization with imides as co-catalysts takes place without any period of induction. The preformed imides replace the amino caproyl caprolactam, which is otherwise primarily formed under the influence of lactamate ions, and get the chain growth going. Each molecule of the imide acts as the starting point of a polyamide chain. On working carefully, you get polymers bearing acylamino groups at the basic ends, but no free amino groups whatsoever. This reaction is a nucleophilic polyaddition of lactamate ions to the carbonylic carbon atom of the terminal acyl lactam ring, so that with each step a cyclic imide residue is newly formed. This process is clearly demonstrated in *Figure 10.*

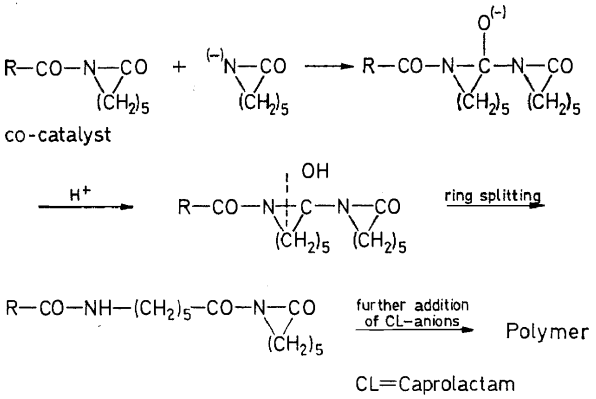


Figure 10. Anionic polymerization of caprolactam tertiary imides (*N*-acyl actams) as co-catalyst

It is indeed regrettable that the great effort in research with its brilliant results in the case of high-speed polymerization is reciprocal to its practical applications. The high-speed polymerization is not yet established for large polycaprolactam fibre production, but rather for making block polymerizates. The reasons for this cannot be treated here in detail, but it

may be stated that the conditions in the case of caprolactam are most complex, while already with the next higher homologue, the oenantholactam, much more uniform results have been achieved.

POLYMERIZATION OF HIGHER LACTAMS

Though caprolactam, because of its availability from benzene (resp. cyclohexane), is a cheap and in normal times unlimited source obviously was the favoured raw material; other lactams with six and more C-atoms in the ring were tested at the same time. The C-alkylated caprolactams were not much promising, they were only considered as possible co-monomers. Besides others they have the essential disadvantage of influencing the polymerization equilibrium in favour of the monomers.

Much more valuable are the higher homologues, at that time not easily accessible. The next member having seven C-atoms in the ring, the oenantholactam, proved to be an eminently suitable monomer. The corresponding polymer Nylon 7 is superior as to the melting point, the crystallinity and last but not the least to the thermal stability. In view of these favourable qualities efforts were made in wartime to find methods for the production of this valuable lactam. But this work, mainly carried out by H. Hopff, did not result in an economic and competitive process. As a rule it is difficult to get into the C_7 series. Ring enlargement methods were not satisfactory in yield. Therefore in order to obtain the polymer the way over the corresponding amino acid or their esters had to be preferred. A process of UCC for some time developed by Chr. Horn and co-workers[8] starts from caprolactone, easily obtained by oxidation of cyclohexanone with peracetic acid or acetaldehyde and oxygen respectively. It leads via bromocaproic acid and cyanocaproic acid ethyl ester on hydrogenation finally to aminoheptanoic acid ethyl ester which is then polycondensed. Another route

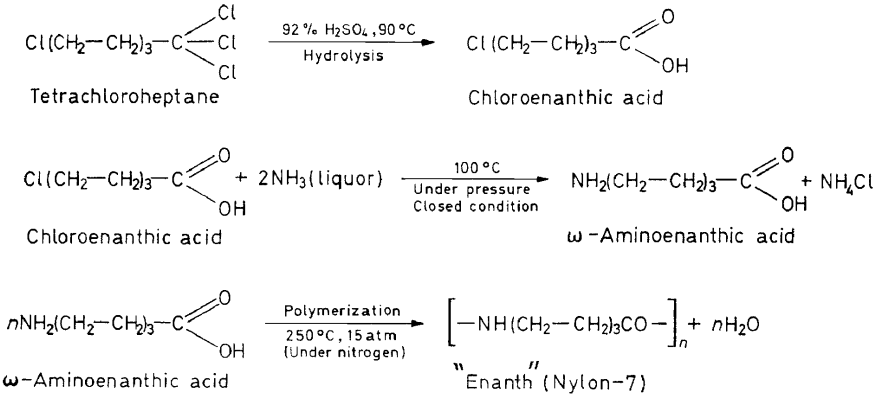


Figure 11. Preparation of Nylon 7

starting from a C_7 telomer of ethylene and tetrachloromethane yields chloroheptanoic acid and finally aminoheptanoic acid (*Figure 11*). In Russia this procedure is used on a small scale for the manufacture of the fibre "Oenanth". Since the yield of the C_7 fraction in telomerization is

relatively small, this process may only be acceptable for expensive special products.

With an increase in the number of ring atoms beyond 6 the reactivity at first rises to an optimum at about C_8, thereafter it falls again. While capryllactam is distinctly easier to polymerize than caprolactam yielding a polymer of very good thermal stability and practically free of monomer similar to the C_7 polyamide, the lauryl lactam (C_{12} lactam), which today is commercially produced on the basis of the cyclotrimer of butadiene is much less active than caprolactam. This remarkable stability of the C_{12} lactam is due to the transconfiguration of the amide group in such large membered lactams as has been demonstrated by R. Huisgen[9]. In polymerizing this C_{12} lactam, however, it is of practical importance that the reaction temperature may be raised to >300°C without any disadvantage, quite in contrast to the conditions given for Polyamides 6 and 66.

β-LACTAMS

A comparatively new group of polyamide-forming monomers is the *C*-substituted β-lactams easily obtainable according to the "Graf synthesis" by reacting *N*-carbonyl-sulphamic acid chloride, the addition product of sulphur trioxide to cyanochloride, with olefines. By anionic polymerization at low temperatures these β-lactams are converted into polymers of remarkably high molecular weight especially in the presence of acylating co-catalysts as used in the polymerization of butyrolactam. Here some lactams of outstanding reactivity such as the β-phenyl-β-lactam can replace the typical acylating agents. In this way amino endgroups can be retained. Since the anionic reaction mechanism is practically the same as with higher lactams, it does not seem necessary to formulate this polymerization here.

Due to the unusually high reactivity of the β-lactams, polymerization may also be initiated otherwise, e.g. by acid chlorides such as oxalic acid chloride. In this case a *N*-acyl derivative may first be formed followed immediately by cleavage of the two lactam rings by hydrogen chloride. The amide dichloride can then attack further lactam molecules and so on (cf. *Figure 12*). The chemistry of the β-lactam polyamides has been reviewed in detail by R. Graf and co-workers[10] in 1962. Fibres of the *C*-methylated

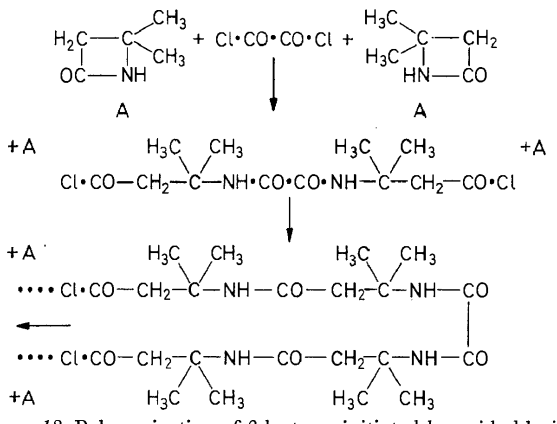
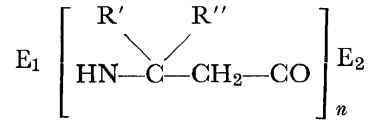


Figure 12. Polymerization of β-lactams initiated by acid chlorides

β-lactams are more similar to silk in aesthetic character than filaments from usual Nylon polyamides.

β-Polyamides prepared by the anionic polymerization of β-lactams corresponding to the general formula given below are not easy to spin.



E_1 E_2 endgroups

R' R'' low alkyl groups especially methyl

Melt-spinning is excluded because of the high melting points and for solution spinning the lack of convenient and cheap solvents is a handicap. The best solvents are acids such as formic acid or sulphuric acid. Surprisingly, however, these acidic solutions are quite unstable. This is not a phenomenon of metastability in a physical sense but a true and comparatively fast hydrolysis followed by a detrimental decrease in viscosity. This unexpected lability is not observed with β-polyamides substituted in α-position, neither with β-monomethylated Nylon 3. To understand this behaviour we have to suppose that in such solutions, e.g. of the β-dimethylated Nylon 3 intermediately and to an equilibrium a more basic heterocycle is formed, which then undergoes hydrolysis as shown in *Figure 13*. The tendency to form such hydroxazine rings is plausible in view of the well-known comformational effect of alkyl groups stabilizing cyclic structures.

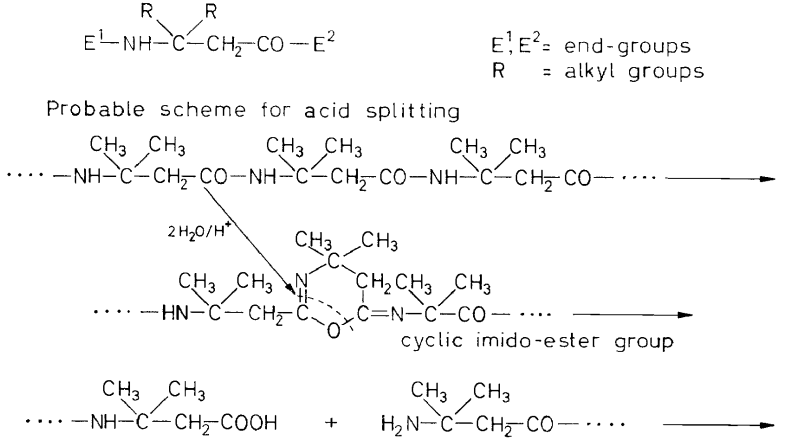


Figure 13. Polyamides of Nylon 3 type

It is worthwhile mentioning that the α-disubstituted Nylon 3 polymer especially the polyamide of amino pivalic acid can be melt-spun without difficulty. The β-alkylated Nylon 3 polyamides are as a class only spinnable from solutions. It may be of interest, however, to know that the polymer of amino pivalic lactam, which unfortunately is not easy to obtain, yields better fibres than the polyamide prepared by melt-condensing the amino acid.

COMMERCIAL PRODUCTION OF CAPROLACTAM

Just as the other polyamide raw materials, especially those containing nitrogen, caprolactam in 1938 had not been an available substance in the chemical industry. It was not even regarded as interesting for production and no desirable outlets were known. Only the detection of the polymerizability of the higher lactams to spinnable polyamides suggested a commercial production and demanded a detailed research for economic and effective production methods.

At first the laboratory route more or less as indicated by O. Wallach[11] was adopted in industry: from phenol to cyclohexanol further to cyclohexanone, then to cyclohexanone oxime with final Beckmann rearrangement of the latter to the lactam. This series of five reaction steps was not really attractive for the manufacturers of organic intermediates looking for modern catalytic processes. Regarding this attitude it is remarkable that the seemingly tedious route which, however, later on could be cheapened somewhat by phenol production via cumene (the Hock process), is practised to a large extent even today. Each step has been worked out to the last detail so that maximum yields of highly pure lactam are obtained.

More and more in the past decade the producers of caprolactam were shifting from the formerly conventional raw material, which was phenol, to cyclohexane. This hydrocarbon today is easily available from petroleum in practically unlimited quantities by hydrogenation of benzene. Replacing phenol made by the Hock process propylene is spared. Moreover, the generation of acetone, at present merely an undesired byproduct, is avoided.

The very interesting process of SNIA which comprises the oxidation of toluene to benzoic acid, hydrogenation of the latter to cyclohexane carboxylic acid and converting this acid in one operation to caprolactam by treating it with nitroso sulphuric acid, does not seem to have been developed much further. Considering the very high purity standard required for caprolactam today it may be difficult to control exactly enough the combined steps of nitrosation, decarboxylation and the rearrangement to the lactam.

The most important methods for the commercial production of caprolactam some of which are, however, not being developed further have been compared in *Figure 14*. Three of these Nos. 6, 7 and 8 are being used at present and may be characterized as follows:

(1) The caprolactam production based on cyclohexanone obtained by air oxidation of cyclohexane has been thoroughly studied and improved during the last ten years. This process has been favoured in spite of the formation of several byproducts, all of which, however, have useful outlets and therefore are no handicap. Some very large plants still under construction will use this route. The theory of this reaction according to W. Langenbeck and W. Pritzkow is shown in *Figure 15*.

(2) The nitrosyl chloride process worked out in Japan by Toyo Rayon (known in Japan as the PCN process) and in Germany by E. Müller at Tübingen adaptable in general to all saturated cyclic paraffins, provides very good yields of the oxime hydrochloride. The oxime is rearranged to caprolactam in the usual way.

(3) The formation of caprolactam by amination of caprolactone which is

easily obtained from cyclohexanone by oxidation with peracetic acid. The lactone is heated with ammonia at a very high temperature under pressure. This procedure has the advantage that no ammonium sulphate is formed as a byproduct whereas all processes comprising

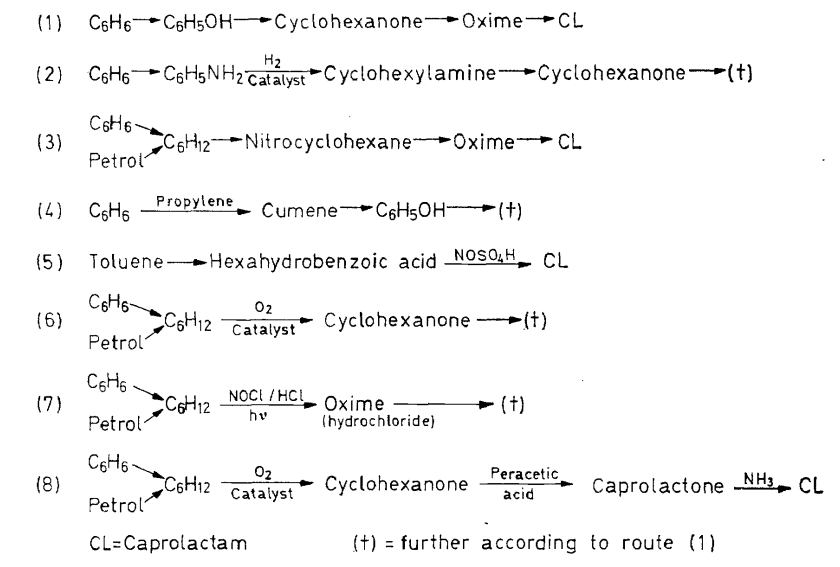


Figure 14. Routes for caprolactam production

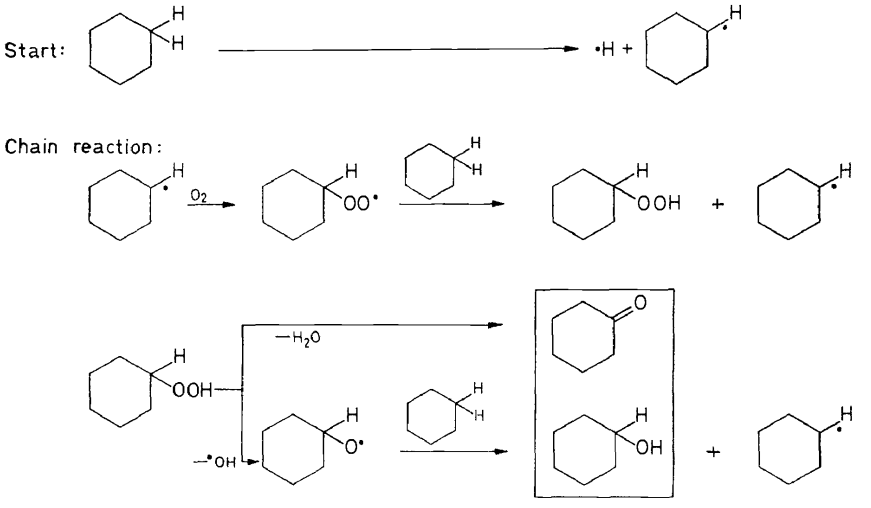


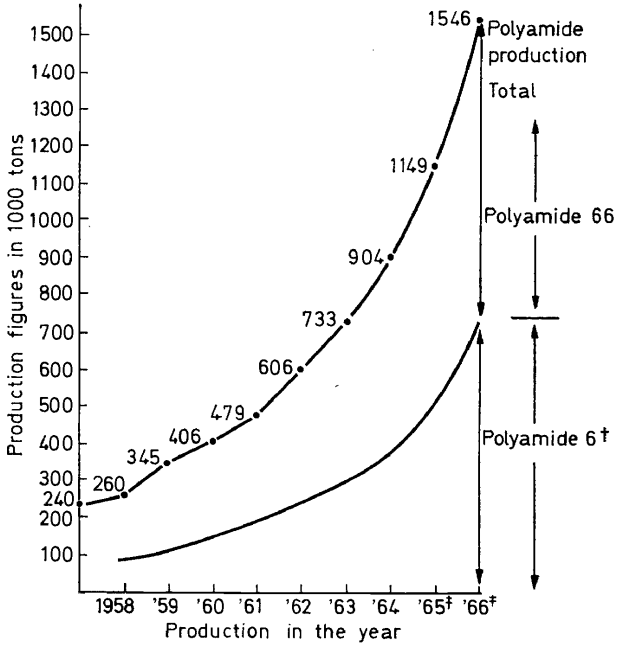
Figure 15. Air oxidation of cyclohexane (W. Langenbeck and W. Pritzkow)

a Beckmann rearrangement in sulphuric acid yield a large amount of ammonium salt, about three times (by weight) as compared with the produced lactam.

This advantage, however, may also be obtained with all processes leading to isolable oxime as intermediate, if the rearrangement is performed catalytically in the vapour-phase using acidic contact substances. According to some patents it now seems to be possible to obtain high yields.

It is not possible here to go further into details. I only wanted you to get a thrilling impression of how much and how successfully the chemical industry was occupied to work out the different processing routes for large lactam production. Today the capacity of the caprolactam plants in the world amounts to more than 500 000 tons per year and the manufacturing costs have been lowered to such an extent that the use of this monomer and its polymer is stimulated also for plastics. Here the anionic polymerization *in situ* at relatively low temperature is of special value. You should, however, consider that because of its comparatively high water regain and the limited melt-stability, polycaprolactam cannot meet all demands. Some uses therefore are reserved for polyamides with higher melt-stability, lower water uptake and better resistance against oxidation at higher temperatures. The polymers of capryl or lauryl lactam have an advantage in this respect if it is supposed that their melting points are satisfactory and their price acceptable as the case may be.

The world production of caprolactam respective Polyamide 6 reached very high figures in the last year as is shown in *Figure 16* which demonstrates



† Including small amounts of Nylon 11
‡ For the years 1965 and 1966 the capacity and not actual production has been taken into consideration

Figure 16. Production figures for Nylon 66 and Nylon 6

graphically the increased production of Nylons 66 and 6 since 1958. For the years 1965 and 1966 this curve does not give the actual production figures but the reported capacities. It is, however, to be taken into account that because of the textile crisis in some important countries the capacities for Nylons 66 and 6 had not been fully exhausted in 1965. *Table 2* shows the

Table 2. World production of Nylon 66 and Nylon 6

	Production in 1000 tons		
Year	*Total*	*Nylon 66*	*Nylon 6*
1958	260	190	70
1959	345	245	100
1960	406	275	131
1961	479	299	180
1962	606	358	248
1963	733	418	315
1964	904	500	404
1965†	1149	620	529
1966†	1546	815	731 (*c.* 48%)

† For the years 1965 and 1966 the figures given are for capacity and not for production.

same figures again; as can be seen from this table Nylon 6 production is supposed to have increased ten times from 1958 to 1966, while Nylon 66 has grown about six times. Here you should remember that Nylon 66, in 1958, had already reached a high production standard.

CONCLUSION

In this short and of course very incomplete survey I have tried to draw a sketchy picture of the development of the lactam chemistry which has at times been quite exciting. The centre was caprolactam being the link between the higher lactams showing, as a rule, a more uniform behaviour and the lower ones representing a group of substances of more different and distinct character of the single members. Since 1938 caprolactam—at that time only a laboratory curiosity—has been raised to a mass-product. The chemical reactions of this apparently so simple substance and its analogues have proved to be surprisingly many-fold so that in spite of the outstanding commercial importance they are not yet exhausted by scientific research.

References

[1] W. H. Carothers. *Chem. Rev.* **8**, 353–426 (1931).
[2] H. Leuchs. *Ber. dtsch. chem. Ges.* **39**, 857 (1906).
[3] W. H. Carothers and G. J. Berchet. *J. Am. Chem. Soc.* **52**, 5289 (1930).
[4] R. M. Joyce and D. M. Ritter. *U.S. Pat.* 2 251 519.
[5] M. Rothe, G. Reinisch, W. Jaeger, and I. Schopov. *Makromol. Chem.* **54**, 183 (1962).
[6] Z. Csürös, Gy. Bertalan, J. Nagy, L. Trezl, and J. Körösi. Paper presented at the IUPAC Symposium on Macromol. Chemistry, Prague, 1965, preprint P 403.
[7] W. O. Ney, Jr., W. R. Nummy, and C. E. Barnes. *U.S. Pat.* 2 638 463.
W. O. Ney, Jr. and M. Crowther. *U.S. Pat* 2 739 959.
O. Wichterle, J. Sebenda, and U. Kralicek. *Fortschr. Hochpolym. Forsch.* 1961, Bd. 2, 578–595, "The anionic polymerization of caprolactam".
[8] C. F. Horn, B. T. Freure, H. Vineyard, and H. J. Decker. *Angew. Chem.* **74**, 531 (1962).
[9] R. Huisgen. *Chem. Ber.* **90**, 1437 (1957).
[10] R. Graf, G. Lohaus, K. Börner, E. Schmidt, and H. Bestian. *Angew. Chem.* **74**, 523 (1962).
[11] O. Wallach. *Liebigs Ann.* **309**, 18 and **312**, 205.