



Description

French Application 83/10,939, filed by the Applicant Company on 28 June 1983 (EP-A-130,927) describes new homogeneous copolyetheramides with a block structure, having, in particular, a high crystallinity so as to offer high melting points and good thermo-mechanical resistance, a glass transition temperature which is as low as possible so as to have high flexibility and elasticity at temperatures as low as those equal to or below -20°C , and a high melt viscosity compatible with easy utilization in the fields of injection moulding and extrusion.

The prior art, of which the French application takes note, consists of US Patent 4,218,351, which describes thermoplastic elastomers consisting of copolyetheramides. This prior art offers a general group of copolyetheramides which are produced by direct reaction of three types of components, each having functional groups capable of taking part in a reaction giving rise to amide groups. The first component (i) is taken from the group formed by a short-chain dicarboxylic acid, a short-chain diamine, a short-chain lactam, a short-chain aminoacid and a mixture of two or more of these species with each other; the second component (ii) is a fatty acid dimer or an amino derivative of a fatty acid dimer; the third component (iii) is a polyoxyalkylenediamine or a polyoxyalkylenedicarboxylic acid. The components taking part in the reaction are chosen so as to contribute substantially equal quantities of NH_2 and COOH groups to the medium. On reading the examples in the abovementioned patent it is noted that the copolyetheramides which are actually prepared are produced substantially by reaction (i) of a mixture of a short-chain diacid or a short-chain diamine or a mixture of a lactam and a short-chain diacid or a short-chain diamine with a reactant of type (ii) and a reactant of type (iii). The copolyetheramides prepared in this way have interesting properties, especially low-temperature flexibility, which is responsible for the good resilience properties announced. However,

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their low melt viscosity, which is generally below 10 Pas at 232°C, does not allow them to be used as adhesives. Now, in the fields of plastics moulding and extrusion there is a need for products having a sufficiently high melt viscosity to be capable of being injection-moulded or being extruded in a suitable manner. In the prior art no description is to be found of means which make it possible to obtain, starting with the reaction mixtures in accordance with the teaching of the abovementioned US patent, copolyetheramides having a sufficiently high melt viscosity to be capable of being employed as technical plastics.

The subject of French Application 83/10,939 relates to copolyetheramides which set out to satisfy the objective of being capable of having available polymers for moulding and extrusion, having a high melt viscosity, in addition to a high flexibility down to temperatures as low as those equal to or below -20°C.

More specifically, the abovementioned French application relates to homogeneous copolyetheramides, with a block structure, having, in particular, a melting or softening point of at least 170°C, a glass transition temperature measured at ZHE of at most -5°C and a melt viscosity of at least 50 Pas, the said copolyetheramides being capable of being obtained in accordance with the operating procedure defined by the following steps:

a) a lactam containing from 4 to 12 carbon atoms is mixed with a solution of a salt of a fatty acid dimer and of a polyoxyalkylenediamine in a solvent medium based on a mixture of water with an aliphatic alcohol containing fewer than 5 carbon atoms, a water/alcohol/lactam mixture (both the alcohol and the lactam employed corresponding to the definitions given above), or lactam itself in a molten state or else, when the lactam is water-soluble, a water/lactam mixture;

b) the stoichiometry of the said salt having been established beforehand by measuring the pH of the salt solution in a solvent mixture based on water and at least one compound chosen from an aliphatic alcohol, an aliphatic

diol or a lactam (both the alcohol and the lactam employed corresponding to the definitions given above, the aliphatic diol containing from 2 to 6 carbon atoms) and by adjusting the composition of the said salt so that the pH reaches, to within ± 0.05 of a pH unit, the value of the pH at the equivalence point, the mixing of the salt solution with the lactam being capable of being omitted when the solution of salt in the solvent medium based on a water/alcohol/lactam mixture, a water/lactam mixture or of lactam itself in the molten state contains sufficient lactam to obtain the copolyetheramide of the required composition;

c) a catalyst consisting of an inorganic oxyacid or an organic oxyacid other than a carboxylic acid, at least one of the acid groups of which, when there are several of these, has an ionization constant pK_a in water at $25^\circ C$ equal to or below 4, is then added to the reaction mixture; and

d) the whole is then subjected to heating to cause the lactam to react with the salt.

Referring to melt viscosity, the abovementioned French application indicates that it is measured at $230^\circ C$, under a shear gradient of 10 s^{-1} by means of a Davenport rheometer in the case of copolyetheramides produced from lactams containing 6 to 12 carbon atoms; in the case of copolyetheramides produced from lactams containing 4 to 5 carbon atoms the melt viscosity is measured as indicated above, but at $260^\circ C$.

It has now been found, and this forms the subject of the present invention, that homogeneous copolyetheramides with a block structure, having the properties referred to in the abovementioned French application may be produced by following an operating procedure which is modified in respect of the definition of the amino compound which serves to form the salt have (sic) reference is made in step (a) and/or in respect of the definition of the catalyst to which reference is made in step (c), and/or in respect of the time of catalyst addition.

More specifically, the present invention relates

to homogeneous copolyetheramides with a block structure having, in particular, a melting or softening point of at least 170°C, a glass transition temperature measured at ZHE of at most -5°C and a melt viscosity of at least

5 50 Pas, the said copolyetheramides being capable of being obtained in accordance with the operating procedure defined by the following steps:

a') a lactam containing from 4 to 12 carbon atoms is mixed with a solution of a salt of a fatty acid dimer and of a suitable amino compound in a solvent medium based on a mixture of water with an aliphatic alcohol containing fewer than 5 carbon atoms, a water/alcohol/lactam mixture (both the alcohol and the lactam employed corresponding to the definitions given above), or lactam itself in a molten state or else, when the lactam is water-soluble, a water/lactam mixture;

b') the stoichiometry of the said salt having been established beforehand by measuring the pH of the salt solution in a diluent mixture based on water and on at least one compound chosen from an aliphatic alcohol, an aliphatic diol or a lactam (both the alcohol and the lactam employed corresponding to the definitions given above, the aliphatic diol containing from 2 to 6 carbon atoms) and by adjusting the composition of the said salt so that the pH reaches, to within ± 0.05 of a pH unit, the pH value at the equivalence point, the mixing of the salt solution with the lactam being capable of being omitted when the solution of the salt in the solvent medium based on a water/alcohol/lactam mixture, a water/lactam mixture or lactam itself in the molten state contains sufficient lactam to obtain the copolyetheramide of the required composition;

c') a catalyst is then added to the reaction mixture; and

35 d') the whole is then subjected to heating to cause the lactam to react with the salt; the said copolyetheramides being characterised in that in step (a') use is made of a salt of a fatty acid dimer and

of a mixture of a polyoxyalkylenediamine with (sic) a tri-
amine and that in step (c') use is made of a catalyst con-
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, at least one of the
acid groups of which, when there are several of these, has
an ionization constant pKa in water at 25°C equal to
or below 4, (beta) denoting an alkali metal salt or an
alkaline-earth metal salt of this acid.

10 The present invention also relates to the copoly-
etheramides having the properties stated above, which are
capable of being produced in accordance with the operating
procedure defined by the steps (a') to (d'), also stated
above, the said copolyetheramides being this time charac-
15 terised in that in step (a') use is made of a salt of a
fatty acid dimer and of a polyoxyalkylenediamine without a
triamine and that in step (c') use is made of a catalyst
consisting of the compound (beta).

The copolyetheramides having the properties stated
20 in the French Application 83/10,939 and in the pre-
sent invention have been described as capable of being
produced by adding the catalyst (alpha) or (beta) to the
reaction mixture comprising the salt of a fatty acid dimer
and the amino compound, the stoichiometry of which has
25 been established beforehand. It has been found that it
may be advantageous, especially when the catalyst is a
strong inorganic or organic oxyacid, to add the catalyst
to the starting solution of the salt of a fatty acid dimer
and of the amino compound and then to carry out the
30 adjustment of the stoichiometry. The present invention
consequently relates also to copolyetheramides having the
properties stated above, capable of being obtained in
accordance with the operating procedure defined by the
following steps:

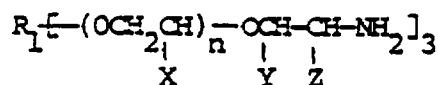
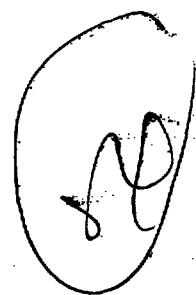
35 a") a lactam containing from 4 to 12 carbon atoms
is mixed with a solution of a salt of a fatty acid dimer
and a suitable amino compound in a solvent medium based
on a mixture of water with an aliphatic alcohol containing

fewer than 5 carbon atoms, a water/alcohol/lactam mixture (both the alcohol and the lactam employed corresponding to the definitions given above), or lactam itself in a molten state, or else, when the lactam is water-soluble, a water/lactam mixture;

b") the stoichiometry of the said solution having been established beforehand by measuring the pH of the solution in a diluent mixture based on water and at least one compound chosen from an aliphatic alcohol, an aliphatic diol or a lactam (both the alcohol and the lactam employed corresponding to the definitions given above, the aliphatic diol containing from 2 to 6 carbon atoms) and by adjusting the composition so that the pH reaches, to within ± 0.05 of a pH unit, the pH value at the equivalence point, the mixing of the salt solution with the lactam being capable of being omitted when the salt solution in the solvent medium based on a water/alcohol/lactam mixture, a water/lactam mixture or lactam itself in a molten state contains sufficient lactam to obtain the copoly-etheramide of the required composition;

c") the lactam is then made to react with the salt by heating in the presence of a catalyst; the said copoly-etheramides being characterised in that the catalyst employed is added to the solution of the salt of a fatty acid dimer and of an amino compound before the adjustment of the stoichiometry of the said solution is carried out, the amino compound consisting of a polyoxyalkylenediamine taken alone or mixed with a triamine and the catalyst consisting either of the compound (alpha), or the compound (beta).

The triamines which may be employed for implementing the present invention are diprimary, secondary or triprimary aliphatic polyamines optionally incorporating one or more ether bridges containing a number of carbon atoms which is at least 8. Mention will be made, in particular, of bis-hexamethylenetriamine of formula $H_2N-(CH_2)_6-NH-(CH_2)_6-NH_2$ and the polyoxyalkylenetriamines corresponding to the general formula:



5 in which:

- R_1 is a trivalent radical which is the residue of a trihydroxylated aliphatic alcohol capable of being polyoxyalkylated, containing from 3 to 10 carbon atoms;

- Z is a straight-chain or branched alkyl radical containing 1 to 18 carbon atoms;

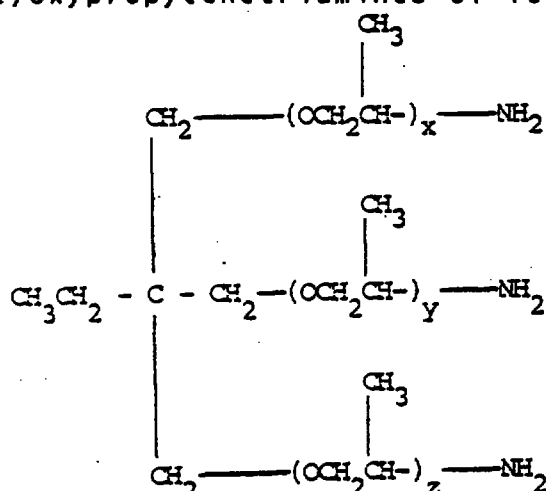
- X and Y, which are identical or different, each denote a hydrogen atom or a radical Z; and

- the symbol n denotes an average number ranging from 0 to 50.

15 These polyoxyalkylenetriamines may be produced according to known processes, such as that described in US Patent 3,654,370.

The triamines which are preferred for carrying out the present invention are the polyoxypropylenetriamines corresponding to the formula (I) given above, in which: R_1 has the definition given above; Z is a methyl radical; X denotes Z; Y is a hydrogen atom and n has an average value ranging from 1 to 16.

25 The triamines which are specially preferred are the polyoxypropylenetriamines of formula:



35 in which (R_1 is thus the trimethylolpropane residue) the symbols x, y and z each denote an average number ranging from 1 to 10, with the total $x + y + z$ ranging from 3 to 30.

The triamines which are most specially preferred are the polyoxypropylenetriamines derived from trimethylolpropane in which the total $x + y + z$ ranges from 5 to 10.

The proportions of triamine which are employed, when its use is required, expressed as the number of millimoles of triamine per 1 kilogramme of final copolyetheramide, are generally between 0.1 and 20, preferably between 1 and 10.

With regard to the strong inorganic or organic oxyacid (alpha) which may be employed, use is made, as indicated in French Application 83/10,939, of an oxygen-containing mono- or polyacid, at least one of the acid groups of which has an ionization constant pK_a (sic) in water at 25°C equal to or below 4.

Suitable strong acids which may be mentioned are, for example:

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

- among the organic oxyacids:

- the organosulphonic acids of formula R_2-SO_3H (III) in which R_2 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 residue 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 $R_3-P(O)(OH)_2$ (IV) in which R_3 denotes an alkyl radical, a phenyl radical or a phenylalkyl radical, each of these radicals having the definition given above for R_2 ;

- the organophosphinic acids of formula $R_4R_5-P(O)(OH)$ (V) in which R_4 and R_5 , which are identical or different, each denote: a straight-chain alkyl radical

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containing from 1 to 3 carbon atoms, a phenyl radical or a phenylalkyl radical, each of these two latter radicals having the definition given above for R_2 ;

- the organophosphonous acids of formula $R_6H-P(O)(OH)$ (VI) in which R_6 denotes: a straight-chain or branched alkyl radical containing from 1 to 4 carbon atoms (branching being excluded for an alkyl radical containing 4 carbon atoms), a phenyl radical or a phenylalkyl radical, each of these two latter radicals having the definition given above for R_2 .

- It is preferable to use as a strong acid (alpha) the acids derived from phosphorus and especially hypophosphorous, phosphorous, orthophosphoric, pyrophosphoric, methylphosphonic, phenylphosphonic, benzylphosphonic, dimethylphosphinic, diphenylphosphinic, methylphenylphosphinic, dibenzylphosphinic, methylphosphonous, phenylphosphonous or benzylphosphonous acids.

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

- As a salt (beta) it is preferable to use those which are completely soluble in the reaction mixture. 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 suitable. The salts (beta) which are most particularly suitable are the sodium and potassium salts derived from the preferred acids derived from phosphorus and particularly mentioned above.

- The proportions of strong acid (alpha) or salt (beta), expressed as a percentage by weight relative to the final copolyetheramide are generally between 0.01 and 1% and preferably between 0.01 and 0.5%.

- The general conditions for putting the present invention into practice are those described in the above-mentioned French application and recalled below.

By way of illustration of the lactams which can be suitable, mention will be made of: γ -butyrolactam,

5 δ -amylolactam, ϵ -caprolactam, oenantholactam, capryllactam, 2-azacycloundecanone, 2-azacyclododecanone and lauro-
lactam. The lactam of which use is preferably made is
 ϵ -caprolactam; the reactant employed then has the same
characteristics as those of the reactant used for the
industrial production of polycaprolactam or nylon 6.

10 The dimer acids employed are obtained by polymerization 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. "Monomeric fatty acids" is intended to de-
note saturated or unsaturated, straight-chain or branched
aliphatic monoacids.

15 Among the saturated straight-chain or branched
monomeric fatty acids mention may be made of: caprylic,
pelargonic, capric, lauric, myristic, palmitic and iso-
palmitic, stearic, arachidic, behenic and lignoceric
acids.

20 Among the straight-chain or branched monomeric
fatty acids containing ethylenic unsaturation(s) mention
may be made of 3-octenoic, 11-dodecenoic, oleic, lauro-
leic, myristoleic, palmitoleic, gadoleic, cetoleic, lino-
leic, linolenic, eicosatetraenoic and chaulmoogric acids.

25 Some acids containing acetylenic unsaturation can also
produce polymeric acids, but they are not found in
appreciable quantities in the natural state and conse-
quently their economic interest is very low.

30 The polymeric fatty acids produced by thermal
polymerization, optionally in the presence of catalysts
such as peroxides or Lewis acids, may be fractionated, for
example, using traditional methods of vacuum distillation
or solvent extraction. They can also be hydrogenated to
reduce their degree of unsaturation and thus to reduce
35 their colouring.

In accordance with the indications of the French
application, the dimer acids which are preferably employed
are fractionated polymeric fatty acids in which the

5 difunctional acid fraction is greater than 94% by weight, the monofunctional acid fraction is below 1% by weight and still more preferably equal to or below 0.5% by weight, the fraction of acid of functionality greater than 2 is below 5% by weight and still more preferably equal to or below 3% by weight.

Still more preferably, the dimer acids employed are the species produced by fractionation (resulting in fractions indicated above) of polymeric fatty acids 10 which have additionally been subjected to a hydrogenation.

The dimer acids which are very specially suitable are, as indicated in the abovementioned French application, the species obtained by fractionation of a hydrogenated composition originating from the catalytic polymerization of monomeric fatty acid(s) containing 18 carbon atoms. 15 In this context, oleic, linoleic and linolenic acids, taken alone or in pairs or preferably in the form of a ternary mixture, are the most particularly preferred starting products for the preparation of the polymeric fatty acids, 20 because of their ready availability and their relatively straightforward polymerization.

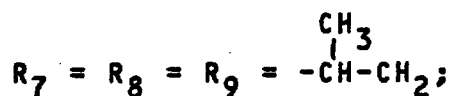
Another reactant employed consists of polyoxyalkylenediamines. As indicated in the abovementioned French application, these compounds may be represented by the 25 general formula:



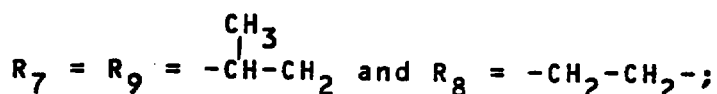
in which the symbols R_7 , R_8 , R_9 , which are identical or different, denote straight-chain or branched divalent saturated aliphatic radicals containing from 1 to 10 carbon atoms and the symbol m is a number determined so as 30 to provide a molecular mass ranging from 100 to 10,000 and, preferably, ranging from 300 to 5,000.

By way of illustration of polyoxyalkylenediamines which are suitable, French Application 83/10,939 mentions, 35 for example:

- polyoxypropylenediamines of formula (VII) in which



- polyoxyethylenediamines of formula (VII) in which



- or polyoxytetramethylenediamines of formula (VII) in
5 which



Naturally, as indicated in the abovementioned
French application, it is possible to use a mixture of two
10 or more polyoxyalkylenediamines.

The process for preparing the copolyetheramides
which accord to the present invention consists in producing,
in a first stage, a solution, in a suitable solvent medium,
which accord to the present invention consists in producing,
15 in a first stage, a solution, in a suitable solvent medium,
of a salt of fatty acid dimer and of polyoxyalkylenedia-
mine taken alone or mixed with a triamine (the said solu-
tion containing or not containing the catalyst), the
stoichiometry of which will then be monitored and adjusted
20 by pH-metering before it is used in the polycondensation
reaction with the lactam (after the catalyst has been
added, where appropriate, when the starting solution does
not contain it).

As mentioned above, the solvent medium for the
25 salt in question and, if appropriate, for the catalyst,
may consist of a water/alcohol mixture (A), a water/alco-
hol/lactam mixture (B), or molten lactam (C) or else, when
the lactam chosen is water-soluble, of a water/lactam mix-
ture (D). The lactam which may then be used is advan-
30 tageously the same as that chosen as a polycondensation
reactant. With regard to the water content of the solvent
media (A) and (D) and to the concentration of the salt in
the media (A), (C) and (D), it is appropriate to refer,
as mentioned by the abovementioned French application, to
35 the indications given by the Applicant Company in French
Patent 2,407,227, pages 2 and 3. Attention will be drawn
to the fact that small changes in relation to the teach-
ing of this prior art may take place in respect of the

respect of the definition of the boundaries within which lie the values of the water content of the solvent media and of the concentration of the salt of fatty acid dimer and of the amino compound; these small changes are substantially attributable to the fact that, in the present invention, on the one hand the salt is prepared from a polyoxyalkylenediamine taken alone or mixed with a triamine, while in the prior art in question the salt is prepared from hexamethylenediamine, and, on the other hand use may now be made of a lactam other than caprolactam, alluded to in this reference. However, the expert will be capable of readily determining these small changes with the aid of simple tests within easy reach. On the subject of the solvent medium (B), although this has not been described in the abovementioned French patent, its composition can, again, be readily determined in the light of the teaching of this document.

With reference to the method of adjusting the stoichiometry of the salt solutions containing or not containing the catalyst, reference should again be made to the teaching of French Patent 2,407,227. As indicated on page 3 of this document, the preferred solvent mixtures used to dilute the salt solution containing or not containing the catalyst, with a view to carrying out the pH measurements, are binary mixtures such as, for example, water/alcohol, water/diol or water/(water-soluble) lactam mixtures, but it is also possible to use ternary mixtures such as, for example, water/alcohol/lactam or water/diol/lactam mixtures, in particular in the case where the lactam chosen is water-insoluble. On the subject of the composition of the diluent mixtures which can be employed, this is the same as that indicated in the prior art in question, with the appearance, if appropriate, of small changes in respect of the definition of the boundaries within which lie the corresponding proportions of each component of these diluent mixtures, these small changes being substantially connected, as indicated before, with the use of a salt of a different kind and, where applicable, the use of a lactam other than

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caprolactam, and which can be readily determined by the expert with the aid of simple tests.

When the lactam-type reactant employed is ϵ -caprolactam, and this corresponds, as already said, to a preferred embodiment, a solvent medium which is particularly recommended for preparing the solution of the salt of fatty acid dimer and of a polyoxyalkylenediamine taken alone or mixed with a triamine (the said solution containing or not containing the catalyst) consists of water/ ϵ -caprolactam mixtures having a water content of between 40 and 80% by weight; with regard to the pH determination of the solution, this is carried out in a highly preferred manner in water/isopropanol diluent mixtures having a water content of between 20 and 60% by weight.

The salt solution (containing or not containing the catalyst), the stoichiometry of which has been strictly monitored and adjusted, is mixed with suitable quantities of lactam (and, where applicable, of catalyst when the starting solution does not contain it), and then the polycondensation of the various monomers involved (lactam, dimer acid and diamine containing ether bridges, taken alone or mixed with a triamine in the form of salt) is carried out.

As indicated in French Application 83/10,939, the polycondensation of the various monomers involved is first carried out by gradually raising the temperature of the reaction mixture between 130°C and 280°C while operating under atmospheric pressure and by providing for uniform distillation of the polycondensation water together with, where applicable, the water and, where appropriate, the alcohol forming part of the constitution of the solvent medium for the salt. The polycondensation is continued by maintaining, after distillation, the melt at the above-mentioned temperatures for a period which can vary from approximately 15 minutes to approximately 2 hours. The polycondensation is completed by then producing a reduced pressure so as gradually to attain a value below $200 \cdot 10^2$ Pa and by maintaining the polycondensation medium at the

abovementioned temperatures for a period which can vary from approximately 15 minutes to approximately 2 hours; this latter stage under reduced pressure offers the advantage of making it possible to remove a large part of the monomers which have not been polycondensed.

The copolyetheramides obtained can, of course, be modified by adding, for example into their preparation medium one or more additives such as, in particular, stabilisers and inhibitors of degradation by oxidation, the ultraviolet, light or heat; lubricants, colouring matter, nucleating agents, antifoam agents, and the like.

In the copolyetheramides according to the present invention, the crystallinity and, consequently, the cohesion and the ease of obtaining high melting points and good thermo-mechanical properties are contributed by the amide blocks; an amide block is understood to denote essentially the concatenation of the segments of formula (VIII) which are derived from the lactam employed by a ring opening:



E denoting the hydrocarbon chain of the lactam. The possibility of obtaining a T_g as low as possible and, as a result, the ability to have high flexibility and elasticity, are contributed by the ether blocks; an ether block is understood to denote essentially the concatenation of segments of formula (IX) which are derived from the condensation of one molecule of polyoxyalkylenediamine with one molecule of dimer acid:



F and G denoting the organic residues joining the functional groups of the polyoxyalkylenediamine and the dimer acid. The triamine, when it is chosen to be employed, will play a minor part in the formation of the amide blocks and/or the ether blocks, depending on its structure. In the case of the polyoxyalkylenetriamines, for example, the triamine takes part in the formation of the ether blocks alone.

The flexibility and the elasticity of the polymer

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obtained can be varied within wide limits by modifying the respective proportions of the amide blocks and the ether blocks in the final copolyetheramide. A good compromise in respect of crystallinity, flexibility and elasticity
5 may be found for weight proportions of amide blocks in the final polymer of between 15 and 85% and preferably between 40 and 60% and for weight proportions of ether blocks of between 85 and 15% and preferably between 60 and 40%. The quantities of reactants employed (lactam and salt of fatty
10 acid dimer and amino compound) are determined, of course, so as to obtain a copolyetheramide having such weight proportions of amide blocks and ether blocks. To calculate these weight proportions it is considered, in the absence of a triamine, that the amide blocks are derived directly
15 from the initial lactam and that the ether blocks are derived from the salt of a dimer acid and a diamine containing ether bridges which is employed by the loss of two moles of water per mole of salt; in the presence, for example, of a polyoxyalkylenetriamine it is considered that the
20 amide blocks are still derived from the starting lactam, while the ether blocks are derived from the salt of dimer acid and of the mixture of diamine containing ether bridges with the triamine containing ether bridges by the loss of one mole of water per COOH group reacting with a
25 NH_2 group originating from the combination of the polyamines.

It has been found, and this in a wholly unexpected manner, that to have both the good compromise just discussed and high melt viscosities it is essential to carry
30 out the polycondensation in the presence of the catalyst which has been specified above in the present description.

Finally, the copolyetheramides obtained have a good thermo-mechanical resistance which is due to their high melting points ranging from 170°C to approximately
35 240°C . They have a T_g , measured at ZHE, which can attain values below -50°C , which endows them with a flexibility and an elasticity (which can be adjusted by modifying the proportions of ether blocks) which can be maintained at

temperatures as low as those between -20°C and -40°C . Their high melt viscosity, measured under the conditions specified above, ranging from 50 poises (sic) to 1000 Pas and even higher, also endows them with an excellent suitability for injection moulding and extrusion. Being perfectly homogeneous, they have, furthermore, good transparency properties. Various applications which rely on the specific qualities of these copolyetheramides may be envisaged in fields as varied as the engineering and building industries, the motor vehicle industry and household appliances.

The following examples illustrate in a non-restrictive manner how the present invention may be implemented in practice.

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

20 - Determination of the pH of the salt solutions:

The pH measurements are carried out at 20°C by means of a pH-meter called Radiometer PHM 62, standardized to a hundredth of a pH unit.

- Microcalorimetric analysis:

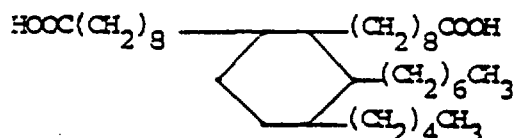
25 The polymers are characterised by melting characteristics such as the melting endotherms E_m and the crystallization exotherms E_c .

These determinations are carried out on a sample subjected to temperature changes of $10^{\circ}\text{C}/\text{min}$ both on heating and on cooling. In this manner, a differential microcalorimetry curve is established on which it is possible to discern the melting point (T_m) and the crystallization point (T_c) on cooling. The difference between T_m and T_c forms the supercooling Δ , which characterises nucleation. Another crystallization characteristic connected with the rate of growth of the crystallites, $\tan \alpha$ was determined; α is the angle formed by the horizontal of the baseline with the initial part of the peak of the

The glass transition temperature (T_g) corresponds to the abrupt drop in the shear modulus as a function of temperature. It can be determined on the diagram showing the changes in the torsion modulus as a function of temperature, changes which are measured by thermomechanical analysis by means of an automatic torsion pendulum.

This is determined at two temperatures: at -20°C and at $+20^{\circ}\text{C}$, by means of an automatic torsion pendulum at a frequency of the order of 1 hertz according to the ISO standard R 537. The specimens are conditioned at ZHE, that is to say they are placed in a desiccator over silica gel and dried for 24 hours at ambient temperature at $0.66-1.33 \cdot 10^2 \text{ Pa}$ before the measurements are carried out. The results are expressed in Mpa.

In the examples which follow, when reference is made to the dimer acid employed, use is made of a compound marketed by Unichema Chemie under the registered 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, the predominant species of which is a saturated compound of formula:



35 The monofunctional acid fraction (the weight content of which will be specified later) consists essentially of oleic acid; as for the fraction of acid of functionality greater than 2 (the weight content of which will also be

specified later), this consists essentially of a mixture of isomeric trimers containing 54 carbon atoms; the average molecular mass of this dimer acid is of the order of 565.

5 Before the notified examples are described, an illustration will be given in the test 1 below of what happens when use is made of the teaching of the prior art, particularly that of US Patent 4,218,351. Test 2 below describes the results obtained when use is made of the
10 method for adjusting the stoichiometry in accordance with the teaching of French Application 83/10,939, but with the polymerization being carried out in the absence of a catalyst.

TEST 1:

15 The apparatus consists of a 1 litre autoclave fitted with :

- a heating system using a heat-transfer fluid,
- a helical band stirrer (speed: 10 revolutions/min to 75 revolutions/min),
- 20 - a distillation column,
- a system permitting pressurization with nitrogen, and
- a circuit permitting the volatile products to be condensed and collected, connected to the head and to the bottom of the distillation column.

25 Into the autoclave, preheated to 75°C, are introduced:

- pure caprolactam: 250 g
- fatty acid dimer marketed under the registered trademark Pripol 1010 by Unichema Chemie, with a monomer content
30 of 0.03% and a trimer content of 3% by weight and having an acidity of between 3.43 meq/g and 3.50 meq/g: 55.4 g
- polyoxyo (sic) propylenediamine marketed by Texaco under the tradename Jeffamine D 2000, having a basicity of between 0.96 meq/g and 0.98 meq/g: 198 g and
- 35 - antioxidant marketed under the registered trademark Irganox 1010 by Ciba Geigy: 0.5 g.

Acidity of the dimer acids: this is determined by potentiometric titration of a solution of dimer acid

in methanol (0.25 g of dimer acid per 80 cm³ of methanol) with a 0.1 N aqueous solution of sodium hydroxide.

Basicity of the polyoxypropylenediamines: this is determined by potentiometric titration of a solution of the diamine in a 50/50 (by volume) water/methanol mixture (0.5 g to 1 g of diamine per 80 cm³ of the solvent mixture) with a 0.1 N aqueous solution of hydrochloric acid and three nitrogen purges are carried out by pressurizing to 3 10⁵ Pa, followed by decompression. With the column set to total reflux, the temperature of the mixture is raised to 175°C in 30 minutes, and then the mixture is kept stirred for 150 minutes at 175°C.

The temperature of the mixture is then raised gradually up to 230°C over approximately 30 minutes while the reaction water is distilled off uniformly. Distillation is continued for 2 hours while the temperature of the reaction mixture is maintained at 230°C.

A pressure of 26.7 10² Pa is then applied gradually over 60 minutes while the temperature of the mixture is maintained at 230°C. The mixture is homogenized at 230°C for 30 minutes under a pressure of 26.7 10² Pa. Stirring is stopped, and then a nitrogen pressure of 3 10⁵ Pa is produced in the autoclave and the polymer is withdrawn. The very fluid polymer extruded from the autoclave is collected on a tray. It is allowed to cool under protection from moisture and it is then cut into small pieces which are stored protected from moisture.

The product obtained is transparent, slightly yellow in colour and has a melt viscosity, measured at 230°C under a shear gradient $\gamma = 10 \text{ s}^{-1}$, of less than 7.5 Pas.

TEST 2:

1. Preparation of the salt of a polyoxypropylene-diamine of molecular mass equal to 2,065 and of the fatty acid dimer in solution at a concentration of 33.33% by weight in a 50/50 (by weight) water/caprolactam mixture:

The following are charged with addition (sic) into a 10 litre round glass flask fitted with a propeller stirrer (three blades; speed of rotation: 100 revolutions/min) and a

dropping funnel and capable of operating under a nitrogen atmosphere:

- demineralized water: 1500 g
- caprolactam: 1,500 g
- 5 - polyoxypropylenediamine of molecular mass equal to 2,065, marketed by BASF under the tradename Etherdiamine 2000: 1,165 g.

The mixture is homogenized for approximately one hour and the free space in the flask is purged with nitrogen.

335 g of fatty acid dimer marketed under the registered trademark Pripol 1010 by Unichema Chemie and having a monomer content of 0.03% and a trimer content of 3% are added to the stirred solution by being poured in at a uniform rate over approximately 30 minutes. The solution is homogenized for 30 minutes.

A small sample of approximately 10 cm³ is taken, which is diluted with a water/isopropanol mixture (42.85/57.15 by weight), so as to adjust the concentration of the salt of the acid dimer and of the polyoxypropylenediamine to 10% by weight. The pH value at 20°C of this diluted solution is lower than that of the pH at the equivalence point.

27.6 g of a solution of polyoxypropylenediamine at a concentration of 33.33% by weight in a water/caprolactam mixture (50/50 by weight) are introduced into the concentrated solution. The solution is homogenized for 30 minutes, and then a pH measurement is again made on a solution diluted to a salt concentration of 10% as previously. The pH value of the diluted solution reaches, to within plus or minus 0.05 of a pH unit, that of the pH at the equivalence point.

The concentrated solution, adjusted in this manner, is stored at 25°C under a nitrogen atmosphere.

2. Preparation of a caprolactam/dimer acid-polyoxypropylenediamine copolyetheramide of molecular mass 2,065, of a weight composition in the region of 50/50 (amide blocks/ether blocks) by using a salt of dimer acid

and of polyoxypropylenediamine, the stoichiometry of which has been established by following the method in accordance with French Application 83/10,939 and by carrying out the polymerization in the absence of an oxyacid having an
5 ionization constant pK_a (sic) in water at 25°C lower than or equal to 4:

The apparatus consists of a 7.5 litre autoclave fitted with:

- a heating system using a heat-transfer fluid,
- 10 - a helical band stirrer (speed: 60 revolutions/min),
- a system permitting pressurization with nitrogen, and
- a circuit permitting the volatile products to be condensed and collected.

Into the autoclave, preheated to 75°C, are introduced:

- a solution of the salt of the acid dimer and of a polyoxypropylenediamine of molecular mass 2,065 at a concentration of 33.33% by weight in a 50/50 (by weight) water/caprolactam mixture from Test 2, part 1: 4,400 g,
- 20 - aqueous solution of caprolactam at a concentration of 60% by weight: 1,150 g,
- antioxidant marketed under the registered trademark Irganox 1010 by Ciba Geigy: 14.7 g, and
- silicone antifoam: 0.5 cm³.

25 The mixture is allowed to homogenize for 15 minutes and three nitrogen purges are carried out by pressurization to $3 \cdot 10^5$ Pa, followed by decompression. The temperature of the stirred mixture is gradually raised up to 150°C over approximately 90 minutes while a uniform
30 distillation of the water is ensured. The temperature of the mixture is maintained at about 150°C until the weight of the distillate reaches 1,782 g (92.5% of the water in the solutions).

The temperature of the mixture is then gradually
35 raised up to 250°C over 45 minutes. The temperature of the stirred mixture is maintained at 250°C for one hour.

A pressure of $66.7 \cdot 10^2$ Pa is then gradually applied over 40 minutes while the mixture is kept

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homogenized at 250°C. The mixture is homogenized at 250°C for 1 hour at a pressure of $66.7 \cdot 10^2$ Pa. 720 g of caprolactam are collected by distillation during the reaction stage under reduced pressure.

5 Stirring is stopped, and then a nitrogen pressure of $3 \cdot 10^5$ Pa is produced in the autoclave and the polymer is withdrawn. The very fluid polymer extruded from the autoclave is collected in cold water and is then cut and dried.

10 The polymer obtained is transparent, pale yellow in colour, and has the following characteristics, measured after drying:

- melt viscosity at 230°C under a shear gradient $\dot{\gamma} = 10 \text{ s}^{-1}$: 48 Pas,

15 - melting point (T_m): 210.5°C,

- crystallization point on cooling (T_c): 153°C,

- $\Delta = T_m - T_c$: 57.5°C,

- $\tan \alpha$: 20.

- Example 1:

20 This example illustrates the modification made to the content of French Application 83/10,939, consisting in the use of a polyoxyalkylenediamine mixed with a triamine.

25 1. Preparation of the salt of a fatty acid dimer and of a mixture of polyoxypropylenediamine of molecular mass equal to 2,065 and of polyoxypropylenetriamine of molecular mass equal to 450, in solution at a concentration of 33.33% by weight in a 50/50 (by weight) water/caprolactam mixture:

30 The following are charged, with stirring, into a 10 litre round glass flask fitted with a propeller stirrer (three blades; speed of rotation: 100 revolutions/min) and a dropping funnel and capable of operating under a nitrogen atmosphere:

35 - demineralized water: 1,500 g

- pure caprolactam: 1,500 g

- polyoxypropylenediamine of molecular mass equal to 2,065, marketed by BASF under the tradename Etherdiamine



2000: 1,168.5 g

- polyoxypropylenetriamine of formula (II) in which the total of $x + y + z$ is in the region of 5.3, with a molecular mass of 450, marketed by Texaco under the trade-name Jeffamine T 403: 8.5 g.

The mixture is homogenized for approximately one hour and the free volume in the flask is purged with nitrogen.

- 323 g of fatty acid dimer marketed under the registered trademark Pripol 1010 by Unichema Chemie, with a monomer content of 0.03% and a trimer content of 3%, are added to the stirred solution by being run in at a uniform rate over approximately 30 minutes. The solution is homogenized for 30 minutes.

- 15 A small sample of approximately 10 cm^3 is taken, which is diluted with a water/isopropanol mixture (42.85/57.15 by weight) so as to adjust the concentration of the salt of the dimer acid and of the polyoxypropyleneamines to 10% by weight. The pH value at 20°C of this diluted solution is higher than that of the pH at the equivalence point.

- 27 g of the fatty acid dimer and 54 g of a 50% strength aqueous solution of caprolactam are added to the concentrated solution. The solution is homogenized for 25 30 minutes and then another pH measurement is made on a solution diluted to 10% salt concentration as before. The pH value of the diluted solution reaches, to within plus or minus 0.05 of a pH unit, that of the pH at the equivalence point.

- 30 The concentrated solution, adjusted in this manner, is stored at 25°C under a nitrogen atmosphere.

2. Preparation of a caprolactam/dimer acid-polyoxypropylenediamine copolyetheramide of molecular mass 2,065-polyoxypropylenetriamine of molecular mass 450, of 35 a weight composition in the region of 50/50 (amide blocks/ether blocks) and with a triamine content in the region of 6.3 millimoles/kg:

The apparatus consists of a 7.5 litre autoclave

fitted with:

- a heating system using a heat-transfer fluid,
- a helical band stirrer (speed: 60 revolutions/min),
- a system permitting pressurization with nitrogen, and
- 5 - a circuit permitting the volatile products to be condensed and collected.

Into the autoclave, preheated to 75°C, are introduced:

- solution of the salt of the dimer acid and of polyoxypropyleneamines at a concentration of 33.33% by weight in a 50/50 (by weight) water/caprolactam mixture from Example 1, part 1: 4,500 g
- aqueous caprolactam solution at a concentration of 60% by weight: 475 g,
- 15 - antioxidant marketed under the registered trademark Irganox 1010 by Ciba Geigy: 15 g,
- hypophosphorous acid in aqueous solution at a concentration of 50% by weight: 3 g, and
- silicone antifoam 0.5 cm³.

20 The mixture is allowed to homogenize for 15 minutes and three nitrogen purges are carried out by pressurization to 3 10⁵ Pa, followed by decompression. The temperature of the stirred mixture is gradually raised up to 150°C over approximately 90 minutes while uniform

25 distillation of the water is ensured. The temperature of the mixture is maintained at about 150°C until the weight of distillate reaches 1,565 g (92.5% of the water in the solution).

The temperature of the mixture is then gradually

30 raised up to 250°C over 45 minutes. The temperature of the stirred mixture in the autoclave is maintained at 250°C for one hour.

A pressure of 72 10² Pa is then produced gradually over 40 minutes while the mixture is kept homogenized at

35 250°C. The mixture is homogenized at 250°C for one hour at a pressure of 72 10² Pa. 330 g of caprolactam are collected by distillation during the reaction stage under reduced pressure.



Stirring is stopped and then a nitrogen pressure of $5 \cdot 10^5$ Pa is produced in the autoclave and the polymer is withdrawn. 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 transparent, slightly opalescent and almost colourless.

It has the following characteristics, measured on dry granules:

- 10 - melting point (T_m): 210°C
- crystallization point on cooling (T_c): 145°C
- $\Delta = T_m - T_c$: 65°C
- $\tan \alpha$: 13
- melt viscosity at 230°C under a shear gradient $\dot{\gamma} = 10 \text{ s}^{-1}$:
15 13,00 Pas.

The physical and mechanical characteristics, measured on injection-moulded, conditioned specimens are as follows:

- glass transition temperature at ZHE: -69°C
- 20 - torsion modulus at ZHE:
 - at $+20^\circ\text{C}$: 54 Mpa
 - at -20°C : 110 MPa.
- Example 2:

Preparation of a caprolactam/dimer acid-polyoxy-propylenediamine of molecular mass equal to 2,065-polyoxy-propylenetriamine of molecular mass 450 copolyetheramide, of weight composition in the region of 50/50 (amide blocks/ether blocks) and having a triamine content in the region of 2.5 millimoles/kg:

30 The operation is carried out following the general operating procedure of Example 1, part 2 but using the following charges:

- solution of the salt of the dimer acid and of the mixture of polyoxypropylenediamine and of polyoxypropylenetriamine at a concentration of 33.33% by weight in a 50/50 (by weight) water/caprolactam mixture as prepared in Example 1, part 1: 1,785 g
- 35 - solution of the salt of the dimer acid and of polyoxy-



propylenediamine at a concentration of 33.33% by weight in a 50/50 (by weight) water/caprolactam mixture, as prepared in Test 2, part 1: 2,715 g

- aqueous solution of caprolactam at a concentration of 5 60% by weight: 475 g
- antioxidant marketed under the registered trademark Irganox 1010 by Ciba Geigy: 15 g
- hypophosphorous acid in aqueous solution at a concentration of 50% by weight: 3 g and
- 10 - silicone antifoam: 0.5 cm³.

320 g of caprolactam are collected by distillation during the reaction stage under reduced pressure.

The transparent, slightly opalescent, almost colourless polymer obtained has the following characteristics, measured on dry granules:

- melting point (T_m): 210°C
- crystallization point on cooling (T_c): 148°C
- Δ = T_m - T_c: 62°C
- tan α : 21
- 20 - melt viscosity at 230°C under a shear gradient $\dot{\gamma} = 10\text{s}^{-1}$: 500 Pas.
- Example 3:

This example illustrates the modification introduced in the content of French Application 83/10,939, consisting in carrying out the adjustment of the stoichiometry of the solution of the salt of a fatty dimer acid and of a polyoxyalkyleneamine in the presence of the catalyst.

1. Preparation of the salt of the fatty dimer acid and of a polyoxypropylenediamine of molecular mass equal 30 to 2,072 in solution at a concentration of 33.33% by weight in a 50/50 (by weight) water/caprolactam mixture, in the presence of phenylphosphonous acid [C₆H₅P(O)H₂OH]:

The following are charged, with stirring, into a 10 litre round glass flask equipped like that described 35 in Example 1:

- demineralized water: 1,490 g
- pure caprolactam: 1,525 g
- polyoxypropylenediamine of molecular mass equal to



2,072, marketed by Texaco under the tradename Jeffamine D 2000: 1,205 g and

- aqueous solution of phenylphosphonous acid at a concentration of 20%: 44 g.

5 The mixture is homogenized for approximately one hour and the free volume of the round flask is purged with nitrogen.

320 g of fatty acid dimer marketed under the registered trademark Pripol 1010 by Unichema Chemie, having a monomer content of 0.03% and a trimer content of 3%,
10 are introduced into the stirred solution by being run in uniformly over approximately 30 minutes. The solution is homogenized for 30 minutes.

A small sample of approximately 10 cm³ is taken
15 and diluted with a water/isopropanol mixture (42.85/57.15 by weight) so as to adjust the concentration of the salt of the dimer acid and of the polyoxypropylenediamine to 10% by weight. The pH value at 20°C of this diluted solution is lower than that of the pH at the equivalence
20 point.

45.9 g of a solution of polyoxypropylenediamine at a concentration of 33.33% by weight in a 50/50 (by weight) water/caprolactam mixture are introduced into the concentrated solution. The solution is homogenized for 30
25 minutes and then another pH measurement is carried out on a solution diluted to 10% salt concentration as before. The pH value of the diluted solution attains, to within plus or minus 0.05 of a pH unit, that of the pH at the equivalence point.

30 The concentrated solution, adjusted in this manner, is stored at 25°C under a nitrogen atmosphere.

2. Preparation of a caprolactam/dimer acid-polyoxypropylenediamine of molecular mass 2,072 copolyetheramide, of weight composition in the region of 50/50 (amide
35 blocks/ether blocks).

Into the autoclave as described in Example 1, part 2, preheated to 75°C, are introduced:

- solution of the salt of the dimer acid and of the

polyoxypropylenediamine of part 1, prepared at a concentration of 33.33% by weight in a 50/50 (by weight) water/caprolactam mixture in the presence of phenylphosphonous acid: 4,500 g.

- 5 - aqueous solution of caprolactam at a concentration of 60% by weight: 550 g, and
- silicone antifoam: 0.5 cm³.

The mixture is allowed to homogenize for 15 minutes and three nitrogen purges are carried out by pressurization to $3 \cdot 10^5$ Pa, followed by decompression. The temperature of the stirred mixture is raised to 115°C over 30 minutes under autogenous pressure. The pressure reached is 210^5 Pa (absolute pressure).

1,485 g of water are distilled at a uniform rate over one hour under this pressure, while the temperature of the mixture increases gradually during this time up to 137°C. The pressure is released down to atmospheric pressure over 10 minutes while the temperature of the mixture is raised to 150°C. During this stage, 160 g of distillate are collected.

The temperature of the mixture is then raised gradually up to 250°C over one hour. The temperature of the stirred mixture is maintained at 250°C for one hour at atmospheric pressure.

A pressure of $66 \cdot 10^2$ Pa is then produced gradually over one hour while the mixture is kept homogenized at 250°C. The mixture is homogenized at 250°C for 20 minutes at a pressure of $66 \cdot 10^2$ Pa. 360 g of caprolactam are collected by distillation during the reaction stage under reduced pressure.

Stirring is stopped and then a nitrogen pressure of $7 \cdot 10^5$ Pa is produced in the autoclave and the polymer is withdrawn. 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 transparent, slightly opalescent and colourless.

It has the following characteristics, measured on

dry granules:

- melting point (T_m): 209.5°C
- crystallization point on cooling (T_c): 142.5°C
- $\Delta = T_m - T_c$: 67°C
- 5 - $\tan \alpha$: 10.5
- melt viscosity at 230°C under a shear gradient $\gamma = 10 \text{ s}^{-1}$: 5500 Pas.
- Example 4:

This example illustrates the modification introduced in the content of French Application 83/10,939, consisting in using a catalyst based on an alkali metal salt of an oxyacid.

1. Preparation of the salt of a polyoxypropylenediamine of molecular mass equal to 2,072 and of the fatty acid dimer in solution at a concentration of 33.33% by weight in a 50/50 (by weight) water/caprolactam mixture:

The dimer acid and the polyoxypropylenediamine of Example 3 are used to prepare this solution in accordance with the general operating procedure described in Test 2, part 1.

2. Preparation of a caprolactam/dimer acid-polyoxypropylenediamine of molecular mass 2,072 copolyetheramide, of weight composition in the region of 50/50 (amide blocks/ether blocks) in the presence of sodium phenyl phosphonite $[\text{C}_6\text{H}_5\text{P}(\text{O})\text{HONa}]$:

The operation is carried out according to the operating procedure of Example 3, part 2, using the following charges:

- solution of the salt of the dimer acid and of the polyoxypropylenediamine of part 1, prepared at a concentration of 33.33% by weight in a 50/50 (by weight) water/caprolactam mixture: 4,500 g,
- aqueous solution of caprolactam at a concentration of 66%: 540 g,
- 35 - 20% concentration aqueous solution of sodium phenyl phosphonite: 45 g, and
- silicone antifoam: 0.5 cm^3 .

The quantity of caprolactam collected during the

reaction stage under reduced pressure is 440 g.

The polymer withdrawn under nitrogen pressure, after the final polymerization stage of 20 minutes at 250°C at a pressure of $66 \cdot 10^2$ Pa, is transparent,

5 slightly opalescent and colourless.

It has the following characteristics, measured on dry granules:

- melting point (T_m): 208°C

- crystallization point on cooling (T_c): 150°C

10 - $\Delta = T_m - T_c$: 58°C

- $\tan \alpha$: 18

- melt viscosity at 230°C under a shear gradient $\dot{\gamma} = 10 \text{ s}^{-1}$: 5000 Pas.

A comparison of the characteristics of the copoly-
15 etheramides of Examples 3 and 4 demonstrates the favourable effect of the catalyst based on a strong acid salt on the crystallizability of the polyetheramide: for a melt vis-
cosity of the same order, the supercooling is reduced by 9°C and $\tan \alpha$ is multiplied by a factor of 1.7

20 when phenylphosphonous acid is replaced by its sodium salt.

- Example 5:

This example illustrates the aspect of the inven-
tion which combines the use of a triamine in the composi-
tion of the parent reactants of the copolyetheramide and
25 the use of an oxyacid salt as a catalyst during the poly-
merization.

Preparation of a caprolactam/dimer acid-polyoxy-
propylenediamine of molecular mass 2,065-polyoxypropylene-
triamine of molecular mass 450 copolyetheramide, of weight
30 composition in the region of 50/50 (amide blocks/ether
blocks), with a triamine content in the region of 2.5
millimoles/kg, polymerized in the presence of sodium
phenylphosphonite.

The operation is carried out according to the
35 general operating procedure of Example 1, part 2, but
using the following charges:

- solution of the salt of the dimer acid and of the mix-
ture of polyoxypropylenediamine of polyoxypropylenetri-

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amine at a concentration of 33.33% by weight in a 50/50 (by weight) water/caprolactam mixture as prepared in Example 1, part 1: 1,785 g,

- 5 - solution of the salt of the dimer acid and of polyoxypropylenediamine at a concentration of 33.33% by weight in a 50/50 (by weight) water/caprolactam mixture, as prepared in Test 2, part 1: 2,715 g,
- aqueous solution of caprolactam at a concentration of 60% by weight: 475 g,
- 10 - a 20% concentration aqueous solution of sodium phenylphosphonite: 7.5 g, and
- silicone antifoam: 0.5 cm³.

320 g of caprolactam are collected during the polymerization stage under reduced pressure. The polymer
15 obtained is transparent, slightly opalescent and colourless.

It has the following characteristics, measured on dry granules:

- melting point T_m : 210°C
- 20 - crystallization point on cooling (T_c): 153°C
- $\Delta = T_m - T_c$: 57°C
- $\tan \alpha$: 25
- melt viscosity at 230°C under a shear gradient $\dot{\gamma} = 10 \text{ s}^{-1}$: 800 Pas.

CLAIMS

1. Homogeneous copolyetheramides, with a block structure, having, in particular, a melting or softening point of at least 170°C, a glass transition temperature measured at ZHE of at most -5°C and a melt viscosity of at least 50 Pas, the said copolyetheramides being capable of being obtained in accordance with the operating procedure defined by the following steps:

a') a lactam containing from 4 to 12 carbon atoms is mixed with a solution of a salt of a fatty acid dimer and a suitable amino compound in a solvent medium based on a mixture of water with an aliphatic alcohol containing fewer than 5 carbon atoms, a water/alcohol/lactam mixture (both the alcohol and the lactam employed corresponding to the definitions given above), or lactam itself in a molten state or else, when the lactam is water-soluble, a water/lactam mixture;

b') the stoichiometry of the said salt having been established beforehand by measuring the pH of the salt solution in a solvent mixture based on water and at least one compound chosen from an aliphatic alcohol, an aliphatic diol or a lactam (both the alcohol and the lactam employed corresponding to the definitions given above, the aliphatic diol containing from 2 to 6 carbon atoms) and by adjusting the composition of the said salt so that the pH reaches, to within ± 0.05 of a pH unit, the value of the pH at the equivalence point, the mixing of the salt solution with the lactam being capable of being omitted when the solution of the salt in the solvent medium based on a water/alcohol/lactam mixture, of a water/lactam mixture or of lactam itself in the molten state contains sufficient lactam to obtain the copolyetheramide of the required composition;

c') a catalyst is then added to the reaction mixture; and

d') the whole is then subjected to heating to cause the lactam to react with the salt; the said copolyetheramides being characterised in that in step



(a') use is made of a salt of a fatty acid dimer and of a mixture of a polyoxyalkylenediamine with a triamine and that in step (c') use is made of 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, at least one of the acid groups of which, when there are several of these, has an ionization constant pka (sic) in water at 25°C which is equal to or below 4, (beta) denoting an alkali metal salt or an alkaline-earth metal salt of this acid.

2. Homogeneous copolyetheramides with a block structure, having, in particular a melting or softening point of at least 170°C, a glass transition temperature measured at ZHE of at most -5°C and a melt viscosity of at least 50 Pas, the said copolyetheramides being capable of being obtained in accordance with the operating procedure defined by the following steps:

a') a lactam containing from 4 to 12 carbon atoms is mixed with a solution of a salt of a fatty acid dimer and of a suitable amino compound in a solvent medium based on a mixture of water with an aliphatic alcohol containing fewer than 5 carbon atoms, a water/alcohol/lactam mixture (both the alcohol and the lactam employed corresponding to the definitions given above), or lactam itself in a molten state or else, when the lactam is water-soluble, a water/lactam mixture;

b') the stoichiometry of the said salt having been established beforehand by measuring the pH of the salt solution in a diluent mixture based on water and on at least one compound chosen from an aliphatic alcohol, an aliphatic diol or a lactam (both the alcohol and the lactam employed corresponding to the definitions given above, the aliphatic diol containing from 2 to 6 carbon atoms) and by adjusting the composition of the said salt so that the pH reaches, to within ± 0.05 of a pH unit, the pH value at the equivalence point, the mixing of the salt solution with the lactam being capable of being omitted when the solution of the salt in the solvent medium based on a



water/alcohol/lactam mixture, a water/lactam mixture or lactam itself in the molten state contains sufficient lactam to obtain the copolyetheramide of the required composition;

c') a catalyst is then added to the reaction mixture; and

d') the whole is then subjected to heating to cause the lactam to react with the salt; the said copolyetheramides being characterised in that in step (a') use is made of a salt of a fatty acid dimer and of a polyoxyalkylenediamine without a triamine and that in step (c') use is made of a catalyst consisting of the compound (beta), such as defined above in Claim 1.

3. Homogeneous copolyetheramides, with a block structure, having, in particular, a melting or softening point of at least 170°C, a glass transition temperature measured at ZHE of at most -5°C and a melt viscosity of at least 50 Pas, the said copolyetheramides being capable of being obtained in accordance with the operating procedure defined by the following steps:

a") a lactam containing from 4 to 12 carbon atoms is mixed with a solution of a salt of a fatty acid dimer and a suitable amino compound in a solvent medium based on a mixture of water with an aliphatic alcohol containing fewer than 5 carbon atoms, a water/alcohol/lactam mixture (both the alcohol and the lactam employed corresponding to the definitions given above), or lactam itself in a molten state or else, when the lactam is water-soluble, a water/lactam mixture;

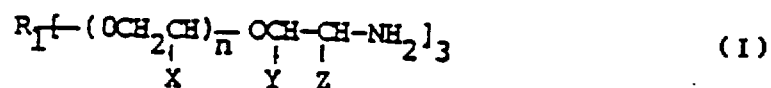
b") the stoichiometry of the said solution having been established beforehand by measuring the pH of the solution in a diluent mixture based on water and at least one compound chosen from an aliphatic alcohol, an aliphatic diol or a lactam (both the alcohol and the lactam employed corresponding to the definitions given above, the aliphatic diol containing from 2 to 6 carbon atoms) and by adjusting the composition so that the pH reaches, to within ± 0.05 of a pH unit, the pH value at the equivalence



point, the mixing of the solution of the salt with the lactam being capable of being omitted when the salt solution in the solvent medium based on a water/alcohol/lactam mixture, a water/lactam mixture or lactam itself in a molten state contains sufficient lactam to obtain the copolyetheramide of the required composition; and

c") the lactam is then made to react with the salt by heating in the presence of a catalyst; the said copolyetheramides being characterised in that the catalyst employed is added to the solution of the salt of a fatty acid dimer and of an amino compound before the adjustment of the stoichiometry of the said solution is carried out, the amino compound consisting of a polyoxyalkylene-diamine taken alone or mixed with a triamine and the catalyst consisting either of the compound (alpha), or the compound (beta), such as defined above in Claim 1.

4. Copolyetheramides according to either of Claims 1 and 3, characterised in that the triamine of which use is made in step (a') or (a'') is a compound taken from the group consisting of bis-hexamethylenetriamine of formula $H_2N-(CH_2)_6-NH-(CH_2)_6-NH_2$ and the polyoxyalkylene-triamines corresponding to the general formula:



in which:

- R_1 is a trivalent radical which is the residue of a trihydroxylated aliphatic alcohol capable of being polyoxyalkylated, containing from 3 to 10 carbon atoms;

- Z is a straight-chain or branched alkyl radical containing 1 to 18 carbon atoms;

- X and Y, which are identical or different, each denote a hydrogen atom or a radical Z; and

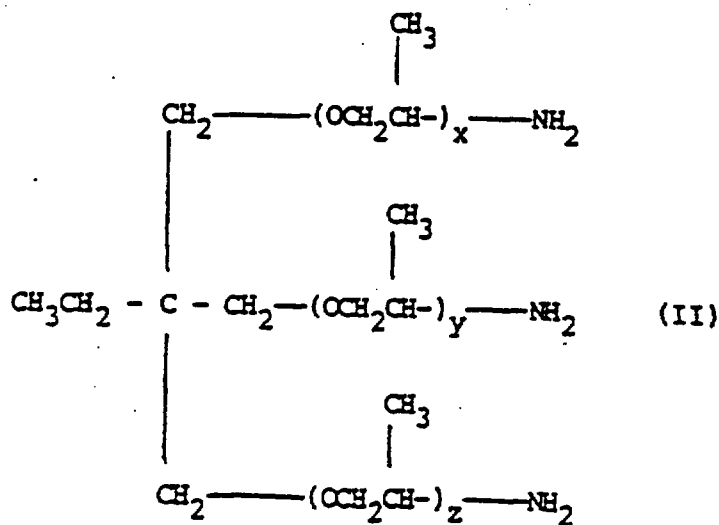
- the symbol n denotes an average number ranging from 0 to 50.

5. Copolyetheramides according to either of Claims 1 and 3, characterised in that the triamine of which use is made in step (a') or (a'') is a compound corresponding



to the formula (I) in which: R_1 has the definition given above in Claim 4; Z is a methyl radical; X denotes Z; Y is a hydrogen atom and n has an average value ranging from 1 to 16.

6. Copolyetheramides according to Claim 5, characterised in that the triamine is a polyoxypropylenetriamine corresponding to the formula



in which the symbols x, y and z each denote an average number ranging from 1 to 10, with the total $x + y + z$ ranging from 3 to 30.

7. Copolyetheramides according to any one of Claims 1 and 3 to 6, characterised in that the proportions of triamine which are employed, expressed as the number of millimoles of triamine per 1 kilogramme of final copolyetheramide are generally between 0.1 and 20, preferably between 1 and 10.

8. Copolyetheramides according to any one of Claims 1 and 3 to 7, characterised in that the catalyst (alpha) of which use is made 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_2-SO_3H (III) in which R_2 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 residue 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 $R_3-P(O)(OH)_2$ (IV) in which R_3 denotes an alkyl radical, a phenyl radical or a phenylalkyl radical, each of these radicals having the definition given above for R_2 ;

- the organophosphinic acids of formula $R_4R_5-P(O)(OH)$ (V) in which R_4 and R_5 , 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 these two latter radicals having the definition given above for R_2 ;

- the organophosphonous acids of formula $R_6H-P(O)(OH)$ (VI) in which R_6 denotes: a straight-chain or branched alkyl radical containing from 1 to 4 carbon atoms (branching being excluded for an alkyl radical containing 4 carbon atoms), a phenyl radical or a phenylalkyl radical, each of these two latter radicals having the definition given above for R_2 .

9. Copolyetheramides according to Claim 8, characterised in that the acids (alpha) of which use is made consist of the acids derived from phosphorus belonging to the group of hypophosphorous, phosphorous, orthophosphoric, pyrophosphoric, methylphosphonic, phenylphosphonic, benzylphosphonic, dimethylphosphinic, diphenylphosphinic, methylphenylphosphinic, dibenzylphosphinic, methylphosphonous, phenylphosphonous or benzylphosphonous acids.

10. Copolyetheramides according to any one of Claims 1 to 7, characterised in that the catalyst (beta) of which



use is made consists of the sodium and potassium salts derived from the acids mentioned above in Claim 8 and, preferably, of the sodium and potassium salts originating from the phosphorus-derived acids mentioned above in Claim 9.

11. Copolyetheramides according to any one of Claims 8 to 10, characterised in that the proportions of strong acid (alpha) or salt (beta), expressed as a percentage by weight relative to the final copolyetheramide, are generally between 0.01 and 1% and preferably between 0.01 and 0.5%.

12. Copolyetheramides according to any one of Claims 1 to 11, characterised in that the lactam of which use is made is ϵ -caprolactam.

13. Copolyetheramides according to any one of Claims 1 to 12, characterised in that the dimer acids employed are obtained by polymerization and fractionation 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 dimer acids comprising a difunctional acid fraction which is greater than 94% by weight, a monofunctional acid fraction which is below 1% by weight and a fraction of acid of functionality greater than 2 which is below 5% by weight.

14. Copolyetheramides according to Claim 13, characterised in that the dimer acids of which use is made 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.

15. Copolyetheramides according to any one of Claims 1 to 14, characterised in that the polyoxyalkylenediamines of which use is made are compounds of general formula



in which the symbols R_7 , R_8 , R_9 , which are identical or different, denote straight-chain or branched divalent



saturated aliphatic radicals containing from 1 to 10 carbon atoms, and the symbol m is a number determined so as to provide a molecular mass ranging from 100 to 10,000 and, preferably, ranging from 300 to 5,000.

16. Copolyetheramides according to Claim 15, characterised in that the polyoxyalkylenediamines of which use is made comprise polyoxypropylenediamines of formula (VII) in which

$R_7 = R_8 = R_9 = -\overset{\text{CH}_3}{\underset{|}{\text{CH}}}-\text{CH}_2-$, polyoxyethylenediamines

of formula (VII) in which $R_7 = R_9 = -\overset{\text{CH}_3}{\underset{|}{\text{CH}}}-\text{CH}_2-$ and $R_8 = -\text{CH}_2-\text{CH}_2-$ or polyoxytetramethylenediamines of formula

(VII) in which $R_7 = R_9 = -\overset{\text{CH}_3}{\underset{|}{\text{CH}}}-\text{CH}_2-$ and $R_8 = -\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$, these compounds having a molecular mass ranging from 100 to 10,000 and, preferably, ranging from 300 to 5,000.

17. Copolyetheramides according to any one of Claims 1 to 16, characterised in that the weight proportions of amide blocks in the final polymer are between 15 and 85% and, preferably, between 40 and 60%, and the weight proportions of ether blocks are between 85 and 15% and preferably, between 60 and 40%.



CLAIMS (for the Contracting State AT)

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1. Process for preparing homogeneous copolyether-amides, with a block structure, having, in particular, a melting or softening point of at least 170°C, a glass transition temperature measured at ZHE of at most -5°C and a melt viscosity of at least 50 Pas, the said process being carried out in accordance with the operating procedure defined by the following steps:

a') a lactam containing from 4 to 12 carbon atoms is mixed with a solution of a salt of a fatty acid dimer and a suitable amino compound in a solvent medium based on a mixture of water with an aliphatic alcohol containing fewer than 5 carbon atoms, a water/alcohol/lactam mixture (both the alcohol and the lactam employed corresponding to the specifications given above), or lactam itself in a molten state or else, when the lactam is water-soluble, a water/lactam mixture;

b') the stoichiometry of the said salt having been established beforehand by measuring the pH of the salt solution in a solvent mixture based on water and at least one compound chosen from an aliphatic alcohol, an aliphatic diol or a lactam (both the alcohol and the lactam employed corresponding to the definitions given above, the aliphatic diol containing from 2 to 6 carbon atoms) and by adjusting the composition of the said salt so that the pH reaches, to within ± 0.05 of a pH unit, the value of the pH at the equivalence point, the mixing of the salt solution with the lactam being capable of being omitted when the solution of the salt in the solvent medium based on a water/alcohol/lactam mixture, of a water/lactam mixture or of lactam itself in the molten state contains sufficient lactam to obtain the copolyetheramide of the required composition;

c') a catalyst is then added to the reaction mixture; and

d') the whole is then subjected to heating to cause the lactam to react with the salt; the said process





being characterised in that in step (a') use is made of a salt of a fatty acid dimer and of a mixture of a polyoxyalkylenediamine with a triamine and that in step (c') use is made of 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, at least one of the acid groups of which, when there are several of these, has an ionization constant pK_a in water at $25^{\circ}C$ which is equal to or below 4, (beta) denoting an alkali metal salt or an alkaline-earth metal salt of this acid.

2. Process for preparing homogeneous copolyetheramides with a block structure, having, in particular a melting or softening point of at least $170^{\circ}C$, a glass transition temperature measured at ZHE of at most $-5^{\circ}C$ and a melt viscosity of at least 50 Pas, the said process being carried out in accordance with the operating procedure specified by the following steps:

a') a lactam containing from 4 to 12 carbon atoms is mixed with a solution of a salt of a fatty acid dimer and a suitable amino compound in a solvent medium based on a mixture of water with an aliphatic alcohol containing fewer than 5 carbon atoms, a water/alcohol/lactam mixture (both the alcohol and the lactam employed corresponding to the specifications given above), or lactam itself in a molten state or else, when the lactam is water-soluble, a water/lactam mixture;

b') the stoichiometry of the said salt having been established beforehand by measuring the pH of the salt solution in a diluent mixture based on water and on at least one compound chosen from an aliphatic alcohol, an aliphatic diol or a lactam (both the alcohol and the lactam employed corresponding to the specifications given above, the aliphatic diol containing from 2 to 6 carbon atoms) and by adjusting the composition of the said salt so that the pH reaches, to within ± 0.05 of a pH unit, the pH value at the equivalence point, the mixing of the solution of the salt with the lactam being capable of being



omitted when the solution of the salt in the solvent medium based on a water/alcohol/lactam mixture, a water/lactam mixture or lactam itself in the molten state contains sufficient lactam to obtain the copolyetheramide of the required composition;

c') a catalyst is then added to the reaction mixture; and

d') the whole is then subjected to heating to cause the lactam to react with the salt; the said process being characterised in that in step (a') use is made of a salt of a fatty acid dimer and of a polyoxyalkylenediamine without a triamine and that in step (c') use is made of a catalyst consisting of the compound (beta), such as specified above in Claim 1.

3. Process for preparing homogeneous copolyetheramides, with a block structure, having, in particular, a melting or softening point of at least 170°C, a glass transition temperature measured at ZHE of at most -5°C and a melt viscosity of at least 50 Pas, the said process being carried out in accordance with the operating procedure defined by the following steps:

a") a lactam containing from 4 to 12 carbon atoms is mixed with a solution of a salt of a fatty acid dimer and a suitable amino compound in a solvent medium based on a mixture of water with an aliphatic alcohol containing fewer than 5 carbon atoms, a water/alcohol/lactam mixture (both the alcohol and the lactam employed corresponding to the specifications given above), or lactam itself in a molten state or else, when the lactam is water-soluble, a water/lactam mixture;

b") the stoichiometry of the said solution having been established beforehand by measuring the pH of the solution in a diluent mixture based on water and at least one compound chosen from an aliphatic alcohol, an aliphatic diol or a lactam (both the alcohol and the lactam employed corresponding to the specifications given above, the aliphatic diol containing from 2 to 6 carbon atoms) and by adjusting the composition so that the pH attains,

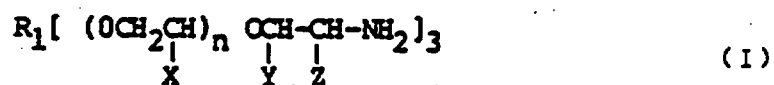


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to within ± 0.05 of a pH unit, the pH value at the equivalence point, the mixing of the solution of the salt with the lactam being capable of being omitted when the salt solution in the solvent medium based on a water/alcohol/lactam mixture, a water/lactam mixture or lactam itself in a molten state contains sufficient lactam to obtain the copolyetheramide with the required composition; and

c") the lactam is then made to react with the salt by heating in the presence of a catalyst; the said process being characterised in that the catalyst employed is added to the solution of the salt of a fatty acid dimer and of an amino compound before the adjustment of the stoichiometry of the said solution is carried out, the amino compound consisting of a polyoxyalkylenediamine taken alone or mixed with a triamine and the catalyst consisting either of the compound (alpha), or the compound (beta), such as defined above in Claim 1.

4. Process according to either of Claims 1 and 3, characterised in that the triamine of which use is made in step (a') or (a'') is a compound taken from the group consisting of bishexamethylenetriamine of formula $H_2N-(CH_2)_6-NH-(CH_2)_6-NH_2$ and the polyoxyalkylenetriamines corresponding to the general formula:



in which:

- R_1 is a trivalent radical which is the residue of a trihydroxylated aliphatic alcohol capable of being polyoxyalkylated, containing from 3 to 10 carbon atoms;
- Z is a straight-chain or branched alkyl radical containing 1 to 18 carbon atoms;
- X and Y, which are identical or different, each denote a hydrogen atom or a radical Z; and
- the symbol n denotes an average number ranging from 0 to 50.

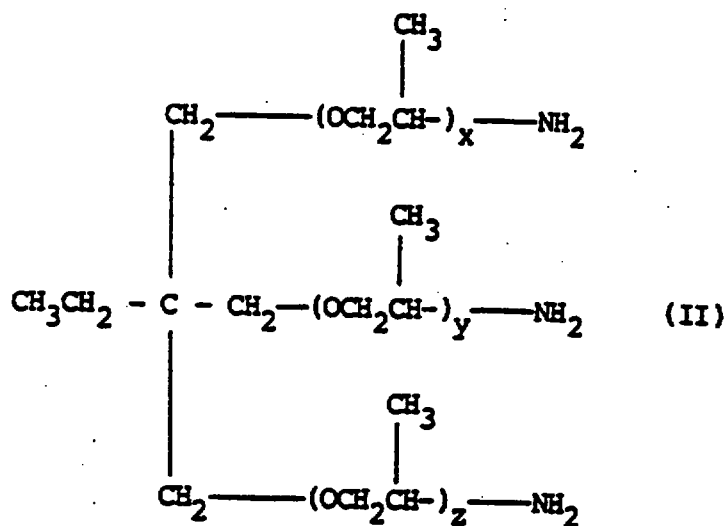
5. Process according to either of Claims 1 and 3, characterised in that the triamine of which use is made



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in step (a') or (a'') is a compound corresponding to the formula (I) in which: R_1 has the definition given above in Claim 4; Z is a methyl radical; X denotes Z; Y is a hydrogen atom and n has an average value ranging from 1 to 16.

6. Process according to Claim 5, characterised in that the triamine is a polyoxypropylenetriamine corresponding to the formula



in which the symbols x, y and z each denote an average number ranging from 1 to 10, with the total of $x + y + z$ ranging from 3 to 30.

7. Process according to any one of Claims 1 and 3 to 6, characterised in that the proportions of triamine which are employed, expressed as the number of millimoles of triamine per 1 kilogramme of final copolyetheramide are generally between 0.1 and 20, preferably between 1 and 10.

8. Process according to any one of Claims 1 and 3 to 7, characterised in that the catalyst (alpha) of which use is made 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 $R_2\text{-SO}_3\text{H}$ (III)

in which R_2 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 residue 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 $R_3-P(O)(OH)_2$ (IV) in which R_3 denotes an alkyl radical, a phenyl radical or a phenylalkyl radical, each of these radicals having the definition given above for R_2 ;

- the organophosphinic acids of formula $R_4R_5-P(O)(OH)$ (V) in which R_4 and R_5 , 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 these latter two radicals having the definition given above for R_2 ;

- the organophosphonous acids of formula $R_6H-P(O)(OH)$ (VI) in which R_6 denotes: a straight-chain or branched alkyl radical containing from 1 to 4 carbon atoms (branching being excluded in the case of an alkyl radical containing 4 carbon atoms), a phenyl radical or a phenylalkyl radical, each of these two latter radicals having the definition given above for R_2 .

9. Process according to Claim 8, characterised in that the acids (alpha) of which use is made consist of the acids derived from phosphorus belonging to the group of hypophosphorous, phosphorous, orthophosphoric, pyrophosphoric, methylphosphonic, phenylphosphonic, benzylphosphonic, dimethylphosphinic, diphenylphosphinic, methylphenylphosphinic, dibenzylphosphinic, methylphosphonous, phenylphosphonous or benzylphosphonous acids.

10. Process according to any one of Claims 1 to 7, characterised in that the catalyst (beta) of which use is made consists of the sodium and potassium salts derived from the acids mentioned above in Claim 8 and, preferably, of the sodium and potassium salts originating from the



phosphorus-derived acids mentioned above in Claim 9.

11. Process according to any one of Claims 8 to 10, characterised in that the proportions of strong acid (alpha) or salt (beta), expressed as a percentage by weight relative to the final copolyetheramide, are generally between 0.01 and 1% and preferably between 0.01 and 0.5%.

12. Process according to any one of Claims 1 to 11, characterised in that the lactam of which use is made is ϵ -caprolactam.

13. Process according to any one of Claims 1 to 12, characterised in that the dimer acids employed are obtained by polymerization and fractionation 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 dimer acids comprising a difunctional acid fraction which is greater than 94% by weight, a monofunctional acid fraction which is smaller than 1% by weight and a fraction of acid of functionality greater than 2 which is below 5% by weight.

14. Process according to Claim 13, characterised in that the dimer acids of which use is made 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.

15. Process according to any one of Claims 1 to 14, characterised in that the polyoxyalkylenediamines of which use is made are compounds of general formula



in which the symbols R_7 , R_8 , R_9 , which are identical or different, denote straight-chain or branched divalent saturated aliphatic radicals containing from 1 to 10 carbon atoms, and the symbol m is a number determined so as to provide a molecular mass ranging from 100 to 10,000 and, preferably, ranging from 300 to 5,000.

16. Process according to Claim 15, characterised in that the polyoxyalkylenediamines of which use is made



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comprise polyoxypropylenediamines of formula (VII) in which

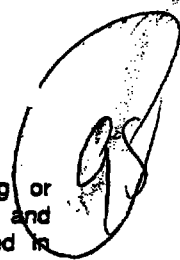
$R_7 = R_8 = R_9 = \overset{\text{CH}_3}{\underset{|}{\text{CH}}}-\text{CH}_2-$, polyoxyethylenediamines

of formula (VII) in which $R_7 = R_9 = \overset{\text{CH}_3}{\underset{|}{\text{CH}}}-\text{CH}_2-$ and $R_8 = -\text{CH}_2-\text{CH}_2-$ or polyoxytetramethylenediamines of formula

(VII) in which $R_7 = R_9 = \overset{\text{CH}_3}{\underset{|}{\text{CH}}}-\text{CH}_2-$ and $R_8 = -\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$, these compounds having a molecular mass ranging from 100 to 10,000 and, preferably, ranging from 300 to 5,000.

17. Process according to any one of Claims 1 to 16, characterised in that the weight proportions of amide blocks in the final polymer are between 15 and 85% and, preferably, between 40 and 60%, and the weight proportions of ether blocks are between 85 and 15% and, preferably, between 60 and 40%.





Claims

1. Homogeneous copolyetheramides, with a block structure, having, in particular, a melting or softening point of at least 170 °C, a glass transition temperature measured at ZHE of at most -5 °C and a melt viscosity of at least 50 Pas, the said copolyetheramides being capable of being obtained in accordance with the operating procedure defined by the following steps :

a') a lactam containing from 4 to 12 carbon atoms is mixed with a solution of a salt of a fatty acid dimer and a suitable amino compound in a solvent medium based on a mixture of water with an aliphatic alcohol containing fewer than 5 carbon atoms, a water/alcohol/lactam mixture (both the alcohol and the lactam employed corresponding to the specifications given above), or lactam itself in a molten state or else, when the lactam is water-soluble, a water/lactam mixture ;

b') the stoichiometry of the said salt having been established beforehand by measuring the pH of the salt solution in a solvent mixture based on water and at least one compound chosen from an aliphatic alcohol, an aliphatic diol or a lactam (both the alcohol and the lactam employed corresponding to the definitions given above, the aliphatic diol containing from 2 to 6 carbon atoms and by adjusting the composition of the said salt so that the pH reaches, to within ± 0.05 of a pH unit, the value of the pH at the equivalence point, the mixing of the salt solution with the lactam being capable of being omitted when the solution of the salt in the solvent medium based on a water/alcohol/lactam mixture, or a water/lactam mixture or of lactam itself in the molten state contains sufficient lactam to obtain the copolyetheramide of the required composition ;

c') a catalyst is then added to the reaction mixture ; and

d') the whole is then subjected to heating to cause the lactam to react with the salt ; the said copolyetheramides being characterised in that in step (a') use is made of a salt of a fatty acid dimer and of a mixture of a polyoxyalkylenediamine with a triamine and that in step (c') use is made of 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, at least one of the acid groups of which, when there are several of these, has an ionization constant pK_a in water at 25 °C which is equal to or below 4, (beta) denoting an alkali metal salt or an alkaline-earth metal salt of this acid.

2. Homogeneous copolyetheramides with a block structure, having, in particular a melting or softening point of at least 170 °C, a glass transition temperature measured at ZHE of at most -5 °C and a melt viscosity of at least 50 Pas, the said copolyetheramides being capable of being obtained in accordance with the operating procedure specified by the following steps :

a') a lactam containing from 4 to 12 carbon atoms is mixed with a solution of a salt of a fatty acid dimer and a suitable amino compound in a solvent medium based on a mixture of water with an aliphatic alcohol containing fewer than 5 carbon atoms, a water/alcohol/lactam mixture (both the alcohol and the lactam employed corresponding to the specifications given above), or lactam itself in a molten state or else, when the lactam is water-soluble, a water/lactam mixture ;

b') the stoichiometry of the said salt having been established beforehand by measuring the pH of the salt solution in a diluent mixture based on water and on at least one compound chosen from an aliphatic alcohol, an aliphatic diol or a lactam (both the alcohol and the lactam employed corresponding to the specifications given above, the aliphatic diol containing from 2 to 6 carbon atoms) and by adjusting the composition of the said salt so that the pH reaches, to within ± 0.05 of a pH unit, the pH value at the equivalence point, the mixing of the solution of the salt with the lactam being capable of being omitted when the solution of the salt in the solvent medium based on a water/alcohol/lactam mixture, a water/lactam mixture or lactam itself in the molten state contains sufficient lactam to obtain the copolyetheramide of the required composition ;

c') a catalyst is then added to the reaction mixture ; and

d') the whole is then subjected to heating to cause the lactam to react with the salt ; the said copolyetheramides being characterised in that in step (a') use is made of a salt of a fatty acid dimer and of a polyoxyalkylenediamine without a triamine and that in step (c') use is made of a catalyst consisting of the compound (beta), such as specified above in Claim 1.

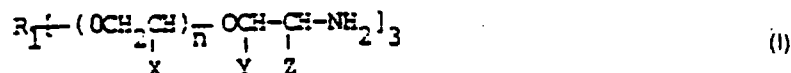
3. Homogeneous copolyetheramides, with a block structure, having, in particular, a melting or softening point of at least 170 °C, a glass transition temperature measured at ZHE of at most -5 °C and a melt viscosity of at least 50 Pas, the said copolyetheramides being capable of being obtained in accordance with the operating procedure defined by the following steps :

a') a lactam containing from 4 to 12 carbon atoms is mixed with a solution of a salt of a fatty acid dimer and a suitable amino compound in a solvent medium based on a mixture of water with an aliphatic alcohol containing fewer than 5 carbon atoms, a water/alcohol/lactam mixture (both the alcohol and the lactam employed corresponding to the specifications given above), or lactam itself in a molten state or else, when the lactam is water-soluble, a water/lactam mixture ;

b') the stoichiometry of the said solution having been established beforehand by measuring the pH of the solution in a diluent mixture based on water and at least one compound chosen from an aliphatic alcohol, an aliphatic diol or a lactam (both the alcohol and the lactam employed corresponding to the specifications given above, the aliphatic diol containing from 2 to 6 carbon atoms) and by adjusting the composition so that the pH attains, to within ± 0.05 of a pH unit, the pH value at the equivalence point, the mixing of the solution of the salt with the lactam being capable of being omitted when the salt solution in the solvent medium based on a water/alcohol/lactam mixture, a water/lactam mixture or lactam itself in a molten state contains sufficient lactam to obtain the copolyetheramide with the required composition ; and

c") the lactam is then made to react with the salt by heating in the presence of a catalyst ; the said copolyetheramides being characterised in that the catalyst employed is added to the solution of the salt of a fatty acid dimer and of an amino compound before the adjustment of the stoichiometry of the said solution is carried out, the amino compound consisting of a polyoxyalkylenediamine taken alone or mixed with a triamine and the catalyst consisting either of the compound (alpha), or the compound (beta), such as defined above in Claim 1.

4. Copolyetheramides according to either of Claims 1 and 3, characterised in that the triamine of which use is made in step (a') or (a'') is a compound taken from the group consisting of bis-hexamethylene-triamine of formula $H_2N-(CH_2)_6-NH-(CH_2)_6-NH_2$ and the polyoxyalkylenetriamines corresponding to the general formula :

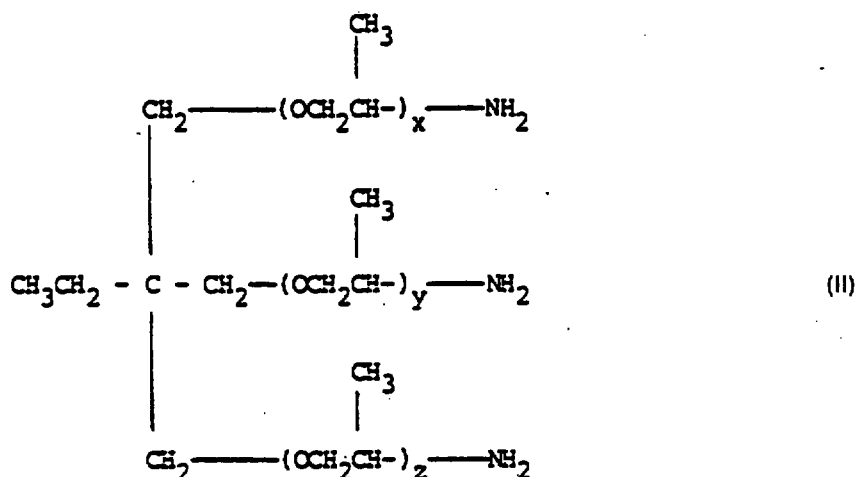


in which :

- . R_1 is a trivalent radical which is the residue of a trihydroxylated aliphatic alcohol capable of being polyoxyalkylated, containing from 3 to 10 carbon atoms ;
- . n is a straight-chain or branched alkyl radical containing 1 to 18 carbon atoms ;
- . X and Y , which are identical or different, each denote a hydrogen atom or a radical Z ; and
- . the symbol n denotes an average number ranging from 0 to 50.

5. Copolyetheramides according to either of Claims 1 and 3, characterised in that the triamine of which use is made in step (a') or (a'') is a compound corresponding to the formula (I) in which : R_1 has the definition given above in Claim 4 ; Z is a methyl radical ; X denotes Z ; Y is a hydrogen atom and n has an average value ranging from 1 to 16.

6. Copolyetheramides according to Claim 5, characterised in that the triamine is a polyoxypropylene-triamine corresponding to the formula



in which the symbols x , y and z each denote an average number ranging from 1 to 10, with the total of $x + y + z$ ranging from 3 to 30.

7. Copolyetheramides according to any one of Claims 1 and 3 to 6, characterised in that the proportions of triamine which are employed, expressed as the number of millimoles of triamine per 1 kilogramme of final copolyetheramide are generally between 0.1 and 20, preferably between 1 and 10.

8. Copolyetheramides according to any one of Claims 1 and 3 to 7, characterised in that the catalyst (alpha) of which use is made 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_2-SO_3H (III) in which R_2 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 residue 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 $R_3-P(O)(OH)_2$ (IV) in which R_3 denotes an alkyl radical, a phenyl radical or a phenylalkyl radical, each of these radicals having the definition given above for R_2 ;

. the organophosphinic acids of formula $R_4R_5-P(O)(OH)$ (V) in which R_4 and R_5 , 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 these latter two radicals having the definition given above for R_2 ;



the organophosphonous acids of formula $R_6H-P(O)(OH)$ (VI) in which R_6 denotes: a straight-chain or branched alkyl radical containing from 1 to 4 carbon atoms (branching being excluded in the case of an alkyl radical containing 4 carbon atoms), a phenyl radical or a phenylalkyl radical, each of these two latter radicals having the definition given above for R_2 .

9. Copolyetheramides according to Claim 8, characterised in that the acids (alpha) of which use is made consist of the acids derived from phosphorus belonging to the group of hypophosphorous,

phosphorous, orthophosphoric, pyrophosphoric, methylphosphonic, phenylphosphonic, benzylphosphonic, dimethylphosphinic, diphenylphosphinic, methylphenylphosphinic, dibenzylphosphinic, methylphosphonous, phenylphosphonous or benzylphosphonous acids.

10. Copolyetheramides according to any one of Claims 1 to 7, characterised in that the catalyst (beta) of which use is made consists of the sodium and potassium salts derived from the acids mentioned above in Claim 8 and, preferably, of the sodium and potassium salts originating from the phosphorus-derived acids mentioned above in Claim 9.

11. Copolyetheramides according to any one of Claims 8 to 10, characterised in that the proportions of strong acid (alpha) or salt (beta), expressed as a percentage by weight relative to the final copolyetheramide, are generally between 0.01 and 1 % and preferably between 0.01 and 0.5 %.

12. Copolyetheramides according to any one of Claims 1 to 11, characterised in that the lactam of which use is made is ϵ -caprolactam.

13. Copolyetheramides according to any one of Claims 1 to 12, characterised in that the dimer acids employed are obtained by polymerization and fractionation 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 dimer acids comprising a difunctional acid fraction which is greater than 94 % by weight, a monofunctional acid fraction which is smaller than 1 % by weight and a fraction of acid of functionality greater than 2 which is below 5 % by weight.

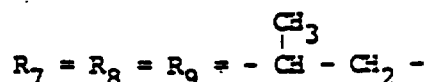
14. Copolyetheramides according to Claim 13, characterised in that the dimer acids of which use is made consist of the species obtained by fractionation of a hydrogenated composition originating from the catalytic polymerization of monomeric fatty acid(s) containing 18 carbon atoms.

15. Copolyetheramides according to any one of Claims 1 to 14, characterised in that the polyoxyalkylenediamines of which use is made are compounds of general formula

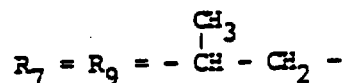


in which the symbols R_7 , R_8 , R_9 , which are identical or different, denote straight-chain or branched divalent saturated aliphatic radicals containing from 1 to 10 carbon atoms, and the symbol m is a number determined so as to provide a molecular mass ranging from 100 to 10,000 and, preferably, ranging from 300 to 5,000.

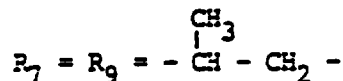
16. Copolyetheramides according to Claim 15, characterised in that the polyoxyalkylenediamines of which use is made comprise polyoxypropylenediamines of formula (VII) in which



polyoxyethylenediamines of formula (VII) in which



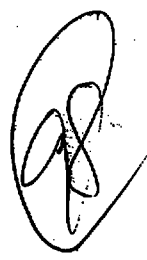
and $R_8 = -\text{CH}_2-\text{CH}_2-$, or polyoxytetramethylenediamines of formula (VII) in which



and $R_8 = -\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$, these compounds having a molecular mass ranging from 100 to 10,000 and, preferably, ranging from 300 to 5,000.

17. Copolyetheramides according to any one of Claims 1 to 16, characterised in that the weight proportions of amide blocks in the final polymer are between 15 and 85 % and, preferably, between 40 and 60 %, and the weight proportions of ether blocks are between 85 and 15 % and preferably, between 60 and 40 %.





Claims (for the Contracting State AT)

1. Process for preparing homogeneous copolyetheramides, with a block structure, having, in particular, a melting or softening point of at least 170 °C, a glass transition temperature measured at ZHE of at most - 5 °C and a melt viscosity of at least 50 Pas, the said process being carried out in accordance with the operating procedure defined by the following steps :

a') a lactam containing from 4 to 12 carbon atoms is mixed with a solution of a salt of a fatty acid dimer and a suitable amino compound in a solvent medium based on a mixture of water with an aliphatic alcohol containing fewer than 5 carbon atoms, a water/alcohol/lactam mixture (both the alcohol and the lactam employed corresponding to the specifications given above), or lactam itself in a molten state or else, when the lactam is water-soluble, a water/lactam mixture ;

b') the stoichiometry of the said salt having been established beforehand by measuring the pH of the salt solution in a solvent mixture based on water and at least one compound chosen from an aliphatic alcohol, an aliphatic diol or a lactam (both the alcohol and the lactam employed corresponding to the definitions given above, the aliphatic diol containing from 2 to 6 carbon atoms) and by adjusting the composition of the said salt so that the pH reaches, to within ± 0.05 of a pH unit, the value of the pH at the equivalence point, the mixing of the salt solution with the lactam being capable of being omitted when the solution of the salt in the solvent medium based on a water/alcohol/lactam mixture, of a water/lactam mixture or of lactam itself in the molten state contains sufficient lactam to obtain the copolyetheramide of the required composition ;

c') a catalyst is then added to the reaction mixture ; and

d') the whole is then subjected to heating to cause the lactam to react with the salt ; the said process being characterised in that in step (a') use is made of a salt of a fatty acid dimer and of a mixture of a polyoxyalkylenediamine with a triamine and that in step (c') use is made of 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, at least one of the acid groups of which, when there are several of these, has an ionization constant pKa in water at 25 °C which is equal to or below 4, (beta) denoting an alkali metal salt or an alkaline-earth metal salt of this acid.

2. Process for preparing homogeneous copolyetheramides with a block structure, having, in particular a melting or softening point of at least 170 °C, a glass transition temperature measured at ZHE of at most - 5 °C and a melt viscosity of at least 50 Pas, the said process being carried out in accordance with the operating procedure specified by the following steps :

a') a lactam containing from 4 to 12 carbon atoms is mixed with a solution of a salt of a fatty acid dimer and a suitable amino compound in a solvent medium based on a mixture of water with an aliphatic alcohol containing fewer than 5 carbon atoms, a water/alcohol/lactam mixture (both the alcohol and the lactam employed corresponding to the specifications given above), or lactam itself in a molten state or else, when the lactam is water-soluble, a water/lactam mixture ;

b') the stoichiometry of the said salt having been established beforehand by measuring the pH of the salt solution in a diluent mixture based on water and on at least one compound chosen from an aliphatic alcohol, an aliphatic diol or a lactam (both the alcohol and the lactam employed corresponding to the specifications given above, the aliphatic diol containing from 2 to 6 carbon atoms) and by adjusting the composition of the said salt so that the pH reaches, to within ± 0.05 of a pH unit, the pH value at the equivalence point, the mixing of the solution of the salt with the lactam being capable of being omitted when the solution of the salt in the solvent medium based on a water/alcohol/lactam mixture, a water/lactam mixture or lactam itself in the molten state contains sufficient lactam to obtain the copolyetheramide of the required composition ;

c') a catalyst is then added to the reaction mixture ; and

d') the whole is then subjected to heating to cause the lactam to react with the salt ; the said process being characterised in that in step (a') use is made of a salt of a fatty acid dimer and of a polyoxyalkylenediamine without a triamine and that in step (c') use is made of a catalyst consisting of the compound (beta), such as specified above in Claim 1.

3. Process for preparing homogeneous copolyetheramides, with a block structure, having, in particular, a melting or softening point of at least 170 °C, a glass transition temperature measured at ZHE of at most - 5 °C and a melt viscosity of at least 50 Pas, the said process being carried out in accordance with the operating procedure defined by the following steps :

a') a lactam containing from 4 to 12 carbon atoms is mixed with a solution of a salt of a fatty acid dimer and a suitable amino compound in a solvent medium based on a mixture of water with an aliphatic alcohol containing fewer than 5 carbon atoms, a water/alcohol/lactam mixture (both the alcohol and the lactam employed corresponding to the specifications given above), or lactam itself in a molten state or else, when the lactam is water-soluble, a water/lactam mixture ;

b') the stoichiometry of the said solution having been established beforehand by measuring the pH of the solution in a diluent mixture based on water and at least one compound chosen from an aliphatic alcohol, an aliphatic diol or a lactam (both the alcohol and the lactam employed corresponding to the specifications given above, the aliphatic diol containing from 2 to 6 carbon atoms) and by adjusting the composition so that the pH attains, to within ± 0.05 of a pH unit, the pH value at the equivalence point, the mixing of the solution of the salt with the lactam being capable of being omitted when the salt solution in the solvent medium based on a water/alcohol/lactam mixture, a water/lactam mixture or lactam itself in a molten state contains sufficient lactam to obtain the copolyetheramide with the required composition ;

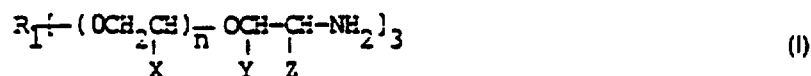
and



c") the lactam is then made to react with the salt by heating in the presence of a catalyst; the said process being characterised in that the catalyst employed is added to the solution of the salt of a fatty acid dimer and of an amino compound before the adjustment of the stoichiometry of the said solution is

carried out, the amino compound consisting of a polyoxyalkylenetriamine taken alone or mixed with a triamine and the catalyst consisting either of the compound (alpha), or the compound (beta), such as defined above in Claim 1.

4. Process according to either of Claims 1 and 3, characterised in that the triamine of which use is made in step (a') or (a'') is a compound taken from the group consisting of bis-hexamethylenetriamine of formula $H_2N-(CH_2)_6-NH-(CH_2)_6-NH_2$ and the polyoxyalkylenetriamines corresponding to the general formula:



in which:

— R_1 is a trivalent radical which is the residue of a trihydroxylated aliphatic alcohol capable of being polyoxyalkylated, containing from 3 to 10 carbon atoms;

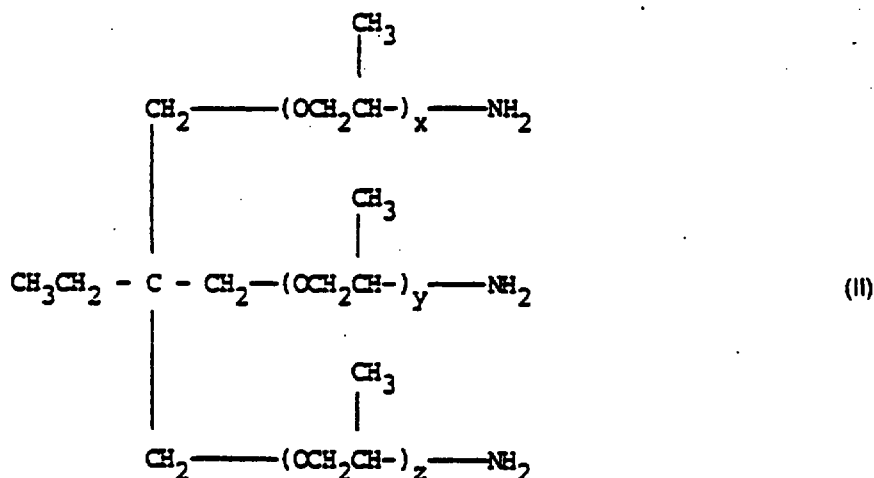
— Z is a straight-chain or branched alkyl radical containing 1 to 18 carbon atoms;

— X and Y, which are identical or different, each denote a hydrogen atom or a radical Z; and

— the symbol n denotes an average number ranging from 0 to 50.

5. Process according to either of Claims 1 and 3, characterised in that the triamine of which use is made in step (a') or (a'') is a compound corresponding to the formula (I) in which: R_1 has the definition given above in Claim 4; Z is a methyl radical; X denotes Z; Y is a hydrogen atom and n has an average value ranging from 1 to 16.

6. Process according to Claim 5, characterised in that the triamine is a polyoxypropylenetriamine corresponding to the formula



in which the symbols x, y and z each denote an average number ranging from 1 to 10, with the total of $x + y + z$ ranging from 3 to 30.

7. Process according to any one of Claims 1 and 3 to 6, characterised in that the proportions of triamine which are employed, expressed as the number of millimoles of triamine per 1 kilogramme of final copolyetheramide are generally between 0.1 and 20, preferably between 1 and 10.

8. Process according to any one of Claims 1 and 3 to 7, characterised in that the catalyst (alpha) of which use is made 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 $R_2-\text{SO}_3\text{H}$ (III) in which R_2 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 residue 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 $R_3-\text{P}(\text{O})(\text{OH})_2$ (IV) in which R_3 denotes an alkyl radical, a phenyl radical or a phenylalkyl radical, each of these radicals having the definition given above for R_2 ;

— the organophosphinic acids of formula $R_4R_5-\text{P}(\text{O})(\text{OH})$ (V) in which R_4 and R_5 , 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 these latter two radicals having the definition given above for R_2 ;



— the organophosphonous acids of formula $R_6H-P(O)(OH)$ (VI) in which R_6 denotes: a straight-chain or branched alkyl radical containing from 1 to 4 carbon atoms (branching being excluded in the case of an alkyl radical containing 4 carbon atoms), a phenyl radical or a phenylalkyl radical, each of these two latter radicals having the definition given above for R_2 .

9. Process according to Claim 8, characterised in that the acids (alpha) of which use is made consist of the acids derived from phosphorus belonging to the group of hypophosphorous, phosphorous, orthophosphoric, pyrophosphoric, methylphosphonic, phenylphosphonic, benzylphosphonic, dimethylphosphinic, diphenylphosphinic, methylphenylphosphinic, dibenzylphosphinic, methylphosphonous, phenylphosphonous or benzylphosphonous acids.

10. Process according to any one of Claims 1 to 7, characterised in that the catalyst (beta) of which use is made consists of the sodium and potassium salts derived from the acids mentioned above in Claim 8 and, preferably, of the sodium and potassium salts originating from the phosphorus-derived acids mentioned above in Claim 9.

11. Process according to any one of Claims 8 to 10, characterised in that the proportions of strong acid (alpha) or salt (beta), expressed as a percentage by weight relative to the final copolyetheramide, are generally between 0.01 and 1 % and preferably between 0.01 and 0.5 %.

12. Process according to any one of Claims 1 to 11, characterised in that the lactam of which use is made is ϵ -caprolactam.

13. Process according to any one of Claims 1 to 12, characterised in that the dimer acids employed are obtained by polymerization and fractionation 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 dimer acids comprising a difunctional acid fraction which is greater than 94 % by weight, a monofunctional acid fraction which is smaller than 1 % by weight and a fraction of acid of functionality greater than 2 which is below 5 % by weight.

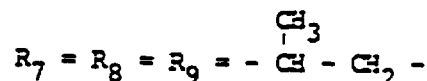
14. Process according to Claim 13, characterised in that the dimer acids of which use is made consist of the species obtained by fractionation of a hydrogenated composition originating from the catalytic polymerization of monomeric fatty acid(s) containing 18 carbon atoms.

15. Process according to any one of Claims 1 to 14, characterised in that the polyoxyalkylenediamines of which use is made are compounds of general formula

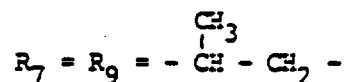


in which the symbols R_7 , R_8 , R_9 , which are identical or different, denote straight-chain or branched divalent saturated aliphatic radicals containing from 1 to 10 carbon atoms, and the symbol m is a number determined so as to provide a molecular mass ranging from 100 to 10,000 and, preferably, ranging from 300 to 5,000.

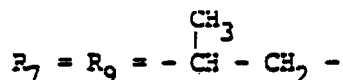
16. Process according to Claim 15, characterised in that the polyoxyalkylenediamines of which use is made comprise polyoxypropylenediamines of formula (VII) in which



polyoxyethylenediamines of formula (VII) in which



and $R_8 = -CH_2-CH_2-$ or polyoxytetramethylenediamines of formula (VII) in which



and $R_8 = -CH_2-CH_2-CH_2-CH_2-$, these compounds having a molecular mass ranging from 100 to 10,000 and, preferably, ranging from 300 to 5,000.

17. Process according to any one of Claims 1 to 16, characterised in that the weight proportions of amide blocks in the final polymer are between 15 and 85 % and, preferably, between 40 and 60 %, and the weight proportions of ether blocks are between 85 and 15 % and, preferably, between 60 and 40 %.



Patentansprüche

1. Homogene Copolyetheramide mit Blockstruktur, die insbesondere einen Schmelzpunkt oder Erweichungspunkt von mindestens gleich 170 °C, eine Glasübergangstemperatur, gemessen bei EHO, höchstens gleich -5 °C und eine Schmelzviskosität mindestens gleich 50 Pas aufweisen, wobei diese Copolyetheramide in der Lage sind, gemäß der durch die folgenden Stufen definierten Arbeitsweise erhalten zu werden:

(a') man vermischt ein Lactam mit 4 bis 12 Kohlenstoffatomen mit einer Lösung eines Salzes eines Fettsäuredimeren und einer geeigneten Aminverbindung in einem Lösungsmilieu auf Basis einer Mischung Wasser-aliphatischer Alkohol mit weniger als 5 Kohlenstoffatomen, eines Gemisches Wasser-Alkohol-Lactam (der verwendete Alkohol und das Lactam entsprechen der einen oder anderen der vorstehend angegebenen Definitionen), des Lactams selbst in geschmolzenem Zustand oder auch, wenn das Lactam in Wasser löslich ist, eines Gemisches Wasser-Lactam;

(b') die Stöchiometrie dieses Salzes wird vorher festgesetzt, indem das pH der Lösung des Salzes in einem Verdünnungsgemisch auf Basis von Wasser und mindestens einer Verbindung, ausgewählt aus einem aliphatischen Alkohol, einem aliphatischen Diol oder einem Lactam (der verwendete Alkohol und das verwendete Lactam entsprechen der einen oder anderen der vorstehend angegebenen Definitionen, das aliphatische Diol hat 2 bis 6 Kohlenstoffatome), gemessen wird und indem die Zusammensetzung dieses Salzes derart eingestellt wird, daß das pH bei $\pm 0,05$ pH-Einheit den pH-Wert im Äquivalenzpunkt erreicht, wobei das Gemisch der Lösung des Salzes mit dem Lactam weggelassen werden kann, wenn die Lösung des Salzes in dem Auflösungsmilieu auf Basis eines Gemisches Wasser-Alkohol-Lactam, eines Gemisches Wasser-Lactam oder Lactam selbst in geschmolzenem Zustand genügend Lactam enthält, um das Copolyetheramid mit der gewünschten Zusammensetzung zu erhalten;

(c') dann gibt man in das Reaktionsgemisch einen Katalysator;

(d') und man unterwirft dann das Ganze einem Erhitzen, um das Lactam mit dem Salz reagieren zu lassen; wobei diese Copolyetheramide dadurch gekennzeichnet sind, daß man in der Stufe (a') ein Salz des Fettsäuredimeren und eines Gemisches Polyoxyalkylendiamin mit einem Triamin einsetzt und daß man in der Stufe (c') einen Katalysator verwendet, der entweder aus einer Verbindung (alpha) oder einer Verbindung (beta) besteht, wobei (alpha) eine Mineraloxysäure oder eine organische Oxysäure, anders als eine Carbonsäure, bezeichnet, wovon wenigstens eine der Säurefunktionen, wenn es davon mehrere gibt, eine Ionisationskonstante pKa in Wasser bei 25 °C gleich oder unterhalb von 4 besitzt, (beta) ein Alkali- oder Erdsalzsäure dieser Säure bezeichnet.

2. Homogene Copolyetheramide mit Blockstruktur, die insbesondere einen Schmelz- oder Erweichungspunkt mindestens gleich 170 °C, eine Glasübergangstemperatur, gemessen bei EHO, höchstens gleich -5 °C und eine Schmelzviskosität mindestens gleich 50 Pas aufweisen, wobei diese Copolyetheramide in der Lage sind, entsprechend der in den folgenden Stufen definierten Arbeitsweise erhalten zu werden:

(a') man vermischt ein Lactam mit 4 bis 12 Kohlenstoffatomen mit einer Lösung eines Salzes von dimerer Fettsäure und einer geeigneten Aminverbindung in einem Auflösungsmilieu auf Basis eines Gemisches Wasser-aliphatischer Alkohol mit weniger als 5 Kohlenstoffatomen, eines Gemisches Wasser-Alkohol-Lactam (der verwendete Alkohol und das verwendete Lactam entsprechen der einen oder anderen der vorstehend gegebenen Definitionen), von Lactam selbst in geschmolzenem Zustand oder auch, wenn das Lactam in Wasser löslich ist, eines Gemisches Wasser-Lactam;

(b') die Stöchiometrie dieses Salzes wird vorher festgestellt, indem das pH der Lösung des Salzes in einem Verdünnungsgemisch auf Basis von Wasser und mindestens einer Verbindung, ausgewählt unter einem aliphatischen Alkohol, einem aliphatischen Diol oder einem Lactam (der verwendete Alkohol und das verwendete Lactam entsprechen der einen oder anderen der vorstehend gegebenen Definitionen, das aliphatische Diol umfaßt 2 bis 6 Kohlenstoffatome), gemessen wird und indem die Zusammensetzung dieses Salzes in der Weise eingestellt wird, daß das pH bei $\pm 0,05$ pH-Einheiten den pH-Wert am Äquivalenzpunkt erreicht und das Gemisch der Lösung des Salzes mit dem Lactam weggelassen werden kann, wenn die Lösung des Salzes in dem Auflösungsmilieu auf Basis eines Gemisches Wasser-Alkohol-Lactam, eines Gemisches Wasser-Lactam oder Lactam selbst in geschmolzenem Zustand genügend Lactam enthält, um das Copolyetheramid der gewünschten Zusammensetzung zu erhalten;

(c') dann gibt man in das Reaktionsgemisch einen Katalysator;

(d') man unterwirft dann das Ganze einem Erhitzen, um das Lactam mit dem Salz reagieren zu lassen; die genannten Copolyetheramide sind dadurch gekennzeichnet, daß man in der Stufe (a') ein Salz von dimerer Fettsäure und Polyoxyalkylendiamin ohne Triamin einsetzt und daß man in der Stufe (c') einen Katalysator verwendet, der aus der Verbindung (beta) besteht, wie sie vorstehend in Anspruch 1 definiert ist.

3. Homogene Copolyetheramide mit Blockstruktur, die insbesondere einen Schmelz- oder Erweichungspunkt von mindestens gleich 170 °C, eine Glasübergangstemperatur, gemessen bei EHO, höchstens gleich -5 °C und eine Schmelzviskosität mindestens gleich 50 Pas aufweisen, wobei diese Copolyetheramide in der Lage sind, entsprechend der durch die folgenden Stufen definierten Arbeitsweise erhalten zu werden:

(a'') man vermischt ein Lactam mit 4 bis 12 Kohlenstoffatomen mit einer Lösung eines Salzes von dimerer Fettsäure und einer geeigneten Aminverbindung in einem Auflösungsmilieu auf Basis eines Gemisches von Wasser-aliphatischem Alkohol mit weniger als 5 Kohlenstoffatomen, eines Gemisches Wasser-Alkohol-Lactam (der verwendete Alkohol und das verwendete Lactam entsprechen der einen und



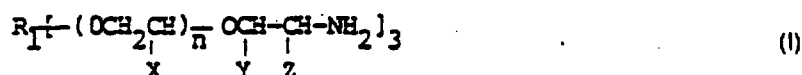
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anderen der vorstehend gegebenen Definitionen), von Lactam selbst in geschmolzenem Zustand oder auch, wenn das Lactam in Wasser löslich ist, eines Gemisches Wasser-Lactam ;

(b") die Stöchiometrie dieser Lösung wird vorher festgesetzt, indem das pH der Lösung in einem Verdünnungsgemisch auf Basis von Wasser und mindestens einer Verbindung, ausgewählt unter einem aliphatischen Alkohol, einem aliphatischen Diol oder einem Lactam (der Alkohol oder das Lactam entsprechen der einen und anderen in den vorstehend gegebenen Definitionen, das aliphatische Diol umfaßt 2 bis 6 Kohlenstoffatome), gemessen wird und indem die Zusammensetzung derart eingestellt wird, daß das pH bei $\pm 0,05$ pH-Einheiten den pH-Wert am Äquivalenzpunkt erreicht, wobei das Gemisch der Lösung des Salzes mit dem Lactam weggelassen werden kann, wenn die Lösung des Salzes in dem Auflösungsmilieu auf Basis eines Gemisches Wasser-Alkohol-Lactam, eines Gemisches Wasser-Lactam oder Lactam selbst in geschmolzenem Zustand hinreichend Lactam enthält, um das Copolyetheramid der gewünschten Zusammensetzung zu erhalten ;

(c") dann läßt man durch Erhitzen das Lactam mit dem Salz in Gegenwart eines Katalysators reagieren, wobei diese Copolyetheramide dadurch gekennzeichnet sind, daß der verwendete Katalysator in die Lösung des Salzes von dimerer Fettsäure und Aminverbindung zugegeben wird, bevor die Stöchiometrie der Lösung reguliert wird, und die Aminverbindung aus einem Polyoxyalkylendiamin allein oder im Gemisch mit einem Triamin besteht und der Katalysator entweder aus der Verbindung (alpha) oder aus der Verbindung (beta), wie vorstehend in Anspruch 1 definiert, besteht.

4. Copolyetheramide gemäß einem der Ansprüche 1 und 3, dadurch gekennzeichnet, daß das Triamin, das man in der Stufe (a') oder (a") verwendet, eine Verbindung ist, ausgewählt aus der Gruppe, die durch Bis-hexamethylentriamin der Formel $\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}-(\text{CH}_2)_6-\text{NH}_2$ und den Polyoxyalkylentriaminen der allgemeinen Formel (I) gebildet ist :



worin

R_1 ein dreiwertiger Rest ist, welcher der Rest eines trihydroxylierten, aliphatischen Alkohols ist, der polyoxyalkyliert werden kann und 3 bis 10 Kohlenstoffatome hat ;

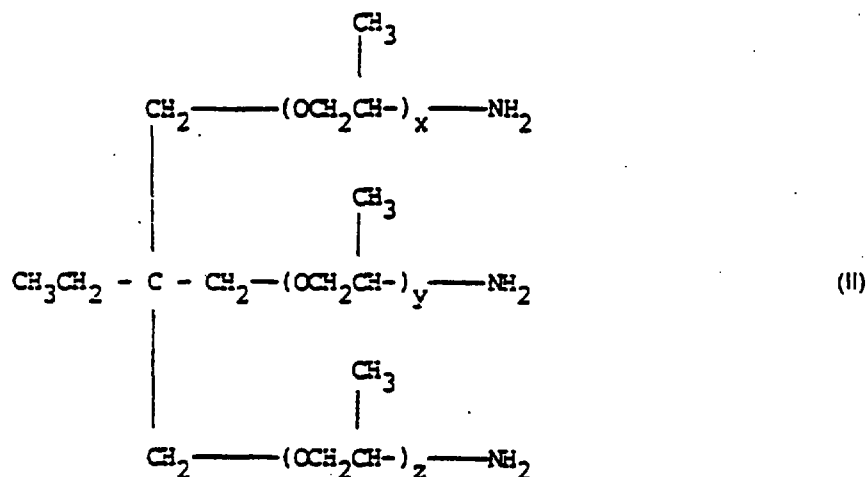
Z ist ein linearer oder verzweigter Alkylrest mit 1 bis 18 Kohlenstoffatomen ;

X und Y, die identisch oder verschieden sind, bedeuten jeweils ein Wasserstoffatom oder einen Rest Z ;

das Symbol n bedeutet eine mittlere Zahl von 0 bis 50.

5. Copolyetheramide gemäß einem der Ansprüche 1 und 3, dadurch gekennzeichnet, daß das Triamin, das in der Stufe (a') oder (a") verwendet wird, eine Verbindung der Formel (I) ist, worin R_1 die vorstehend in Anspruch 4 gegebene Definition hat ; Z ein Methylrest ist ; X für Z steht ; Y ein Wasserstoffatom ist und n den mittleren Wert von 1 bis 16 hat.

6. Copolyetheramide gemäß Anspruch 5, dadurch gekennzeichnet, daß das Triamin ein Polyoxypolyentriamin der Formel (II) ist :



worin die Symbole x, y und z jeweils eine mittlere Zahl von 1 bis 10 bedeuten mit der Summe $x + y + z$ von 3 bis 30.

7. Copolyetheramide gemäß einem der Ansprüche 1 und 3 bis 6, dadurch gekennzeichnet, daß die eingesetzten Mengen an Triamin, ausgedrückt als Millimol Triamin pro 1 kg End-Copolyetheramid, im allgemeinen zwischen 0,1 und 20, vorzugsweise zwischen 1 und 10, liegen.

8. Copolyetheramide gemäß einem der Ansprüche 1 und 3 bis 7, dadurch gekennzeichnet, daß der Katalysator (alpha), der verwendet wird, aus den folgenden Gruppen besteht :



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unter den mineralischen Oxyssäuren: Schweflige Säure, Schwefelsäure, Hypophosphorige Säure, Phosphorige Säure, Orthophosphorsäure oder Pyrophosphorsäure;

unter den organischen Oxyssäuren:

die Organosulfonsäuren der Formel R_2-SO_3H (III), worin R_2 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 $R_3-P(O)(OH)_2$ (IV) worin R_3 einen Alkylrest, einen Phenylrest oder einen Phenylalkylrest bedeutet, wobei jeder dieser Reste die vorstehend für R_2 angegebene Definition hat;

die Organophosphinsäuren der Formel $R_4R_5-P(O)(OH)$ (V) worin R_4 und R_5 identisch oder verschieden sind und jeweils bedeuten: einen geraden Alkylrest mit 1 bis 3 Kohlenstoffatomen; einen Phenylrest oder einen Phenylalkylrest, wobei jeder dieser zwei letztgenannten Reste die vorstehend für R_2 gegebene Definition hat;

die Organophosphonigsäuren der Formel $R_6H-P(O)(OH)$ (VI), worin R_6 bedeutet: einen linearen oder verzweigten Alkylrest mit 1 bis 4 Kohlenstoffatomen (die Verzweigung ist für einen Alkylrest mit 4 Kohlenstoffatomen ausgeschlossen); einen Phenylrest oder einen Phenylalkylrest, wobei jeder dieser beiden letztgenannten Reste die vorstehend für R_2 gegebene Definition hat.

9. Copolyetheramide gemäß Anspruch 8, dadurch gekennzeichnet, daß die (alpha) Säuren, welche verwendet werden, bestehen aus Säuren, abgeleitet von Phosphor, gehörend zu der Gruppe der Hypophosphorigen-, Phosphorigen-, Orthophosphor-, Pyrophosphor-, Methylphosphon-, Phenylphosphon-, Benzylphosphon-, Dimethylphosphin-, Diphenylphosphin-, Methylphenylphosphin-, Dibenzylphosphin-, Methylphosphonige-, Phenylphosphonige- oder Benzylphosphonigesäuren.

10. Copolyetheramide gemäß einem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß der Katalysator (beta), der verwendet wird, aus Natrium- und Kaliumsalzen von den vorstehend in Anspruch 8 zitierten Säuren besteht und vorzugsweise aus Natrium- und Kaliumsalzen von Säuren, die von Phosphor abgeleitet sind, wie sie vorstehend in Anspruch 9 genannt sind.

11. Copolyetheramide gemäß einem der Ansprüche 8 bis 10, dadurch gekennzeichnet, daß die Mengenverhältnisse von starker Säure (alpha) oder Salz (beta), ausgedrückt in Gewichtsprozenten in bezug auf das End-Copolyetheramid, im allgemeinen zwischen 0,01 und 1 % und vorzugsweise zwischen 0,01 und 0,5 % liegen.

12. Copolyetheramide gemäß einem der Ansprüche 1 bis 11, dadurch gekennzeichnet, daß das verwendete Lactam ϵ -Caprolactam ist.

13. Copolyetheramide gemäß einem der Ansprüche 1 bis 12, dadurch gekennzeichnet, daß die verwendeten dimeren Säuren erhalten sind durch Polymerisation und Fraktionierung von Verbindungen, enthaltend 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 eine Fraktion an difunktioneller Säure enthalten, die größer als 94 Gew.% ist, eine Fraktion an monofunktioneller Säure, die unterhalb 1 Gew.% ist, und eine Fraktion an Säure mit Funktionalität über 2, welche unterhalb 5 Gew.% liegt.

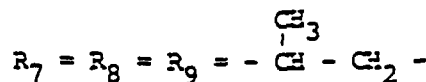
14. Copolyetheramide gemäß Anspruch 13, dadurch gekennzeichnet, daß die verwendeten dimeren Säuren aus Arten bestehen, die durch Fraktionierung einer hydrierten Zusammensetzung von der katalytischen Polymerisation von monomerer(n) Fettsäure(n) mit 18 Kohlenstoffatomen erhalten wurden.

15. Copolyetheramide gemäß einem der Ansprüche 1 bis 14, dadurch gekennzeichnet, daß die verwendeten Polyoxyalkylendiamine Verbindungen der allgemeinen Formel

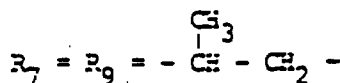


sind, worin die Symbole R_7 , R_8 und R_9 , die identisch oder verschieden sind, zweiwertige, gesättigte, aliphatische Reste, gerade oder verzweigt, mit 1 bis 10 Kohlenstoffatomen sind und das Symbol m ist eine Zahl, die derart bestimmt ist, daß eine Molekularmasse von 100 bis 10 000 und vorzugsweise von 300 bis 5000 erhalten wird.

16. Copolyetheramide gemäß Anspruch 15, dadurch gekennzeichnet, daß die verwendeten Polyoxyalkylendiamine Polyoxypropylendiamine der Formel (VII) sind, worin



Polyoxyethylendiamine der Formel (VII), worin



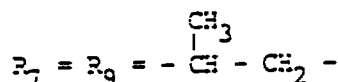


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und $R_5 = -CH_2-CH_2-$, oder Polyoxytetramethylen-diamine der Formel (VII), worin



und $R_8 = -CH_2-CH_2-CH_2-CH_2-$, wobei diese Verbindungen eine Molekularmasse von 100 bis 10 000 und vorzugsweise von 300 bis 5000 haben.

17. Copolyetheramide gemäß einem der Ansprüche 1 bis 16, dadurch gekennzeichnet, daß die Gewichtsverhältnisse der Amidblöcke in dem endgültigen Polymeren zwischen 15 und 85 % und vorzugsweise zwischen 40 und 60 % liegen und daß die Gewichtsanteile der Etherblöcke zwischen 85 und 15 % und vorzugsweise zwischen 60 und 40 % liegen.

Patentansprüche (für den Vertragsstaat AT)

1. Verfahren zur Herstellung von homogenen Copolyetheramiden mit Blockstruktur, die insbesondere einen Schmelz- oder Erweichungspunkt mindestens gleich 170 °C, eine Glasübergangstemperatur, gemessen bei EHO, höchstens gleich -5 °C und eine Schmelzviskosität mindestens gleich 50 Pas aufweisen, wobei dieses Verfahren entsprechend der durch die folgenden Stufen definierten Arbeitsweise durchgeführt wird:

(a') man vermischt ein Lactam mit 4 bis 12 Kohlenstoffatomen mit einer Lösung eines Salzes eines Fettsäuredimeren und einer geeigneten Aminverbindung in einem Lösungsmilieu auf Basis einer Mischung Wasser-aliphatischer Alkohol mit weniger als 5 Kohlenstoffatomen, eines Gemisches Wasser-Alkohol-Lactam (der verwendete Alkohol und das Lactam entsprechen der einen oder anderen der vorstehend angegebenen Definitionen), des Lactams selbst in geschmolzenem Zustand oder auch, wenn das Lactam in Wasser löslich ist, eines Gemisches Wasser-Lactam;

(b') die Stöchiometrie dieses Salzes wird vorher festgesetzt, indem das pH der Lösung des Salzes in einem Verdünnungsgemisch auf Basis von Wasser und mindestens einer Verbindung, ausgewählt aus einem aliphatischen Alkohol, einem aliphatischen Diol oder einem Lactam (der verwendete Alkohol und das verwendete Lactam entsprechen der einen oder anderen der vorstehend angegebenen Definitionen, das aliphatische Diol hat 2 bis 6 Kohlenstoffatome), gemessen wird und indem die Zusammensetzung dieses Salzes derart eingestellt wird, daß das pH bei $\pm 0,05$ pH-Einheit den pH-Wert im Äquivalenzpunkt erreicht, wobei das Gemisch der Lösung des Salzes mit dem Lactam weggelassen werden kann, wenn die Lösung des Salzes in dem Auflösungsmilieu auf Basis eines Gemisches Wasser-Alkohol-Lactam, eines Gemisches Wasser-Lactam oder Lactam selbst in geschmolzenem Zustand genügend Lactam enthält, um das Copolyetheramid mit der gewünschten Zusammensetzung zu erhalten;

(c') dann gibt man in das Reaktionsgemisch einen Katalysator;

(d') und man unterwirft dann das Ganze einem Erhitzen, um das Lactam mit dem Salz reagieren zu lassen; wobei dieses Verfahren dadurch gekennzeichnet ist, daß man in der Stufe (a') ein Salz des Fettsäuredimeren und eines Gemisches Polyoxyalkylen-diamin mit einem Triamin einsetzt und daß man in der Stufe (c') einen Katalysator verwendet, der entweder aus einer Verbindung (alpha) oder einer Verbindung (beta) besteht, wobei (alpha) eine Mineraloxysäure oder eine organische Oxysäure, anders als eine Carbonsäure, bezeichnet, wovon wenigstens eine der Säurefunktionen, wenn es davon mehrere gibt, eine Ionisationskonstante pK_a in Wasser bei 25 °C gleich oder unterhalb von 4 besitzt, (beta) ein Alkali- oder Erdalkalisalz dieser Säure bezeichnet.

2. Verfahren zur Herstellung von homogenen Copolyetheramiden mit Blockstruktur, die insbesondere einen Schmelz- oder Erweichungspunkt mindestens gleich 170 °C, eine Glasübergangstemperatur, gemessen bei EHO, höchstens gleich -5 °C und eine Schmelzviskosität mindestens gleich 50 Pas aufweisen, wobei dieses Verfahren entsprechend der durch die folgenden Stufen definierten Arbeitsweise durchgeführt wird:

(a') man vermischt ein Lactam mit 4 bis 12 Kohlenstoffatomen mit einer Lösung eines Salzes von dimerer Fettsäure und einer geeigneten Aminverbindung in einem Auflösungsmilieu auf Basis eines Gemisches Wasser-aliphatischer Alkohol mit weniger als 5 Kohlenstoffatomen, eines Gemisches Wasser-Alkohol-Lactam (der verwendete Alkohol und das verwendete Lactam entsprechen der einen oder anderen der vorstehend gegebenen Definitionen), von Lactam selbst in geschmolzenem Zustand oder auch, wenn das Lactam in Wasser löslich ist, eines Gemisches Wasser-Lactam;

(b') die Stöchiometrie dieses Salzes wird vorher festgestellt, indem das pH der Lösung des Salzes in einem Verdünnungsgemisch auf Basis von Wasser und mindestens einer Verbindung, ausgewählt unter einem aliphatischen Alkohol, einem aliphatischen Diol oder einem Lactam (der verwendete Alkohol und das verwendete Lactam entsprechen der einen oder anderen der vorstehend gegebenen Definitionen, das aliphatische Diol umfaßt 2 bis 6 Kohlenstoffatome), gemessen wird und indem die Zusammensetzung dieses Salzes in der Weise eingestellt wird, daß das pH bei $\pm 0,05$ pH-Einheiten den pH-Wert am Äquivalenzpunkt erreicht und das Gemisch der Lösung des Salzes mit dem Lactam weggelassen werden

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kann, wenn die Lösung des Salzes in dem Auflösungsmilieu auf Basis eines Gemisches Wasser-Alkohol-Lactam, eines Gemisches Wasser-Lactam oder Lactam selbst in geschmolzenem Zustand genügend Lactam enthält, um das Copolyetheramid der gewünschten Zusammensetzung zu erhalten ;

(c') dann gibt man in das Reaktionsgemisch einen Katalysator ;

(d') man unterwirft dann das Ganze einem Erhitzen, um das Lactam mit dem Salz reagieren zu lassen ; wobei das genannte Verfahren dadurch gekennzeichnet ist, daß man in der Stufe (a') ein Salz von dimerer Fettsäure und Polyoxyalkylendiamin ohne Triamin einsetzt und daß man in der Stufe (c') einen katalysator verwendet, der aus der Verbindung (beta) besteht, wie sie vorstehend in Anspruch 1 definiert ist.

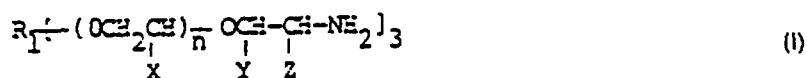
3. Verfahren zur Herstellung von homogenen Copolyetheramiden mit Blockstruktur, die insbesondere einen Schmelz- oder Erweichungspunkt mindestens gleich 170 °C, eine Glasübergangstemperatur, gemessen bei EHO, höchstens gleich -5 °C und eine Schmelzviskosität mindestens gleich 50 Pas aufweisen, wobei dieses Verfahren entsprechend der durch die folgenden Stufen definierten Arbeitsweise durchgeführt wird :

(a'') man vermischt ein Lactam mit 4 bis 12 Kohlenstoffatomen mit einer Lösung eines Salzes von dimerer Fettsäure und einer geeigneten Aminverbindung in einem Auflösungsmilieu auf Basis eines Gemisches von Wasser-aliphatischem Alkohol mit weniger als 5 Kohlenstoffatomen, eines Gemisches Wasser-Alkohol-Lactam (der verwendete Alkohol und das verwendete Lactam entsprechen der einen und anderen der vorstehend gegebenen Definitionen), von Lactam selbst in geschmolzenem Zustand oder auch, wenn das Lactam in Wasser löslich ist, eines Gemisches Wasser-Lactam ;

(b'') die Stöchiometrie dieser Lösung wird vorher festgesetzt, indem das pH der Lösung in einem Verdünnungsgemisch auf Basis von Wasser und mindestens einer Verbindung, ausgewählt unter einem aliphatischen Alkohol, einem aliphatischen Diol oder einem Lactam (der Alkohol oder das Lactam entsprechen der einen und anderen der vorstehend gegebenen Definitionen, das aliphatische Diol umfaßt 2 bis 6 Kohlenstoffatome), gemessen wird und indem die Zusammensetzung derart eingestellt wird, daß das pH bei ±0,05 pH-Einheiten den pH-Wert am Äquivalenzpunkt erreicht, wobei das Gemisch der Lösung des Salzes mit dem Lactam weggelassen werden kann, wenn die Lösung des Salzes in dem Auflösungsmilieu auf Basis eines Gemisches Wasser-Alkohol-Lactam, eines Gemisches Wasser-Lactam oder Lactam selbst in geschmolzenem Zustand hinreichend Lactam enthält, um das Copolyetheramid der gewünschten Zusammensetzung zu erhalten ;

(c'') dann läßt man durch Erhitzen das Lactam mit dem Salz in Gegenwart eines Katalysators reagieren, wobei dieses Verfahren dadurch gekennzeichnet ist, daß der verwendete Katalysator in die Lösung des Salzes von dimerer Fettsäure und Aminverbindung zugegeben wird, bevor die Stöchiometrie der Lösung reguliert wird, und die Aminverbindung aus einem Polyoxyalkylendiamin allein oder im Gemisch mit einem Triamin besteht und der Katalysator entweder aus der Verbindung (alpha) oder aus der Verbindung (beta), wie vorstehend in Anspruch 1 definiert, besteht.

4. Verfahren gemäß einem der Ansprüche 1 und 3, dadurch gekennzeichnet, daß das Triamin, das man in der Stufe (a') oder (a'') verwendet, eine Verbindung ist, ausgewählt aus der Gruppe, die durch Bis-hexamethylentriamin der Formel $H_2N-(CH_2)_6-NH-(CH_2)_6-NH_2$ und den Polyoxyalkylentriaminen der Formel (I) gebildet ist :



worin

R_1 , ein dreiwertiger Rest ist, welcher der Rest eines trihydroxylierten, aliphatischen Alkohols ist, der polyoxyalkyliert werden kann und 3 bis 10 Kohlenstoffatome hat ;

Z ist ein linearer oder verzweigter Alkylrest mit 1 bis 18 Kohlenstoffatomen ;

X und Y, die identisch oder verschieden sind, bedeuten jeweils ein Wasserstoffatom oder einen Rest Z ;

das Symbol n bedeutet eine mittlere Zahl von 0 bis 50.

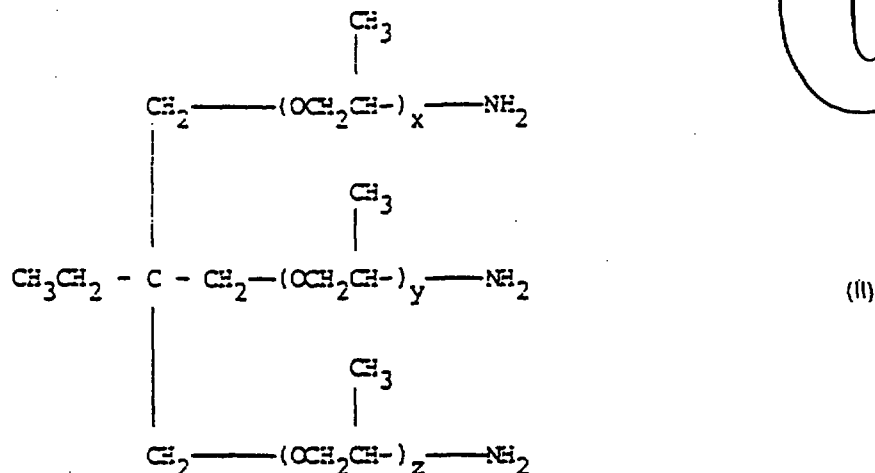
5. Verfahren gemäß einem der Ansprüche 1 und 3, dadurch gekennzeichnet, daß das Triamin, das in der Stufe (a') oder (a'') verwendet wird, eine Verbindung der Formel (I) ist, worin R_1 die vorstehend in Anspruch 4 gegebene Definition hat ; Z ein Methylrest ist ; X für Z steht ; Y ein Wasserstoffatom ist und n den mittleren Wert von 1 bis 16 hat.

6. Verfahren gemäß Anspruch 5, dadurch gekennzeichnet, daß das Triamin ein Polyoxypropylentriamin der Formel (II) ist :

(Siehe Formel II Seite 32 f.)



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worin die Symbole x, y und z jeweils eine mittlere Zahl von 1 bis 10 bedeuten mit der Summe x + y + z von 3 bis 30.

7. Verfahren gemäß einem der Ansprüche 1 und 3 bis 6, dadurch gekennzeichnet, daß die eingesetzten Mengen an Triamin, ausgedrückt als Millimol Triamin pro 1 kg End-Copolyetheramid, im allgemeinen zwischen 0,1 und 20, vorzugsweise zwischen 1 und 10, liegen.

8. Verfahren gemäß einem der Ansprüche 1 und 3 bis 7, dadurch gekennzeichnet, daß der Katalysator (alpha), der verwendet wird, aus den folgenden Gruppen besteht:

unter den mineralischen Oxy Säuren; Schweflige Säure, Schwefelsäure, Hypophosphorige Säure, Phosphorige Säure, Orthophosphorsäure oder Pyrophosphorsäure;

unter den organischen Oxy Säuren:

die Organosulfonsäuren der Formel $\text{R}_2\text{—SO}_3\text{H}$ (III), worin R_2 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 $\text{R}_3\text{—P(O)(OH)}_2$ (IV) worin R_3 einen Alkylrest, einen Phenylrest oder einen Phenylalkylrest bedeutet, wobei jeder dieser Reste die vorstehend für R_2 angegebene Definition hat;

die Organophosphinsäuren der Formel $\text{R}_4\text{R}_5\text{—P(O)(OH)}$ (V) worin R_4 und R_5 identisch oder verschieden sind und jeweils bedeuten: einen geraden Alkylrest mit 1 bis 3 Kohlenstoffatomen; einen Phenylrest oder einen Phenylalkylrest, wobei jeder dieser zwei letztgenannten Reste die vorstehend für R_2 gegebene Definition hat;

die Organophosphonigsäuren der Formel $\text{R}_6\text{H—P(O)(OH)}$ (VI), worin R_6 bedeutet: einen linearen oder verzweigten Alkylrest mit 1 bis 4 Kohlenstoffatomen (die Verzweigung ist für einen Alkylrest mit 4 Kohlenstoffatomen ausgeschlossen); einen Phenylrest oder einen Phenylalkylrest, wobei jeder dieser beiden letztgenannten Reste die vorstehend für R_2 gegebene Definition hat.

9. Verfahren gemäß Anspruch 8, dadurch gekennzeichnet, daß die (alpha) Säuren, welche verwendet werden, bestehen aus Säuren, abgeleitet von Phosphor, gehörend zu der Gruppe der Hypophosphorigen-, Phosphorigen-, Orthophosphor-, Pyrophosphor-, Methylphosphon-, Phenylphosphon-, Benzylphosphon-, Dimethylphosphin-, Diphenylphosphin-, Methylphenylphosphin-, Dibenzylphosphin-, Methylphosphonige-, Phenylphosphonige- oder Benzylphosphonigesäuren.

10. Verfahren gemäß einem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß der Katalysator (beta), der verwendet wird, aus Natrium- und Kaliumsalzen von den vorstehend in Anspruch 8 zitierten Säuren besteht und vorzugsweise aus Natrium- und Kaliumsalzen von Säuren, die von Phosphor abgeleitet sind, wie sie vorstehend in Anspruch 9 genannt sind.

11. Verfahren gemäß einem der Ansprüche 8 bis 10, dadurch gekennzeichnet, daß die Mengenverhältnisse von starker Säuren (alpha) oder Salz (beta), ausgedrückt in Gewichtsprozenten in bezug auf das End-Copolyetheramid, im allgemeinen zwischen 0,01 und 1 % und vorzugsweise zwischen 0,01 und 0,5 % liegen.

12. Verfahren gemäß einem der Ansprüche 1 bis 11, dadurch gekennzeichnet, daß das verwendete Lactam ε-Caprolactam ist.

13. Verfahren gemäß einem der Ansprüche 1 bis 12, dadurch gekennzeichnet, daß die verwendeten dimeren Säuren erhalten sind durch Polymerisation und Fraktionierung von Verbindungen, enthaltend 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 eine Fraktion an difunktioneller Säure enthalten, die größer als 94 Gew.% ist, eine Fraktion an



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monofunktioneller Säure, die unterhalb 1 Gew.% ist, und eine Fraktion an Säure mit Funktionalität über 2, welche unterhalb 5 Gew.% liegt.

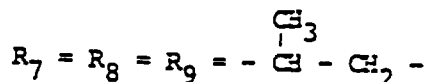
14. Verfahren gemäß Anspruch 13, dadurch gekennzeichnet, daß die verwendeten dimeren Säuren aus Arten bestehen, die durch Fraktionierung einer hydrierten Zusammensetzung von der katalytischen Polymerisation von monomerer(n) Fettsäure(n) mit 18 Kohlenstoffatomen erhalten wurden.

15. Verfahren gemäß einem der Ansprüche 1 bis 14, dadurch gekennzeichnet, daß die verwendeten Polyoxyalkylendiamine Verbindungen der allgemeinen Formel

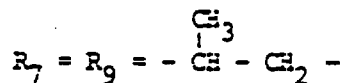


sind, worin die Symbole R_7 , R_8 und R_9 , die identisch oder verschieden sind, zweiwertige, gesättigte, aliphatische Reste, gerade oder verzweigt, mit 1 bis 10 Kohlenstoffatomen sind und das Symbol m ist eine Zahl, die derart bestimmt ist, daß eine Molekularmasse von 100 bis 10 000 und vorzugsweise von 300 bis 5 000 erhalten wird.

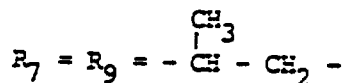
16. Verfahren gemäß Anspruch 15, dadurch gekennzeichnet, daß die verwendeten Polyoxyalkylendiamine Polyoxypropylendiamine der Formel (VII) sind, worin



Polyoxyethylendiamine der Formel (VII), worin



und $\text{R}_8 = -\text{CH}_2-\text{CH}_2-$, oder Polyoxytetramethylendiamine der Formel (VII), worin



und $\text{R}_8 = -\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$, wobei diese Verbindungen eine Molekularmasse von 100 bis 10 000 und vorzugsweise von 300 bis 5 000 haben.

17. Verfahren gemäß einem der Ansprüche 1 bis 16, dadurch gekennzeichnet, daß die Gewichtsverhältnisse der Amidblöcke in dem endgültigen Polymeren zwischen 15 und 85 % und vorzugsweise zwischen 40 und 60 % liegen und daß die Gewichtsanteile der Etherblöcke zwischen 85 und 15 % und vorzugsweise zwischen 60 und 40 % liegen.

