

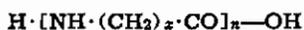
ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE PRODUCTION OF HIGH POLYMERIC COMPOUNDS

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This invention relates to the production of high polymeric compounds. The superpolyamides known at the present time and used in the production of artificial filaments, fibers, foils etc., obtained from monobasic amino carboxylic acids by outer amide formation correspond to the formula



These polymers possess between the —NH— and the —CO— group in the practically utilizable form within the n -times recurring structure-unit at least 5 C-atoms and more. This corresponds in the formula above to an $x=7$ or 8. The superpolyamides hitherto known with structural units between the —NH— and the —CO— group of less than 6 C-atoms are brittle and of bad mechanical qualities, even though they contain this structural unit in the molecule to a certain percentage only.

According to this invention it has been found that mechanically valuable mixed superpolyamides, containing between the —NH— and the —CO— group in the structural unit 4 C-atoms and less, are obtained, if this short structural unit contains an aromatic radical. This aromatic radical may be introduced by aromatic substitution of the structural unit at any place, that means in the —NH— or —CH₂— group, or may be placed as member between the —NH— and —CO— group. Such mixed polymers, besides their better mechanical qualities, are more easily obtainable, because they are formed at lower temperature and in shorter time. They also show noteworthy qualities for the production of foils.

Besides their usefulness for textile purposes in the form of filaments they are well suited for the production of films (for photographic and other purposes), plates (as substitute for glass), sheets or foils (for electric insulation, coating foils for cigarette tips, wrapping foils, adhesive foils, light filters, patterns, stencils, supports for prints or the like), sound records (either those in which the sound track is cut mechanically into the support or is impressed therein without removal of material (the Edison or the Berliner method)), masses for the reproduction and printing arts, masses for die-casting and molding by pressure (production of camera parts and casings for rollfilms or filmpacks by pressing or rolling, production of spools or parts thereof for photographic rollfilms by the molding method), as adhesive or intermediate layers for composite glass. The sheets or foils made from the materials according to this invention may be pro-

vided with a metallic coating according to a known process.

It is therefore an object of the present invention to provide a process of producing high polymeric compounds by polymerising ω -amino carboxylic acids with amino carboxylic acids containing an aromatic radical.

A further object is the provision of a process by which polymerisates can be obtained, which are capable of being worked up into fibers, films, sheets, foils and the like.

Another object is the provision of a polymerization process, which is carried out in the absence of oxygen.

An additional object resides in the provision of suitable polymerization catalysts.

Another object is the provision of a process in which the molten reaction product is heated up at a temperature above the reaction temperature, if necessary by a vacuum treatment.

A still further object is the provision of a continuous process for the production of said high polymeric compound.

A still further object of the invention resides in a process, in which the reaction takes place under a protective layer consisting of a molten indifferent material.

Other additional objects will become apparent as the description proceeds.

This invention is based on the observation that very valuable polymers of the kind referred to are obtained by inter-condensation or polymerization with ω -amino carboxylic acids possessing not more than 4 C-atoms and containing an aromatic radical. The amino carboxylic acids may be used in this form or in the form of their condensable derivatives like anhydrides, acid chlorides, lactams, esters. As to the amino carboxylic acids containing an aromatic radical, compounds are used like phenyl- and naphthylalanine, phenyl-amino acetic acid and tyrosine. The aromatic radical may be directly built in between the —NH— and —CO— group, for instance, as in the 3-aminobenzoic acid and in aromatic amino carboxylic acids of similar constitution.

The molar proportion between the components is widely variable, but preferably the amino carboxylic acids with a longer chain, that means the one not containing the aromatic radical, should prevail. As example for such amino carboxylic acids there is mentioned the ω -aminocaproic acid and its similar derivatives like the anhydride, the lactam, the acid amide, the acid halides and esters.

The reaction between the two different amino

carboxylic acids may be accomplished in different ways. The components may be melted together. Thereby an indifferent component, for instance paraffin of a melting point 40 to 80°C not being a solvent for one or both components, may be added in order to reduce the heat of reaction or to facilitate the separation of the water. It is also possible to choose the diluent so, that it is a solvent for the final product for instance, like aniline at higher temperature. This should be added, if desired, towards the end of the reaction. The components however may be caused to react on each other in an indifferent solvent like phenols of all kind. According to the nature and qualities of the reaction product such compounds are added, in which the high polymer is soluble or not soluble.

The reaction temperature lies practically between 175 and 250° C. At temperatures below 175° C the formation of high polymeric compounds in some cases also sets in, proceeding, however, very slowly and not leading to products with improved mechanical qualities. Decisive for the quality of high polymeric final products is the absolute purity of the starting material and the careful exclusion of oxygen during the reaction. One works best therefore in the atmosphere of an indifferent gas such as CO₂, N₂ etc. and care has to be taken during the manufacturing process to exclude oxygen at temperatures above 150° C. In most cases it is sufficient to carry out the reaction at normal atmospheric pressure. If one of the reaction components shows great tendency to sublime, this may be counter acted by application of pressure, which is also applicable in such cases, where the reaction of the different components represents a true polymerization without splitting off of water. If the reaction however takes place without separation of water, it is advisable to avoid the undesirable points of certain reaction equilibria by application of pressure in excess and to work at a certain vacuum. In such cases it is most convenient, as mentioned, to apply a dissolving or not dissolving medium, which enhances the removal of water by lowering the partial pressure of the water vapor. The reaction may be advantageously performed as a continuous operation.

According to the constitution of the reaction components it is often practical to accelerate the polymerization and condensation by adding a catalyst. Advantageously, the accelerating materials used, if desired in conjunction with water or hydroxyl or sulphhydryl compounds, are acids, bases or salts or substances or mixtures of substances which form these. Correspondingly, acceleration occurs already if a small portion of water or of a hydroxyl compound or of a mercaptan is added. Since these substances, at least when the operation is conducted in a closed vessel, react in part stoichiometrically or in part until a definite equilibrium is attained, their proportion must in most cases be exactly adjusted in order that good reproducible results may be obtained. This is especially the case with alcohols and mercaptans of high molecular weight. In the case of materials of lower molecular weight, an equilibrium may occur rather in the course of the heating, particularly in the final phase. In certain cases, for instance when phenols are used, a considerable excess may be employed. Instead of free acids, functional derivatives thereof may be used, insofar as they have a tendency to acylate reactive hydrogen, especially acid chlorides, also, however, freely reactive acid esters, for instance

phenol esters of carboxylic acids and acid amides.

Especially favourable have proved salts of amino compounds capable of acylation, particularly those having primary amino nitrogen. Salts of secondary amines are in general less advantageous, since they appear to accelerate also the elimination of ammonia. Of the salts of primary amines, those of the amino acids are of special interest, because they favour a very uniform course of reaction. Since the number of the finally present end-groups and therewith the degree of polymerization is associated with the proportion of the catalyst, this proportion will in general be kept within comparatively narrow limits, at least when production of very highly polymeric products is desired. In most cases, it has proved advantageous to keep during the main reaction period a proportion of the substance which determines the formation of the end-groups below 1/50 equivalent in relation to the reaction that forms the end-groups. It has been remarked, however, that in many cases one cannot ascertain with certainty what the amount of the added accelerator is in fact consumed for the formation of the end-groups. Occasionally, suitable substances for forming end-groups are so changed that they cannot be regenerated. In the case of amimosulphonic acids, for instance sulphanilic acid, it has been observed that the sulpho groups are eliminated.

When the promoting substance is decomposed in the course of heating without formation of stable end-groups, it volatilises or becomes chemically inactive and may obviously be added in a larger proportion; for example when mixtures of lactams and amino acid esters are heated or when vapour of ammonia or an amine of low molecular weight is passed through molten lactam or mixture of lactams at a suitably high temperature, if desired under pressure.

The nature of the final product may be influenced both by the chemical composition of the catalyst and also by the proportion and the mode in which it is added. When the accelerator used is one which is practically not decomposed and acts as a true catalyst, for instance an inorganic halide in the presence of a trace of water, large variations in the proportion may have no essential influence on the properties of the final product. The position is otherwise, however, as has already been indicated, when the accelerator or constituent thereof, for example the cationic portion of a salt, is decomposed during the reaction more or less profoundly for the formation of the end-groups or of substances producing the end-groups. In such cases the desired degree of polymerization may be controlled and predetermined by using the accelerator in doses within certain limits. This is an essential advantage of the process. Moreover, the substances forming the end-groups may be determined in dependence on the substituents present and also on their electro-chemical character.

The higher the degree of polymerization, the more must the capacity for binding acid and therewith the quantitative adsorption of acid dyestuffs by the polymerisate or by the structure formed therefrom diminish. This retrogression in affinity for dyestuffs may be counteracted if as the accelerator there are used compounds forming end-groups capable of forming such end-groups as may be acylated, which compounds, besides the groups capable of acylation and of reaction with the lactam, for instance hydroxyl or amino groups or both, contain basic groups

which are incapable or only feebly capable of being acylated. Such materials are, for example, unsymmetrical dimethylpropylenediamine, ω -piperidopentylamine, and others having more than one nitrogen atom listed in the aforesaid table. By suitable choice of the accelerator forming the end-groups the capacity of the structure as a wetting agent and for swelling may be influenced within certain limits.

Table

Substances which are applicable as accelerators of the reaction:

1. *Inorganic compounds.*—Hydrogen bromide (as aqueous acid having a specific gravity of 1.48), Mixture of sulphuric acid and water in proportion of 98:36, Ammoniumfluoride, lithium chloride, hydroxylaminohydrochloride, magnesium chloride, zinc chloride, borofluoridedihydrate, aluminium chloride and other catalysts for Friedel Crafts reactions, sodium amide, lithium hydroxide.

2. *Organic hydroxyl- and sulphhydryl compounds.*—Benzyl alcohol, ω -dimethylamino-paraethylphenol, dodecylalcohol, cholestrin, thioglycollic acid dodecyl ester, iso-octylphenol and iso-octylphenol ethyl ether.

3. *Amines and salts of organic amino compounds.*—Benzylamine, octadecylamine, octamethylenediamine, guanidine carbonate, N-butylaminofluorosulphonate, dodecylaminohydrochloride, abietinylaminohydrochloride, 9-amino-pentatriacontane hydrochloride, butanolamino hydrochloride, β -chloroethylaminohydrochloride, triethylenetetramine-tetrahydrochloride, $\beta\beta$ -diamino-diethylether-dihydrochloride, $\beta\beta$ -diaminodithiethylsulphidedihydrochloride, anilinohydrochloride, benzidine-dihydrochloride, para-aminothlophenolhydrochloride, pyridine-camphorsulphonate, histaminedihydrochloride, melaminehydrochloride, sarcosinehydrochloride, cyclohexane- α -aminocarboxylic acid hydrobromide, para-aminobenzoic acid hydrobromide, para-aminophenyl acid ester hydrochloride, aminoethanesulphonic acid, sulphanic acid.

4. *Organic acids and acid derivatives.*—Toluenesulphonic acid, naphtanlenesulphonic acid, meta-sulphobenzoic acid (these above preferably in the presence of small quantities of water, of mono- or polyvalent alcohols, phenols or mercaptans, for example of benzyl alcohol, phenoxyethyl alcohol, diethylene-glycol, hexamethylene-glycol, vinyloctadecyl ether), oxyethanesulphonic acid, adipic acid, terephthalic acid chloride, cyanuric chloride, 1:3:5-benzenetricarboxylic acid chloride, laurylcyanamide, toluenesulphonic acid ethyl ester in presence of very small quantities of water (1/200 mol ester + 1/200 mol water to 1 mol lactam).

5. *Salt-like organic compounds especially such as are of preponderant basic character.*—Carbazole potassium, aluminium ethylate, magnesium oleate, potassium acetate in combination with cyclohexanol or dodecylalcohol, sulphosalicylic acid sodium.

6. *Substances which react with formation of organic acids.*—Benzyl chloride, para-xylylene bromide, butylchloromethyl ether, especially in presence of small quantities of water, alcohols, phenols or mercaptans, which may be present in small excess as compared with the halogen compound.

One may omit, however, to add special catalysts especially when the longer reaction component is employed in the form of its lactam. Most

probably the other amino carboxylic acid, containing the aromatic radical proofs enough reaction accelerating.

The shorter reaction time is very characteristic for the formation of mixed polymers according to this invention, which in most cases does not exceed 6-9 hours and which therefore is much shorter than that for the superpolyamides hitherto known without containing aromatic radicals.

In using promoters forming end-groups, which have more than two reactive groups, for example hydrochlorides of tri- and polybasic amines, especially primary amines or acid chlorides of free or polybasic carboxylic and sulphonic acids, there may be produced three-dimensional products which are fusible and soluble and chemically not net-like, which for many purposes are of especial interest, since by the action of substances having in the molecule at least two amino- and/or carboxyl groups, as compared with groups functionally reactive with formation of covalent linking, may be hardened or tanned, thus diminishing its capacity for swelling and raising the melting point.

Suitable substances are polyfunctional compounds having alkylating and/or acylating groups; also reactive carbonyl compounds and functional derivatives thereof, for instance dicarboxylic acids and their derivatives, such as adipic acid, maleic acid anhydride, diphenylcarbonate, dimethyloxalate, cyanuric chloride, diisocyanates, for instance para-phenylene-diisocyanate, and such substances produced by heating, such as hexamethylene-bis-carbamic acid methyl ester, hexamethylene-bis-carbamic acid phenyl ester; compounds having both alkylating and acylating function, for instance methylchloroacetate, methacrylate; polyvalent alkylating agents, for instance 1:4-dichlorobutene, epichlorhydrin, tetrachloroxypropylammonium chloride, butadiene-dioxide, butadiene-disulphide, $\alpha:\alpha'$ -dichlorodimethyl ether; also formaldehyde and quinone.

Such subsequent structural variations which, if they occur less fundamentally or in several stages, may be realised or induced before the shaping operation, but in many cases at the same time as the shaping or subsequently thereto, are, although less pronounced, occasionally possible also in products with only two-dimensional unbranched chains, especially when groups with certain specific reactivity are comprised. Such groups are, for instance (especially end-groups) of the phenolic kind as well as primary carbamide groups, guanidine groups and biguanide groups. Since these reactions are generally limited to end-groups, there is no danger that the elasticity of the structure will be lost by too profound a network. After-treatment with freely reactive substances, for instance, formaldehyde, may with advantage be undertaken in connection with an improvement of the shaped structure, for instance a stretching operation, in which latter case the variation of form must be accompanied by a fixing.

The presence of the polymerization accelerator of saline or salt-forming character or a conversion product thereof does not disturb in general the working-up of the product of the process, and its shaping to the desired structure. Occasionally, indeed, it may be attended by certain advantages, for example when the object is to produce staple fibres which, for facilitating their spinning, ought to be strongly crimped. In other

cases, to be sure, the catalyst residue favours the coloring of the material and at the same time corrosion of the apparatus may occur. A coloring effect is produced by the presence of acid accelerators, for example strong acids and salts of strong acids with organic bases, so that the structures obtained from the polymerides adsorb acid dyestuffs very rapidly and in some cases unequally. This fault may be remedied by a preliminary washing before the dyeing, in which the washing liquid may contain with advantage a mild alkali, for example an alkali acetate, borax, ammonia or ammonium carbonate, for the complete removal of the acid anions.

Even if one sets aside this special point in connection with the dyeing, it is in many cases of advantage to add towards the end of the polymerization, if desired before or during the degasification, an alkaline or acid binding agent. Here there come into question also substances which unite with acids or acid groups to form non-ionogenic compounds, and if desired also can give rise to substitution at amino groups.

In this connection there may be named, for instance, alkaline compounds such as ammonia, alkali acetate, alkali stearate. Preferable, however, are the usual organic bases or organic substances which yield such bases, for example salts of the bases with feeble acids or acids which, in comparison with the base, are volatile; for instance amines, amine salts (amine soaps), amides, for example amides belonging to the group of carbonic acid derivatives. Among the amines are especially the polyamines, especially those of high molecular weight, and of resinous character. Particular materials suitable for this stage of the process are cyclohexylamine, cyclohexylamine-oleate, or -stearate, octamethylenediamine, octadecylamine, octadecylamine-acetate, octadecylpolyethylene-imine, resinous condensation products from alkylene-imines and isocyanates, cyclohexylureas, dicyandiamide, melamine, guanidine salts, cyclic and acyclic iso-urea ethers and isothioureas ethers.

Favourable results are obtained also if for eliminating or compensating acid properties there is added afterwards a reactive alkylating agent and/or aminating agent which reacts with the acid or basic groups present. There may be used either the ordinary alkylating agents of the ester type or substances which yield these, for instance quaternary salts in presence of a separate acid binding agent, for instance magnesium oxide, or with special advantage a cyclic alkylating agent having a tendency to combine with the reactive groups with ring scission. Of these latter the following may be named:

Ethylene oxide, propylene oxide, butadiene dioxide, epichlorhydrin, phenoxypropene oxide, para-phenylene-dioxypropene oxide, piperidopropene oxide, N-didecyl-methylaminopropene oxide, propylene sulphide, butadienedisulphide, ethylenimine, N-cyclohexylethylenimine, N-butylethylene-imine, C-phenyl-ethylenimine, dodecylethylenimine. The alkylene-imines and their derivatives react particularly freely if the substratum contains ionogenic halogen.

Insofar as the added reactive substances containing basic nitrogen are fixed in this structure, so that they cannot be washed out or themselves react with the polymeride, there is simultaneously obtained an increase in the total affinity which is desirable for attaining dyeing properties similar to those of vegetable fibres, especially

when the material worked has a high degree of polymerization.

If the first desideratum is to enhance the basic character of the artificial material, polyamines of high molecular weight or high degree of polymerization may be used which can react with the lactam polymerisate without formation of amide, for example those having exclusively tertiary basic nitrogen or even polyamines of high molecular weight in the form of any desired salt so far as these are miscible with the molten mass or the solution, for instance salts of polymeric alkylene polyamines with organic sulphonic acids. It is of especial advantage to use salts when the free amine bases are not sufficiently stable to heat.

The application of the products in form of films, filaments and the like takes place according to known processes: di-casting, casting from the melt or from solutions, drawing from the molten mass or under pressure below the softening point, warm- and cold stretching, rolling in order to effect an orientation of the molecules in one or several directions, etc.

EXAMPLE I

16 grams ϵ -aminocaprolactam are well mixed in a glass tube with 4 grams carefully dried phenylalanine and heated up within an hour at 220° with exclusion of air. After 8 hours heating a feebly colored viscous melt is obtained, which after cooling solidifies into rods of slightly yellowed color and of great hardness. By careful remelting films may be drawn directly from the melt.

EXAMPLE II

8.1 grams ϵ -aminocaprolactam and 1.9 grams phenylglycocoll are polymerized as in Example I. The slightly brown tinted reaction mass may be transferred from a solution in formic acid (0.5 grams for 1.5 cc. formic acid) into a feebly milky film.

EXAMPLE III

18 grams ϵ -aminocaprolactam and 2 grams tyrosine are heated in a vacuum of 150-200 mm pressure for 7 hours at 220°. The brown reaction mass may be formed into fine filaments in a known manner under slight excess pressure by a spinning nozzle with fine boreholes. If these filaments are simultaneously stretched at room temperature, they assume high tenacity and high tensile strength.

EXAMPLE IV

150 grams ϵ -aminocaprolactam of the diffusion point 69/72° are mixed with 50 grams anthranilic acid, recrystallized three times from methanol, carefully melted together in a glass vessel and placed in an electrically heated oil bath. The air in the reaction vessel is replaced by carbon dioxide freed from air. The reaction product is heated within half an hour at 200°C in an atmosphere of carbon dioxide and kept at that temperature during 5 hours. A high viscous, bright and colorless melt is formed, which may be drawn directly to clear films of high tenacity and good tensile strength. The softening point lies at 205-210°C.

EXAMPLE V

If a mixing proportion of 350 grams ϵ -aminocaprolactam and 60 grams of anthranilic acid is used and the heating carried out under the same conditions, molten masses are obtained, the softening point of which lies about 10° higher. A reaction product of the same qualities is ob-

tained if instead of in a carbon dioxide atmosphere the mass is heated in a vacuum of about 50 mm. If a sealed reaction tube is applied and the water, which is formed during the reaction not eliminated, the resultant high polymeric melt is of a feebly brown tint.

EXAMPLE VI

180 grams ϵ -aminocaprolactam are melted together with 120 grams anthranilic acid under the precautions described in Example IV and heated during 6 hours at 200°C. Instead of supplying the apparatus with a continuous stream of car-

bon dioxide, it is sealed by quicksilver after a complete removal of oxygen, which allows an excess pressure of about 30-50 mm, but blows off at higher temperature. The softening point of the reaction product lies between 195 and 200°C.

EXAMPLE VII

18 grams ϵ -aminocaprolactam are melted together under carbon dioxide with 2 grams p-aminobenzoic acid and heated for 6 hours at 190-200°C. The hard, feebly brownish melt yields clear films of good mechanical strength.

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