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Description

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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 mole %.

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 only 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 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 underlies the fact that the copolymers in question have thermomechanical properties which can be readily reproduced, in addition to good transparency properties. A copolymer having good flexibility is intended to define a copolyamide whose flexural modulus is significantly lower than that of the conventional polyamides such as polyhexamethylenediamine (nylon 66) or polycaprolactam (nylon 6) and is of the order of, or lower than, that of the polyamides considered to be flexible

such as, for example, polyundecanamide (nylon 11).

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 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 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 mole %, copolyamides are obtained whose melting point will be more or less high and whose flexibility will be greater or lesser. The copolyamides in which the quantity of short acid is in the range from 70 to 90 mole % 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 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 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 mole % and that the contents of amino groups and of carboxylic groups do not differ by more than 5 % as an absolute value, the polymerization 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);
2. - a homogenization 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;

- 5 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
10 30 minutes to several hours.

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

1. - Prepolymers are prepared in a heterogeneous
15 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 mole % and
20 that the contents of amino groups and of carboxylic groups differ by more than 5 % as an absolute value, the pre-polymerization reaction consisting in taking the starting mixture to a temperature corresponding to the beginning of the following phase (2), in a gradual and uniform
25 manner, over a period of time ranging from 30 minutes to several hours;

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

- 30 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
35 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 mole % 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 state inert towards the amidification reactants and reactions.

While continuing work in this field of technology, the Applicant Company has now found that homogeneous copolyamides can be prepared by making use of a process permitting independence:

- of the use of an intermediate homogenization 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.

More specifically, the present invention relates 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 present being in the range from 50 to 99 mole %, the said process being characterized 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, the compounds consisting:
 - (i) either of the mixture of the following constituents: adipic acid, optionally at least one other short-chain dicarboxylic acid of a saturated cycloaliphatic or aromatic type, hexamethylenediamine, and 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 ionization constant pK_a in water at $25^{\circ}C$ which does not exceed 4, (beta) denoting an alkali metal or alkaline-earth metal salt of this acid,

- 5 - (ii) or of the 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 in an optionally
- 10 closed system of the autoclave type by raising the starting mixture gradually by heating under an autogenous water vapour pressure in the range from atmospheric pressure to 3 MPa, and then by removing the water present in the reaction mixture by distillation so as to bring the tem-
- 15 perature of the mass at the end of this step to a value ranging from 170 to $250^{\circ}C$;
- in a second step (b), the prepolymer obtained is reacted with the fatty acid dimer, this polycondensation being carried out by operating at a temperature ranging from
- 20 250 to $280^{\circ}C$, at a water vapour pressure which gradually decreases from a value equal to the prepolymerization pressure to a value which can be atmospheric pressure [in the case where the step (a) is carried out under a pressure above atmospheric pressure] or a pressure below
- 25 the latter [in the case where the step (a) is carried out at a pressure higher than or equal to atmospheric pressure] and for a period which is sufficient to produce a copolyamide with the required viscosity;
- the proportions of the various constituents are such
- 30 that:
- the quantity of short acid(s) relative to the combination of short acid(s) + dimer acid ranges from 50 to 99 mole %,
- the ratio r_1 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
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hexamethylenediamine which makes it possible to compensate for the loss of this reactant which may occur in step (a) during the distillation and/or in step (b) during the decompression,

- 5 - the ratio r_2 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_1 .

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

 The "water present in the reaction mixture" is intended to define the water which is formed during the polycondensation of the short acid(s) with hexamethylenediamine, plus, if appropriate, the water initially introduced with the constituents of the reaction mixture. The
15 quantity of water which may be introduced at the outset is not critical and can vary within wide limits.

 The "copolyamide of the required viscosity" is intended to define a copolyamide which has a sufficiently
20 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
25 3,000 and 60,000 poises.

 On the subject of the loss of hexamethylenediamine, referred to above, this can arise, for example, when the equipment employed does not incorporate a distillation column; under these conditions, for a given equipment and
30 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 starting reaction mixture to preserve the equivalence between the amino groups and the
35 carboxy groups which react. In general, when a loss of hexamethylenediamine occurs, it is moderate, and it has been found that the use of quantities of this reactant which result in the ratios r_1 and r_2 having values ranging from a number greater than 1 to 1.3 are suitable.

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 cycloaliphatic or aromatic nature. More precisely, cycloaliphatic and/or aromatic dicarboxylic acids which can come within the scope of the present invention are compounds containing at most 12 carbon atoms; 1,4-cyclohexanedicarboxylic acid, isophthalic acid, and terephthalic acid may be mentioned as suitable diacids of this type.

5 The proportion of adipic acid in the mixture of short diacids which may be employed usually represents at least 70 mole %.

It is thought that during the homogenization step employed in the abovementioned French patent, the amino and carboxy groups, which no longer undergo an amidification reaction at this time, are used to form breaks in the block oligomers of adipic acid with hexamethylenediamine 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 dimer acid whose oligomers with hexamethylenediamine are, however, incompatible with those of the preformed polyhexamethylene amide.

15 The dimer acids employed are obtained by polymerization 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, arachidic, 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, lino-
5 leic, 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
10 interest is very low.

The polymeric fatty acids obtained by thermal polymerization, in the presence of catalysts such as peroxides or Lewis acids if appropriate, may be fractionated for example by using conventional vacuum distillation or
15 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
20 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
25 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.

30 The dimer acids which are most especially suitable are the species obtained by fractionation of a hydrogenated composition originating from the catalytic polymerization of monomeric fatty acid(s) containing 18 carbon atoms. In this context, owing to their ready availability of supply
35 and their relatively easy polymerization, 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 oxy-acid (alpha) which is employed as catalyst, use is made, as indicated above, of an oxygen-containing mono- or poly-acid in which at least one of the acid groups has an ionization constant pka 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 form $R_2-P(O)(OH)_2$ (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 form $R_5H-P(O)(OH)$ (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 4 carbon atoms); a phenyl radical or a phenylalkyl radical, each of the latter two radicals having the definition

given above for R₁.

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.

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 action during the polycondensation reaction, 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 present invention is to be ensured, care will be taken to observe the corresponding proportions of the various constituents employed as perfectly as possible. According to a preferred embodiment of the invention, in step (a) the short diacid(s) is (or are) used in the form of its (or of 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 of stoichiometry between free hexamethylenediamine and the dimer acid, the operation may be carried out by precise weighing of the reactants the assay of which is known accurately at the time of use. The

5 stoichiometry of the salt(s) of the short acid(s) can be monitored by 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

10 reaction between the free amino groups in the prepolymer and the 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).

15 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

20 aqueous solution.

Concerning the carrying out of step (a) of the process according to the invention, the operation is preferably carried out in a closed system under an autogenous water vapour pressure which is above atmospheric pressure

25 and does not exceed 2 MPa. It will be indicated that the autogenous water vapour pressure which is required to conduct the distillation is produced by gradual heating, for example over a period ranging from 10 minutes to 2 hours, up to a temperature ranging from 150 to 220°C.

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

35 - either all of the dimer acid, or a part of the dimer acid representing, for example, 70 to 95 % of the total quantity to be introduced into the polymer, is added gradually, for example over a period ranging from 10 minutes to 2 hours,

- while the pressure is reduced at the same time from the initial prepolymerization value down to the value of atmospheric pressure,

5 - while the temperature of the reaction mixture is also raised for the same period to a value above the temperature reached at the end of step (a) and lying in the range from 250 to 280°C,

- and while ensuring simultaneous distillation of water,

10 - when the abovementioned addition of dimer acid is finished, after stirring of the reaction mixture has continued, if appropriate, at the abovementioned temperature and at atmospheric pressure for a period ranging, for example, from 10 minutes to 1 hour, a reduced pressure not
15 exceeding 200×10^2 Pa is then gradually established over a period ranging, for example, from 5 minutes to 1 hour,
- when the reduced pressure has been established, the remainder of the dimer acid is added where applicable and the polycondensation is completed by continuing to stir
20 the mixture at the abovementioned temperature which lies in the range from 250 to 280°C, at the reduced pressure indicated above, for a period ranging, for example, from 10 minutes to 1 hour, while simultaneously ensuring a distillation of residual water.

25 In the case where step (a) is carried out under an autogenous pressure above atmospheric pressure, it may be advantageous, when this pressure is close (or equal) to the maximum value of the pressure indicated above in the present description, to carry out, before introducing all
30 or part of the dimer acid, a slight pressure reduction which reduces the autogenous water vapour pressure to a value p_1 which is from 5 to 30 % lower than the prepolymerization pressure. It should then be understood, within the scope of the preferred use of the step (b) referred to above,
35 that all or part of the dimer acid is added gradually while the pressure is reduced at the same time, no longer from the initial prepolymerization value, but from the value p_1 down to the value of atmospheric pressure.

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: stabilizers or inhibitors of degradation due to oxidation, to ultraviolet, to light or heat; lubricants; colorants; nucleating agents; antifoaming agents and inorganic fillers.

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 according to the usual injection-moulding, extrusion or spinning methods to give shaped articles: components, films or fibres of very high uniformity.

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

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.

25 - MICROCALORIMETRIC ANALYSIS:

The polymers are characterized by melting characteristics such as the melting endotherms E_m and the crystallization exotherms E_c .

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 (T_m) and crystallization on cooling (T_c) points.

35 - MELT VISCOSITY:

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:

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
5 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 stand-
10 ardisied 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.

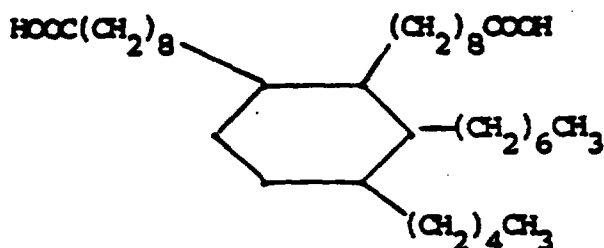
- DETERMINATION OF TENSILE MECHANICAL PROPERTIES:

15 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
20 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:

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

In the following examples, wherever reference is made to the dimer acid employed, the compound used is that
30 marketed by Unichema Chemie under the trademark Pripol 1 010, 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
35 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.

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 at a pressure below atmospheric pressure.

- Step (a):

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

- hexamethylenediamine salt of adipic acid, in dry solid form: 2,086.7 g (7.955 moles),
- demineralized water: 700 g,
- aqueous solution containing 32.5 % by weight of hexamethylenediamine: 746.5 g (2.088 moles),
- aqueous solution containing 50 % by weight of hypophosphorous acid: 6 g,
- silicone antifoam marketed by Rhone-Poulenc Specialites Chimiques under the trademark Rhodorsil Si 454: 0.3 g.

Stirring is commenced and five nitrogen purges are carried out by pressurization to 7×10^5 Pa, followed by pressure release. The temperature of the stirred mixture is gradually raised to 217°C over 1 hour 15 minutes while the autogenous pressure is maintained; this reaches 1.8 MPa. Water is distilled off under pressure over 2 hours to reach a mixture temperature of 250°C .

- Step (b):

The pressure is released down to 1.5 MPa while the temperature is maintained at 250°C. 895 g (1.567 moles) of fatty acid dimer marketed by Unichema Chemie under the trademark Pripol 1 010, having a monomer content of 0.03 %
5 by weight and a trimer content of 3 % by weight are then added to the stirred mixture by steady pouring over 1 hour 35 minutes; during the time when the dimer acid is being added, the autoclave pressure is gradually reduced to
10 atmospheric pressure and the temperature of the mixture is gradually raised to 270°C.

A pressure of 133×10^2 Pa is then established gradually over 40 minutes while the mixture is maintained at 270°C. When the reduced pressure has been established,
15 a further 90 g (0.158 mole) of dimer acid are added by steady pouring. The polycondensation is completed by continuing to stir the mixture for 30 minutes at 270°C under 133×10^2 Pa.

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

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

- melting point (T_m): 241°C,
- crystallization point on cooling (T_c): 191°C,
- end group contents:
30
 - COOH: 1.75 meq/kg
 - NH₂: 116.4 meq/kg
- melt viscosity at 260°C under a shear gradient:
 $\gamma = 18.6 \text{ s}^{-1}$: 6,000 poises.
- tensile mechanical properties:
35
 - break strength: 64.3 MPa,
 - elongation at break: 270 %,
 - tensile modulus: 750 MPa,
- torsional thermomechanical properties; torsional modulus at:



- -20°C: 600 MPa,
- 0°C: 570 MPa,
- +20°C: 500 MPa,
- +40°C: 320 MPa,
- +60°C: 125 MPa.

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EXAMPLE 2:

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

- Step (a):

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

- hexamethylenediamine salt of adipic acid, in dry solid form: 1,043.3 g (3.978 moles),
- aqueous solution containing 32.15 % by weight of hexamethylenediamine: 1,424 g (3.939 moles),
- aqueous solution containing 50 % by weight of hypophosphorous acid: 6 g,
- silicone antifoam described above in Example 1: 0.3 g.

15

Stirring is commenced and five nitrogen purges are carried out by pressurisation to 1 MPa, followed by pressure release. The temperature of the stirred mixture is raised gradually to 217°C over 1 hour while autogenous pressure is maintained. This reaches 1.8 MPa. Water is distilled off under pressure over 1 hour so that the mixture attains a temperature of 230°C.

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- Step (b):

Pressure is reduced to 1 x 5 MPa while the temperature is maintained at 230°C. 1,566 g (2.743 moles) of Pripol 1 010 fatty acid dimer described earlier in Example 1 are then added to the stirred mixture by steady pouring over 1 hour 30 minutes; during the time when the dimer acid is being added the autoclave pressure is gradually reduced to atmospheric pressure and the temperature of the mixture is gradually raised to 260°C. The mixture is stirred for 30 minutes at 260°C at atmospheric pressure.

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A pressure of 133×10^2 Pa is then established gradually over 30 minutes while the mixture is maintained at 260°C. When the reduced pressure has been established, a further 220 g (0.385 mole) of dimer acid are added by

steady pouring. The polycondensation is completed by continuing to stir the mixture for 30 minutes at 260°C under $133 \times 10^2 \text{ Pa}$.

5 Stirring is stopped, and then a nitrogen pressure of $5 \times 10^5 \text{ Pa}$ is established in the autoclave and the polymer is drawn off. The latter, extruded from the autoclave in lace form, is cooled by passing through a cold water bath and is then granulated and dried.

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

- melting point (T_m): 214°C ,
- crystallization point on cooling (T_c): 145°C ,
- end group contents:
 - 15 - COOH : 54.48 meq/kg,
 - NH_2 : 9.47 meq/kg,
- melt viscosity at 260°C under a shear gradient:
 $\gamma = 10 \text{ s}^{-1}$: 4,000 poises.
- torsional mechanical properties:
 - 20 - break strength: 49.7 MPa,
 - elongation at break: 300 %,
 - tensile modulus: 325 MPa.
- torsional thermomechanical properties; torsional modulus at:
 - 25 - -20°C : 470 MPa,
 - 0°C : 400 MPa,
 - $+20^{\circ}\text{C}$: 235 MPa,
 - $+40^{\circ}\text{C}$: 100 MPa.

30 By way of a comparative test, the above example is reproduced, but this time without the use of catalyst (hypophosphorous acid); the reactant charges are as follows:

- Step (a):
 - 35 - hexamethylenediamine salt of adipic acid, in dry solid form: 1,043.3 g (3.978 moles),
 - aqueous solution containing 32.15 % by weight of hexamethylenediamine: 1,244.8 g (3.450 moles),
 - silicone antifoam Si 454: 0.3 g.

- Step (b):

- first addition of dimer acid: 1,716 g (3.005 moles),
- second addition of dimer acid: 126 g (0.220 mole).

5 The polymer obtained is perfectly transparent and consequently homogeneous. But the end group contents which are obtained:

- COOH: 68.5 meq/kg,
- NH₂: 55 meq/kg

10 are high, and this result is indicative of a slowing down of the polycondensation in the absence of hypophosphorous acid. It is noted, furthermore, that the melt viscosity, measured at 260°C under a gradient $\gamma = 10 \text{ s}^{-1}$, is low, being of the order of 900 poises.

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CLAIMS

1. Process for the preparation of homogeneous copoly-
amides having both a high melting point and good flexibi-
lity, from hexamethylenediamine, short-chain dicarboxylic
acid(s) and a fatty acid dimer, the quantity of short
5 acid(s) relative to the total quantity of the acids pre-
sent being in the range from 50 to 99 mole %, the said pro-
cess being characterized by the following points:
- in a first step (a), a prepolymer having amino end
groups is prepared by reacting, optionally in the presence
10 of water, the compounds consisting:
- (i) either of the mixture of the following consti-
tuents: adipic acid, optionally at least one other short-
chain dicarboxylic acid of a saturated cycloaliphatic or
aromatic type, hexamethylenediamine, and a catalyst con-
15 sisting 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 ionization constant pKa in water at 25°C which does
20 not exceed 4, (beta) denoting an alkali metal or alkaline-
earth metal salt of this acid,
- (ii) or of the mixture of the following consti-
tuents: stoichiometric salt(s) of the abovementioned
short acid(s) with hexamethylenediamine, free hexamethy-
25 lenediamine and the catalyst defined above,
this first step (a) being carried out in an optionally
closed system of the autoclave type by raising the star-
ting mixture gradually by heating under an autogenous water
vapour pressure in the range from atmospheric pressure



* C L H S *

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to 3 MPa, and then by removing the water present in the reaction mixture by distillation so as to bring the temperature of the mass at the end of this step to a value ranging from 170 to 250°C;

- 5 - in a second step (b), the prepolymer obtained is reacted with the fatty acid dimer, this polycondensation being carried out by operating at a temperature ranging from 250 to 280°C, at a water vapour pressure which gradually decreases from a value equal to the prepolymerization
- 10 pressure to a value which can be atmospheric pressure or a pressure below the latter and for a period which is sufficient to produce a copolyamide with the required viscosity;

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

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

- the ratio r_1 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
- 20 hexamethylenediamine which makes it possible to compensate for the loss of this reactant which may occur in step (a) during the distillation and/or in step (b) during the decompression,

- the ratio r_2 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_1 .
- 30

2. Process according to Claim 1, characterized in that the short acids used consist of adipic acid by itself or
- 35 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



* C L H S *

70 mole %.

3. Process according to either of Claims 1 and 2, characterized in that the dimer acids used are obtained by polymerization and fractionation of compounds comprising 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 dimer acids comprising a difunctional acid fraction which is greater than 94 % by weight, a monofunctional acid fraction which is less than 1 % by weight and a fraction of acid of functionality greater than 2 which is less than 5 % by weight.

4. Process according to Claim 3, characterized in that the dimer acids which are used consist of the species obtained by fractionation of a hydrogenated composition originating from the catalytic polymerization of monomeric fatty acid(s) containing 18 carbon atoms.

5. Process according to any one of Claims 1 to 4, characterized 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 for 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 .

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

7. Process according to any one of Claims 1 to 4, characterized in that the catalyst (beta) which is used consists of the sodium and potassium salts derived from the acids referred to above in Claim 4 and, preferably, of the sodium and potassium salts originating from the phosphorus-derived acids mentioned above in Claim 5.

8. Process according to any one of Claims 5 to 7, characterized 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 0.5 %.

9. Process according to any one of Claims 1 to 8, characterized in that step (a) is carried out in a closed system under autogenous water vapour pressure which is greater than atmospheric pressure and does not exceed 2 MPa.



10. Process according to Claim 9, characterized in that step (b) is carried out by linking the following steps:

- 5 - either all of the dimer acid, or a part of the dimer acid representing 70 to 95 % of the total quantity to be introduced into the polymer, is added gradually, over a period ranging from 10 minutes to 2 hours,
 - 10 - while the pressure is reduced at the same time from the initial prepolymerization value down to the value of atmospheric pressure,
 - while the temperature of the reaction mixture is also raised for the same period to a value above the temperature reached at the end of step (a) and lying in the range from 250 to 280°C,
 - 15 - and while ensuring simultaneous distillation of water,
 - when the abovementioned addition of dimer acid is finished, after stirring of the reaction mixture has continued, if appropriate, at the abovementioned temperature and at atmospheric pressure for a period ranging from 10 minutes to 1 hour, a reduced pressure not exceeding 200 x 10² Pa is then gradually established over a period ranging from 5 minutes to 1 hour,
 - when the reduced pressure has been established, the 25 remainder of the dimer acid is added where applicable and the polycondensation is completed by continuing to stir the mixture at the abovementioned temperature which lies in the range from 250 to 280°C, at the reduced pressure indicated above, for a period ranging from 10 minutes to 30 1 hour, while simultaneously also ensuring a distillation of residual water.





As printed.

Claims

1. 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 present being in the range from 50 to 99 mole%, the said process being characterized 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, the compounds consisting :

(i) either of the mixture of the following constituents : adipic acid, optionally at least one other short-chain dicarboxylic acid of a saturated cycloaliphatic or aromatic type, hexamethylenediamine, and 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 ionization 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 the 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 in an optionally closed system of the autoclave type by raising the starting mixture gradually by heating under an autogenous water vapour pressure in the range from atmospheric pressure to 3 MPa, and then by removing the water present in the reaction mixture by distillation so as to bring the temperature of the mass at the end of this step to a value ranging from 170 to 250 °C :

in a second step (b), the prepolymer obtained is reacted with the fatty acid dimer, this polycondensation being carried out by operating at a temperature ranging from 250 to 280 °C, at a water vapour pressure which gradually decreases from a value equal to the prepolymerization pressure to a value which can be atmospheric pressure or a pressure below the latter and 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 combination of short acid(s) + dimer acid ranges from 50 to 99 mole%,

— the ratio r_1 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 (a) during the distillation and/or in step (b) during the decomposition,

— the ratio r_2 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_1 .

2. Process according to Claim 1, characterized 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 mole%.

3. Process according to either of Claims 1 and 2, characterized in that the dimer acids used are obtained by polymerization and fractionation of compounds comprising 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 dimer acids comprising a difunctional acid fraction which is greater than 94 % by weight, a monofunctional acid fraction which is less than 1 % by weight and a fraction of acid of functionality greater than 2 which is less than 5 % by weight.

4. Process according to Claim 3, characterized in that the dimer acids which are used consist of the species obtained by fractionation of a hydrogenated composition originating from the catalytic polymerization of monomeric fatty acid(s) containing 18 carbon atoms.

5. Process according to any one of Claims 1 to 4, characterized in that the catalyst (alpha) which is



and 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 for 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 .

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

7. Process according to any one of Claims 1 to 4, characterized in that the catalyst (beta) which is used consists of the sodium and potassium salts derived from the acids referred to above in Claim 4 and, preferably of the sodium and potassium salts originating from the phosphorus-derived acids mentioned above in Claim 5.

8. Process according to any one of Claims 5 to 7, characterized 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 0.5 %.

9. Process according to any one of Claims 1 to 8, characterized in that step (a) is carried out in a closed system under autogenous water vapour pressure which is greater than atmospheric pressure and does not exceed 2 MPa.

10. Process according to Claim 9, characterized in that step (b) is carried out by linking the following steps :

either all of the dimer acid, or a part of the dimer acid representing 70 to 95 % of the total quantity to be introduced into the polymer, is added gradually, over a period ranging from 10 minutes to 2 hours,

— while the pressure is reduced at the same time from the initial prepolymerization value down to the value of atmospheric pressure,

— while the temperature of the reaction mixture is also raised for the same period, to a value above the temperature reached at the end of step (a) and lying in the range from 250 to 280 °C,

— and while ensuring simultaneous distillation of water,

when the abovementioned addition of dimer acid is finished, after stirring of the reaction mixture has continued, if appropriate, at the abovementioned temperature and at atmospheric pressure for a period ranging from 10 minutes to 1 hour, a reduced pressure not exceeding $200 \cdot 10^2$ Pa is then gradually established over a period ranging from 5 minutes to 1 hour,

when the reduced pressure has been established, the remainder of the dimer acid is added where applicable and the polycondensation is completed by continuing to stir the mixture at the abovementioned temperature which lies in the range from 250 to 280 °C, at the reduced pressure indicated above, for a period ranging from 10 minutes to 1 hour, while simultaneously also ensuring a distillation of residual water.

Patentansprüche

1. Verfahren zur Herstellung von homogenen Copolyamiden, die gleichzeitig einen hohen Schmelzpunkt und gute Biegsamkeit haben, ausgehend von Hexamethylendiamin, Dicarbonsäure(n) mit kurzer Kette und einem Fettsäuredimeren, wobei die Menge an kurzer(kurzen) Säure(n) in bezug auf die Gesamtmenge der vorhandenen Säuren im Bereich von 50 bis 99 Mol-% liegt, wobei das Verfahren durch folgende Punkte gekennzeichnet ist :

in einer ersten Stufe (a) stellt man ein Präpolymere mit aminierten Endgruppen her, indem gegebenenfalls in Gegenwart von Wasser die Verbindungen umgesetzt werden, bestehend aus :

(i) entweder dem Gemisch der folgenden Bestandteile : Adipinsäure, gegebenenfalls mindestens



...andere Dicarbonsäure mit kurzer Kette von cycloaliphatischer gesättigter oder aromatischer Natur, Hexamethyldiamin und einem Katalysator, bestehend entweder aus einer Verbindung (alpha) oder aus einer Verbindung (beta), wobei (alpha) eine Mineraloxysäure oder eine organische Oxsäure, anders als eine Carbonsäure, ist, von der mindestens eine der Säurefunktionen, wenn mehrere vorhanden sind, eine Ionisationskonstante pK_a in Wasser bei 25 °C gleich oder unterhalb 4 besitzt, (beta) ein Alkali- oder Erdalkalisalz dieser Säure ist, oder

(ii) einem Gemisch der folgenden Bestandteile: stöchiometrische(s) Salz(e) der vorgenannten kurzen Säure(n) und Hexamethyldiamin, freies Hexamethyldiamin und dem vorstehend definierten Katalysator,

wobei diese erste Stufe (a) in einem gegebenenfalls geschlossenen System vom Typ Autoklav durchgeführt wird, indem das Ausgangsgemisch durch Erhitzen fortschreitend unter einen autogenen Wasserstoffdruck in dem Bereich von atmosphärischem Druck bis 3 MPa geführt wird, indem dann durch Destillation das in dem Reaktionsgemisch vorhandene Wasser derart entfernt wird, daß die Temperatur der Masse am Ende dieser Stufe auf einen Wert von 170 bis 250 °C geführt wird;

in einer zweiten Stufe (b) wird das erhaltene Präpolymere mit dem Fettsäuredimeren umgesetzt, wobei diese Polykondensation durchgeführt wird, indem bei einer Temperatur von 250 bis 280 °C unter einem Wasserdampfdruck gearbeitet wird, der fortschreitend von einem Wert gleich dem Präpolymerisationsdruck bis zu einem Wert, der Atmosphärendruck oder ein Druck unterhalb des letzteren sein kann, absinkt, und während einer Dauer, die ausreicht, um ein Copolyamid der gewünschten Viskosität zu erhalten;

wobei die Mengenverhältnisse dieser verschiedenen Bestandteile derart sind, daß:

— die Menge der kurzen Säure(n) in bezug auf die Gesamtheit der kurzen Säure(n) + dimere Säure von 50 bis 99 Mol-% geht,

— das Verhältnis r_1 der Zahl der eingesetzten Mole Hexamethyldiamin in der Stufe (a), Alternative (i), in bezug auf die Gesamtzahl der Mole kurze Säuren(n) und dimere Säure gleich 1 oder gegebenenfalls gleich einem Wert oberhalb der Stöchiometrie ist, bestimmt derart, daß in das Reaktionsgemisch ein Überschuß an Hexamethyldiamin eingeführt wird, der es erlaubt, den Verlust dieses Reaktanten, der in der Stufe (a) während der Destillation und/oder in der Stufe (b) während der Entspannung eintreten kann, zu kompensieren,

— das Verhältnis r_2 der Anzahl der in der Stufe (a), Alternative (ii), eingesetzten Mole freies Hexamethyldiamin in bezug auf die Anzahl der Mole dimere Säure die vorstehend für das Verhältnis r_1 angegebenen Werte besitzt.

2. Verfahren gemäß Anspruch 1, dadurch gekennzeichnet, daß die verwendeten kurzen Säuren in Adipinsäure, allein genommen oder im Gemisch mit wenigstens einer anderen Dicarbonsäure, ausgewählt aus der Gruppe, gebildet von der 1,4-Cyclohexandicarbonsäure, Isophthalsäure, Terephthalsäure, bestehen, wobei das Verhältnis der Adipinsäure in dem Gemisch mindestens 70 Mol-% beträgt.

3. Verfahren gemäß einem der Ansprüche 1 oder 2, dadurch gekennzeichnet, daß die verwendeten dimeren Säuren erhalten sind durch Polymerisation und Fraktionierung von Verbindungen, umfassend 80 bis 100 Gew.% monomere Fettsäure(n) mit 16 bis 20 Kohlenstoffatomen und 20 bis 0 Gew.% monomere Fettsäure(n) mit 8 bis 15 Kohlenstoffatomen und/oder 21 bis 24 Kohlenstoffatomen, wobei diese dimeren Säuren umfassen eine Fraktion an difunktioneller Säure, die oberhalb 94 Gew.% ist, eine Fraktion an monofunktioneller Säure, die unterhalb 1 Gew.% ist, und eine Fraktion an Säure mit einer Funktionalität oberhalb 2, die unterhalb 5 Gew.% ist.

4. Verfahren gemäß Anspruch 3, dadurch gekennzeichnet, daß die verwendeten dimeren Säuren in den Arten bestehen, die durch Fraktionierung einer hydrierten Zusammensetzung erhalten werden, die von der katalytischen Polymerisation der monomeren Fettsäure(n) mit 18 Kohlenstoffatomen stammt.

5. Verfahren gemäß einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß der verwendete Katalysator (alpha) aus folgenden Arten besteht:

unter den Mineraloxysäuren die Schweflige Säure, Schwefelsäure, Hypophosphorige Säure, Phosphorige Säure, Orthophosphorsäure oder Pyrophosphorsäure;

unter den organischen Oxsäuren:

— die Organosulfonsäuren der Formel R_1-SO_3H (I), worin R_1 bedeutet: einen geraden 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, dessen Benzolkern gegebenenfalls durch 1 bis 3 Alkylreste mit 1 bis 3 Kohlenstoffatomen substituiert sein kann; 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 gegebene 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 geraden 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





...n oder verzweigten Alkylrest mit 1 bis 4 Kohlenstoffatomen (die Verzweigung ist für einen Alkylrest, Kohlenstoffatomen ausgeschlossen); einen Phenylrest oder einen Phenylalkylrest, wobei jeder der beiden letzteren Reste die vorstehend für R₁ angegebene Definition hat.

6. Verfahren gemäß Anspruch 5, dadurch gekennzeichnet, daß die verwendeten Säuren (alpha) in Säuren, abgeleitet von Phosphor, bestehen, gehörend zur Gruppe der Hypophosphorigen Säure, Phosphorigen Säure, Orthophosphorsäure, Pyrophosphorsäure, Methylphosphonsäure, Phenylphosphonsäure, Benzylphosphonsäure, Dimethylphosphinsäure, Diphenylphosphinsäure, Methylphenylphosphinsäure, Dibenzylphosphinsäure, Methylphosphonige Säure, Phenylphosphonige Säure oder Benzylphosphonige Säure.

7. Verfahren gemäß einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß der verwendete Katalysator (beta) in den Natrium- und Kaliumsalzen besteht, die von den vorstehend in Anspruch 4 genannten Säuren stammen, und vorzugsweise in den Natrium- und Kaliumsalzen, die von Säuren stammen, die von Phosphor abgeleitet sind, die vorstehend in Anspruch 5 genannt sind.

8. Verfahren gemäß einem der Ansprüche 5 bis 7, dadurch gekennzeichnet, daß die Mengenverhältnisse starke Säure (alpha) oder Salz (beta), ausgedrückt in Gewichtsprozent in bezug auf das Endcopolyamid, im allgemeinen zwischen 0,01 und 1 % und vorzugsweise zwischen 0,01 und 0,5 % liegen.

9. Verfahren gemäß einem der Ansprüche 1 bis 8, dadurch gekennzeichnet, daß die Stufe (a) in einem geschlossenen System unter einem autogenen Wasserdampfdruck durchgeführt wird, der oberhalb des Atmosphärendrucks und höchstens gleich 2 MPa ist.

10. Verfahren gemäß Anspruch 9, dadurch gekennzeichnet, daß die Stufe (b) durchgeführt wird, indem die folgenden Stufen aneinandergereiht werden:

- man führt fortschreitend während einer Zeitdauer von 10 Minuten bis 2 Stunden entweder die Gesamtmenge der dimeren Säure oder einen Teil der dimeren Säure, bestehend aus 70 bis 95 % der Gesamtmenge, die in das Polymere eingeführt wird, ein,

- indem gleichzeitig der Druck von dem Anfangswert der Präpolymerisation bis zum Wert des Atmosphärendrucks erniedrigt wird,

- indem noch gleichzeitig die Temperatur des Reaktionsgemisches auf einen Wert oberhalb der am Ende der Stufe (a) erreichten Temperatur erhöht wird und die in dem Bereich von 250 bis 280 °C liegt,

- und indem eine gleichzeitige Destillation von Wasser sichergestellt wird,

wobei bei beendeter Zugabe der vorstehend erwähnten dimeren Säure, nachdem gegebenenfalls das Rühren des Reaktionsgemisches bei der vorstehend erwähnten Temperatur und unter Atmosphärendruck während einer Dauer von 10 Minuten bis 1 Stunde fortgesetzt worden ist, man dann fortschreitend während einer Zeitdauer von 5 Minuten bis 1 Stunde einen verminderten Druck gleich oder unterhalb 200×10^2 Pa herstellt,

- nach Herstellung des verminderten Drucks fügt man gegebenenfalls die verbleibende dimere Säure zu und beendet die Polykondensation, indem man fortfährt, das Milieu bei der vorstehend erwähnten Temperatur in dem Bereich von 250 bis 280 °C unter dem vorstehend angegebenen, verminderten Druck während einer Zeitdauer von 10 Minuten bis 1 Stunde zu rühren, wobei noch eine gleichzeitige Destillation von restlichem Wasser sichergestellt wird.

