

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE MANUFACTURE OF HIGH MOLECULAR POLYAMIDE COMPOUNDS

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This invention relates to the manufacture of high molecular polyamide compounds.

When simple bifunctional urethane compounds are condensed in the heat for themselves or together with other substances reactive with urethane compounds, high molecular polyamides are obtained. Such substances were obtained by self-condensation of urethane carboxylic acids with at least 5 atoms between the nitrogen atom and the carbonyl group, by heating of such urethane carboxylic acids with α - ω -diamines, by condensing diurethanes, with $\alpha\omega$ -diamines and finally also by heating of diurethanes for themselves.

There were used until now for the condensation only such urethane compounds, in which the carbamic acid radical is esterified with an aliphatic alcohol. Fundamentally the same reactions show also urethanes with cyclo-aliphatic or aromatic substituted aliphatic alcohols, for instance carbamic acid esters of the benzyl alcohol or of the phenyl ethanol.

It is an object of this invention to produce high molecular polyamide compounds.

A further object is the preparation of filaments, fibers, ribbons from these materials.

Still further objects will become apparent from the detailed specification following hereinafter.

It has been found that the condensation reactions between urethane compounds and other substances condensable together with them proceed by far smoother, when there are used bifunctional starting materials containing the radical of the carbamic acid in esterified form containing at least once the radical of the carbamic acid with an aromatic or enolic hydroxyl compound, and when these products are caused to react at a temperature suitable for the reaction with other bifunctional compounds which show free carboxyl groups or hydroxyl-, sulfhydryl- or amino-groups capable of being acetylated. The reactions take place as a rule already at relatively low temperature and proceed especially in the beginning rather quickly, so that monomeric reaction components not being volatile are not present any more already after a short time. In many cases therefore one can work without excessive pressure, also when relatively volatile substances, for instance 1,4-butylene glycol or diethylene glycol are used. Also when working under pressure advantages are to be found, since displacements of concentrations, caused by distillation are little or not at all to be feared. Furthermore the reaction usually proceeds much more uniformly, as the self-condensation, which happens easily at high temperatures with car-

bamic acid esters of the low aliphatic alcohols, does not occur in this case. It leads also less easily to cross-linking.

The uniformity of the reaction in many cases is of considerable importance, as substances structurally uniform can be more extensively oriented during or after the forming process than irregular mixed condensates or mixtures. Besides that they are usually characterized by a higher melting point. It is therefore easily possible to produce mixed condensates showing a regular arrangement of different components. A very uniform mixed condensate for instance is obtained, when hexamethylene-bis-carbamic acid diphenyl ester (f. p. 138° C.) is condensed with octamethylenediamine or dodecamethylenediamine. This for instance is not as easily accomplished when hexamethylene-bis-carbamic acid dimethylester is heated with octamethylenediamine, or if a mixture of hexamethylenediamine and octamethylenediamine is condensed with a neutral carbamic ester or urea.

Similarly this applies to the condensation with glycols being here of special importance. If for instance hexamethylene-bis-carbamic acid dimethylester is condensed with 1,4-butylene glycol in equivalent proportions, part of the glycol as a rule remains unchanged on account of the simultaneous self-condensation, whereas when working with the different diarylesters, for instance with the diphenylester or a chlorophenylester, the polyurethane formation proceeds uniformly in the desired way. Simple and substituted phenols are first of all to be mentioned as hydroxyl components for the manufacture of the carbamic acid ester, for instance phenol, m-cresol, the various halogen- and polyhalogenphenols, naphthols, oxydiphenyls. Especially useful are halogen substituted phenols, as they have very little tendency to decolorize.

Instead of the phenols there may be employed with the same success also hydroxyl compounds of other ring systems, in which the hydroxyl group is connected to a double linked carbon atom, for instance oxypyridine, 4-oxypyrazol.

Just as well react the carbamic acid esters of aliphatic or alicyclic enols which may be easily saponified, for instance the carbamic acid esters from aliphatic diisocyanates like hexamethylenediisocyanate and ω -formylacetophenone, from methylidihydroresorazine or dimethyldihydroresorazine, acetyl acetone, ethyl aceto acetate.

To manufacture carbamic acid esters the corresponding chloroformic acid aryl esters may be caused to act on the amino compounds or when

working under exclusion of water and in the heat on their salts, especially when the latter contain hydrogenhalide. In the latter case it is of advantage to employ an indifferent solvent, for instance benzene, toluene, chlorobenzene. Furthermore they are obtained by a reaction of the amino compounds with the corresponding carbonic esters, whereby it is useful to discharge gradually the amine into a solution of the carbonic ester. It was found hereby that for uniform course of the reaction it is of great importance, if a solvent is chosen, in which the carbamic acid ester to be expected is as little soluble as possible. Especially suitable are hydrocarbons like benzene or chlorobenzene. The carbonic ester may preferably be used in excess, if for instance the reaction product on account of the solubility may be easily separated from the excess of the ester.

Needless to say the carbamic acid esters are also obtainable by a reaction of phenols with isocyanates or the corresponding carbamic acid chlorides. As far as amine compounds with a secondary amine nitrogen are concerned it is best to work with carbamic acid chlorides.

Derivatives of secondary amino compounds, for instance carbamic acid esters from symmetric dimethyltetramethylene-diamine are preferably suited for the reaction with amino compounds, for instance hexamethylenediamine.

For the condensation in principle also such carbamic acid esters may be used, the carbon chains of which are interrupted by so called hetero atoms or groups like O, S, N, SO₂. To insert also sulfamide groups into the carbon chain of the carbamic acid ester is possible according to German Patent application I. 64 124 /12 o, filed March 20, 1939. In the same way also the bifunctional compounds condensable with the carbamic acid esters, for instance the diamines or glycols may contain such groupings or atoms interrupting the chain.

In order to produce condensation products, nearly equimolecular quantities of the components are heated in the presence or absence of a solvent. As a rule it is useful to start the condensation at a relatively low temperature and to apply higher temperatures only then, if the monomeric starting materials have practically disappeared. The oxy compound which is split off, for instance a phenol, may be distilled off at the end, if one does not prefer to work up the finished polyamide with a precipitant, if necessary after dilution. A working method practical in many cases is to employ the carbamic acid ester of an oxy compound being solid at room-temperature and to remove the split off oxy compound with a solvent, for instance acetone, after disintegration by grinding from the finished solidified polyamide. The reaction product remains then in the form of a coarse powder, which can be moulded.

The products separated by precipitation may be again condensed by remelting and reheating at correspondingly high temperature, preferably in vacuo. Hereby also a small amount of bifunctional amide forming compounds are preferably added, for instance dicarboxylic acids like sebacic acid, or diamines like hexamethylenediamine.

The condensations may be increased and facilitated especially in the production of polyurethanes by adding catalysts, for instance small amounts alkali alcoholate, alkali phenolate, tertiary amines or acid reacting compounds like

hydrogen halide, aryl sulfonic acids, hydrohalic acids of amines and amino acids. Especially when condensing with amino compounds the degree of the desired condensation may be extensively influenced by adding acid compounds, for instance amino hydrochlorides, amino-acid-hydrochlorides, -phosphates, -toluenesulfonates.

The high molecular condensation products according to the present invention may be worked up into filaments, ribbons, foils, directly from the melt or from the solutions, for instance in phenols, acetic acid, formic acid, and the like. The spun filaments, especially those obtained directly from the melt, show high elasticity and obtain excellent tenacity by the drawing process. Structures may be also obtained from the polyamides by casting, dye-casting, injection moulding or pressing.

Example I

1 mol hexamethylene diisocyanate is dissolved in 2.5 parts phenol, whereby the diurethane is formed. There is then added 1 mol 1,4-butane-diol and $\frac{1}{200}$ mol lithium phenolate. The mixture is then heated up to 160° C for 3 hours. The phenol is distilled off in vacuo (1-2 mm). The last parts of the phenol are removed in vacuo by conducting over large surfaces the liquid now heated at 220° C in the presence of nitrogen, the melt for instance is thereby caused to flow through an evacuated funnel in the form of a film. The mass melting at 175° C may be directly spun. The process may be performed continuously.

Example II

1 mol hexamethylenediamine in 5 times the quantity of benzene is added at 80° C, while stirring, to a solution of 1 mol diphenylcarbonate also in 5 times its quantity of benzene. When standing, the hexamethylene-bis-carbamic acid diphenyl ester is separated in colorless crystals (f. p. 138° C). It can be recrystallized from hot benzene.

1 mol of this carbamic acid ester is mixed with $\frac{1}{200}$ mol lithium phenolate and 1 mol diethylene glycol, then heated at 100° C for 2 hours and finally at 140° C for 5 hours. The reaction product is dissolved in glycol monomethyl ether and precipitated with acetone.

Example III

1 mol tetramethylene diamine, then 1 mol tetramethylene glycol is added to a 20% solution of polymeric ϵ -caprolactam (2 mols) in phenol. The mixture is then caused to flow continuously through a tube heated at 150° C, then through another tube heated at 180° C which, if necessary, is rotatively constructed. After the mass has left the two tubes within 4 hours, it flows into an inclined vacuum vessel, evacuated at about 2 mm. As described in Example I, the mass flows here over a large heating surface, whereby the last portions of the phenol and monomeric lactam are evaporated. The homogeneously melting mass is finally fed to the spinnerets by pumps.

Example IV

2 mols chloroformic acid phenyl ester are added to a solution of 1 mol hexamethylene diamine in chlorobenzene. The mass is heated until the development of hydrogenchloride ceases. When working it up the hexamethylenedicarbamic acid diphenyl ester remains in colorless crystals (f. p. 138° C). 1 mol of the diurethane is melted with 1 mol sebacic acid and heated first at

180° for 3 hours, then at 240° C still another 3 hours in vacuo (2 mm), whereby the phenol is distilled off. The polyamide thus obtained is excellently spinnable from the melt.

Example V

1 mol hexamethylene-bis-carbamic acid diphenylester is melted together with 1 mol octamethyl diamine. The melt is heated gradually at 180° C and kept at this temperature for 3 hours. The phenol is distilled off in vacuo under exclusion of atmospheric oxygen, whereby the temperature is gradually raised up to 240° C. The reaction product is a hard, nearly white resin which is easily formed by mechanical means. It is not identical with the product obtained when 1 mol hexamethylene diamine and 1 mol octamethylene diamine are condensed together in the heat with 2 mols butylcarbonate.

Example VI

Half a mol ϵ -amino caproic acid methyl ester in benzene is added, while cooling, to a solution of 1 mol chloroformic acid phenyl ester in benzene. After the benzene is distilled off the ϵ -phenylcarbaminyl caproic acid methyl ester is separated from the amino caproic acid methyl ester hydrochloride by adding water. The dried urethane ester (1 mol) is then mixed with 1 mol hexamethylenediamine and heated at 100° C for 2 hours, then at 240° C for further 4 hours and finally heated in vacuo. The polyamide thus obtained can be spun from the melt.

Example VII

Hexamethylene dimercaptane is melted with the calculated amount hexamethylene-bis-carbamic acid diphenyl ester and the melt heated at 150° C for 3 hours. Then the phenol thus formed is distilled off in vacuo (2 mm) at a bath temperature increasing from 150-200° C. in a nitrogen atmosphere free from oxygen within 3 hours. The remaining melt may be formed into elastic filaments which may be oriented by drawing.

Instead of the mercaptane also one of its salts, for instance the lithium compounds may be employed. There is formed the respective phenolate as by-product. This is washed out with alcohol from the melt which solidifies, when cooled down. Also amine salts of mercaptanes may be employed. Volatile amines are then distilled off together with phenols.

Example VIII

2 mols chloroformic acid phenyl ester are dissolved in o-dichlorobenzene and there is added gradually 1 mol hexamethylene diamine dissolved in o-dichlorobenzene. The hexamethylene diamine hydrochloride and more or less also hexamethylene dicarbamic acid phenyl ester is hereby precipitated. The mass is heated, while stirring, until all is again dissolved. Then there is added 1 mol decamethylene glycol. The mass is then heated at 150° C for 5 hours, the temperature then increased for 1 hour until boiling and the solvent and the phenol thus formed is distilled off in vacuo, whereby the temperature is finally raised up to 220° C. The liquid residue is then extruded by a nozzle as skein into cold water.

Example IX

Symmetrical dimethyl-1,4-tetramethylene diamine is transformed with phosgene in the usual way in tetramethylene-bis-carbamic acid chloride and the latter converted by heating with phenol dissolved in benzene into the tetramethylene-bis-carbamic acid diphenyl ester. After the hydrogen chloride development is finished, the equivalent amount $\beta\beta'$ -diamino-diethylether is added. The benzene is distilled off, the residue heated to 180° C within several hours. The phenol thus separated is finally distilled off in vacuo. The product thus obtained may be drawn into filaments from the melt.

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