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(54) COPOLYMERES GREFFES A BASE DE POLYAMIDE
(54) POLYAMIDE GRAFT COPOLYMERS

(57) A graft copolymer which contains the following monomer units: a) from 0.5 to 25% by weight, based on the graft copolymer, of a polyamine having at least 11 nitrogen atoms and a number-average molar mass M_n of at least 500 g/mol; and b) an equimolar combination of diamine and dicarboxylic acid as polyamide-forming monomers is suitable, inter alia, as a blend component or as a hot-melt adhesive.

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Abstract:

A graft copolymer which contains the following monomer units:

a) from 0.5 to 25% by weight, based on the graft copolymer, of a polyamine having at least 11 nitrogen atoms and a number-average molar mass M_n of at least 500 g/mol; and

b) an equimolar combination of diamine and dicarboxylic acid as polyamide-forming monomers

is suitable, inter alia, as a blend component or as a hot-melt adhesive.

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Polyamide graft copolymers

FIELD OF THE INVENTION

The invention relates to polyamide graft copolymers which are composed of a polyamine moiety and grafted-on polyamide chains.

BACKGROUND OF THE INVENTION

Graft copolymers based on polyamine and polyamide are known. They may be prepared, for example, by cationic polymerization of caprolactam in the presence of polyethyleneimine hydrochloride dendrimers as core molecule (J.M. Warakomski, Chem. Mater. 1992, 4, 1000 - 1004). Compared with linear nylon-6, nylon-6 dendrimers of this type have markedly reduced melt viscosity and solution viscosity, but unchanged tensile strength, stiffness, melting points, enthalpies of fusion and barrier action with respect to oxygen.

Graft copolymers based on polyvinylamine and polyamide are known from U.S. Patent No. 2 615 863. U.S. Patent No. 3 442 975 describes graft copolymers which are prepared by polymerizing lactams in the presence of high-molecular-weight polyethyleneimine.

German Patent Publication No. 19 15 772 describes blends made from a polyimine-polyamide graft copolymer, and also from a polyolefin and/or polyester, which are processed to give fibers which are easy to color.

Finally, German Patent Publication No. 196 54 179 describes H-shaped polyamides which are prepared from lactams or aminocarboxylic acids, from an at least trifunctional amine, from dibasic carboxylic acids and from monobasic carboxylic acid. There is a certain ratio here of the two last-named compounds to one another and of these to the functional groups of the at least trifunctional amine. The products have improved melt stability.

Polyamide graft copolymers of this type are suitable, for example, as a blend component for giving a molding composition better processing performance or better compatibility with other polymers. However, the compatibility of currently known graft copolymers, mainly containing nylon-6 graft chains, with respect to polyamides derived from a combination of diamine and dicarboxylic acid is not always ideal when these polyamides are used as a base for molding compositions.

There has to date been no disclosure of analogous polyamide graft copolymers which contain graft chains derived from a combination of a diamine and a dicarboxylic acid. A possible reason for this is that attempts to prepare them from a diamine, a dicarboxylic acid and a polyamine give a crosslinked product.

SUMMARY OF THE INVENTION

In one aspect, the invention provides a graft copolymer which comprises the following monomer units:

a) from 0.5 to 25% by weight, preferably from 1 to 20% by weight and particularly preferably from 1.5 to 16% by weight based on the graft copolymer, of a polyamine having at least 11 nitrogen atoms and a number-average molecular weight M_n of at least 500 and preferably at least 800;

b) an equimolar combination of a diamine and a dicarboxylic acid as polyamide-forming monomers; and

c) optionally, a lactam and/or ω-aminocarboxylic acid as a further polyamide-forming monomer, in an amount of not more than 95% by weight, preferably not more than 90% by weight, particularly preferably not more than 70% by weight and very particularly preferably not more than 50% by weight, of the polyamide graft chains.

DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

The following classes of substances may, for example, be used as the polyamine:

- polyvinylamines (Römpp Chemie Lexikon [Römpp's Chemical Encyclopedia], 9th edition, vol. 6, p. 4921, Georg Thieme Verlag Stuttgart 1992)

- polyamines prepared from alternating polyketones (German Patent Publication No. 196 54 058)

- dendrimers, such as $((H_2N-(CH_2)_3)_2N-(CH_2)_3)_2-N-(CH_2)_2-N((CH_2)_2-N((CH_2)_3-NH_2)_2)_2$ (German Patent Publication No. 196 54 179) or 3,15-bis(2-aminoethyl)-6,12-bis[2-[bis(2-aminoethyl)amino]ethyl]-9-[2-[bis[2-bis(2-aminoethyl)amino]ethyl]amino]ethyl]-3,6,9,12,15-pentaazaheptadecane-1,17-diamine (J. M. Warakomski, Chem. Mat. 1992, 4, 1000 - 1004);

- linear polyethyleneimines which can be prepared by polymerizing 4,5-dihydro-1,3-oxazoles followed by hydrolysis (Houben-Weyl, Methoden der Organischen Chemie [Methods of Organic Chemistry], vol. E20, pp. 1482 - 1487, Georg Thieme Verlag Stuttgart, 1987);

- branched polyethyleneimines obtainable by polymerizing aziridines (Houben Weyl, Methoden der Organischen Chemie [Methods of Organic Chemistry], vol. E20, pp. 1482 - 1487, Georg Thieme Verlag Stuttgart, 1987) and which generally have the following amino group distribution: from 25 to 46% of primary amino groups, from 30 to 45% of secondary amino groups, and from 16 to 40% of tertiary amino groups.

The polyamine preferably has a number-average molecular weight M_n of not more than 20,000, particularly preferably not more than 10,000 and in particular not more than 5,000. In certain embodiments, the amount of the polyamine is from 0.8 to 5% based on the graft copolymer.

Examples of combinations of the diamine and the dicarboxylic acid are hexamethylenediamine/adipic acid, hexamethylenediamine/dodecanedioic acid, octamethylenediamine/sebacic acid, decamethylenediamine/sebacic acid, decamethylenediamine/dodecanedioic acid, dodecamethylenediamine/dodecanedioic acid and dodecamethylenediamine/2,6-naphthalenedicarboxylic acid. However, besides these it is also possible to use any other combination, such as decamethylenediamine/dodecanedioic acid/terephthalic acid, hexamethylenediamine/adipic acid/terephthalic acid, hexamethylenediamine/adipic acid/carprolactam, decamethylenediamine/dodecanedioic acid/ω-aminoundecanoic acid, decamethylenediamine/dodecanedioic acid/laurolactam, decamethylenediamine/terephthalic acid/laurolactam or dodecamethylenediamine/2,6-naphthalenedicarboxylic acid/laurolactam.

Lactams or ω-aminocarboxylic acids which may optionally be used as polyamide-forming monomers may contain from 4 to 19 carbon atoms, in particular from 6 to 12 carbon atoms. Particular preference is given to ε-caprolactam, ε-aminocaproic acid, caprylolactam, ω-aminocaprylic acid, laurolactam, ω-aminododecanoic acid and/or ω-aminoundecanoic acid.

In one preferred embodiment the graft copolymer is prepared with concomitant use of an oligocarboxylic acid which has been selected from the group consisting of from 0.015 to about 3 mol% of a dicarboxylic acid and from 0.01 to about 1.2 mol% of a tricarboxylic acid, based in each case on the total of the other polyamide-forming monomers. In this calculation each of the monomers in the equimolar combination of the diamine and the dicarboxylic acid is treated separately. The polyamide-forming monomers therefore have overall a slight excess of carboxyl groups. The upper limits given for the dicarboxylic acid and the tricarboxylic acid are merely intended to ensure that the resultant graft copolymer is thermoplastic and not crosslinked. According to current understanding, these upper limits are good guideline values. However, in individual cases, especially when using relatively high amounts of polyamine, higher amounts of oligocarboxylic acid may be added. Graft copolymers of this type are also within the scope of the invention. If a dicarboxylic acid is used it is preferable to use from 0.03 to 2.2 mol%, particularly preferably from 0.05 to 1.5 mol%, very particularly preferably from 0.1 to 1 mol% and in particular from 0.15 to 0.65 mol%. If a tricarboxylic acid is used the amount is preferably from 0.02 to 0.9 mol%, particularly preferably from 0.025 to 0.6 mol%, very particularly preferably from 0.05 to 0.4 mol% and in particular from 0.03 to 0.25 mol%. The concomitant use of the oligocarboxylic acid markedly improves solvent resistance and fuel resistance, and in particular resistance to hydrolysis and alcoholysis, and environmental stress cracking resistance, but also improves swelling behavior and, associated therewith, dimensional stability, and also barrier action with respect to diffusion.

The oligocarboxylic acid may be any desired di- or tricarboxylic acid and may have from 6 to 24 carbon atoms, such as adipic acid, subaric acid, azelaic acid, sebacic acid, dodecanedioic acid, isophthalic acid, 2,6-naphthalenedicarboxylic acid, cyclohexane-1,4-dicarboxylic acid, trimesic acid and/or trimellitic acid.

If desired, use may also be made, as regulators, of aliphatic, alicyclic, aromatic, arylalkyl and/or alkylaryl monocarboxylic acids having from 3 to 50 carbon atoms, e.g. lauric acid, unsaturated fatty acids, (e.g., acrylic acid) or benzoic acid. These regulators can reduce the concentration of amino groups without altering the form of the molecule. This method also allows the introduction of functional groups, such as double bonds or triple bonds, etc. It is, however, desirable for the graft copolymer to have a substantial number of amino groups. The amino group concentration in the graft copolymer is preferably from 100 to 2500 mmol/kg, particularly preferably from 150 to 1500 mmol/kg and very particularly preferably from 250 to 1300 mmol/kg. For the purposes of the present invention, here and below amino groups are not only terminal amino groups but also any secondary or tertiary amine functions which may be present in the polyamine.

Various processes may be used to prepare the novel graft copolymers. In general, a polyamide prepolymer is reacted with the polyamine.

One preferred process has two stages of which the first is the prepolymerization of the diamine and the dicarboxylic acid, and also of the optional cocomponents a lactam or ω-aminocarboxylic acid. In the second step the polyamine is added, while the oligocarboxylic acid which may be used concomitantly, if desired, is metered in prior to, during or after the prepolymerization. The pressure is then reduced at from 200 to 290°C and the polycondensation carried out under a stream of nitrogen or in vacuo.

Another preferred process consists in the hydrolytic degradation of a polyamide to give a prepolymer and simultaneous or subsequent reaction with the polyamine. The polyamides used are preferably those in which the terminal group difference is approximately zero or those which already incorporate the oligocarboxylic acid which may, if desired, be used concomitantly.

However, the oligocarboxylic acid may also be added at the beginning or during the course of the degradation reaction.

These processes can be used to prepare extremely highly branched polyamides with acid numbers below 40 mmol/kg, preferably below 20 mmol/kg and particularly preferably below 10 mmol/kg. Virtually complete conversion is achieved after reaction times as short as from one to five hours at temperatures of from 200°C to 290°C.

A vacuum phase lasting a number of hours may follow, if desired, as a further process step. This lasts at least four hours, preferably at least six hours and particularly preferably at least eight hours, at from 200 to 290°C. After an induction period of a number of hours, an increase in the melt viscosity is then observed, probably due to a reaction of terminal amino groups with one another with elimination of ammonia and chain-linking. The resultant further increase in molecular weight is particularly advantageous in molding compositions intended for extrusion.

If it is not desirable to carry out the reaction to completion in the melt, the extremely highly branched polyamide may also be post-condensed in the solid state as in the prior art.

The novel graft copolymers may be used for molding compositions intended for injection molding or extrusion. They may also be used as a blend component for modifying performance characteristics, or as hot-melt adhesives.

The results listed in the examples were determined with the aid of the following test methods.

To determine carboxyl end groups, 1 g of graft copolymer was dissolved in 50 ml of benzyl alcohol under nitrogen. The time required for this was not more than 20 min. The solution was titrated with a solution of KOH in ethylene glycol (0.05 mol KOH/l) using phenolphthalene as indicator, until the color changed.

To determine amino groups, 1 g of the graft copolymer was dissolved in 50 ml of m-cresol at 25°C. The solution was titrated potentiometrically with perchloric acid.

Solution viscosity η_{rel} (relative viscosity) was determined using a 0.5% strength by weight m-cresol solution at 25°C as in DIN 53727/ISO 307.

Comparative Example 1:

5.570 kg of adipic acid (38.12 mol) were melted at 160°C and transferred into a polymerization vessel heated to 180°C. A mixture made from 4.430 kg of hexamethylenediamine (38.12 mol), 440 g of water and 86 g of polyethyleneimine (Lupasol* G 100 from BASF AG, Ludwigshafen, Germany) was then metered in and the mixture brought to 220°C. The condensation was then started under a pressure of 20 bar for a period of 1.5 hours, followed by stepwise pressure reduction to atmospheric pressure, while at the same time the temperature was increased to 280°C. The viscosity of the reaction mixture rose sharply during this procedure, causing the stirrer to stop. It was impossible to discharge the product from the vessel.

Example 1:

8.0 kg of nylon-6,6 (Ultramid* A3 from BASF AG, Ludwigshafen, Germany) and 320 g of water were transferred into a pressure-tight polycondensation vessel with a gauge pressure of 0.2 bar set using nitrogen. This was followed by heating, without stirring, at 270°C for 7 hours, whereupon the pressure

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rose to 20 bar. The stirrer was then switched on and the pressure reduced to a residual water vapor pressure of 5 bar within a period of 3 hours. 80 g of polyethyleneimine (Lupasol* G 100 from BASF AG, Ludwigshafen, Germany) were then metered in and incorporated under autogenic pressure, and the pressure was then reduced to atmospheric pressure and nitrogen passed over the mixture at 270°C for 2 hours. The clear melt was discharged via a melt pump in the form of an extrudate, cooled in a water bath and then pelletized.

η_{rel}: 1.62
melting point T_m: 259°C
amino group concentration: 201 mmol/kg
carboxyl end group concentration: < 20 mmol/kg

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CLAIMS:

1. A graft copolymer which comprises the following monomer units:

a) from 0.5 to 25% by weight, based on the graft copolymer, of a polyamine having at least 11 nitrogen atoms and a number-average molecular weight M_n of at least 500; and

b) an equimolar combination of a diamine and a dicarboxylic acid as polyamide-forming monomers.

2. A graft copolymer as claimed in claim 1,

wherein the combination of the diamine and the dicarboxylic acid is hexamethylenediamine/adipic acid, hexamethylenediamine/dodecanedioic acid, octamethylenediamine/sebacic acid, decamethylenediamine/sebacic acid, decamethylenediamine/dodecanedioic acid, dodecamethylenediamine/dodecanedioic acid, dodecamethylenediamine/2,6-naphthalenedicarboxylic acid, decamethylenediamine/dodecanedioic acid/terephthalic acid, hexamethylenediamine/adipic and acid/terephthalic acid.

3. A graft copolymer as claimed in claim 1, wherein the combination of the diamine and the dicarboxylic acid is hexamethylenediamine/adipic acid.

4. A graft copolymer as claimed in any one of claims 1 to 3,

wherein the polyamine is a member selected from the group consisting of:

(i) a polyvinylamine,

(ii) a polyamine prepared from an alternating polyketone,

(iii) a dendrimer that is $((H_2N-(CH_2)_3)_2N-(CH_2)_3)_2-N-(CH_2)_2-N((CH_2)_2N((CH_2)_3NH_2)_2)_2$ or 3,15-bis(2-aminoethyl)-6,12-bis[2-[bis(2-aminoethyl)amino]ethyl]-9-[2-[bis[2-bis(2-aminoethyl)amino]ethyl]amino]ethyl-3,6,9,12,15-pentaazaheptadecane-1,17-diamine,

(iv) a linear polyethyleneimine prepared by polymerizing 4,5-dihydro-1,3-oxazole followed by hydrolysis, and

(v) a branched polyethyleneimine obtainable by polymerizing aziridine and having the following amino acid group distribution:

25-46% of primary amino groups;

30-45% of secondary amino groups; and

16-40% of tertiary amino groups.

5. A graft copolymer as claimed in claim 4, wherein the polyamine is the branched polyethyleneimine (v).

6. A graft copolymer as claimed in claim 4 or 5, wherein the polyamine has a number-average molecular weight M_n of 800 to 20,000.

7. A graft copolymer as claimed in any one of claims 1 to 6, which has an amino group concentration of from 100 to 2500 mmol/kg and an acid number of below 40 mmol/kg.

8. A graft copolymer as claimed in any one of claims 1 to 7, further comprising:

c) 95% or less by weight, based on the weight of polyamide graft chains, of a lactam, a ω-aminocarboxylic acid, or a combination thereof, as polyamide-forming monomer.

9. A graft copolymer as claimed in any one of claims 1 to 8, further comprising:

d) an oligocarboxylic acid, selected from the group consisting of from 0.015 to about 3 mol% of a dicarboxylic acid and from 0.01 to about 1.2 mol% of a tricarboxylic acid, based in each case on the total of the polyamide-forming monomers.

10. A process for preparing a graft copolymer as claimed in any one of claims 1 to 7, which comprises:

reacting a polyamide prepolymer with the polyamine, wherein the polyamide prepolymer consists essentially of the polyamide-forming monomers.

11. A process according to claim 10, which comprises:

a hydrolytic degradation of a polyamide consisting essentially of the polyamide-forming monomers to give the polyamide prepolymer;

simultaneously or subsequently reacting the polyamide prepolymer with the polyamine; and

then subjecting the reaction product of the polyamide prepolymer and the polyamine to a polycondensation at a temperature of 200 to 290°C under a stream of nitrogen or in vacuo.

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PATENT AGENTS