

0,022,048

Description

The present invention relates to new homogeneous copolyamides based on hexamethylenediamine, adipic acid and fatty acid dimers and to specific processes for obtaining them.

5 For some applications of plastics, there is a need for polymers which have a whole range of chemical and physical properties which can be found, in part, in polyamides. It may be necessary to add flexibility properties to the chemical resistance and the toughness properties of conventional polyamides: good elongation and
10 hence good energy absorption. Many copolymers have been proposed for this purpose; however, the whole range of properties sought is rarely obtained, as any modification to improve a particular property results in a deterioration of another property.
15

A progress has been achieved with the provision of flexible copolymers based on caprolactam, fatty acid dimers and hexamethylenediamine, which comprise a good flexibility, a tensile strength greater than 5 daN/mm²
20 and a good water resistance: French Patent Application no. 77/33,341.

For certain applications, there may be a need for copolymers which have a better thermal behaviour and therefore higher melting points. Various trials have
25 been carried out according to known processes in order to

obtain copolyamides based on polyhexamethylenediamine adipate and which have the properties sought; however, they always ran into problems with homogeneity of the copolymers.

5 Flexible and homogeneous copolyamides have now been found, based on adipic acid, fatty acid dimers obtained by the fractionation of polymerized fatty acids and containing more than 95% by weight of dimers and hexamethylenediamine, characterized in that, on the one hand,
10 the dimers originate from fatty acids obtained by the polymerization of mixtures of C_{18} acids and, on the other hand, the molar ratio of adipic acid relative to the total acids is between 0.5 and 0.99 and finally, the point obtained by plotting the molar fraction of adipic acid along
15 the abscissa and the melting point of the copolyamide, determined by differential microcalorimetry with a temperature change of 10°C per minute, along the ordinate is within the area A B C D plotted on the graph given in the appendix.

20 Flexible copolyamide means a copolyamide, the flexural modulus of which will be substantially lower (for example by 1 to 10 times) than that of conventional polyamides such as polyhexamethylene adipamide or polycaprolactam and will be of the order of or even less than
25 that of polyamides which are regarded as flexible, such as, for example, polyundecanamide.

Homogeneous copolyamide means a copolymer which

has only a single phase in the molten state or in the solid state, and can be observed, for example, by scanning electron microscopy, visualizing any dispersed phase by phosphotungstic acid fixation.

5 A much simpler means to observe this homogeneity consists in examining the state of transparency, on the one hand, of a molten mass with a thickness of approximately 0.2 to 0.5 cm, heated to a temperature at least 10°C above its melting point and, on the other hand, of
10 a film or rod obtained from this molten mass after rapid cooling, for example, by immersing in water at ambient temperature. An absolutely transparent film or rod indicates a perfect homogeneity of the polymer; a film or rod which has cloudy areas or which is translucent is the
15 sign of a certain heterogeneity; a white film containing streaks or inclusions (for example knots) is the sign of significant heterogeneity.

 Another means for determining the homogeneity which is based on melting points, as will be described
20 later, was preferred to this visual examination, the evaluation based on which is partly subjective.

 The C₁₈ monomeric fatty acids mentioned above are saturated or unsaturated aliphatic monoacids.

 Polymeric fatty acids obtained by polymerization,
25 most frequently in the presence of peroxides or Lewis acids, may be fractionated. They may also be hydrogenated in order to reduce their level of unsaturation and thereby

reduce their colour.

The most commonly used starting products are compositions which originate from hydrogenated oleic and linoleic acids and which contain:

- 5 from 1 to 15% by weight of monobasic acid.
 up to 98% by weight of dibasic acid and
 from 1 to 25% by weight of tribasic acid or above.

In order to obtain the copolyamides according to the invention, compositions with a dimeric acid fraction
10 greater than 95% are employed. Dimeric acids of which a monofunctional acid content is less than 0.5% by weight and of which the content of acid of functionality greater than 2 is less than 5% by weight will be preferred.

If it is desired to obtain copolymers which have
15 a high melting point, the molar percentage of adipic acid relative to the total quantity of acids, adipic acid plus dimeric acids, will be greater than 50%. If it is desired to maintain the flexibility properties provided by the dimeric acids, this percentage will be less than 99%. It
20 is self-evident that within the range of copolymers obtained by varying the adipic acid content from 99% to 50%, products of variable flexibility and with variable melting point will be obtained. Products with a molar fraction of adipic acid between 0.95 and 0.80 are of particular
25 value because they have both a high melting point and a good flexibility.

In fact, it has been found that the melting points

of the homogeneous copolyamides according to the invention were located on a curve determined more or less accurately, so as to take into account possible errors due to the melting point determination method and due to the very nature of the copolyamides, within an area defined by the curves representing an error of $\pm 2^{\circ}\text{C}$ relative to the mean theoretical melting point curve. This area A B C D is plotted on the figure attached.

The molar fraction of adipic acid is plotted along the abscissa and the melting point of the copolymer determined by differential microcalorimetry with a temperature change of 10°C per minute along the ordinate.

The homogeneous copolyamides according to the invention have single melting points which are located within the area A B C D. The heterogeneous copolyamides differ from the former either in having a single melting point which is, however, significantly higher than that expected and therefore outside the area A B C D or in having two melting points, one of which is close to the melting point of polyhexamethylene adipamide.

Another subject of the invention relates to processes for obtaining flexible and homogeneous copolyamides which have a molar ratio of adipic acid of between 0.5 and 0.99% relative to the total acids employed.

In fact, neither the conventional processes for the polycondensation of polyamides nor the specific process claimed in French Patent 2,395,076 for the preparation

of copolyamide, based on adipic acid (molar fraction less than 0.5), dimeric acid and hexamethylenediamine, can be applied in the preparation of the copolyamides according to our invention.

5 In fact, with these two types of processes, heterogeneous copolymers with physical properties which can be reproduced with difficulty and which are unsuitable for fibre extrusion or extrusion are obtained.

 It has been found that it was possible to prepare
10 homogeneous copolyamides according to the invention by preparing, in a heterogeneous medium, prepolymers starting with a mixture of adipic acid, dimeric acid and hexamethylenediamine or the corresponding salts thereof, these prepolymers being then homogenized under conditions such
15 that the equilibrium state of the amidification reactions was not modified, and then by converting the homogeneous prepolymers thereby obtained into high molecular weight polycondensates.

 In a first process, the reaction is carried out
20 starting with compositions containing either adipic and dimeric acids and hexamethylenediamine, or the salt of adipic acid and hexamethylenediamine and the salt of dimeric acid and hexamethylenediamine, or one of the salts and the free state constituents of the other salt, the
25 quantities of the constituents of the starting composition being such that the amino group and the carboxylic group contents do not differ by more than 5% and preferably

by more than 1%.

If it is desired to ensure a perfect reliability of the process, it is advisable to prepare stoichiometric compositions as accurately as possible.

5 It has been found that in order to obtain the new copolyamides with a high adipic acid content according to the invention, it was indispensable to carry out a homogenization phase lasting approximately 30 min to 5 hours at high temperature (of the order of 280°C), at a high
10 steam pressure (of the order of 20 bars).

The conditions under which the homogenization phase is carried out are critical. The parameters to be considered are adipic acid content, temperature, pressure and the duration of this phase; these parameters are not
15 independent.

For a given adipic acid content (which content varies from 0.5 to 0.99 in molar fraction), the duration may vary from 30 minutes to approximately 5 hours and preferably from 1 hour to 4 hours. This duration depends on
20 the temperature and the pressure. This temperature is between 270°C and 290°C . Steam pressure in itself varies between 13 and 25 bars, preferably between 15 and 20 bars.

The ranges claimed correspond to the conditions which are industrially the most profitable; however, it
25 is self-evident that it is possible to obtain a good homogenization by using a value for a parameter which is outside the values claimed and by compensating for the effect

produced by varying another parameter.

During this phase, it is indispensable that there is no significant shift in the equilibrium of the amidification reactions. This condition will be achieved by preventing any loss of volatile product.

The procedure for implementing the process will comprise a number of successive stages which will be described below in a non-limiting way.

The salt of the dimeric acid and hexamethylenediamine is not compatible with aqueous solutions of hexamethylenediamine adipate. The initial stoichiometry between the dimeric acid and the hexamethylenediamine, which stoichiometry is essential for obtaining high molecular weight polymers, may be achieved either by accurately weighing reagents of well known purity at the time of implementation (which method is difficult to employ on an industrial scale) or by preparing the dimeric acid salt in an alcoholic solution, the pH of which may then be adjusted (which method leads to copolyamides which are more coloured).

A variant of this first process, which can easily be applied on an industrial scale and which enables the initial stoichiometry between adipic acid, the dimeric acid and the hexamethylenediamine to be achieved consists in preparing an emulsion of the salt of the dimeric acid and the hexamethylenediamine in an aqueous solution of hexamethylenediamine adipate, the stoichiometry being monitored

by determining the pH of sample solutions obtained by diluting the emulsion with an alcohol.

The composition of the starting products thus prepared is placed in an inert atmosphere and then brought gradually uniformly to the state of chemical equilibrium corresponding to the initial stage of the following phase. A particularly suitable method consists in heating the composition under self-generated pressure so as to bring it to the pressure chosen for the homogenization phase which follows. The temperature is then gradually brought to that chosen for the homogenization phase by gradual distillation of water.

The next phase is the homogenization phase described above.

The final phase enables the polycondensation to be completed according to known processes.

For example, it is possible to carry out a gradual decompression with simultaneous distillation of residual water and, if required, a lowering of temperature to that chosen for the "cooking", i.e. the thermal treatment leading to the final polymer. The temperature corresponding to this phase is generally between 260 and 290°C and preferably between 275 and 285°C. The pressure may be atmospheric pressure or a lower pressure. The copolyamide is finally recovered by extrusion under an inert gas pressure of 1 to 5 bars.

A second process which does not require the use

of high pressure has been developed; however, the use of a certain pressure could be technologically advantageous. The choice of starting products is very open.

The principle of this process consists in preparing, at high temperature, a prepolymer containing carboxylic or amino end groups with a molar average molecular mass less than 10,000 and preferably less than 5,000. This prepolymer then undergoes a homogenization phase between 265°C and 290°C, preferably between 270°C and 285°C for a period which depends on the temperature chosen and the composition of the polymer, but which generally varies from 10 min to approximately 2 h.

The prepolymer obtained at the end of this phase is maintained at a temperature between 260°C and 290°C during the gradual addition of the reagent or of a mixture of reagents in deficit until a copolycondensate with the desired viscosity is obtained.

Although it is possible to prepare a prepolymer containing end groups which are essentially of the amino type, the preparation of a prepolymer containing end groups which are essentially of the carboxylic acid type, for which the risks of branching due to secondary reactions are lower, will be preferred. In the latter case, during the reaction of completion of the condensation, it is possible to reach the stoichiometry or, depending on the case, to obtain copolyamides containing a small proportion of acid end groups, which is preferable, or even possibly exceed

the stoichiometry and reach copolyamides containing a small proportion of amino end groups; however, the products obtained are chemically less stable.

This adjustment of viscosity is advantageously
5 carried out by the in situ determination of the load moment of the stirrer of the polymerizer. The hexamethylenediamine may be added either in the molten form or in the form of an aqueous solution. However, in this case, the addition must be very gradual and must be made so that
10 it does not cause a significant lowering of the temperature of the mass.

As indicated above, one of the advantages of this second process consists in the very open choice of the starting products.

15 Thus, it is possible to start with a mixture of adipic acid, dimeric acid and hexamethylenediamine, the latter product being in a deficit of at least 5% and preferably of approximately 5 to 20% by weight relative to the quantity theoretically required to obtain the stoichiometry.
20

It is also possible to start with the adipic acid salt of hexamethylenediamine, the dimeric acid and the hexamethylenediamine in a deficit of at least 5% and preferably of 5 to 20% by weight as above.

25 A variant which is advantageous from a practical point of view consists in preparing, in a first stage, a dispersion of adipic acid in dimeric acid at a temperature

between 130 and 150°C and then adding molten hexamethylene-diamine. A very well dispersed reaction mass is thus obtained.

It is also possible to start with the composition employed in the first process and which consists of an emulsion of the salt of the dimeric acid and the hexamethylenediamine in an aqueous solution of hexamethylene-diamine adipate: it is then essential to add to the composition an excess of adipic acid or of dimeric acid so as to achieve conditions which enable a prepolymer containing carboxylic acid end groups to be obtained in a first stage.

A third type of process which consists in preparing the prepolymer of the copolyamide in a homogeneous phase at a temperature between 150 and 300°C and preferably between 190°C and 250°C has been developed. This homogeneous phase condition may be achieved by adding a solvent which has a number of properties to the reaction mixture.

According to this process, it will be especially advantageous to start with a reaction mixture essentially consisting of adipic acid, dimeric acid and hexamethylenediamine or of the corresponding salts thereof, the contents of the amino and the carboxylic acid groups not being different by more than 5% and preferably by more than 1%.

The solvent employed must be inert towards the

base reagents and towards the amidification reactions. The physical properties thereof, especially the boiling point thereof, must be compatible with the high temperature conditions required for the amidification reactions.

5 Thus, this solvent will advantageously have a boiling point between 170°C and 250°C. It has been found that N-methylpyrrolidone led to particularly advantageous results. This is generally employed.

The prepolymer thus obtained is then converted by
10 heating to a temperature between 200°C and 290°C, during which the middle part of the solvent is removed by distillation.

The residual amounts of solvent may be removed at the end of this phase by subjecting to vacuum.

15 It is self-evident that in all the processes described here, according to the invention, the composition of the starting reagents may also contain various additives which are commonly employed during the preparation of conventional polyamides. These additives are, in particular, chain-limiting agents such as, mainly, monocarb-
20 oxylic acids such as, for example, acetic acid, nucleating agents and stabilizers of different types.

The use of compositions which contain, in addition to the three essential constituents, minor quantities of other polyamide producing reagents, whether they
25 are diacids, diamines, amino acids or lactams, will not constitute a departure from the invention.

The processes according to the invention enable homogeneous copolyamides which have an improved flexibility, a high toughness related to a good resistance to hydrolysis and a good thermal behaviour at the same time to be
5 obtained. Being perfectly homogeneous, they have improved transparency properties and may be employed according to conventional techniques of injection, extrusion or fibre extrusion to give shaped objects: articles, films or threads of very high uniformity.

10 The following examples enable the invention to be illustrated.

Example 1

Preparation of the salt of the dimeric acid and the hexa-
15 methylenediamine as an emulsion in an aqueous solution of hexamethylenediamine adipate.

A 3 litre glass reactor equipped with a stirrer and maintained swept with a slight nitrogen current is charged with:

20 crystalline hexamethylenediamine adipate (N salt):
834.6 g (3.185 moles); and
deionized water: 1150 g.

The mixture is stirred at 25°C until the N salt is completely dissolved.

25 The following are then introduced:

crystalline hexamethylenediamine: 80.6 g (0.695 mole); and

deionized water: 181 g.

The mixture is stirred at 25°C until the hexamethylenediamine is completely dissolved.

421.7 g of a dimeric acid sold under the name
5 Empol 1010 ($\approx$ 0.74 mole) and containing 0.05% by weight of monomer and 95.55% of dimer are introduced slowly, with stirring.

The emulsion is stirred for 2 hours.

20 g of emulsion are withdrawn and diluted with
10 17.8 g of a water:isopropanol (21.9:78.1 w/w) mixture. The pH of the solution at 20°C is 7.63 (10% solution of the dimeric acid salt in an 18.4:40.8:40.8 by weight mixture of N salt:water:isopropanol).

14 g of a 30% aqueous solution of hexamethylenediamine are added, the mixture is stirred for 1 hour and
15 the pH is checked on a 20 g sample as before. The pH at 20°C is 8.40 and corresponds, within $\pm$ 0.1 pH unit, to the pH at stoichiometry, determined under the same conditions of concentrations and solvent by pH measurement.

20 An emulsion which is relatively stable at 25°C, with a dry extract content of 50%, containing a 62.2:37.8 by weight mixture of N salt and dimeric acid salt, which can be used directly in the preparation of the new copolyamides, is obtained.

Example 2

Preparation of the new copolyamides

The general procedure for obtaining these copolyamides is as follows:

- 5 the reaction is carried out in a stainless steel autoclave which is stirred and equipped for operating at up to 300°C, at 25 bars.

The following reagents are added, in the cold state, into the apparatus:

- 10 either (process a):

N salt in the form of a 50% aqueous solution
+ hexamethylenediamine in the form of a 30% aqueous solution
+ dimeric acid weighed according to stoichiometry
15 + chain-limiting agent (either an excess of dimeric acid or an aqueous solution of acetic acid)

or (process b):

- an emulsion of the type of that in example 1
+ if required, a 50% aqueous solution of N salt
20 adjustment of the copolymer composition
+ chain-limiting agent.

The apparatus is purged with nitrogen and the temperature of the mass is raised to 225°C, maintaining the self-generated pressure. A pressure of 20 bars is reached.

- 25 Water is distilled for 1 hour under pressure so as to reach a high mass temperature of 60°C. The distillation is stopped in order to carry out the homogenization phase

lasting x minutes at $\theta^{\circ}\text{C}$ mass temperature, at a steam pressure of P bars.

The apparatus is decompressed to atmospheric pressure over 30-90 minutes, maintaining the temperature at $\theta^{\circ}\text{C}$.

The polymer, which has been kept stirred since the time when the temperature of the mass exceeded 250°C , is maintained stirred at $\theta^{\circ}\text{C}$, at atmospheric pressure, for 30 minutes, extruded under nitrogen pressure (2-6 bars) and granulated after cooling with water.

The properties of the polymers obtained are collated in the table below.

The melting point (m.p. $^{\circ}\text{C}$) and point of crystallization on cooling (c.p. $^{\circ}\text{C}$) were determined by differential microcalorimetry ($10^{\circ}\text{C}/\text{minute}$ under nitrogen).

The inherent viscosities were determined at 25°C in a 0.5 g/100 ml m-cresol solution:

$$\eta_{\text{inh}} = \frac{1}{C} \log \frac{t}{t_0}$$

t = solution flow time

t_0 = pure solvent flow time

C = concentration in g/dl

The NH_2 group contents were determined by the analysis of a solution of the polymer in a phenol:water (90:10) mixture, with glycolic potassium hydroxide in the presence of phenolphthalein.

TABLE

Ex.	COMPOSITION OF COPOLYAMIDES MOLAR FRACTION OF ADIPIC ACID IN THE ACID MIXTURE	CHAIN-LIMITING AGENT		CONDITIONS OF HOMOGENIZATION PHASE			PROPERTIES OF THE COPOLYAMIDE					
		Type	% content /mole of salts	0 °C	P bars	x min- utes	Appearance	m.p. °C	c.p. °C	Y inh of l/g	COOH meq/ kg	NH ₂ meq/ kg
2 A	0.742	0	0	285	18	0	heterogeneous	260				
2 B	0.87	0	0	275	18	0	heterogeneous	260		1.089		
2 C	0.656	0	0	280	18	120	homogeneous	225	170	0.971	80	29
2 D	0.742	0	0	280	18	60	heterogeneous	250	195		80	26
2 E	"	0	0	280	20	60	heterogeneous	250	202	0.967	83.7	36
2 F	"	0	0	280	20	90	almost homogeneous	248	197	0.997	60.2	53
2 G	"	0	0	280	20	120	homogeneous	236	184	0.987	70	56.8
2 H	"	0	0	280	20	120	homogeneous	237	186	1.12	58.4	46.3
2 I	0.812	0	0	280	20	120	homogeneous	245	195	1.157	77.75	37.8
2 J	0.842	0	0	280	20	120	homogeneous	247	198	1.054	94.6	32.7
2 K	"	0	0	280	20	240	homogeneous	246	198	1.034	78.6	84.0
2 L	0.87	0	0	280	20	60	heterogeneous	257	206	1.21	73	43.8
2 M	"	0	0	280	20	120	homogeneous	248	200	1.09	75.7	56
2 N	"	di- meric	0.05	280	20	120	homogeneous	247	201	1.1	63.3	64.3
2 O	"	di- meric	0.05	280	20	120	homogeneous	248	205	1.08	69.5	53.6
2 P	0.92	0	0	280	20	90	heterogeneous	254	211	1.13	70.4	50
2 Q	"	0	0	280	18	120	heterogeneous	255	200	1.08	58	65.5
2 R	"	0	0	280	20	180	homogeneous	247	205	1.22	51.4	79.5
2 S	0.963	0	0	280	20	180	heterogeneous	254	205	1.22	58.9	79.3
2 T	"	0	0	280	20	240	homogeneous	254	209	1.25	71.4	64.7
2 U	0.982	0	0	280	20	240	homogeneous	257	211	1.21	75.8	62.3

The COOH group contents were determined by the analysis of a solution of the polymer in benzyl alcohol at 200°C, with glycolic potassium hydroxide in the presence of phenolphthalein.

5 These two contents are expressed in milliequivalents per kg (meq/kg).

 Examples 2C, 2G, 2H, 2I, 2J, 2K, 2M, 2N, 2O, 2R, 2T and 2U illustrate the preparation and some properties of the new copolyamides. It is observed that at a temperature of 280°C and a steam pressure of 20 bars, the duration of the homogenization phase must be increased from approximately 2 hours to approximately 4 hours when the molar fraction of adipic acid passes from 0.65 to 0.98.

10 Examples 2A and 2B show that the polyamide 66 process does not enable homogeneous copolyamides derived from adipic acid and dimeric acid with a molar fraction of adipic acid > 0.5 to be obtained.

 Examples 2D, 2E, 2F, 2L, 2P, 2Q and 2S show that inadequate homogenization conditions also lead to non-homogeneous copolyamides with a molar fraction of adipic acid > 0.5.

Example 3

25 Polycondensation starting with the base reagents operating by acidolysis

 The reaction is carried out in a 1 litre stainless steel autoclave equipped with a stirrer which can

rotate at 50 rpm and a dropping funnel thermostated at 80°C which enables the remaining amount of hexamethylenediamine to be introduced.

Charges: 169.65 g (which is 1.161 moles) of pure adipic acid

253 g (which is 0.443 mole) of dimeric acid

167.55 g (which is 1.444 moles) of

hexamethylenediamine

which amounts to 90% of the theoretical quantity required to obtain the stoichiometry.

The adipic and the dimeric acids are charged, in the cold state, into the autoclave.

The contents are stirred at 15 rpm. The autoclave is purged 6 times under a nitrogen pressure of 8 bars.

The mass is gradually heated to 150°C.

The contents are then stirred at 50 rpm and molten hexamethylenediamine is added in the course of 20 min.

The reaction mass is then heated to 285°C in the course of approximately 45 min and maintained at this temperature for 1 hour. 17 g of molten hexamethylenediamine (0.146 mole) are then introduced in the course of 10 min. The contents are stirred again for 1 hour at 280°C returning the rate of stirring to 10 rpm. The copolyamide is collected in cold water. It is perfectly transparent and therefore homogeneous.

The properties of the product obtained were as

follows:

m.p.: 239°C

c.p.: 191°C

γ inh: 1.02

5 Acid content in meq/kg: 80.30

Amine content in meq/kg: 32.5

Example 4

Polycondensation starting with the base reagents by
10 acidolysis

The reaction is carried out by preparing, in a first stage, a homogeneous prepolymer with a 17% deficit of diamine in a 1 litre glass reactor equipped with a scraping anchor type of stainless steel stirrer and for
15 heating with a temperature controlled oil bath.

Charges: hexamethylenediamine: 181 g (1.560 moles)

adipic acid: 205.6 g (1.408 mole)

dimeric acid: 280 g (0.4857 mole)

hexamethylenediamine for adjustment: 38.70 g
20 (0.334 mole)

181 g of hexamethylenediamine, 205.6 g of adipic acid and 280 g of dimeric acid are charged into the reactor at ambient temperature. The reactor is purged 5 times by creating vacuum and then introducing nitrogen. The
25 apparatus is then maintained under a slight current of nitrogen. The reactor is then immersed in an oil bath preheated to 140°C. The contents are stirred and the

bath temperature is increased to 280-285°C in the course of 1 h 10 min. On stirring for 30 min at 280°C, the mass is perfectly homogeneous and not very viscous. 38.7 g of molten hexamethylenediamine are then introduced in the course of 30 min so as to re-establish stoichiometry. The contents are stirred again for 1 hour at 280-285°C. The viscosity of the mass increases. The copolyamide obtained is collected by pouring into cold water.

The properties of the copolymer are as follows:
product in the form of a 3 to 5 mm-diameter tube is transparent
inherent viscosity: 0.90 dl/g
melting point determined by differential microcalorimetry: 235°C
point of crystallization on cooling: 186°C.

Example 5

Polycondensation in a homogeneous medium

The reaction is carried out in the presence of N-methylpyrrolidone (NMP) which plays the role of solvent and enables a homogeneous medium to be obtained rapidly when the reagents are employed in stoichiometric quantities.

The following are charged into a 1 litre glass reactor equipped with a scraping anchor type of stainless steel stirrer and for heating with a temperature controlled oil bath:

adipic acid: 205.6 g (1.408 mole)

hexamethylenediamine: 219.7 g (1.894 mole)

dimeric acid: 280 g (0.486 mole)

NMP: 200 g

The reagents are introduced at ambient temperature and the reactor is purged 5 times by creating vacuum and then introducing nitrogen. The apparatus is then maintained under a slight current of nitrogen. The temperature is increased to 200°C, at which temperature the homogeneity of the medium is obtained. The temperature is maintained at a plateau of 200-210°C for 30 min in order to remove the major part of NMP. The temperature is then increased to 275°C in the course of 1 hour and maintained at this level for 1 hour. Vacuum is then created in the course of 30 min in order to remove the NMP. The mass obtained at the end of the reaction is very viscous.

The properties of the copolyamide are as follows:

m.p. determined by differential microcalorimetry:

248°C

t.° of crystallization on cooling: 214°C

inherent viscosity: 0.911 dl/g.



Claims for the contracting States: BE CH DE GB IT LI
LU NL SE

1. Flexible and homogeneous copolyamides based on adipic acid, fatty acid dimers obtained by the fractionation of polymerized fatty acids and containing more than 95% by weight of dimers and hexamethylenediamine characterized in that, on the one hand, the dimers originate from fatty acids obtained by the polymerization of mixtures of C₁₈ acids and, on the other hand, the molar ratio of adipic acid relative to the total acids is between 0.5 and 0.99 and finally, the point obtained by plotting the molar fraction of adipic acid along the abscissa and the melting point of the copolyamide, determined by differential microcalorimetry with a temperature change of 10°C per minute along the ordinate is within the area A B C D plotted on the graph given in the appendix.
2. Copolyamides according to Claim 1, characterized in that the fatty acid dimer contains a monomer fraction less than 0.5%, the remaining amount being of functionality greater than 2.
3. Process for obtaining copolyamides according to Claim 1, characterized by the preparation, in a heterogeneous medium, of prepolymers starting with a mixture of adipic acid, dimeric acid and hexamethylenediamine or the corresponding salts thereof, these prepolymers being then homogenized under conditions such that the equilibrium



state of the amidification reactions is not modified, the homogeneous prepolymers being finally converted into high molecular weight polycondensates.

4. Process according to Claim 3, characterized:

1 - by the use of a composition essentially consisting of a mixture of adipic acid, dimeric acid and hexamethylenediamine or the corresponding salt thereof, such that the amino group and the carboxylic group contents do not differ by more than a maximum of 5% in absolute value, which use consists in bringing the composition gradually and uniformly by heating to 270°C under a steam pressure between 13 and 25 bars, which is the chemical equilibrium state corresponding to the initial stage of the following phase;

2 - by a homogenization phase lasting for a period between 0.5 and 5 hours, at a temperature between 270°C and 290°C, at a water pressure between 13 and 25 bars, during which the equilibrium state of the amidification reactions is not modified, followed by a polycondensation according to known processes.

5. Process according to Claim 4, characterized in that the amino group and the carboxylic group contents do not differ by more than 1%.

6. Process according to Claim 4, characterized in that the starting composition is an emulsion of the salt of dimeric acid and hexamethylenediamine in an aqueous solution of the salt of adipic acid and hexamethylene-



diamine and the stoichiometry of which is adjusted by pH determination.

7. Process according to Claim 3, characterized:

1 - by the use of a composition essentially consisting of a mixture of adipic acid, dimeric acid and hexamethylenediamine and/or the corresponding salts thereof, such that the amino group and the carboxylic acid group contents do not differ by more than 5%, which use consists in bringing the composition gradually and uniformly to a temperature corresponding to the initial stage of the following phase;

2 - by a homogenization phase lasting between 10 min and 2 hours at a temperature between 265°C and 290°C, followed by the gradual addition of the reagent in deficit at temperatures between 260° and 290°C until the copolycondensate of desired viscosity is obtained.

8. Process according to Claim 7, characterized in that the excess of one of the amino or the acid reagents is between 5 and 20 mol %.

9. Process according to Claim 7, characterized in that the reagent in deficit is hexamethylenediamine.

10. Process according to Claim 7, characterized in that the homogenization phase is carried out at a temperature between 270 and 285°C.

11. Process for obtaining copolyamides according to Claim 1, characterized by the direct preparation, at a temperature between 150 and 300°C, in a homogeneous medium,



of copolymers starting with a mixture of adipic acid, dimeric acid and hexamethylenediamine, the medium being made homogeneous by the use of a third solvent for the mixture of the three starting products or of the corresponding salts and/or the oligomers of adipic acid and hexamethylenediamine, and of dimeric acid and hexamethylenediamine, of molar mass less than 5,000, this solvent being inert towards the reagents and the amidification reactions.

12. Process according to Claim 11, characterized in that the solvent has a boiling point between 170° and 250°C.

13. Process according to Claim 12, characterized in that the solvent is N-methylpyrrolidone.

14. Process according to Claim 11, characterized in that the copolycondensation temperature is between 190° and 280°C.

Claims for the contracting State: AT

1. Process for obtaining flexible and homogeneous copolyamides based on adipic acid, fatty acid dimers obtained by the fractionation of polymerized fatty acids and containing more than 95% by weight of dimers and hexamethylenediamine, characterized in that:

prepolymers are prepared, in a heterogeneous medium, starting with a mixture of adipic acid, dimeric acid originating from fatty acids obtained by the



polymerization of mixtures of C₁₈ acids and hexamethylenediamine or the corresponding salts thereof, the molar ratio of adipic acid relative to the total acids being between 0.5 and 0.99,

these prepolymers are then homogenized under conditions such that the equilibrium state of the amidification reactions is not modified,

and finally, the homogeneous prepolymers thus obtained are converted into high molecular weight polycondensates for which, the point obtained by plotting the molar fraction of adipic acid along the abscissa and the melting point of the copolyamide obtained, determined by differential microcalorimetry with a temperature change of 10°C per minute along the ordinate is within the area ABCD plotted on the graph given in the appendix.

2. Process according to Claim 1, characterized:

(1) - by the use of a composition essentially consisting of a mixture of adipic acid, dimeric acid and hexamethylenediamine or the corresponding salts thereof, such that the amino group and the carboxylic group contents do not differ by more than a maximum of 5% in absolute value, which use consists in bringing the composition gradually and uniformly by heating to 270°C under a steam pressure between 13 and 25 bars, which is the chemical equilibrium state corresponding to the initial stage of the following phase;

(2) - by a homogenization phase lasting for a



period between 0.5 and 5 hours, at a temperature between 270°C and 290°C at a water pressure between 13 and 25 bars, during which the equilibrium state of the amidification reactions is not modified, followed by a polycondensation according to known processes.

3. Process according to Claim 2, characterized in that the amino group and the carboxylic group contents do not differ by more than 1%.

4. Process according to Claim 2, characterized in that the starting composition is an emulsion of the salt of dimeric acid and hexamethylenediamine in an aqueous solution of the salt of adipic acid and hexamethylenediamine and the stoichiometry of which is adjusted by pH determination.

5. Process according to Claim 1, characterized:

(1) - by the use of a composition essentially consisting of a mixture of adipic acid, dimeric acid and hexamethylenediamine and/or the corresponding salts thereof, such that the amino group and the carboxylic group contents do not differ by more than 5%, which use consists in bringing the composition gradually and uniformly to a temperature corresponding to the initial stage of the following phase;

(2) - by a homogenization phase lasting between 10 min and 2 hours at a temperature between 265°C and 290°C, followed by the gradual addition of the reagent in deficit at temperatures between 260°C and 290°C until the



copolycondensate of desired viscosity is obtained.

6. Process according to Claim 5, characterized in that the excess of one of the amine or the acid reagents is between 5 and 20 mol %.

7. Process according to Claim 5, characterized in that the reagent in deficit is hexamethylenediamine.

8. Process according to Claim 5, characterized in that the homogenization phase is carried out at a temperature between 270 and 285°C.

9. Process for obtaining flexible and homogeneous copolyamides based on adipic acid, fatty acid dimers obtained by the fractionation of polymerized fatty acids and containing more than 95% by weight of dimers and hexamethylenediamine, characterized in that copolymers are prepared directly at a temperature between 150 and 300°C, starting with a mixture of adipic acid, dimeric acid resulting from fatty acids obtained by the polymerization of mixtures of C₁₈ acids and hexamethylenediamine, the molar ratio of adipic acid relative to the total acids being between 0.5 and 0.99, the medium being made homogeneous by the use of a third solvent for the mixture of the three starting products or of the corresponding salts and/or the oligomers of adipic acid and hexamethylenediamine, and of dimeric acid and hexamethylenediamine, of molar mass less than 5,000, the said solvent being inert towards the reagents and the amidification reactions, the copolymer thus obtained having a point, obtained by plotting the molar

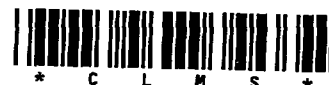


fraction of adipic acid along the abscissa and the melting point determined as mentioned in Claim 1 along the ordinate, which is within the area ABCD plotted in the graph given in the appendix.

10. Process according to Claim 9, characterized in that the solvent has a boiling point between 170°C and 250°C.

11. Process according to Claim 10, characterized in that the solvent is N-methylpyrrolidone.

12. Process according to Claim 9, characterized in that the copolycondensation temperature is between 190°C and 280°C.



Patentansprüche für die Vertragsstaaten: BE CH DE GB IT LI LU NL SE (as printed)

1. Flexible und homogene Copolyamide auf Basis von Adipinsäure, Fettsäuredimeren, die durch Fraktionierung von polymerisierten Fettsäuren herstellbar sind und mehr als 95 Gew.-% Dimere enthalten, und von Hexamethylendiamin, dadurch gekennzeichnet, daß einerseits die Dimeren von Fettsäuren abgeleitet sind, die durch Polymerisation von Mischungen von C_{18} -Säuren herstellbar sind, und daß andererseits das molare Verhältnis von Adipinsäure, bezogen auf die gesamten Säuren, 0,5 bis 0,99 beträgt und daß schließlich der Punkt, den man erhält, wenn man auf der Abszisse den molaren Anteil an Adipinsäure und auf der Ordinate die Schmelztemperatur des Copolyamids, bestimmt durch Differentialmikrocalorimetrie mit einer Temperaturvariation von 10°C pro Minute, aufträgt, innerhalb der auf der beiliegenden Zeichnung dargestellten Fläche ABCD liegt.

2. Copolyamide nach Anspruch 1, dadurch gekennzeichnet, daß das Fettsäuredimere einen Monomeranteil von weniger als 0,5% enthält, wobei der Rest eine Funktionalität von mehr als 2 aufweist.

3. Verfahren zur Herstellung von Copolyamiden nach Anspruch 1, dadurch gekennzeichnet, daß man in heterogenem Milieu Präpolymere aus einer Mischung von Adipinsäure, dimerer Säure und Hexamethylendiamin oder ihren entsprechenden Salzen herstellt, welche Präpolymere anschließend unter solchen Bedingungen homogenisiert werden, daß der Gleichgewichtszustand der Amidifikationsreaktionen nicht verändert wird, und daß die homogenen Präpolymere schließlich in Polykondensate mit hohem Molekulargewicht überführt werden.

4. Verfahren nach Anspruch 3, dadurch gekennzeichnet, daß man

1 — eine Masse herstellt, die im wesentlichen aus einer Mischung von Adipinsäure, dimerer Säure und Hexamethylendiamin oder ihren entsprechenden Salzen besteht, wobei sich die Gehalte an Amingruppen und Carbonsäuregruppen um nicht mehr als maximal 5%, ausgedrückt in absoluten Zahlen, unterscheiden, daß man dazu die Masse fortschreitend und gleichmäßig durch Erhitzen auf 270°C bei einem Wasserdampfdruck zwischen 13 und 25 bar bringt, welches der dem Beginn der folgenden Phase entsprechende chemische Gleichgewichtszustand ist;

2 — eine Homogenisationsphase mit einer Dauer von 0,5 bis 5 Stunden bei einer Temperatur zwischen 270°C und 290°C unter einem Druck von 13 bis 25 bar durchführt, während welcher der Gleichgewichtszustand der Amidifikationsreaktionen nicht verändert wird, und anschließend eine Polykondensation nach bekannten Verfahren ausführt.

5. Verfahren nach Anspruch 4, dadurch gekennzeichnet, daß sich die Gehalte an Amingruppen und Carbonsäuregruppen um nicht mehr als höchstens 1% unterscheiden.

6. Verfahren nach Anspruch 4, dadurch gekennzeichnet, daß die Ausgangsmasse eine Emulsion des Salzes von dimerer Säure und Hexamethylendiamin in der wässrigen Lösung des Salzes von Adipinsäure und Hexamethylendiamin ist, deren Stöchiometrie durch Messung des pH-Werts eingestellt wird.

7. Verfahren nach Anspruch 3, dadurch gekennzeichnet, daß man

1 — eine Masse herstellt, die im wesentlichen aus einer Mischung von Adipinsäure, dimerer Säure und Hexamethylendiamin und/oder ihren entsprechenden Salzen besteht, wobei sich die Gehalte an Amingruppen und Carbonsäuregruppen um mehr als 5% unterscheiden, daß man dazu die Masse fortschreitend und gleichmäßig auf eine Temperatur, entsprechend dem Beginn der folgenden Phase, bringt;

2 — eine Homogenisationsphase mit einer Dauer von 10 Minuten bis 2 Stunden bei einer Temperatur zwischen 265°C und 290°C durchführt, und anschließend fortschreitend fehlendes Reagens bei Temperaturen zwischen 260°C und 290°C zusetzt, bis ein Copolykondensat mit der gewünschten Viskosität hergestellt ist.

8. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß der Überschuß an einem der aminierten oder sauren Reagentien 5 bis 20 Mol% beträgt.

9. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß das fehlende Reagens Hexamethylendiamin ist.

10. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß die Homogenisationsphase bei einer Temperatur zwischen 270 und 285°C ausgeführt wird.

11. Verfahren zur Herstellung von Copolyamiden nach Anspruch 1, dadurch gekennzeichnet, daß man bei einer Temperatur zwischen 150 und 300°C in homogenem Milieu direkt Copolymere aus einer Mischung von Adipinsäure, dimerer Säure und Hexamethylendiamin herstellt, wobei das Milieu homogen gemacht wird durch Verwendung eines Drittlösungsmittels für die Mischung der drei Ausgangsmaterialien oder von deren entsprechenden Salzen und/oder der Oligomeren von Adipinsäure und Hexamethylendiamin und dimerer Säure und Hexamethylendiamin mit einer molekularen Masse kleiner 5000, welches Lösungsmittel inert gegenüber den Reagenzien und Amidifikationsreaktionen ist.

12. Verfahren nach Anspruch 11, dadurch gekennzeichnet, daß das Lösungsmittel einen Siedepunkt zwischen 170 und 250°C hat.

13. Verfahren nach Anspruch 12, dadurch gekennzeichnet, daß das Lösungsmittel N-Methylpyrrolidon ist.

14. Verfahren nach Anspruch 11, dadurch gekennzeichnet, daß die Copolykondensationstemperatur 190° bis 280°C beträgt.



Patentansprüche für den Vertragsstaat: AT (as printed)

1. Verfahren zur Herstellung von flexiblen und homogenen Copolyamiden auf Basis von Adipinsäure, Fettsäuredimeren, die durch Fraktionierung von polymerisierten Fettsäuren herstellbar sind und mehr als 95 Gew.-% Dimere enthalten, und Hexamethyldiamin, dadurch gekennzeichnet, daß man — in heterogenem Milieu Präpolymere aus einer Mischung von Adipinsäure, dimerer Säure, die von Fettsäuren, hergestellt durch Polymerisation von Mischungen von C_{18} -Säuren, abgeleitet ist, und Hexamethyldiamin oder ihren entsprechenden Salzen, wobei das molare Verhältnis an Adipinsäure zu dem Gesamtgehalt an Säuren 0,5 bis 0,99 beträgt, herstellt,

— dann diese Präpolymeren unter solchen Bedingungen homogenisiert, daß der Gleichgewichtszustand der Amidifikationsreaktionen nicht verändert wird,

— schließlich die so erhaltenen homogenen Präpolymeren in Polykondensate mit hohem Molekulargewicht umwandelt, die einen Punkt aufweisen, den man erhält, wenn man auf der Abszisse den molaren Anteil an Adipinsäure und auf der Ordinate die Schmelztemperatur des erhaltenen Copolyamids, bestimmt durch Differentialmikrocalorimetrie mit einer Temperaturvariation von 10°C pro Minute, aufträgt, innerhalb der auf der beiliegenden Zeichnung dargestellten Fläche ABCD liegt.

2. Verfahren nach Anspruch 1, gekennzeichnet durch:

(1) — die Herstellung einer Masse, die im wesentlichen aus einer Mischung von Adipinsäure, dimerer Säure und Hexamethyldiamin oder ihren entsprechenden Salzen besteht, wobei sich die Gehalte an Amingruppen und Carbonsäuregruppen um nicht mehr als maximal 5%, ausgedrückt in absoluten Zahlen, unterscheiden, wozu man die Masse fortschreitend und gleichmäßig durch Erhitzen auf 270°C bei einem Wasserdampfdruck von 13 bis 25 bar bringt, welches der dem Beginn der folgenden Phase entsprechende chemische Gleichgewichtszustand ist;

(2) — eine Homogenisationsphase mit einer Dauer von 0,5 bis 5 Stunden bei einer Temperatur von 270°C bis 290°C unter einem Wasserdruck von 13 bis 25 bar, während welcher der Gleichgewichtszustand der Amidifikationsreaktionen nicht verändert wird, gefolgt von einer Polykondensation nach bekannten Verfahren.

3. Verfahren nach Anspruch 2, dadurch gekennzeichnet, daß sich die Gehalte an Amingruppen und Carbonsäuregruppen um nicht mehr als höchstens 1% unterscheiden.

4. Verfahren nach Anspruch 2, dadurch gekennzeichnet, daß die Ausgangsmasse eine Emulsion des Salzes von dimerer Säure und Hexamethyldiamin in der wässrigen Lösung des Salzes von Adipinsäure und Hexamethyldiamin ist, deren Stöchiometrie durch Messung des pH-Werts eingestellt wird.

5. Verfahren nach Anspruch 1, gekennzeichnet durch:

(1) — die Herstellung einer Masse, die im wesentlichen aus einer Mischung von Adipinsäure, dimerer Säure und Hexamethyldiamin und/oder ihren entsprechenden Salzen besteht, wobei sich die Gehalte an Amingruppen und Carbonsäuregruppen um mehr als 5% unterscheiden, wozu man die Masse fortschreitend und gleichmäßig auf eine Temperatur, entsprechend dem Beginn der folgenden Phase, bringt;

(2) — eine Homogenisationsphase mit einer Dauer von 10 Minuten bis 2 Stunden bei einer Temperatur zwischen 265°C und 290°C, gefolgt von der fortschreitenden Zugabe des fehlenden Reagens bei Temperaturen zwischen 260°C und 290°C bis zur Herstellung des Copolykondensats mit der gewünschten Viskosität.

6. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß der Überschuß an einem der aminierten oder sauren Reagentien 5 bis 20 Mol% beträgt.

7. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß das fehlende Reagens Hexamethyldiamin ist.

8. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß die Homogenisierungsphase bei einer Temperatur zwischen 270 und 285°C ausgeführt wird.

9. Verfahren zur Herstellung von flexiblen und homogenen Copolyamiden auf Basis von Adipinsäure, Fettsäuredimeren, die durch Fraktionierung von polymerisierten Fettsäuren herstellbar sind und mehr als 95 Gew.-% Dimere enthalten, und Hexamethyldiamin, dadurch gekennzeichnet, daß man bei einer Temperatur zwischen 150 und 300°C in homogenem Milieu direkt Copolymere aus einer Mischung von Adipinsäure, dimerer Säure, die von Fettsäuren, hergestellt durch Polymerisation von Mischungen von C_{18} -Säuren, abgeleitet ist, und Hexamethyldiamin, wobei das molare Verhältnis an Adipinsäure zum Gesamtgehalt an Säuren zwischen 0,5 und 0,99 liegt und das Milieu durch Verwendung eines Drittlösungsmittels für die Mischung der drei Ausgangsmaterialien oder ihrer entsprechenden Salze und/oder der Oligomeren von Adipinsäure und Hexamethyldiamin und dimerer Säure und Hexamethyldiamin mit einer molekularen Masse kleiner 5000 homogen gemacht wird, welches Lösungsmittel inert gegenüber den Reagenzien und den Amidifikationsreaktionen ist, und wobei die so erhaltenen Copolymeren einen Punkt aufweisen, den man erhält, wenn man auf der Abszisse den molaren Anteil an Adipinsäure und auf der Ordinate die Schmelztemperatur, bestimmt wie im Anspruch 1 angegeben, aufträgt, innerhalb der auf der beiliegenden Zeichnung dargestellten Fläche ABCD liegt.

10. Verfahren nach Anspruch 9, dadurch gekennzeichnet, daß das Lösungsmittel einen Siedepunkt zwischen 170°C und 250°C hat.

11. Verfahren nach Anspruch 10, dadurch gekennzeichnet, daß das Lösungsmittel N-Methylpyrrolidon ist.

12. Verfahren nach Anspruch 9, dadurch gekennzeichnet, daß die Polykondensationstemperatur zwischen 190°C und 280°C liegt.



Claims for the Contracting States: BE CH DE GB IT LI LU NL SE (as printed)

1. Flexible, homogeneous copolyamides based on adipic acid and on dimers of fatty acids obtained by fractionating polymerised fatty acids and containing more than 95% by weight of dimers and of hexamethylenediamine, characterised in that, on the one hand, the dimers originate from fatty acids obtained by polymerising mixtures of C_{18} acids and, on the other hand, the molar ratio of adipic acid to the total acids is between 0.5 and 0.99 and finally the point obtained by plotting the molar fraction of adipic acid as abscissa and the melting point of the copolyamide as ordinate, this temperature being determined by differential microcalorimetry with a temperature change of 10°C per minute, is located in the region ABCD plotted on the attached graph.

2. Copolyamides according to Claim 1, characterised in that the fatty acid dimer contains a monomer fraction which is less than 0.5%, the remainder having a functionality greater than 2.

3. A process for obtaining copolyamides according to Claim 1, characterised by preparing, in a heterogeneous medium, prepolymers from a mixture of adipic acid, dimer acid and hexamethylenediamine or there corresponding salts, these prepolymers being then homogenised under conditions such that the state of equilibrium of the amide-forming reactions is unaltered, the homogeneous prepolymers being finally converted into polycondensates of high molecular weight.

4. A process according to Claim 3, characterised:

1 — by the use of a composition consisting substantially of a mixture of adipic acid, dimer acid and hexamethylene diamine or of their corresponding salts, such that the contents of amino groups and of carboxyl groups do not differ by more than a maximum of 5% in absolute value, the use consisting in bringing the composition by heating gradually and steadily up to 270°C under a steam pressure of between 13 and 25 bars, which is the state of chemical equilibrium corresponding to the start of the following stage;

2 — by a homogenisation stage with a duration of between 0.5 and 5 hours, at a temperature between 270°C and 290°C under a steam pressure between 13 and 25 bars, during which the state of equilibrium of the amide-forming reactions is unaltered, followed by a polycondensation according to the known processes.

5. A process according to Claim 4, characterised in that the contents of amino groups and of carboxyl groups do not differ by more than 1%.

6. A process according to Claim 4, characterised in that the starting composition is an emulsion of the salt of the dimer acid with hexamethylenediamine in the aqueous solution of the salt of adipic acid with hexamethylenediamine and whose stoichiometry is adjusted by pH measurement.

7. A process according to Claim 3, characterised:

1 — by using a composition consisting substantially of a mixture of adipic acid, dimer acid and hexamethylenediamine and/or their corresponding salts, such that the contents of amino groups and carboxyl groups differ by more than 5%, the use consisting in bringing the composition gradually and steadily to a temperature which corresponds to the start of the following stage;

2 — by a homogenisation stage with a duration of between 10 minutes and 2 hours at a temperature between 265°C and 290°C followed by the gradual addition of the deficient reactant at temperatures between 260° and 290°C until the copolycondensate having the desired viscosity is obtained.

8. A process according to Claim 7, characterised in that the excess of one of the amine or acid reactants is between 5 and 20 mol%.

9. A process according to Claim 7, characterised in that the deficient reactant is hexamethylenediamine.

10. A process according to Claim 7, characterised in that the homogenisation stage is carried out at a temperature between 270 and 285°C .

11. A process for obtaining copolyamides according to Claim 1, characterised by direct preparation, at a temperature between 150 and 300°C , in a homogeneous medium, of copolymers from a mixture of adipic acid, dimer acid and hexamethylenediamine, the medium being made homogeneous by using a third solvent for the mixture of the three starting materials or the corresponding salts and/or the oligomers of adipic acid with hexamethylenediamine and of dimer acid with hexamethylenediamine, of molecular weight below 5,000, this solvent being unreactive in respect of the reactants and the amide-forming reactions.

12. A process according to Claim 11, characterised in that the solvent has a boiling point between 170° and 250°C .

13. A process according to Claim 12, characterised in that the solvent is N-methylpyrrolidone.

14. A process according to Claim 11, characterised in that the temperature of copolycondensation is between 190° and 280°C .



Claims for the Contracting State: AT (as printed)

1. A process for obtaining flexible, homogeneous copolyamides based on adipic acid, fatty acid dimers obtained by fractionating polymerised fatty acids containing more than 95% by weight of dimers and hexamethylenediamine, characterised by:

— preparing, in a heterogeneous medium, prepolymers from a mixture of adipic acid, the dimer acid originating from fatty acids obtained by polymerising mixtures of C_{18} acids and hexamethylenediamine or their corresponding salts, the molar ratio of adipic acid to the total acids being between 0.5 and 0.99,

— then homogenising these prepolymers under such conditions that the state of equilibrium of the amide-forming reactions is unaltered,

— and finally converting the homogeneous prepolymers thus obtained into polycondensates of high molecular weight in respect of which the point obtained by plotting the molar fraction of adipic acid as abscissa and the melting point of the copolyamide obtained as ordinate, this temperature being determined by differential microcalorimetry with a temperature change of 10°C per minute, is located in the region ABCD plotted on the attached graph.

2. A process according to Claim 1, characterised:

(1) by using a composition consisting substantially of a mixture of adipic acid, dimer acid and hexamethylenediamine or their corresponding salts, such that the contents of amino groups and carboxyl groups do not differ by more than a maximum of 5% in absolute value, the use consisting in bringing the composition by heating gradually and steadily to 270°C under a steam pressure between 13 and 25 bars, which is the state of chemical equilibrium corresponding to the start of the following stage;

(2) by a homogenisation stage with a duration of between 0.5 and 5 hours, at a temperature between 270°C and 290°C under a steam pressure between 13 and 25 bars during which the state of equilibrium of the amide-forming reactions is unaltered, followed by a polycondensation according to the known processes.

3. A process according to Claim 2, characterised in that the contents of amino groups and of carboxyl groups do not differ by more than 1%.

4. A process according to Claim 2, characterised in that the starting composition is an emulsion of the salt of the dimer acid with hexamethylenediamine in the aqueous solution of the salt of adipic acid with hexamethylenediamine and whose stoichiometry is adjusted by pH measurement.

5. A process according to Claim 1, characterised:

(1) by using a composition consisting substantially of a mixture of adipic acid, dimer acid and hexamethylene diamine and/or their corresponding salts, such that the contents of amino groups and carboxyl groups differ by more than 5%, the use consisting in bringing the composition gradually and steadily to a temperature which corresponds to the start of the following stage;

(2) by a homogenisation stage with a duration of between 10 minutes and 2 hours at a temperature between 265°C and 290°C followed by the gradual addition of the deficient reactant at temperatures between 260° and 290°C until the copolycondensate having the desired viscosity is obtained.

6. A process according to Claim 5, characterised in that the excess of one of the amine or acid reactants is between 5 and 20 mol%.

7. A process according to Claim 5, characterised in that the deficient reactant is hexamethylenediamine.

8. A process according to Claim 5, characterised in that the homogenisation stage is carried out at a temperature between 270 and 285°C.

9. A process for obtaining flexible, homogeneous copolyamides based on adipic acid, dimers of fatty acids obtained by fractionating polymerised fatty acids containing more than 95% by weight of dimers and hexamethylenediamine, characterised by preparing directly, at a temperature between 150 and 300°C, in a homogeneous medium, copolymers from a mixture of adipic acid, dimer acid originating from fatty acids obtained by polymerising mixtures of C_{18} acids with hexamethylenediamine, the molar ratio of adipic acid to the total acids being between 0.5 and 0.99, the medium being made homogeneous by using a third solvent for the mixture of the three starting materials or the corresponding salts and/or oligomers of adipic acid with hexamethylenediamine and the dimer acid with hexamethylenediamine with a molecular weight of less than 5,000, the said solvent being unreactive in respect of the reactants and the amide-forming reactions, the copolymer thus obtained having a point, obtained by plotting the molar fraction of adipic acid as abscissa and the melting point, determined as indicated in Claim 1, as ordinate, which is located in the region ABCD plotted on the attached graph.

10. A process according to Claim 9, characterised in that the solvent has a boiling point between 170°C and 250°C.

11. A process according to Claim 10, characterised in that the solvent is N-methylpyrrolidone.

12. A process according to Claim 9, characterised in that the temperature of copolycondensation is between 190°C and 280°C.