

The present invention relates to a process for the preparation of homogeneous copolyamides having both a high melting point and good flexibility, from hexamethylenediamine, adipic acid by itself or mixed with at least one other short-chain dicarboxylic acid and a fatty acid dimer, the quantity of short diacid(s) relative to the total quantity of the acids present [short acid(s) + dimer acid] being in the range from 50 to 99 mol%.

Copolyamides of this type, based on hexamethylenediamine, adipic acid and dimer acid, are already described by the Applicant Company in French Patent 2,459,810. A homogeneous copolyamide is intended to define a copolymer which forms a single phase in the melt state or a single amorphous phase in the solid state, as can be determined, for example, by scanning electron microscopy which reveals any dispersed phase which may be present by fixing with phosphotungstic acid.

A much simpler means for determining this homogeneity consists in observing the transparency state of, on the one hand, a melt with a thickness of approximately 0.2 to 0.5 cm, heated at a temperature of at least 10°C above its melting point and, on the other hand, a small-diameter rod or film obtained from this melt after rapid cooling, for example by immersion in water at ambient temperature. An absolutely transparent rod or film indicates perfect homogeneity of the polymer; when the film is greater in thickness or when the cooling has been slower, a translucent zone may be the sign of some degree of crystallinity; a white film incorporating streaks or inclusions (eyes, for example) is the sign of a major heterogeneity. This homogeneity underlines the fact that the copolymers in question have thermomechanical properties which can be readily reproduced, in addition to good transparency properties. A copolyamide having good flexibility is intended to define a copolyamide whose flexural modulus is significantly lower than that of the conventional polyamides such as polyhexamethylene adipamide (nylon 66) or polycaprolactam (nylon 6) and

will be of the order of, or lower than, that of the polyamides considered to be flexible such as, for example, polyundecanamide (nylon 11).

5 In the copolyamides of the type of this prior art, the crystallinity and, consequently, the ability to obtain high melting points and good thermomechanical properties are essentially contributed by the group of segments which are derived from the condensation of the short acid molecules (adipic acid) with a part of the
10 hexamethylenediamine molecules. The ability to have flexibility and good elasticity is substantially contributed by the group of segments which are derived from the condensation of the fatty acid dimer molecules with the other part of the hexamethylenediamine molecules. It is
15 self-evident that, by changing the quantity of short acid relative to the total quantity of the acids present in the range from 50 to 99 mol%, copolyamides are obtained whose melting point will be more or less high and whose flexibility will be greater or lesser. The copolyamides
20 in which the quantity of short acid is in the range from 70 to 90 mol% are of particular interest because they have both a high melting point and excellent flexibility.

Several specific processes which make it possible to prepare such homogeneous copolyamides are also
25 described in the abovementioned French patent. According to a first process, the following steps are carried out:

1. prepolymers are prepared in a heterogeneous medium from a mixture of adipic acid, dimer acid and hexamethylenediamine or of their corresponding salts, the
30 quantities of the constituents of the starting mixture being such that the quantity of adipic acid relative to the total acids is in the range from 50 to 99 mol% and that the contents of amino groups and of carboxylic groups do not differ by more than 5% as an absolute
35 value, the polymerisation reaction consisting in taking the starting mixture up to 270°C by heating it in a gradual and uniform manner over a period of time ranging from 30 minutes to several hours, at a water vapour pressure of between 1.3 and 2.5 MPa, which is the

chemical equilibrium state corresponding to the start of the following phase (2);

5 2. a homogenisation phase is then carried out for a period of between 0.5 and 5 hours, at a temperature of between 270 and 290°C under a water vapour pressure of between 1.3 and 2.5 MPa, during which the equilibrium state of the amidification reactions is not altered;

10 3. and, lastly, a polycondensation is carried out so as to convert the homogeneous prepolymers thus obtained into the required copolyamides, the polycondensation reaction being carried out in a conventional manner at a temperature of between 260 and 290°C at atmospheric pressure or at a lower pressure, for a period ranging from 30 minutes to several hours.

15 According to a second process, the following steps are carried out:

20 1. prepolymers are prepared in a heterogeneous medium from a mixture of adipic acid, dimer acid and hexamethylenediamine or of their corresponding salts, the quantities of the constituents of the starting mixture being such that the quantity of adipic acid relative to the total acids is in the range from 50 to 99 mol% and that the contents of amino groups and of carboxylic groups differ by more than 5% as an absolute value, the
25 prepolymerisation reaction consisting in taking the starting mixture to a temperature corresponding to the beginning of the following phase (2) in a gradual and uniform manner, over a period of time ranging from 30 minutes to several hours;

30 2. a homogenisation phase is then carried out for a period between 10 minutes and 2 hours at a temperature of between 265 and 290°C;

35 3. and, lastly, the gradual addition of the deficient reactant is carried out in a conventional manner and the polycondensation is completed at temperatures of between 260 and 290°C at atmospheric pressure or at a lower pressure for a period ranging from 30 minutes to several hours until the required copolyamides are obtained.

Lastly, according to a third process, copolymers are prepared directly at a temperature of between 150 and 300°C, in a homogeneous medium, from a mixture of adipic acid, dimer acid and hexamethylenediamine, the quantity of adipic acid relative to the total acids being in the range from 50 to 99 mol% and the contents of amino groups and of carboxylic groups not differing by more than 5% as an absolute value, the medium being made homogeneous by the use of a third solvent for the mixture of the three starting products or of the corresponding salts and/or the oligomers of adipic acid and hexamethylenediamine and dimer acid and hexamethylenediamine with a molecular weight of below 5,000, the said solvent being inert towards the amidification reactants and reactions.

While continuing work in this field of technology, the Applicant Company has shown in EP-A-196,981 (published after the priority date of the present invention) that homogeneous copolyamides can be prepared by making use of a fourth process permitting independence:

- of the use of an intermediate homogenisation step at a high temperature, which is liable to lengthen excessively the time of occupation of industrial reactors and to result prematurely in some degradation of the copolyamides, and

- of the use of an organic solvent, the recovery of which is liable to give rise to additional difficulties.

According to this fourth process in accordance with the abovementioned EP, an unbalanced prepolymer containing NH_2 end groups is prepared in a first step from excess hexamethylenediamine and a short acid like adipic acid by driving the polycondensation forward by removing the water present in the reaction mixture by distillation under an appropriate autogenous pressure, and the prepolymer obtained is then reacted, in a second step, with the dimer acid.

A process in which the dimer acid is added after the formation of a polymer of hexamethylenediamine and adipic acid has already been described in US-A-3,329,633, but in this prior art the polymer in question is

balanced, that is to say it contains NH_2 and COOH end groups in equivalent numbers, and it has been found that this balanced structure produces a heterogeneous copolyamide after the addition of dimer acid.

5 The Applicant Company has now found a fifth process for the preparation of homogeneous copolyamides based on hexamethylenediamine, short acid(s) and a dimer acid, which does not rely on the use of an intermediate homogenisation stage or of an organic solvent. Like the
10 fourth process, this fifth process has two separate steps, including a first step for the preparation of an unbalanced prepolymer, but this first step is now conducted without performing a distillation.

 More specifically, the present invention relates
15 to a process for the preparation of homogeneous copolyamides having both a high melting point and good flexibility, from hexamethylenediamine, short-chain dicarboxylic acid(s) and a fatty acid dimer, the quantity of short acid(s) relative to the total quantity of the acids
20 present being in the range from 50 to 99 mol%, the said process being characterised by the following points:

- in a first step (a), a prepolymer having amino end groups is prepared by reacting, optionally in the presence of water at the beginning of this step, the
25 compounds consisting:

- (i) either a mixture of the following constituents: adipic acid, optionally at least one other short-chain dicarboxylic acid of a saturated alicyclic or aromatic type, hexamethylenediamine, and a catalyst
30 consisting either of a compound (alpha) or of a compound (beta), (alpha) denoting an inorganic oxyacid or an organic oxyacid other than a carboxylic acid, in which at least one of the acid groups, when there are several of these, has an ionisation constant pK_a in water at 25°C
35 which does not exceed 4, (beta) denoting an alkali metal or alkaline-earth metal salt of this acid,

- (ii) or of a mixture of the following constituents: stoichiometric salt(s) of the abovementioned short acid(s) with hexamethylenediamine, free

hexamethylenediamine and the catalyst defined above, this first step (a) being carried out, without performing water distillation in a closed system of the autoclave type, under the following conditions:

- 5 - the quantity of water initially present, when there is any, in the reaction mixture, expressed as a percentage by weight based on the total quantity of water initially present + reactants, does not exceed 45%,
- 10 - the starting mixture is gradually raised, by heating, to a temperature in the range from 200 to 250°C and the reactants are allowed to react at this temperature and at an autogenous pressure which is higher than atmospheric pressure for a period of time which is sufficient to enable the reaction mixture to reach the state of chemical equilibrium of the amidification reactions corresponding to the beginning of the following step (b);
- 15
- 20 - in a second step (b), the prepolymer obtained is reacted with the fatty acid dimer, which is added gradually to the reaction mixture, the following points being observed:
 - 25 - the operation is carried out at a temperature situated in the range from 200 to 280°C,
 - the operation is carried out at an autogenous pressure which, during the period of addition of the dimer acid, is equal to the prepolymerisation pressure (case a) or is higher than this pressure (case b) or gradually decreases from the prepolymerisation pressure to atmospheric pressure (case c) and which, after the addition of the dimer acid, decreases gradually to a value which may be atmospheric pressure (in cases a and b) or a pressure which is lower than the latter (in cases a, b and c) or remains equal to atmospheric pressure (in case c),
 - 30
 - 35 - a simultaneous distillation of water is

ensured, on the one hand, if desired, during the period of addition of the dimer acid and, on the other hand, during the period following the addition of the dimer acid,

- 5 - care is taken that, at the end of the period of addition of the dimer acid, the ratio r_1 , defined below:

10
$$\frac{\text{weight of reactants in step (a)} + \text{weight of dimer acid}}{\text{weight of reactants in step (a)} + \text{weight of dimer acid} + \text{weight of residual water}}$$

has a value situated in the range from 0.915 to 1, if need be by removing water by distillation during the period of addition of the dimer acid, and

- 15 - the dimer acid, once its introduction is complete, is reacted for a period which is sufficient to produce a copolyamide with the required viscosity,

- 20 - the proportions of the various constituents are such that:

 - the quantity of short acid(s) relative to the combination of short acid(s) + dimer acid ranges from 50 to 99 mol%,

- 25 - the ratio r_2 of the number of moles of hexamethylenediamine employed in step (a), alternative (i), relative to the total number of moles of short acid(s) and of dimer acid is equal to 1 or optionally equal to a value which is higher than the stoichiometry and is determined so as to introduce into the reaction mixture an excess of hexamethylenediamine which makes it possible to compensate for the loss of this reactant which may occur in step (b) during the pressure release,

- 30 - the ratio r_3 of the number of moles of free hexamethylenediamine employed in step (a), variant (ii), relative to the number of moles of dimer acid has the values indicated above for the ratio r_2 .

35 A preferred process according to the present invention is that consisting in carrying out steps (a) and (b) as defined above as a sequence, but with the

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presence of water in the reaction mixture at the beginning of step (a), the quantity of water initially present not exceeding 45%, as indicated above.

5 In the present description, the pressure under discussion is always absolute pressure.

10 The "water initially present in the reaction mixture" is intended to define the water which is initially introduced, in addition to the reactants, into the reaction mixture in step (a), plus, if appropriate, the water used as solvent for the reactants employed in the form of solution. In this case, the term "reactants" includes the short diacid(s), hexamethylenediamine and the catalyst and, unless indicated otherwise, the substances involved are in the dry state.

15 "Residual water" is taken as: either the quantity of water present at the beginning of step (a), when no water has been distilled off until the end of the addition of the dimer acid, or, when water has been distilled off during the addition of the dimer acid, the difference: quantity of water initially present - quantity of water distilled off until the end of the addition of the dimer acid.

25 It is obvious that, when the step (a) is performed without the presence of water at the beginning of this step, the period of addition of the dimer acid will elapse without water distillation taking place and the quantity of residual water will be nil and the ratio r_1 referred to above will be equal to 1. This ratio will also be equal to 1 when the quantity of water distilled off until the end of the addition of the dimer acid corresponds to the quantity of water present at the beginning of step (a).

30 The term "copolyamide of the required viscosity" is intended to define a copolyamide which has a sufficiently high melt viscosity to be capable of being injection-moulded or extruded in a convenient manner. More precisely, it is intended to define a copolyamide with a melt viscosity (measured under conditions which are defined hereinafter) of at least 1,500 poises and

preferably between 3,000 and 60,000 poises.

On the subject of the loss of hexamethylene-
diamine, referred to above, this can arise, for example,
when the equipment employed does not incorporate a
5 distillation column; under these conditions, for given
equipment and for given charges, simple methods may be
used to determine the quantity of hexamethylenediamine
entrained during each operation and, consequently, the
excess of this reactant to be introduced into the initial
10 reaction mixture to preserve the equivalence between the
amino groups and the carboxyl groups which react. In
general, when a loss of hexamethylenediamine occurs, it
is very moderate, and this is one of the advantages of
the process according to the present invention; it has
15 been found that the use of quantities of this reactant
which result in the ratios r_2 and r_3 having values ranging
from a number greater than 1 to 1.1 are suitable. The
loss of hexamethylenediamine, expressed as a weight
percentage based on the total quantity of diamine
20 employed, generally amounts to less than 1% and may even
reach values as low as those below 0.3%.

It is obvious that "short acid(s)" is intended to
denote adipic acid by itself or mixed with at least one
other short-chain dicarboxylic acid of a saturated
25 alicyclic or aromatic nature. More precisely, alicyclic
and/or aromatic dicarboxylic acids which can come within
the scope of the present invention are compounds con-
taining at most 12 carbon atoms; 1,4-cyclohexanedi-
carboxylic acid, isophthalic acid, and terephthalic acid
30 may be mentioned as suitable diacids of this type. The
proportion of adipic acid in the mixture of short diacids
which may be employed usually represents at least
70 mol%.

It is thought that during the homogenisation step
35 employed in the abovementioned French patent, the amino
and carboxyl groups, which no longer undergo an amidifi-
cation reaction at this time, are used to form breaks in
the block oligomers of adipic acid with hexamethylene-
diamine and/or oligomers of dimer acid with

hexamethylenediamine and that, as a result, a homogeneous random prepolymer is formed. It is thought that, in the process according to the present invention, the prepolymer formed in step (a) is in the form of a homogeneous preformed polyhexamethylene amide structure whose homogeneity, surprisingly, is not altered by the subsequent addition of a dimer acid whose oligomers with hexamethylenediamine are, however, incompatible with those of the preformed polyhexamethylene amide.

The dimer acids employed are obtained by polymerisation of compounds containing 80 to 100% by weight of monomeric fatty acid(s) containing from 16 to 20 carbon atoms and 20 to 0% by weight of monomeric fatty acid(s) containing from 8 to 15 carbon atoms and/or from 21 to 24 carbon atoms. Monomeric fatty acids are intended to denote saturated or unsaturated, straight-chain or branched aliphatic monoacids.

Among the straight-chain or branched saturated monomeric fatty acids there may be mentioned: caprylic, pelargonic, capric, lauric, myristic, palmitic and isopalmitic, stearic, archidic, behenic and lignoceric acids.

Among the straight-chain or branched monomeric fatty acids containing ethylenic unsaturation(s) there may be mentioned: 3-octenoic, 11-dodecenoic, oleic, lauroleic, myristoleic, palmitoleic, gadoleic, cetoleic, linoleic, linolenic, eicosatetraenoic and chaulmoogric acids. Some acids containing acetylenic unsaturation may also result in polymeric acids, but they do not occur naturally in quantities of interest and as a result their economic interest is very low.

The polymeric fatty acids obtained by thermal polymerisation, in the presence of catalysts such as peroxides or Lewis acids if appropriate, may be fractionated, for example by using conventional vacuum distillation or solvent extraction methods. They can also be hydrogenated to reduce their degree of unsaturation and thus to reduce their colour.

The dimer acids which are preferably employed in

the present invention are fractionated polymeric fatty acids in which the difunctional acid fraction is greater than 94% by weight, the monofunctional acid fraction is less than 1% by weight and still more preferably does not exceed 0.5% by weight, the fraction of acid with a functionality greater than 2 is less than 5% by weight and still more preferably does not exceed 3% by weight.

Still more preferably, the dimer acids employed are the species obtained by fractionation (resulting in the fractions indicated above) of polymeric fatty acids which have additionally undergone a hydrogenation.

The dimer acids which are most especially suitable are the species obtained by fractionation of a hydrogenated composition originating from the catalytic polymerisation of monomeric fatty acid(s) containing 18 carbon atoms. In this context, owing to their ready availability of supply and their relatively easy polymerisation, oleic, linoleic and linolenic acids, taken by themselves or in pairs or preferably in the form of a ternary mixture, are the starting materials which are most especially preferred for the preparation of the polymeric fatty acids.

Concerning the strong organic or inorganic oxyacid (α) which is employed as catalyst, use is made, as indicated above, of an oxygen-containing mono- or polyacid in which at least one of the acid groups has an ionisation constant pK_a in water at 25°C which does not exceed 4.

As strong acids which are suitable there may be mentioned, for example:

- among the inorganic oxyacids, sulphurous, sulphuric, hypophosphorous, phosphorous, orthophosphoric or pyrophosphoric acids;

- among the organic oxyacids:

- the organosulphonic acids of formula R_1-SO_3H (I) in which R_1 denotes: a straight-chain or branched alkyl radical containing from 1 to 6 carbon atoms; a phenyl radical optionally substituted by 1 to 3 alkyl radicals containing from 1 to 3 carbon atoms; a phenylalkyl

radical containing from 1 to 3 carbon atoms in the alkyl moiety and in which the benzene nucleus may optionally be substituted by 1 to 3 alkyl radicals containing from 1 to 3 carbon atoms; or a naphthyl radical optionally substituted by 1 to 4 alkyl radicals containing from 1 to 3 carbon atoms;

- the organophosphonic acids of formula $R_2-P(O)(OH)_2$ (II) in which R_2 denotes an alkyl radical, a phenyl radical or a phenylalkyl radical, each of these radicals having the definition given above for R_1 ;

- the organophosphinic acids of formula $R_3R_4-P(O)(OH)$ (III) in which R_3 and R_4 , which are identical or different, each denote: a straight-chain alkyl radical containing from 1 to 3 carbon atoms; a phenyl radical or a phenylalkyl radical, each of the latter two radicals having the definition given above for R_1 ;

- the organophosphonous acids of formula $R_5H-P(O)(OH)$ (IV) in which R_5 denotes: a straight-chain or branched alkyl radical containing from 1 to 4 carbon atoms (the branching being excluded for an alkyl radical containing four carbon atoms); a phenyl radical or a phenylalkyl radical, each of the latter two radicals having the definition given above for R_1 .

As a strong acid (alpha), it is preferred to use the acids derived from phosphorus, and more particularly the hypophosphorous, phosphorous, orthophosphoric, pyrophosphoric, methylphosphonic, phenylphosphonic, benzylphosphonic, dimethylphosphinic, diphenylphosphinic, methylphenylphosphinic, dibenzylphosphinic, methylphosphonous, phenylphosphonous or benzylphosphonous acids.

Where the acid salt (beta) is concerned, use is generally made of alkali metal or alkaline-earth metal salts derived from inorganic or organic oxyacids (alpha).

Salts which are completely soluble in the reaction mixture are preferably used as the salt (beta). Among these preferred salts (beta), the sodium and potassium salts derived from the particular suitable types of inorganic or organic oxyacids (alpha), referred

to above, are very suitable. The salts (beta) which are especially suitable are sodium and potassium salts originating from the preferred phosphorus-derived acids referred to by name above.

5 The proportions of strong acid (alpha) or salt (beta), expressed as a weight percentage relative to the final copolyamide, are generally between 0.01 and 1%, and preferably between 0.01 and 0.5%. In addition to a catalytic effect during the polycondensation reaction,
10 the strong acids (alpha) or their salts (beta) and especially the phosphorus-derived compounds of this type, have the advantage of giving the final copolyamide some protection against degradation due to light.

 If good operation of the process according to the
15 present invention is to be ensured, care will be taken particularly to observe as perfectly as possible the corresponding proportions of the various constituents employed. According to a preferred embodiment of the invention, in step (a) the short diacid(s) is (or are)
20 used in the form of its (or their) salt(s) with hexamethylenediamine (variant ii). In order to ensure, on the one hand, stoichiometry in the manufacture of the salt(s) of short acid(s) with hexamethylenediamine and, on the other hand, the stoichiometry or the intended overshoot
25 of stoichiometry between free hexamethylenediamine and the dimer acid, the operation may be carried out by precise weighing of the reactants whose concentration is accurately known at the time of use. The stoichiometry of the salt(s) of the short acid(s) can be monitored by
30 measuring the pH of specimen solutions produced by diluting the salt(s) in a suitable solvent. It is also possible to monitor the stoichiometry or the intended overshoot of stoichiometry in the amidification reaction between the free amino groups in the prepolymer and the
35 dimer acid by control of the viscosity, which may be advantageously assessed by in situ measurement of the resistant torque of mechanical stirring of the polycondensation mixture in step (b).

 To carry out the process according to the

invention, hexamethylenediamine may be used in solid form, in melt form or in the form of an aqueous solution. The salt(s) of short acid(s) and hexamethylenediamine may also be used in solid form, in melt form or in the form of an aqueous solution.

Concerning the carrying out of step (a) of the preferred process according to the invention [performed in the presence of water at the beginning of step (a)], the quantity of water initially present in the reaction mixture is preferably situated in the range from 5 to 45% and, still more preferably, from 9 to 40% and the reactants are preferably allowed to react at a temperature situated in the range from 205 to 230°C for a period which depends on the temperature chosen, ranging, for example, from 20 minutes (when the temperature chosen is 230°C) to 2 hours (when the temperature chosen is 205°C) at an autogenous pressure ranging from 1.1 to 3 MPa.

Concerning the carrying out of step (b) which follows step (a), carried out in the preferred manner as indicated above, the operation is preferably carried out by linking the following steps:

- all of the dimer acid is introduced gradually, for example over a period ranging from 10 minutes to 2 hours, the following points being observed:

- the temperature of the reaction mixture is kept equal to the prepolymerisation temperature,

- the pressure is kept equal to the prepolymerisation pressure or is raised to a value which is 5 to 40% higher than the prepolymerisation pressure,

- it is ensured, if desired by removing water by distillation, that the ratio r_1 , defined above, has a value situated in the range from 0.930 to 1 at the end of the period of addition of the dimer acid,

- when the abovementioned addition of dimer acid is finished, after stirring of the reaction mixture has continued, if appropriate, at the abovementioned pressure for a period ranging, for example, from 10 minutes to

1 hour, the temperature being increased, if appropriate, over the same period to a value above that employed during the period of addition of the dimer acid and situated in the range from a value above 205 to 240°C, the following operations are then carried out:

- the pressure is gradually lowered, over a period ranging, for example, from 10 minutes to 2 hours, from the value employed during the period of addition of the dimer acid to the value of atmospheric pressure,
- the temperature of the reaction mixture is raised over the same time to a value higher than the temperature which is either that employed during the period of addition of the dimer acid or that reached at the end of the period (if any) of superheating which immediately follows the period of addition of the dimer acid, this temperature, once raised, being situated in the range from a value above 205°C to 280°C,
- a steady distillation of water is further ensured over the same time, and
- a reduced pressure equal to or lower than 600×10^2 Pa is then gradually established over a period ranging, for example, from 5 minutes to 1 hour,
- the polycondensation is then terminated while the mixture continues to be stirred at the abovementioned temperature situated in the range from a value above 205°C to 280°C, at the reduced pressure indicated above, for a period ranging, for example, from 10 minutes to 1 hour, while a simultaneous distillation of water is maintained.

It is possible to add to the mixture for preparing the copolyamides produced in accordance with the present process, without inconvenience, one or more additives such as especially: stabilisers or inhibitors of degradation due to oxidation, to ultraviolet, to light

or heat; lubricants; colorants; nucleating agents; antifoaming agents and inorganic fillers.

5 In the case where the reaction mixture in step (a) initially contains a quantity of water which is greater than 45%, it is obvious that in a first stage, before commencing step (a), an operation to concentrate the reaction mixture may be carried out, for example by distilling off water at atmospheric pressure or under reduced pressure and under low temperature conditions 10 which do not permit an amidification reaction to develop in any way, so as to reduce the quantity of water present at the beginning of step (a) to the indicated value not exceeding 45%.

15 The process according to the invention makes it possible to obtain homogeneous copolyamides which have good thermal resistance and mechanical strength due to their high melting points and an improved flexibility at the same time. Being perfectly homogeneous, they have improved transparency properties and may be employed 20 according to the usual injection-moulding, extrusion or spinning methods to give shaped articles: components, films or fibres of very high uniformity.

25 The following examples illustrate, without implying any limitation, how the present invention may be implemented.

30 A number of controls are carried out in these examples. Similarly, various properties are measured. The operating methods and/or the standards according to which these controls and measurements are carried out are indicated below.

- MICROCALORIMETRIC ANALYSIS:

The polymers are characterised by melting characteristics such as the melting endotherms E_m and the crystallisation exotherms E_c .

35 These determinations are carried out using a specimen subjected to temperature variations of $10^\circ\text{C}/\text{minute}$ both upwards and downwards. In this way, a differential microcalorimetry curve is determined, on which it is possible to observe the melting point (T_m)

and the point of crystallisation on cooling (T_c).

- MELT VISCOSITY:

5 This is measured at 260°C under a variable shear gradient (indicated in the examples below) with the aid of a Davenport rheometer. The results are expressed in poises.

- DETERMINATION OF THE END GROUPS IN THE COPOLYAMIDE:

10 The method described below makes it possible to estimate both types of end groups on a single test sample and with a single acidimetric titration. The polyamide is dissolved with stirring in a mixture of trifluoroethanol and chloroform at ambient temperature. After it has dissolved, a 0.05 N aqueous alcoholic solution of tetrabutylammonium hydroxide is added and a potentiometric titration is finally carried out using a standardised solution of 0.05 N hydrochloric acid under a stream of nitrogen. The use of the potentiometric curve exhibiting two potential steps enables the two types of end groups to be determined.

20 - DETERMINATION OF TENSILE MECHANICAL PROPERTIES:

25 These are determined at 25°C on specimens conditioned at an RH of 0 according to the French standard NF T 51 034 (in an Instron-type tensometer at a traction speed of 10 mm/min). Conditioning at an RH of 0: the specimens are placed over silica gel in a desiccator and are dried for 24 hours at ambient temperature at 0.66 to 1.33×10^2 Pa before the measurements are carried out.

- TORSIONAL MODULUS:

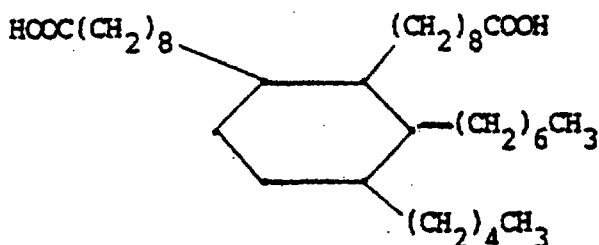
30 This is determined at several temperatures (-20°C, 0°C, +20°C, +40°C, +60°C) with an automatic torsion pendulum at a frequency of the order of 1 hertz in accordance with the ISO standard R 537. The specimens are conditioned at an RH of 0. The results are expressed in MPa.

35 - DETERMINATION OF THE LOSS OF HEXAMETHYLENEDIAMINE:

A quantitative estimation is done at the end of step (b) on an aliquot portion of the total aqueous distillate collected. A potentiometric titration is carried out using a standardised 0.1 N solution of

hydrochloric acid. The loss of hexamethylenediamine is expressed as a weight percentage based on the total quantity of diamine employed [free diamine + any diamine present as a constituent of the salt(s) of short acid(s)].

In the following examples, wherever reference is made to the dimer acid employed, the compound used is that marketed by Unichema Chemie under the trademark Pripol 1010, in which the difunctional acid fraction is greater than 95% by weight. This difunctional acid fraction consists of a mixture of isomers containing 36 carbon atoms, in which the predominant species is a saturated compound of formula:



The monofunctional acid fraction (the weight proportion of which will be detailed later) consists substantially of oleic acid; as for the fraction of acid with a functionality greater than 2 (the weight proportion of which will also be detailed later), this consists substantially of a mixture of isomeric trimers containing 54 carbon atoms; the mean molecular mass of this dimer acid is of the order of 571.

EXAMPLES

EXAMPLE 1

The operation is carried out in a 7.5-litre stainless steel autoclave fitted with mechanical stirring, a heating system and a system which makes it possible to operate at a pressure above atmospheric pressure or below atmospheric pressure. The plant also comprises a device permitting a liquid reactant to be introduced into the autoclave, under pressure, and a device permitting water to be removed.

Step (a):

The following charges are introduced into the apparatus at ambient temperature:

- 5 - hexamethylenediamine salt of adipic acid, in equimolar proportions, in dry solid form: 2086.7 g (7.955 moles),
- demineralised water: 1,048 g,
- 10 - aqueous solution containing 32.5% by weight of hexamethylenediamine: 746.5 g, i.e. 242.6 g of pure hexamethylenediamine (2.088 moles) and 503.9 g of water of solution,
- aqueous solution containing 50% by weight of hypophosphorous acid: 6 g, i.e. 3 g of water of solution,
- 15 - silicone antifoam marketed by Rhône-Poulenc Spécialités Chimiques under the trademark Rhodorsil Si 454 : 0.2 g.

20 With these charges, the quantity of water initially present in the reaction mixture is 1,554.9 g and it represents 40% by weight of the total : water initially present + reactants.

25 Stirring is commenced and 5 nitrogen purges are carried out by pressurisation to 7×10^5 Pa, followed by pressure release. The temperature of the stirred mixture is gradually raised to 210°C over 1 hour (an autogenous pressure of 1.8 MPa) and the reactants are allowed to react under these conditions for 1 hour.

Step (b):

30 While the abovementioned temperature and pressure conditions are maintained, 1,140 g (1.996 moles) of a fatty acid dimer marketed under the trademark Pripol 1010 by Unichema Chemie, which has a monomer content of 0.03% by weight and a trimer content of 3% by weight, are introduced into the stirred mixture by being run in

35 steadily over 1 hour 10 minutes; during the period of addition of the dimer acid, a steady distillation of water is ensured under rate conditions which enable 1,320 g of water to be collected at the end of the addition of the dimer acid.

At the end of the addition of the dimer acid the weight of residual water is 234.9 g and the ratio r_1 defined earlier in the present description has a value of 0.937.

5 Water distillation is continued to a small extent for 30 minutes to reach a temperature of 230°C at a pressure of 1.8 MPa.

10 The autoclave pressure is then released gradually, over a period of 90 minutes, down to atmospheric pressure and the temperature is raised gradually to 260°C over the same period while a steady distillation of water continues to be ensured.

15 A pressure of 120×10^2 Pa is then established gradually over 30 minutes while the mixture is maintained at 260°C and the polymerisation is finished off by continuing to stir the mixture at 260°C and 120×10^2 Pa for 20 minutes while a steady distillation of water continues to be ensured.

20 The loss of hexamethylenediamine, measured at the end of step (b), is 0.29%.

25 Stirring is stopped, and then a nitrogen pressure of 5×10^5 Pa is established in the autoclave and the polymer is drawn off. The latter, extruded from the autoclave in rod form, is cooled by passing through a cold water bath, and is then granulated and dried.

The polymer obtained is perfectly transparent and consequently homogeneous. It has the following characteristics, measured on dry granules:

- 30 - melting point (T_m): 240°C,
- crystallisation point on cooling (T_c): 186°C,
- end group contents:
 - COOH: 85.62 meq/kg
 - NH_2 : 4.92 meq/kg
- melt viscosity at 260°C under a shear gradient:
35 $\gamma = 10 \text{ s}^{-1}$: 11,000 poises.
- tensile mechanical properties:
 - break strength: 64.3 MPa,
 - elongation at break: 260%,
 - tensile modulus: 760 MPa,

- torsional thermomechanical properties; torsional modulus at:

- -20°C: 690 MPa,
- 0°C: 660 MPa,
- +20°C: 580 MPa,
- +40°C: 320 MPa,
- +60°C: 150 MPa.

COMPARATIVE EXAMPLE A

In this example it is shown (with all the remaining operating conditions of the invention being observed) that when the quantity of water initially present in the reaction mixture (expressed as a percentage by weight based on the total of water initially present + reactants) is greater than 45%, the polymer obtained is opaque and heterogeneous.

The operation is carried out in a 7.5-litre stainless steel autoclave as indicated in Example 1.

Step (a):

Charges:

- hexamethylenediamine salt of adipic acid, in dry solid form: 2,086.7 g (7.955 moles),
- demineralised water: 1,825.4 g,
- aqueous solution containing 32.5% by weight of hexamethylenediamine: 746.5 g, i.e. 242.6 g of hexamethylenediamine (2.088 moles) and 503.9 g of water of solution,
- aqueous solution containing 50% by weight of hypophosphorous acid: 6 g, i.e. 3 g of water of solution,
- silicone antifoam of Example 1: 0.2 g.

With these charges, the quantity of water initially present in the reaction mixture is 2,332.3 g and it represents 50% by weight of the total of water initially present + reactants.

The operating procedure is identical to that indicated in Example 1.

Step (b):

Charges:

- dimer acid: 1,140 g (1.996 moles).

The operating procedure is identical to that indicated in Example 1, the only changes being as follows:

5 2.091 g of water are collected by distillation at the end of the addition of the dimer acid; the weight of residual water is 241.3 g and the ratio r_1 also has a value of 0.935 in this case.

The reduced pressure which is established is 400×10^2 Pa.

10 The polymer obtained is opaque and consequently heterogeneous. It has the following characteristics, measured on dry granules:

- melting point (T_m): 248°C ,
- crystallisation point on cooling (T_c): 188°C ,
- 15 - end group contents:
 - COOH: 32.7 meq/kg
 - NH_2 : 25.5 meq/kg.

COMPARATIVE EXAMPLE B

20 In this example it is shown (with all the remaining operating conditions of the invention being observed) that when the ratio r_1 has a value which is lower than 0.915 at the end of the period of addition of the dimer acid, the polymer obtained is opaque and heterogeneous.

25 The operation is carried out in a 7.5-litre stainless steel autoclave equipped as stated in Example 1.

Step (a):

Charges:

- hexamethylenediamine salt of adipic acid, in dry solid form: 2,086.7 g (7.955 moles),
- 30 - demineralised water: 1,048 g,
- aqueous solution containing 32.5% by weight of hexamethylenediamine: 746.5 g, i.e. 242.6 g of hexamethylenediamine (2.088 moles) and 503.9 g
- 35 of water of solution,
- aqueous solution containing 50% by weight of hypophosphorous acid: 6 g, i.e. 3 g of water of solution,
- silicone antifoam of Example 1: 0.2 g.

With these charges, the quantity of water initially present in the reaction mixture is 1,554.9 g and it represents 40% by weight of the total of water initially present + reactants.

5 The operating procedure is identical to that indicated in Example 1.

Step (b):

Charges:

- dimer acid: 1,140 g (1.996 moles).

10 The operating procedure is identical to that indicated in Example 1, the only changes being as follows:

15 1,170 g of water are collected by distillation at the end of the addition of the dimer acid; the weight of residual water is 384.9 g and the ratio r_1 then has a value of 0.900.

The reduced pressure which is established is 500×10^2 Pa.

20 The polymer obtained is opaque and consequently heterogeneous. It has the following characteristics, measured on dry granules:

- melting point (T_m): 245°C,

- crystallisation point on cooling (T_c): 189°C.

EXAMPLE 2

25 The operation is carried out in a 7.5-litre stainless steel autoclave equipped as stated in Example 1.

Step (a):

Charges:

30 - hexamethylenediamine salt of adipic acid, in dry solid form: 1,739 g (6.629 moles),

- demineralised water: 203.6 g,

- pure hexamethylenediamine: 177.5 g (1.527 moles) aqueous solution containing 50% by weight of

35 - hypophosphorous acid: 2.5 g, i.e. 1.25 g of water of solution,

- silicone antifoam of Example 1: 0.2 g.

With these charges, the quantity of water initially present in the reaction mixture is 204.85 g and

it represents 9.65% by weight of the total of water initially present + reactants.

5 Stirring is commenced and 5 nitrogen purges are carried out by pressurisation to 7×10^5 Pa, followed by pressure release. The temperature of the stirred mixture is raised gradually to 210°C over 1 hour (an autogenous pressure of 1.4 MPa) and the reactants are allowed to react for 30 minutes under these conditions.

Step (b):

10 While the abovementioned temperature and pressure conditions are maintained, 872 g (1.527 moles) of a fatty acid dimer marketed under the trademark Pripol 1010 by Unichema Chemie, which has a monomer content of 0.03% by weight and a trimer content of 3% by weight, are introduced into the stirred mixture by being steadily run in
15 over 40 minutes; no water distillation is carried out during the period of addition of the dimer acid and the autogenous pressure rises to 1.7 MPa.

20 At the end of the addition of the dimer acid the weight of residual water is 204.85 g and the ratio r_1 , defined earlier in the present description, has a value of 0.932.

25 The autoclave pressure is then gradually released down to atmospheric pressure over a period of 1 hour 40 minutes, and the temperature is gradually increased to 260°C over the same period while water is simultaneously distilled off.

30 A pressure of 500×10^2 Pa is then gradually established over 30 minutes while the mixture is maintained at 260°C and the polycondensation is finished off by continuing to stir the mixture for 40 minutes at 260°C and 120×10^2 Pa while a steady distillation of water continues to be ensured.

35 The loss of hexamethylenediamine, measured at the end of step (b), is 0.15%.

 Stirring is stopped and then a nitrogen pressure of 5×10^5 Pa is established in the autoclave and the polymer is drawn off. The latter, extruded from the autoclave in rod form, is cooled by passing through a

cold water bath and is then granulated and dried.

The polymer obtained is perfectly transparent and consequently homogeneous. It has the following characteristics, measured on dry granules:

- 5 - melting point (T_m): 242°C,
- crystallisation point on cooling (T_c): 194°C,
- end group contents:
 - COOH: 60.16 meq/kg
 - NH_2 : 19.78 meq/kg
- 10 - melt viscosity at 260°C under a shear gradient:
 $\gamma = 10 \text{ s}^{-1}$: 26,000 poises.
- tensile mechanical properties:
 - break strength: 72 MPa,
 - elongation at break: 350%,
- 15 - tensile modulus: 630 MPa,
- torsional thermomechanical properties; torsional
 modulus at:
 - -20°C: 720 MPa
 - 0°C: 700 MPa,
 - 20 - +20°C: 580 MPa,
 - +40°C: 320 MPa,
 - +60°C: 160 MPa.

CLAIMS

1. Process for the preparation of homogeneous copolyamides having both a high melting point and good flexibility, from hexamethylenediamine, dicarboxylic acid(s) containing not more than 12 carbon atoms and a fatty acid dimer taken from the group of dimer acids obtained by polymerisation of compounds containing 80 to 100 % by weight of monomeric fatty acid(s) containing from 16 to 20 carbon atoms and 20 to 0 % by weight of monomeric fatty acid(s) containing from 8 to 15 carbon atoms and/or from 21 to 24 carbon atoms, the said process being characterised by the following points:
- in a first step (a), a prepolymer having amino end groups is prepared by reacting, optionally in the presence of water at the beginning of this step, the compounds consisting:
 - (i) either of a mixture of the following constituents: short acids(s) consisting of adipic acid, taken by itself or in a mixture with at least one other dicarboxylic acid of a saturated cycloaliphatic or aromatic type containing not more than 12 carbon atoms + hexamethylenediamine + a catalyst consisting either of a compound (alpha) or of a compound (beta), (alpha) denoting an inorganic oxyacid or an organic oxyacid other than a carboxylic acid, in which at least one of the acid groups, when there are several of these, has an ionisation constant pKa in water at 25°C which does not exceed 4, (beta) denoting an alkali metal or alkaline-earth metal salt of this acid,
 - (ii) or of a mixture of the following constituents: stoichiometric salt(s) of the abovementioned short acid(s) with hexamethylenediamine + free hexamethylenediamine + the catalyst defined above,this first step (a) being carried out, without performing water distillation in a closed system of the autoclave type, under the following conditions:
 - the quantity of water initially present, when there is any, in the reaction mixture expressed as a percentage by weight based on the total quantity of water initially present + reactants does not exceed 45%,



- 40



if need be by removing water by distillation during the period of addition of the dimer acid, and

- the dimer acid, once its introduction is complete, is reacted for a period which is sufficient to produce a copolyamide with the required viscosity,
- the proportions of the various constituents are such that:

- the quantity of short acid(s) relative to the total of short acid(s) + dimer acid ranges from 50 to 99 mol%,

- the ratio r_2 of the number of moles of hexamethylenediamine employed in step (a), variant (i), relative to the total number of moles of short acid(s) and of dimer acid is equal to 1 or optionally equal to a value which is higher than the stoichiometry and is determined so as to introduce into the reaction mixture an excess of hexamethylenediamine which makes it possible to compensate for the loss of this reactant which may occur in step (b) during the pressure release,

- the ratio r_3 of the number of moles of free hexamethylenediamine employed in step (a), variant (ii), relative to the number of moles of dimer acid has the values indicated above for the ratio r_2 .

2. Process according to Claim 1, characterised in that the steps (a) and (b) are performed as a sequence, but with a presence of water in the reaction mixture at the beginning of step (a), the quantity of water initially present not exceeding 45%.

3. Process according to either of Claims 1 and 2, characterised in that the short acids used consist of adipic acid by itself or mixed with at least one other dicarboxylic acid taken from the group consisting of 1,4-cyclohexanedicarboxylic acid, isophthalic acid, and terephthalic acid, the proportion of adipic acid in the mixture representing at least 70 mol%.

4. Process according to any one of Claims 1 to 3, characterised in that the dimer acids used are fractionated polymeric fatty acids in which the difunctional acid fraction is greater than 94% by weight, the monofunctional acid fraction is less than 1% by weight and



the fraction of acid of functionality greater than 2 is less than 5% by weight.

5. Process according to Claim 4, characterised in that the dimer acids which are used consist of the species obtained by fractionation of a hydrogenated composition originating from the catalytic polymerisation of monomeric fatty acid(s) containing 18 carbon atoms.

6. Process according to any one of Claims 1 to 5, characterised in that the catalyst (alpha) which is used consists of the following species:

- among the inorganic oxyacids: sulphurous, sulphuric, hypophosphorous, phosphorous, orthophosphoric or pyrophosphoric acids;

- among the organic oxyacids:

- the organosulphonic acids of formula R_1-SO_3H (I) in which R_1 denotes: a straight-chain or branched alkyl radical containing from 1 to 6 carbon atoms; a phenyl radical optionally substituted by 1 to 3 alkyl radicals containing from 1 to 3 carbon atoms, a phenylalkyl radical containing from 1 to 3 carbon atoms in the alkyl moiety and in which the benzene nucleus may optionally be substituted by 1 to 3 alkyl radicals containing from 1 to 3 carbon atoms; or a naphthyl radical optionally substituted by 1 to 4 alkyl radicals containing from 1 to 3 carbon atoms;

- the organophosphonic acids of formula $R_2-P(O)(OH)_2$ (II) in which R_2 denotes an alkyl radical, a phenyl radical or a phenylalkyl radical, each of these radicals having the definition given above for R_1 ;

- the organophosphinic acids of formula $R_3R_4-P(O)(OH)$ (III) in which R_3 and R_4 , which are identical or different, each denote: a straight-chain alkyl radical containing from 1 to 3 carbon atoms; a phenyl radical or a phenylalkyl radical, each of the latter two radicals having the definition given above for R_1 ;

- the organophosphonous acids of formula $R_5H-P(O)(OH)$ (IV) in which R_5 denotes: a straight-chain or branched alkyl radical containing from 1 to 4 carbon atoms (the branching being excluded in the case of an alkyl radical



containing 4 carbon atoms); a phenyl radical or a phenylalkyl radical, each of the latter two radicals having the definition given above for R_1 .

5 7. Process according to Claim 6, characterised in that the acids (alpha) which are used consist of the phosphorous-derived acids belonging to the group of hypophosphorous, phosphorous, orthophosphoric, pyrophosphoric, methylphosphonic, phenylphosphonic, benzylphosphonic, dimethylphosphinic, diphenylphosphinic, methylphenylphosphinic, dibenzylphosphinic, methylphosphonous, 10. phenylphosphonous or benzylphosphonous acids.

8. Process according to any one of Claims 1 to 5, characterised in that the catalyst (beta) which is used consists of the sodium and potassium salts derived from 15 the acids referred to above in Claim 6 and, preferably, of the sodium and potassium salts originating from the phosphorus-derived acids mentioned above in Claim 7.

9. Process according to any one of Claims 6 to 8, characterised in that the proportions of strong acid 20 (alpha) or of salt (beta), expressed as a weight percentage relative to the final copolyamide, are generally between 0.01 and 1% and preferably between 0.01 and 0.5%.



Process for the preparation of homogeneous copolyamides having both a high melting point and good flexibility, from hexamethylenediamine, dicarboxylic acid(s) containing not more than 12 carbon atoms and a fatty acid dimer taken from the group of dimer acids obtained by polymerisation of compounds containing 80 to 100 % by weight of monomeric fatty acid(s) containing from 16 to 20 carbon atoms and 20 to 0 % by weight of monomeric fatty acid(s) containing from 8 to 15 carbon atoms and/or from 1 to 24 carbon atoms, the said process being characterised by the following points:

- in a first step (a), a prepolymer having amino end groups is prepared by reacting, optionally in the presence of water at the beginning of this step, the compounds consisting:
 - (i) either of a mixture of the following constituents: short acids(s) consisting of adipic acid, taken by itself or in a mixture with at least one other dicarboxylic acid of a saturated cycloaliphatic or aromatic type containing not more than 12 carbon atoms + hexamethylenediamine + a catalyst consisting either of a compound (alpha) or of a compound (beta), (alpha) denoting an inorganic oxyacid or an organic oxyacid other than a carboxylic acid, in which at least one of the acid groups, when there are several of these, has an ionisation constant pKa in water at 25 °C which does not exceed 4, (beta) denoting an alkali metal or alkaline-earth metal salt of this acid,
 - (ii) or of a mixture of the following constituents: stoichiometric salt(s) of the abovementioned short acid(s) with hexamethylenediamine + free hexamethylenediamine + the catalyst defined above, this first step (a) being carried out, without performing water distillation in a closed system of the autoclave type, under the following conditions:
 - the quantity of water initially present, when there is any, in the reaction mixture expressed as a percentage by weight based on the total quantity of water initially present + reactants does not exceed 45%.
 - the starting mixture is raised gradually, by heating, to a temperature situated in the range from 200 to 250 °C and the reactants are allowed to react at this temperature and at an autogenous pressure which is higher than atmospheric pressure for a period of time which is sufficient to enable the reaction mixture to reach the state of chemical equilibrium of the amidification reactions corresponding to the beginning of the following step (b);
- in a second step (b), the prepolymer obtained is reacted with the fatty acid dimer, which is added gradually to the reaction mixture, the following points being observed:
 - the operation is carried out at a temperature situated in the range from 200 to 280 °C,
 - the operation is carried out at an autogenous pressure which, during the period of addition of the dimer acid, is equal to the prepolymerisation pressure (case a) or is higher than this pressure (case b) or decreases gradually from the prepolymerisation pressure to atmospheric pressure (case c) and which, after the addition of the dimer acid, decreases gradually to a value which may be atmospheric pressure (in cases a and b) or a pressure which is lower than the latter (in cases a, b and c) or remains equal to atmospheric pressure (in case c),
 - a simultaneous distillation of water is ensured, on the one hand, if desired, during the period of addition of the dimer acid and, on the other hand, during the period following the addition of the dimer acid,
 - care is taken that, at the end of the period of addition of the dimer acid, the ratio r_1 defined below:

$$r_1 = \frac{\text{weight of reactants in step (a)} + \text{weight of dimer acid}}{\text{weight of reactants in step (a)} + \text{weight of dimer acid} + \text{weight of residual water}}$$

has a value situated in the range from 0.915 to 1, if need be by removing water by distillation during the period of addition of the dimer acid, and

- the dimer acid, once its introduction is complete, is reacted for a period which is sufficient to produce a copolyamide with the required viscosity,
- the proportions of the various constituents are such that:
 - the quantity of short acid(s) relative to the total of short acid(s) + dimer acid ranges from 50 to



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- 99 mol%,
 - the ratio r_2 of the number of moles of hexamethylenediamine employed in step (a), variant (i), relative to the total number of moles of short acid(s) and of dimer acid is equal to 1 or optionally equal to a value which is higher than the stoichiometry and is determined so as to introduce into the reaction mixture an excess of hexamethylenediamine which makes it possible to compensate for the loss of this reactant which may occur in step (b) during the pressure release,
 - the ratio r_3 of the number of moles of free hexamethylenediamine employed in step (a), variant (ii), relative to the number of moles of dimer acid has the values indicated above for the ratio r_2 .
2. Process according to Claim 1, characterised in that the steps (a) and (b) are performed as a sequence, but with a presence of water in the reaction mixture at the beginning of step (a), the quantity of water initially present not exceeding 45%.
 3. Process according to either of Claims 1 and 2, characterised in that the short acids used consist of adipic acid by itself or mixed with at least one other dicarboxylic acid taken from the group consisting of 1,4-cyclohexanedicarboxylic acid, isophthalic acid, and terephthalic acid, the proportion of adipic acid in the mixture representing at least 70 mol%.
 4. Process according to any one of Claims 1 to 3, characterised in that the dimer acids used are fractionated polymeric fatty acids in which the difunctional acid fraction is greater than 94% by weight, the monofunctional acid fraction is less than 1% by weight and the fraction of acid of functionality greater than 2 is less than 5% by weight.
 5. Process according to Claim 4, characterised in that the dimer acids which are used consist of the species obtained by fractionation of a hydrogenated composition originating from the catalytic polymerisation of monomeric fatty acid(s) containing 18 carbon atoms.
 6. Process according to any one of Claims 1 to 5, characterised in that the catalyst (alpha) which is used consists of the following species:
 - among the inorganic oxyacids: sulphurous, sulphuric, hypophosphorous, phosphorous, orthophosphoric or pyrophosphoric acids;
 - among the organic oxyacids:
 - the organosulphonic acids of formula $R_1\text{-SO}_3\text{H}$ (I) in which R_1 denotes: a straight-chain or branched alkyl radical containing from 1 to 6 carbon atoms; a phenyl radical optionally substituted by 1 to 3 alkyl radicals containing from 1 to 3 carbon atoms, a phenylalkyl radical containing from 1 to 3 carbon atoms in the alkyl moiety and in which the benzene nucleus may optionally be substituted by 1 to 3 alkyl radicals containing from 1 to 3 carbon atoms; or a naphthyl radical optionally substituted by 1 to 4 alkyl radicals containing from 1 to 3 carbon atoms;
 - the organophosphonic acids of formula $R_2\text{-P(O)(OH)}_2$ (II) in which R_2 denotes an alkyl radical, a phenyl radical or a phenylalkyl radical, each of these radicals having the definition given above for R_1 ;
 - the organophosphinic acids of formula $R_3R_4\text{-P(O)(OH)}$ (III) in which R_3 and R_4 , which are identical or different, each denote: a straight-chain alkyl radical containing from 1 to 3 carbon atoms; a phenyl radical or a phenylalkyl radical, each of the latter two radicals having the definition given above for R_1 ;
 - the organophosphonous acids of formula $R_5\text{H-P(O)(OH)}$ (IV) in which R_5 denotes: a straight-chain or branched alkyl radical containing from 1 to 4 carbon atoms (the branching being excluded in the case of an alkyl radical containing 4 carbon atoms); a phenyl radical or a phenylalkyl radical, each of the latter two radicals having the definition given above for R_1 .
 7. Process according to Claim 6, characterised in that the acids (alpha) which are used consist of the phosphorous-derived acids belonging to the group of hypophosphorous, phosphorous, orthophosphoric, pyrophosphoric, methylphosphonic, phenylphosphonic, benzylphosphonic, dimethylphosphinic, diphenylphosphinic, methylphenylphosphinic, dibenzylphosphinic, methylphosphonous, phenylphosphonous or benzylphosphonous acids.



Process according to any one of Claims 1 to 5, characterised in that the catalyst (beta) which is used consists of the sodium and potassium salts derived from the acids referred to above in Claim 6 and, preferably, of the sodium and potassium salts originating from the phosphorus-derived acids mentioned above in Claim 7.

Process according to any one of Claims 6 to 8, characterised in that the proportions of strong acid (alpha) or of salt (beta), expressed as a weight percentage relative to the final copolyamide, are generally between 0.01 and 1% and preferably between 0.01 and 0.05%.

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Antansprüche

Verfahren zur Herstellung von homogenen Copolyamiden, die gleichzeitig einen hohen Schmelzpunkt und eine gute Biegsamkeit haben, ausgehend von Hexamethyldiamin, Dicarbonsäure/n mit höchstens 12 Kohlenstoffatomen und einem Fettsäuredimeren, das genommen ist aus der Gruppe gebildet durch die dimeren Säuren, erhalten durch Polymerisation von Verbindungen mit 80 bis 100 Gew.-% monomerer/n Fettsäure/n mit 16 bis 20 Kohlenstoffatomen und 20 bis 0 Gew.-% monomerer/n Fettsäure/n mit 8 bis 15 Kohlenstoffatomen und/oder 21 bis 24 Kohlenstoffatomen, wobei dieses Verfahren durch die folgenden Punkte gekennzeichnet ist:

- in einer ersten Stufe (a) stellt man ein Präpolymere mit endständigen Aminogruppen her, indem in Gegenwart oder nicht von Wasser zu Beginn dieser Stufe reagieren gelassen werden die Verbindungen bestehend aus:

- (i) entweder aus dem Gemisch der folgenden Bestandteile: kurze Säure/n bestehend aus Adipinsäure, allein genommen oder im Gemisch mit mindestens einer anderen Dicarbonsäure, gesättigter cycloaliphatischer oder aromatischer Natur mit höchstens 12 Kohlenstoffatomen, + Hexamethyldiamin + Katalysator, bestehend entweder aus einer Verbindung (alpha) oder einer Verbindung (beta), wobei (alpha) eine mineralische Oxysäure oder eine organische Oxysäure anders als eine Carbonsäure bezeichnet, wovon mindestens eine der Säurefunktionen, falls es mehrere gibt, eine Ionisationskonstante pKa in Wasser bei 25 °C gleich oder unter 4 besitzt, und (beta) ein Alkali- oder Erdalkalisalz dieser Säure bedeutet,
- (ii) oder aus dem Gemisch der folgenden Bestandteile stöchiometrische/s Salz/e der vorerwähnten kurzen Säure/n mit Hexamethyldiamin + freies Hexamethyldiamin + vorstehend definierter Katalysator,

wobei diese erste Stufe (a) durchgeführt wird ohne Destillation von Wasser, in einem geschlossenen System vom Typ Autoklav unter den folgenden Bedingungen:

- die zu Beginn in dem Reaktionsgemisch vorhandene Wassermenge, wenn es vorhanden ist, ausgedrückt in Gewichtsprozent in bezug auf die gesamte Wassermenge, vorhanden zu Beginn + Reaktanten, ist höchstens gleich 45 %,
- man führt das Ausgangsgemisch fortschreitend durch Erhitzen auf eine Temperatur in dem Bereich von 200 bis 250 °C und läßt die Reaktanten bei dieser Temperatur und unter einem autogenen Druck höher als Atmosphärendruck während einer Zeitdauer reagieren, die ausreicht, um zu erlauben, das Reaktionsgemisch in den Zustand des chemischen Gleichgewichts der Amidifikationsreaktionen entsprechend dem Beginn der folgenden Stufe (b) zu führen;
- in einer zweiten Stufe (b) läßt man das erhaltene Präpolymere mit der dimeren Fettsäure reagieren, die fortschreitend in das Reaktionsgemisch zugegeben wird, indem die folgenden Punkte beachtet werden:
 - man arbeitet bei einer Temperatur im Bereich von 200 bis 280 °C,
 - man arbeitet unter einem autogenen Druck, der während der Zugabeperiode der dimeren Säure gleich dem Präpolymerisationsdruck ist (Fall a) oder höher als dieser Druck ist (Fall b), oder fortschreitend von dem Präpolymerisationsdruck bis zu Atmosphärendruck absinkt (Fall c) und der nach Zugabe der dimeren Säure fortschreitend absinkt bis auf einen Wert, der atmosphärischer Druck (für die Fälle a und b) oder ein Druck unterhalb dieses letzteren (für die Fälle a, b und c) sein kann, oder gleich dem Atmosphärendruck bleibt (für den Fall c),
 - man stellt eine gleichzeitige Destillation von Wasser einerseits gegebenenfalls während der



Zugabeperiode der dimeren Säure und andererseits während der Periode, die der Zugabe der dimeren Säure folgt, sicher, man achtet darauf, daß am Ende der Zugabeperiode der dimeren Säure, falls erforderlich, indem Wasser während der Zugabeperiode der dimeren Säure durch Destillation entfernt wird, das nachstehend definierte Verhältnis r_1 :

$$\frac{\text{Gewicht der Reaktanten der Stufe (a)} + \text{Gewicht dimere Säure}}{\text{Gewicht der Reaktanten der Stufe (a)} + \text{Gewicht dimere Säure} + \text{Gewicht Restwasser}}$$

einen Wert aufweist, der im Bereich von 0,915 bis 1 liegt,

und man läßt die dimere Säure, wenn diese letztere einmal vollständig eingesetzt ist, während einer ausreichenden Zeitdauer reagieren, um ein Copolyamid der gewünschten Viskosität zu erhalten,

- die Mengenverhältnisse der verschiedenen Bestandteile sind derart daß:
 - die Menge an kurzer/n Säure/n in bezug auf die Gesamtheit kurze Säure/n + dimere Säure von 50 bis 99 Mol-% geht,
 - das Verhältnis r_2 der Zahl der Mole Hexamethylendiamin, die in der Stufe (a), Alternative (i), eingesetzt sind, in bezug auf die Gesamtzahl der Mole kurze Säure/n und dimere Säure gleich 1 ist oder gegebenenfalls gleich einem Wert, der über der Stöchiometrie ist, bestimmt derart, daß in das Reaktionsgemisch ein Überschuß an Hexamethylendiamin eingeführt wird, der es erlaubt, den Verlust dieses Reaktanten, der während der Stufe (b) während der Druckverminderung auftreten kann, zu kompensieren,
 - das Verhältnis r_3 der Zahl der Mole freies Hexamethylendiamin, die in Stufe (a), Alternative (ii), eingesetzt werden, in bezug auf die Zahl der Mole an dimerer Säure besitzt die vorstehend angegebenen Werte für das Verhältnis r_2 .
2. Verfahren gemäß Anspruch 1, dadurch gekennzeichnet, daß es darin besteht, die Stufen (a) und (b) aneinander zu reihen, jedoch mit Anwesenheit von Wasser in dem Reaktionsgemisch zu Beginn der Stufe (a), wobei die zu Beginn vorhandene Wassermenge höchstens gleich 45 % beträgt.
 3. Verfahren gemäß einem der Ansprüche 1 oder 2, dadurch gekennzeichnet, daß die verwendeten kurzen Säuren in der Adipinsäure allein genommen oder in einem Gemisch mit mindestens einer anderen Dicarbonsäure bestehen, genommen aus der Gruppe gebildet durch die 1,4-Cyclohexandicarbonsäure, die Isophthalsäure, die Terephthalsäure, wobei das Mengenverhältnis von Adipinsäure in dem Gemisch mindestens 70 Mol-% beträgt.
 4. Verfahren gemäß einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß die verwendeten dimeren Säuren fraktionierte polymere Fettsäuren sind, worin die Fraktion an difunktioneller Säure über 94 Gew.-% ist, die Fraktion an monofunktioneller Säure unter 1 Gew.-% ist, und die Fraktion an Säure mit einer Funktionalität höher als 2 unter 5 Gew.-% ist.
 5. Verfahren gemäß Anspruch 4, dadurch gekennzeichnet, daß die dimeren Säuren, die verwendet werden, aus Gattungen bestehen, die durch Fraktionierung einer hydrierten Zusammensetzung erhalten wurden, welche von der katalytischen Polymerisation monomerer Fettsäure/n mit 18 Kohlenstoffatomen stammen.
 6. Verfahren gemäß einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß der Katalysator (alpha), der verwendet wird, aus den folgenden Sorten besteht:
 - unter den mineralischen Oxyssäuren die schweflige Säure, Schwefelsäure, hypophosphorige Säure, phosphorige Säure, Orthophosphorsäure oder Pyrophosphorsäure;
 - unter den organischen Oxyssäuren: die Organosulfonsäuren der Formel $R_1\text{-SO}_3\text{H}$ (I), worin R_1 bedeutet: einen linearen oder verzweigten Alkylrest mit 1 bis 6 Kohlenstoffatomen; einen Phenylrest, gegebenenfalls substituiert durch 1 bis 3 Alkylreste mit 1 bis 3 Kohlenstoffatomen; einen Phenylalkylrest mit 1 bis 3 Kohlenstoffatomen im Alkylrest und dessen Benzolring gegebenenfalls



- substituiert sein kann durch 1 bis 3 Alkylreste mit 1 bis 3 Kohlenstoffatomen; oder einen Naphthylrest, gegebenenfalls substituiert durch 1 bis 4 Alkylreste mit 1 bis 3 Kohlenstoffatomen;
- die Organophosphonsäuren der Formel $R_2-P(O)(OH)_2$ (II), worin R_2 einen Alkylrest, einen Phenylrest oder einen Phenylalkylrest bedeutet, wobei jeder dieser Reste die vorstehend für R_1 angegebene Definition hat;
 - die Organophosphinsäuren der Formel $R_3R_4-P(O)(OH)$ (III), worin R_3 und R_4 , die identisch oder verschieden sind, jeweils bedeuten: einen linearen Alkylrest mit 1 bis 3 Kohlenstoffatomen; einen Phenylrest oder einen Phenylalkylrest, wobei jeder dieser beiden letzteren Reste die vorstehend für R_1 angegebene Definition hat;
 - die organophosphonigen Säuren der Formel $R_5H-P(O)(OH)$ (IV), worin R_5 bedeutet: einen linearen oder verzweigten Alkylrest mit 1 bis 4 Kohlenstoffatomen (die Verzweigung für einen Alkylrest mit 4 Kohlenstoffatomen ist ausgeschlossen); einen Phenylrest oder einen Phenylalkylrest, wobei jeder dieser zwei letzteren Reste die vorstehend für R_1 angegebene Definition hat.

Verfahren gemäß Anspruch 6, dadurch gekennzeichnet, daß die Säuren (alpha), welche verwendet werden, in den Säuren, die von Phosphor abgeleitet sind, bestehen, gehörend zu der Gruppe der hypophosphorigen, phosphorigen, Orthophosphor-, Pyrophosphor-, Methylphosphon-, Phenylphosphon-, Benzylphosphon-, Dimethylphosphin-, Diphenylphosphin-, Methylphenylphosphin-, Dibenzylphosphin-, methylphosphonigen, phenylphosphonigen oder benzylophosphonigen Säure.

- Verfahren gemäß einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß der Katalysator (beta), der verwendet wird, in den Natrium- und Kaliumsalzen der vorstehend in Anspruch 6 erwähnten Säuren besteht und vorzugsweise in den Natrium- und Kaliumsalzen der Säuren, abgeleitet von Phosphor, die vorstehend in Anspruch 7 erwähnt sind.
9. Verfahren gemäß einem der Ansprüche 6 bis 8, dadurch gekennzeichnet, daß die Mengenverhältnisse an starker Säure (alpha) oder Salz (beta), ausgedrückt in Gewichtsprozent in bezug auf das Endcopolymid, im allgemeinen zwischen 0,01 und 1 % und vorzugsweise zwischen 0,01 und 0,5 % liegen.

