

Process for the manufacture of polyamide

The present invention relates to a process for the manufacture of polyamide. The
5 polyamide is of the type of those obtained by polycondensation from diacids and
diamines and/or of the type of those obtained by polycondensation from lactams and/or
amino acids. The process is entirely suitable for the manufacture of polyhexamethylene
adipamide.

Polyamides are polymers of great industrial and commercial importance.
10 Thermoplastic polyamides are obtained either by reaction between two different
monomers or by polycondensation of a single monomer. The invention applies, on the
one hand, to polyamides resulting from two different monomers, the most important
polyamide of which is poly(hexamethylene adipamide). Of course, these polyamides can
be obtained from a mixture of diacids and diamines. Thus, in the case of
15 poly(hexamethylene adipamide), the main monomers are hexamethylenediamine and
adipic acid. However, these monomers can comprise up to 25 mol% of other diamine or
diacid monomers or even amino acid or lactam monomers. The invention applies, on the
other hand, to polyamides resulting from a single monomer, the most important
polyamide of which is polycaprolactam. Of course, these polyamides can be obtained
20 from a mixture of lactams and/or amino acids. Thus, in the case of polycaprolactam, the
main monomer is caprolactam. However, these monomers can comprise up to 25 mol%
of other amino acid or lactam monomers or even diamine or diacid monomers.

The class of polyamides resulting from two different monomers is generally
manufactured by using, as starting material, a salt obtained by mixing a diacid with a
25 diamine in stoichiometric amount, generally in a solvent, such as water.

Thus, in the manufacture of poly(hexamethylene adipamide), adipic acid is mixed
with hexamethylenediamine, generally in water, to produce hexamethylenediammonium
adipate, better known under the name of Nylon salt or "N salt".

The solution of the N salt is optionally concentrated by partial or complete
30 evaporation of the water.

The class of polyamides resulting from a single monomer is generally manufactured
by using, as starting material, a lactam and/or an amino acid, and a small amount of
water; the proportion by weight of water is generally between 1 and 15%.

The polyamide is obtained by heating, at high temperature and high pressure, an
35 aqueous solution of the monomers (for example, a solution of Nylon salt as described
above) or a liquid comprising the monomers, in order to evaporate the water while
avoiding any formation of solid phase so as to prevent the mixture from setting solid.

Several processes using different types of devices are known for the manufacture of polyamides.

Processes are known during which the polycondensation is carried out in the molten phase comprising the solution of N salt or the liquid comprising the monomers, the reaction stream flowing at low speed in the lower part of a reactor in a horizontal axis. The upper part of the reactor comprises steam, evaporated from the starting solution or produced by the polycondensation reaction. The molten reaction stream is in the presence of a gas phase which exhibits substantially the same pressure throughout the reactor. The steam is partially evacuated, so as to control the pressure. The polycondensation reaction is thus carried out at a pressure of approximately 0.5-2.5 MPa at a temperature of approximately 215-300°C. The reaction stream is subsequently subjected to a nonadiabatic pressure reduction down to atmospheric pressure by passing through a flasher, that is to say a heated tubular device exhibiting a sufficient exchange surface area to prevent crystallization of the product. During this operation, the residual water present in the material stream is evaporated. The vapour and the liquid stream are subsequently separated in a gas/liquid separator. The polycondensation is continued in the molten phase at atmospheric or reduced pressure so as to achieve the desired degree of progression.

Other processes are known during which the polycondensation is carried out in the molten phase in a tubular reactor exhibiting a high length/diameter ratio. The reaction stream flows at high speed, occupying the entire cross section of the reactor. The hydrodynamic state of this reactor is such that the steam resulting from the reaction is mixed with a material stream, for example in the form of bubbles. The speed, the composition, the pressure and the temperature of the steam gas phase varies along the reactor. The surface area for exchange between reaction medium and heat-exchange fluid is high, which promotes transfers of heat. The residence times are generally shorter than in the processes described above.

Tubular reactors are generally coils included in a chamber comprising a heat-exchange fluid or included in a jacket for circulation of heat-exchange fluid. Such plants exhibit the advantage of being highly compact.

Processes for the manufacture of polyamide in a tubular reactor are described in the documents FR 1 505 307, FR 1 352 650 and FR 1 520 190. In the processes described, a stream of a solution of N salt is injected at a pressure of the order of 1 to 5 MPa into a coil, the diameter of which gradually increases.

The stream of bulk material undergoes polycondensation, releasing steam. It undergoes a gradual pressure reduction along the reactor by head loss.

The polyamide exits from the coil at atmospheric pressure with a high degree of

progression of polymerization and thus a high melt viscosity sufficient to ensure its buildup in weight in a subsequent finishing stage. These processes exhibit the advantage of employing highly compact plants and of being very easy to carry out.

However, they do exhibit disadvantages. At the end of the coil, the speed of flow of the molten polyamide is low and that of the steam is high. The flow state can be annular, with a very rapid stream of vapour at the centre and a slow stream of very viscous molten polyamide at the periphery. Solid deposits of decomposed polyamide form by accumulation over time on the walls. These deposits are capable of unexpectedly detaching, thus detrimentally affecting the final quality of the polyamide. Furthermore, they modify the flows and thus the functioning of the process. They make it necessary to frequently clean the plants and thus to shut down production and dismantle, resulting in high maintenance costs. Furthermore, these processes are not very flexible. This is because the functioning thereof (pressure, temperature, progression) is directly related to the geometry of the plants. A modification to the throughputs according to production requirements modifies the flow and heat exchange states. In particular, for a given geometry, when the throughput decreases, the flow state has a tendency to promote the formation of deposits.

The present invention provides an improved continuous process for the manufacture of polyamide, in particular in a tubular reactor. The process employs a compact plant. The process is flexible and easy to carry out.

To this end, the invention provides a process for the continuous manufacture of a polyamide comprising at least the following stages:

- Stage 1: Polycondensation in a reactor of a liquid stream comprising the monomers, at a pressure P1 greater than atmospheric pressure, the stream of material at the outlet of the reactor being composed of a vapour phase comprising at least steam and of a liquid phase comprising at least the polycondensation product
- Stage 2: Feeding the stream of material to a chamber, evacuating at least a portion of the vapour phase from the chamber and recovering at least the liquid phase comprising at least the polycondensation product, the pressure P2 in the chamber being regulated at a set value such that it is greater than atmospheric pressure and that the residence time of the liquid phase in the chamber is less than 5 minutes, preferably less than 1 minute
- Stage 3: Pressure reduction of at least the liquid phase comprising at least the stream of polycondensation product recovered during Stage 2.

The manufacturing process according to the invention is a process for the manufacture of polyamides of the type of those obtained from dicarboxylic acids and

diamines and/or of the type of those obtained by polycondensation from lactams and/or amino acids.

The lactam or amino acid monomers can, for example, be chosen from caprolactam, 6-aminoheptanoic acid; 5-aminopentanoic acid, 7-aminoheptanoic acid, aminoundecanoic acid or dodecanolactam. The preferred lactam is caprolactam.

The dicarboxylic acid monomers can, for example, be chosen from glutaric acid, adipic acid, suberic acid, sebacic acid, dodecanedioic acid; 1,2- or 1,3-cyclohexanedicarboxylic acid; 1,2- or 1,3-phenylenediacetic acid; 1,2- or 1,3-cyclohexanediacyclic acid; isophthalic acid; terephthalic acid; 4,4'-benzophenonedicarboxylic acid; 2,5-naphthalenedicarboxylic acid; and p-(tert-butyl)isophthalic acid. The preferred dicarboxylic acid is adipic acid.

The diamine monomers can, for example, be chosen from hexamethylenediamine; butanediamine; 2-methylpentamethylenediamine; 2-methylhexamethylenediamine; 3-methylhexamethylenediamine; 2,5-dimethylhexamethylenediamine; 2,2-dimethylpentamethylenediamine; nonanediamine; 5-methylnonanediamine; dodecamethylenediamine; 2,2,4- and 2,4,4-trimethylhexamethylenediamine; 2,2,7,7-tetramethyloctamethylenediamine; meta-xylylenediamine; para-xylylenediamine; isophoronediamine; diaminodicyclohexylmethane and C₂-C₁₆ aliphatic diamines which can be substituted by one or more alkyl groups. The preferred diamine is hexamethylenediamine.

This is a continuous manufacturing process, the conversion is taking place on streams of material. The streams of material undergo conversions during the various stages carried out in one or more parts. The process comprises at least the three successive stages described above. They can obviously comprise others upstream or downstream of them or even between them.

The main conversion carried out during the implementation of the process is generally the polycondensation of a dicarboxylic acid with a diamine or of a lactam and/or amino acid. This conversion is well known to a person skilled in the art, for example for the manufacture of polyamide 66 from adipic acid and hexamethylenediamine or for the manufacture of polyamide 6 from caprolactam. This polycondensation generally releases water in the vapour form.

The degree of progression of the polycondensation is defined as follows:

$$\text{Degree of progression (\%)} = [(\text{number of moles of amide units formed}) / (\text{number of moles of initial reactive functional groups in deficit})] * 100$$

The number of moles of initial reactive functional groups in deficit is:

- either the number of moles of carboxylic acid functional groups resulting from the monomers initially present in the reaction medium, if the reactive functional groups in deficit initially in this medium are the carboxylic acid functional groups (with respect to the

amine functional groups),

- or the number of moles of amine functional groups resulting from the monomers initially present in the reaction medium, if the reactive functional groups in deficit initially in this medium are the amine functional groups (with respect to the carboxylic acid functional groups).

Depending on the degree of progression of the polycondensation, the product obtained can be described as amidate, polyamide oligomer, polyamide prepolymer or polyamide.

The polycondensation is preferably mainly carried out during Stage 1. It is during this stage that the degree of progression increases the most. The polycondensation can, however, continue during Stage 2 or Stage 3 or during subsequent stages.

The degree of progression of the polycondensation on conclusion of Stage 3 is advantageously greater than 60%, preferably greater than 90%.

The temperature during Stage 1 is such that the stream of material does not solidify.

The polycondensation requires a supply of heat, the heat temperature generally being far below the melting point of the final polymer. The plants used for the implementation of the process thus comprise heat supply means for the purpose of maintaining the reaction medium at a sufficient temperature to prevent the appearance of a solid phase. They likewise comprise all the means which may be necessary for its implementation, such as pumps, analytical means, control means, valves, means for introducing or storing the stream of material, or static mixers.

For the implementation of Stage 1, of polycondensation, a liquid stream comprising the monomers of the polyamide to be prepared is introduced into the reactor. In order to prepare a polyamide of the PA66 type, the monomers are dicarboxylic acids and diamines. In order to prepare a polyamide of PA6 type, the monomers are lactams and/or amino acids. These compounds constitute the main monomers. An aqueous solution may be involved. The acid and the diamine are advantageously in substantially stoichiometric proportions, in the case of the preparation of a polyamide of PA66 type.

The dicarboxylic acid is preferably adipic acid and the diamine is preferably hexamethylenediamine. The stream can comprise other monomers, such as other dicarboxylic acids or other diamines, or amino acids or lactams, such as caprolactam.

The lactam is preferably caprolactam. The stream can comprise other monomers, such as other lactams and/or amino acids, or dicarboxylic acids or diamines, such as hexamethylenediamine or adipic acid.

For the preparation of a polyamide of PA66 type, the stream fed in is preferably a stream of an aqueous solution of N salt, comprising adipic acid or one of its ionic forms

and hexamethylenediamine or one of its ionic forms, in substantially stoichiometric proportions. For the preparation of a polyamide of PA6 type, the stream fed in is preferably composed of a mixture of caprolactam and of water. The stream fed in advantageously comprises 50 to 100% by weight of monomers; for example, it preferably
5 comprises 50 to 80% of N salt in the case of the production of PA66.

Such a solution can, for example, be obtained by dissolution of a solid salt or by dissolution of the acid and of the diamine with monitoring of the stoichiometry using an appropriate means, for example pH-metric or near infrared analysis. The solution may have been subjected to a preheating operation before introduction into the reactor. The
10 solution may have been subjected to a concentrating operation, by evaporation of water, and/or a preheating operation before introduction into the reactor.

The stream comprising the dicarboxylic acid and the diamine can also be obtained by heating the solid salt or the acid and the diamine.

The stream comprising the monomers is fed to the reactor at a pressure greater
15 than atmospheric pressure and at a temperature such that the stream is liquid.

The stream comprising the monomers is fed to the reactor. The stream of material flows in the reactor. During the progression of the stream in the reactor, in particular in the tubular reactor, polycondensation occurs between the diamine and the diacid to form polyamide chains, with the formation of water, a portion of which can evaporate.

20 The stream of material, before the outlet of the reactor, can be composed solely of a liquid phase comprising the polycondensation product and dissolved water. In this case, a vapour phase is produced, comprising water which is evaporated from the liquid phase, for example by employing a valve immediately before the outlet of the reactor.

The stream of material at the outlet of the reactor comprises a liquid phase
25 comprising at least the polycondensation product in the molten form and optionally dissolved water and a vapour phase comprising at least steam. The hydrodynamic state in the reactor will depend on the arrangement chosen and on the operating conditions, it being possible for the gas phase comprising steam and the liquid phase to be mixed or not to be mixed. A gas/liquid flow then exists. The two phases flow cocurrentwise in the
30 reactor.

The reactor is maintained at a temperature sufficient for polycondensation to take place. The reactor can advantageously be fed with a preheated stream, the temperature which is close to the temperature for the start of polycondensation.

The pressure P1 in the reactor is generally between 0.5 and 3.5 MPa and the
35 temperature is generally between 180 and 320°C.

According to a specific embodiment of the process of the invention, in Stage 1, the liquid stream is fed at a pressure P'1 greater than atmospheric pressure, the stream of

material at the outlet of the reactor being at a pressure $P''1$ lower than the feed pressure $P'1$ and greater than atmospheric pressure.

The feed pressure $P'1$ of the stream into the reactor is advantageously greater than 1 MPa, preferably greater than 1.5 MPa, more preferably still greater than 1.8 MPa or even 3.0 MPa, for example if the production throughput is high.

The reactor is preferably a tubular reactor. It advantageously exhibits a length to diameter ratio of greater than 100. It is preferably greater than 500. In the reactor, the surface speed of the liquid phase is preferably greater than 0.1 m/second. The speed is defined by the ratio of the throughput by volume of the liquid phase to the cross section of the flow of the stream of material. The residence time of the liquid phase in the reactor is advantageously greater than 1 minute, preferably greater than 5 min. It preferably does not exceed 60 minutes.

The degree of progression of the polycondensation at the outlet of the reactor is advantageously greater than 60%, preferably greater than 90%. The length and the diameter of the tubular reactor and the speed of the stream can be adjusted and controlled in order to obtain the desired degree of progression.

The pressure in the polycondensation reactor generally decreases by head loss from the inlet towards the outlet of the reactor. The outlet pressure $P''1$ is, however, greater than atmospheric pressure. It is advantageously greater than 0.5 MPa, preferably greater than 1.0 MPa.

According to a preferred embodiment of the invention, the tubular reactor is a coil with a length to diameter ratio of greater than 500. The length of the coil is preferably greater than 200 m. The internal diameter is preferably less than 200 mm.

The coil can comprise several parts with different diameters, the diameter increasing gradually or in sequential fashion from the inlet towards the outlet of the reactor. Such a device makes it possible to reduce the pressure in a controlled and gradual fashion and also to reduce overall the difference in pressure between the inlet pressure and the outlet pressure of the reactor. The length/diameter ratio of the reactor when it comprises several parts of different diameter is advantageously greater than 10, preferably greater than 500.

The tubular reactor is generally placed in a chamber or a jacket comprising a heat-exchange fluid. The heat-exchange fluid is, for example, Therminol VP-1®. When the heat-exchange fluid is in the vapour form, it is maintained in this form using a boiler. The reactor is, for example, a helical coil placed in a chamber thus heated.

According to the invention, the liquid phase comprising the polycondensation product and the vapour phase comprising steam at the outlet of the reactor are fed to a device intended to evacuate at least a portion of the steam.

The liquid phase comprising the polycondensation product will be directed to the bottom of the chamber and the vapour phase will occupy the upper part. The pressure P_2 in the chamber is greater than atmospheric pressure. It is preferably between 0.5 and 2.5 MPa. The pressure P_2 is less than or equal to the pressure P''_1 .

- 5 The evacuation device comprises a means for evacuating the vapour phase and a means for recovering the liquid phase comprising the polycondensation product in the molten form.

10 The pressure P_2 in the chamber can be regulated by the evacuation throughput of the vapour phase. In order to increase the pressure, it is possible, for example, to reduce the degree of opening of the valve for evacuation of the vapour phase.

15 The pressure P_2 in the chamber is advantageously regulated so that there is no retention of the liquid phase in the chamber. It is preferable for the residence time of the liquid phase in the evacuation chamber to be reduced to a minimum, indeed even for it to be virtually zero (that is to say, less than a few seconds, indeed even a few tenths of a second, or of the order of a few seconds, indeed even a few tenths of a second). The residence time of the liquid phase in the chamber is comparable to a passage time of this liquid phase in the chamber.

20 According to a preferred embodiment, the evacuated vapour stream, and thus also the pressure in the chamber, are subject to the control of liquid level detection in the chamber where the evacuation is carried out, more particularly in the part of the chamber intended for the recovery of the liquid phase. A set level of the liquid phase in the part of the chamber intended for the recovery of the liquid phase, for example a liquid height in this chamber part, is chosen. When the liquid level exceeds the set level, a valve for evacuation of the vapour phase is actuated in order to limit the stream of vapour phase evacuated and thus to increase the pressure in the chamber. The increase in the pressure promotes the flow of the liquid phase comprising the polycondensation product into the pressure-reducing device of Stage 3, which has the effect of reducing the liquid level in the chamber. The set level is advantageously chosen so that the amount of liquid phase in the evacuation chamber is at a minimum. For example, if the set level is a given liquid height in the part of the chamber intended for the recovery of the liquid phase, this set height will preferably be chosen to be as low as possible. It is possible, if this level is adjusted to a sufficiently low value, for a portion of the vapour phase originating from the chamber to accompany the liquid phase into the device of Stage 3.

35 One method which can be used to determine the residence time of the liquid phase in the chamber consists in injecting a tracer upstream of the chamber, in recovering it downstream of the chamber and in measuring the time between the injection and the recovery of the tracer. The tracer is an inert substance which does not interact chemically

or physically with the reaction medium. This method is known to a person skilled in the art and is described in particular in the work "Génie de la réaction chimique" [Engineering of the Chemical Reaction], Daniel Schweich, published by Technique et Documentation, 2001, pp. 137-141. The residence time of the liquid phase in the chamber can also be
5 determined, in the case where the liquid level in the part of the chamber intended for the recovery of the liquid phase is being controlled, by the ratio of the volume of this part of the chamber to the throughput by volume of liquid.

The evacuation device is preferably a device of cyclone type. Such a device is known to a person skilled in the art. It comprises a cylindrical part into which the stream of
10 material resulting from Stage 1 is fed tangentially, a conical part intended for the recovery of the liquid phase comprising the polycondensation product, and a device for evacuation of the vapour phase. In the conical part, the stream of material forms a film on the walls of the cyclone. According to a useful form, the cyclone is provided with means for measuring the level of the liquid polycondensation product recovered, the operating pressure of the
15 cyclone being subject to control by this measurement. When a set level is exceeded, the pressure in the cyclone is then increased by reducing the throughput for evacuation of the vapour phase. The cyclone can be heated by a heat-exchange fluid.

During Stage 3, the stream of polycondensation product resulting from Stage 2 is subjected to a nonadiabatic pressure reduction in order to achieve a pressure generally in
20 the vicinity of atmospheric pressure. This pressure reduction is preferably carried out by head loss in a heated tubular device proportioned so that the flow generates a head loss substantially equal to the difference between the operating pressure desired for the chamber of Stage 2 and atmospheric pressure. This tubular device is advantageously placed in a chamber comprising a heat-exchange fluid. The pressure-reducing device can
25 be a helical coil composed, if appropriate, of several sections. The same chamber may be involved as that comprising the tubular reactor. This arrangement exhibits the advantage of being highly compact.

It is possible for the degree of progression of the polycondensation to increase during this stage.

30 The stream on conclusion of Stage 3 advantageously exhibits a degree of progression of the polycondensation of greater than 90%.

The polycondensation product resulting from Stage 3 is a molten polymer or prepolymer. It can comprise a vapour phase essentially composed of steam which may have been formed and/or evaporated during the pressure-reducing phase.

35 This product can be subjected to vapour-phase separating and finishing stages in order to achieve the degree of polycondensation desired. The separation of the vapour phase can, for example, be carried out in a device of cyclone type. Such devices are

known.

The finishing consists in maintaining the polycondensation product in the molten state, under a pressure in the vicinity of atmospheric pressure or under reduced pressure, for a time sufficient to achieve the desired degree of progression. Such an operation is
5 known to a person skilled in the art. The temperature of the finishing stage is advantageously greater than or equal to 200°C and in all cases greater than the solidification temperature of the polymer. The residence time in the finishing device is preferably greater than or equal to 5 minutes.

The stream of liquid resulting from Stage 3 or from the finishing stage can also be
10 subjected to a stage of postcondensation in a solid phase. This stage is known to a person skilled in the art and makes it possible to increase the degree of polycondensation to a desired value.

The polyamide obtained at the end of the finishing stage can be cooled and put into the form of granules. It preferably exhibits, after the finishing stage or stage of
15 postcondensation in the solid phase, a degree of progression of the polycondensation of greater than 99%.

According to a specific alternative form of the invention, the process comprises several successive stages of polycondensation/evacuation of the liquid phase and of the vapour phase which precede the stage of pressure reduction to the pressure in the vicinity of atmospheric pressure. According to a specific embodiment of the invention, the
20 process comprises, between Stage 2 and Stage 3, at least one series of successive stages of polycondensation i and of evacuation j which are respectively analogous to Stage 1 and Stage 2, starting from the liquid phase resulting from Stage 2, the pressures in the tubular polycondensation reactor of stage i and in the evacuation chamber of
25 stage j being greater than atmospheric pressure and the inlet pressure P^i in the tubular polycondensation reactor of stage i being greater than the outlet pressure $P''i$ of the latter. Stages i and j can be repeated at least twice, the feed stream of the polycondensation stage $i+1$ resulting from the evacuation stage j . The pressure P_j is less than or equal to the pressure $P''i$. In practice, several tubular polycondensation reactors and several
30 evacuation devices, such as the cyclones described above, are arranged in series. Preferably they are placed in the same chamber comprising a heat-exchange fluid. The parameters, in particular of pressure, temperature, residence time or geometry, in the various polycondensation reactors are chosen according to the degree of polycondensation desired on conclusion of each polycondensation stage and according
35 to the final degree of polycondensation desired. Each evacuation device, such as a cyclone, is employed at a pressure greater than atmospheric pressure and the pressure inside each cyclone is regulated so that there is little or no retention of the liquid phase in

the evacuation chamber, for example by subjecting the throughput of evacuated vapour phase to the control of a set level of liquid present in the evacuation chamber.

The polyamide obtained by the process of the invention in the molten form can be directly formed or can be extruded and granulated for a subsequent forming after melting.

5 The polyamide can be used for a large number of applications, in particular for the manufacture of yarns, fibres or filaments or for forming articles by injection moulding or extrusion. It can in particular be used in industrial plastic compositions.

10 The process of the invention has many advantages. It is a continuous process which makes it possible to obtain a uniform product, on the one hand, and great flexibility in the operating throughput, by adjusting the throughput for evacuation of the vapour phase in the evacuation device, while limiting the fouling of the plant by solid residues resulting from decomposed polymer. This process minimizes the number of rotating machines to be employed (for example the number of pumps) and pollution by organic compounds present in the effluents (for example hexamethylenediamine present in the vapour phase). In addition, the pressurized gas phase evacuated in the evacuation device, essentially composed of steam, can be easily recovered and reused as energy source, for example for heating the feed stream of monomers.

Other details or advantages of the invention will become more apparent in the light of the example given below.

20 Viscosity number: Measured in 90% formic acid according to Standard ISO 307:2003.

EXAMPLE

25 1157 kg/h of an aqueous solution comprising 70% by weight of hexamethylene-diammonium adipate are fed at 150°C into a spirally wound pipe made of stainless steel situated in a cylindrical chamber with a diameter of 1 m and a height of 4 m heated by a thermal fluid at 280°C. This pipe, with an internal diameter of 40.9 mm and a length of 440 metres, conveys the reaction stream to a separator of cyclone type, also heated by a thermal fluid at 280°C. The stream exiting from the pipe and entering the separator is composed of an aqueous solution of prepolymer with a viscosity number of approximately equal to 30 ml/g and of a vapour phase predominantly composed of water.

30 The duration of the reaction in the pipe is approximately 15 minutes and the pressure at the inlet of the pipe is equal to 2.6 MPa. The pressure in the separator is regulated at 1.9 MPa using a pressure-reducing valve which makes it possible to remove a portion of the vapour phase at a level of 346 kg/h. The remaining stream, composed of the liquid phase and of the balance of vapour phase, is evacuated into a pressure-reducing device composed of a series of spirally wound pipes which is also incorporated

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in the heated chamber and which makes it possible to reduce the pressure of the medium down to a pressure in the vicinity of atmospheric pressure. This series of pipes consists of a first winding with a length of 163 metres and an internal diameter of 32.5 mm, followed by a second winding with a length of 27 metres and an internal diameter of 36.6 mm. The
5 duration of the pressure-reducing stage is approximately 4 minutes. A vapour phase and a liquid prepolymer with a viscosity number of 47 ml/g are obtained.

This reaction mixture is introduced at a temperature in the vicinity of 280°C into a vertical finisher operating at a pressure in the vicinity of atmospheric pressure and equipped with an outlet for the vapour phase. A polymer with a viscosity number equal to
10 131 ml/g is withdrawn from this finisher at a throughput of 698 kg/h.

CLAIMS

1. Process for the continuous manufacture of a polyamide comprising at least the following stages:
 - 5 - Stage 1: Polycondensation in a reactor of a liquid stream comprising the monomers, at a pressure P1 greater than atmospheric pressure, the stream of material at the outlet of the reactor being composed of a vapour phase comprising at least steam and of a liquid phase comprising at least the polycondensation product
 - 10 - Stage 2: Feeding the stream of material to a chamber, evacuating at least a portion of the vapour phase from the chamber and recovering at least the liquid phase comprising at least the polycondensation product, the pressure P2 in the chamber being regulated at a set value such that it is greater than atmospheric pressure and that the residence time of the liquid phase in the chamber is less
15 than 5 minutes, preferably less than 1 minute
 - Stage 3: Pressure reduction of at least the liquid phase comprising at least the stream of polycondensation product recovered during Stage 2.
2. Process according to Claim 1, characterized in that, in Stage 1, the stream of liquid is
20 fed at a pressure P'1 greater than atmospheric pressure, the stream of material at the outlet of the reactor being at a pressure P''1 which is lower than the feed pressure P'1 and greater than atmospheric pressure.
3. Process according to Claim 1 or 2, characterized in that, in Stage 2, the pressure P2
25 in the chamber is regulated at a set value such that there is no retention of the liquid phase in the chamber.
4. Process according to one of the preceding claims, characterized in that the reactor is
30 a tubular reactor.
5. Process according to one of the preceding claims, characterized in that the monomers are a dicarboxylic acid and a diamine.
6. Process according to Claim 5, characterized in that the polyamide is a polyamide 66
35 or a copolyamide, the majority of the repeat units of which are polyamide 66 units, the dicarboxylic acid being adipic acid and the diamine being hexamethylenediamine.

7. Process according to one of Claims 1 to 4, characterized in that the monomers are a lactam and/or an amino acid.
8. Process according to Claim 7, characterized in that the polyamide is a polyamide 6 or a copolyamide, the majority of the repeat units of which are polyamide 6 units, the lactam being caprolactam and/or the amino acid being aminohexanoic acid.
9. Process according to one of the preceding claims, characterized in that the liquid stream comprising the monomers is an aqueous solution.
10. Process according to one of the preceding claims, characterized in that the liquid stream comprises between 50% and 100% by weight of monomers.
11. Process according to one of the preceding claims, characterized in that the stream fed to the tubular reactor is at a pressure $P'1$ of greater than 1 MPa, preferably of greater than or equal to 1.5 MPa.
12. Process according to one of the preceding claims, characterized in that the stream of material at the outlet of the tubular reactor is at a pressure $P''1$ of greater than 0.5 MPa, preferably of greater than or equal to 1 MPa, and at a temperature of greater than 200°C.
13. Process according to one of the preceding claims, characterized in that the degree of progression of a polycondensation at the outlet of the reactor is greater than 90% for a polyamide 66.
14. Process according to one of the preceding claims, characterized in that the residence time of the liquid phase in the reactor is greater than 5 minutes.
15. Process according to one of the preceding claims, characterized in that the tubular reactor comprises one or more segments of different diameters, the length/diameter ratio of which is greater than 100, preferably greater than 500.
16. Process according to one of the preceding claims, characterized in that the tubular reactor comprises several segments, the diameter of which increases from the inlet towards the outlet of the reactor.

17. Process according to one of the preceding claims, characterized in that the surface speed of the liquid phase in the reactor is greater than 0.1 m/s.
18. Process according to one of the preceding claims, characterized in that the reactor is placed in a chamber or jacket comprising a heat-exchange fluid.
19. Process according to one of the preceding claims, characterized in that the pressure P2 in the chamber where evacuation is carried out is regulated at a set value such that P2 is between 0.5 and 2.5 MPa.
20. Process according to one of the preceding claims, characterized in that the throughput of evacuated vapour phase is subject to the control of detection of the level of the liquid phase in the chamber where evacuation is carried out, more particularly in the part of the chamber intended for the recovery of the liquid phase, the throughput for evacuation of the vapour phase being reduced when a set level is exceeded.
21. Process according to one of the preceding claims, characterized in that the evacuation is carried out in a device of cyclone type comprising a cylindrical part into which the stream of material is fed, a conical part intended for the recovery of the liquid phase of the polycondensation product and a device for evacuation of the vapour phase.
22. Process according to one of the preceding claims, characterized in that the pressure reduction of at least the liquid phase comprising at least the stream of polycondensation product is carried out in a tubular device optionally comprising several segments with increasing cross sections.
23. Process according to Claim 22, characterized in that the tubular pressure-reducing device is placed in a chamber or a jacket comprising a heat-exchange fluid.
24. Process according to Claim 23, characterized in that a generator of thermal fluid in the form of vapour is present in the chamber.
25. Process according to one of the preceding claims, characterized in that the degree of progression of the polycondensation of the stream of product resulting from Stage 3 is preferably greater than 90% for a polyamide 66.

26. Process according to one of the preceding claims, characterized in that Stage 3 is followed by a stage of finishing the polycondensation, in the molten phase, or by a postcondensation in the solid phase.

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27. Process according to Claim 26, characterized in that the finishing stage or the stage of postcondensation in the solid phase is preceded by a stage of separation of the vapour phase present in the stream exiting from the pressure-reducing stage.

10 28. Process according to Claims 26 or 27, characterized in that the finishing device is heated using a heat-exchange fluid.

29. Process according to one of the preceding claims, characterized in that it comprises, between Stage 2 and Stage 3, at least one series of successive stages of
15 polycondensation i and of evacuation j which are respectively analogous to Stage 1 and Stage 2, starting from the liquid phase resulting from Stage 2, the pressures in the tubular polycondensation reactor of stage i and in the evacuation chamber of stage j being greater than atmospheric pressure and the inlet pressure P^i in the tubular polycondensation reactor of stage i being greater than the outlet pressure P''^i
20 of the latter.