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(54) **POLYESTERAMIDES BIODEGRADABLES A SEGMENTS
POLYESTERS ET POLYAMIDES EN BLOCS**
(54) **BIODEGRADABLE POLYESTER AMIDES WITH
BLOCK-SHAPED POLYESTER AND POLYAMIDE
SEGMENTS**

(57) L'invention concerne des polyesteramides en blocs à structure amide ou ester, qui contiennent les monomères suivants: dialcools aliphatiques ou diols cycloaliphatiques, acide dicarboxylique aliphatique, également sous forme de l'ester correspondant, acides dicarboxyliques aromatiques, également sous forme des esters correspondants, acides hydroxycarboxyliques et lactones, amino-alcools, lactames cycliques, acides .omega.-aminocarboxyliques ou bien mélanges (sels dans un rapport 1:1) d'acides dicarboxyliques et de diamines. On obtient les polyesteramides selon l'invention par polycondensation d'un bloc ester à terminaison hydroxyle, acide ou ester et d'un bloc amide à terminaison amino-acide ou ester, la teneur en ester du polyesteramide étant comprise entre 20 et 80 % en poids et la teneur en amide entre 80 et 20 % en poids.

(57) The invention relates to block-shaped polyester amides with an amide or ester structure, containing the following monomers: aliphatic dialcohols or cycloaliphatic diols and/or aliphatic dicarboxylic acid also in the form of a corresponding ester and/or aromatic dicarboxylic acids also in the form of a corresponding ester and/or hydroxy carboxylic acids and lactone and/or amino alcohols and/or cyclic lactames, and/or .omega. amino carboxylic acids and/or mixtures (1:1 salts) of dicarboxylic acids and diamines, whereby the polyester amides can be obtained by polycondensation of a hydroxy, acid or ester terminated ester block and an amino acid or ester terminated amide block, whereby the ester content of the polyester amide is 20-80 wt. % and the amide content is 80-20 %.



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<p>(54) Title: BIODEGRADABLE POLYESTER AMIDES WITH BLOCK-SHAPED POLYESTER AND POLYAMIDE SEGMENTS</p>		
<p>(54) Bezeichnung: BIOLOGISCH ABBAUBARE POLYESTERAMIDE MIT BLOCKARTIG AUFGEBAUTEN POLYESTER- UND POLYAMID-SEGMENTEN</p>		
<p>(57) Abstract</p>		
<p>The invention relates to block-shaped polyester amides with an amide or ester structure, containing the following monomers: aliphatic dialcohols or cycloaliphatic diols and/or aliphatic dicarboxylic acid also in the form of a corresponding ester and/or aromatic dicarboxylic acids also in the form of a corresponding ester and/or hydroxy carboxylic acids and lactone and/or amino alcohols and/or cyclic lactams, and/or ω amino carboxylic acids and/or mixtures (1:1 salts) of dicarboxylic acids and diamines, whereby the polyester amides can be obtained by polycondensation of a hydroxy, acid or ester terminated ester block and an amino acid or ester terminated amide block, whereby the ester content of the polyester amide is 20-80 wt. % and the amide content is 80-20 %.</p>		
<p>(57) Zusammenfassung</p>		
<p>Gegenstand der Erfindung sind blockartig aufgebaute Polyesteramide mit Amid- oder Esterstruktur, die folgende Monomere enthalten: aliphatische Dialkohole oder cycloaliphatische Dirole und/oder aliphatische Dicarbonsäure auch in Form ihrer jeweiligen Ester und/oder aromatische Dicarbonsäuren auch in der Form ihrer jeweiligen Ester und/oder Hydroxycarbonsäuren und Lactone und/oder Aminoalkohole und/oder cyclische Lactame und/oder ω-Aminocarbonsäuren und/oder Mischungen (1:1 Salze) aus Dicarbonsäuren und Diaminen, wobei die Polyesteramide durch Polykondensation eines hydroxyl-, säure- oder esterterminierten Esterblocks und eines aminosäure- oder esterterminierten Amidblocks erhältlich sind und wobei der Estergehalt des Polyesteramids zwischen 20 und 80 Gew. % und der Amidgehalt 80 bis 20 Gew.-% beträgt.</p>		

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Biodegradable polyesteramides having polyester segments and polyamide segments of block construction

Compostable aliphatic polyesteramides are known (for example, EP-A 641 817). Compostable aliphatic-aromatic polyesteramides are also described (WO 92/21689, WO 96/21690, WO 96/21691 and WO 96/21692).

The structures described are constructed purely statistically and have no segmented block construction at all.

Polyesteramides of block construction are also known. Polyesteramides of block construction obtained by transesterification-/transamidation reactions of higher-molecular weight polyamides with higher molecular weight polyesters are described in EP-A 717 064, JP 0 430 6229, JP 0 701 0988 and JP 0 715 7557. Such reactions are reproducible only with difficulty, as the extent of the reactions depends very greatly on the operating conditions. Polyesteramides having such a block construction are not however sufficiently biodegradable.

The object of this invention is to provide segmented polyesteramides in block form, which are completely degradable biologically and by enzymes.

It has been found that acid-, ester-, hydroxyl- or amine-terminated short oligomers having amide or ester structures and molecular weights of not more than 3,000 are reacted with one another under mild conditions in such a way that this segmented structure is preserved.

The invention accordingly provides polyesteramides of block construction and having an amide structure or ester structure, which polyesteramides can be synthesised from the following monomers:

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- aliphatic dialcohols having preferably 2 to 12 carbon atoms, such as ethylene glycol, diethylene glycol, 1,4-butanediol, 1,3-propanediol, 1,6-hexanediol and cycloaliphatic diols such as cyclohexanedimethanol, and/or
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- aliphatic dicarboxylic acid having preferably 2 to 12 carbon atoms, such as oxalic acid, succinic acid, adipic acid, and others, also in the form of its respective esters (methyl, ethyl, etc.), and/or
- 10 - aromatic dicarboxylic acids, such as terephthalic acid, isophthalic acid, phthalic acid, and others, also in the form of their respective esters (methyl, ethyl, etc.), and/or
- Hydroxycarboxylic acids having preferably 2 to 12 C atoms, lactones, such as
15 caprolactone and others, and/or
- aminoalcohols having preferably 2 to 12 C atoms, such as ethanolamine, propanolamine, etc., and/or
- 20 - cyclic lactams, such as ϵ -caprolactam or lauryl lactam, etc., and/or
- ω -aminocarboxylic acids, such as aminocaproic acid, etc., and/or
- mixtures (1 : 1 salts) of dicarboxylic acids having preferably 2 to 12 C atoms,
25 such as adipic acid, succinic acid, terephthalic acid, etc., and of diamines having preferably 2 to 10 C atoms in the alkyl group, such as hexamethylenediamine, diaminobutane, etc.,

30 the polyesteramides being obtainable by polycondensation of a hydroxyl-, acid- or ester-terminated ester block and of an amino acid-terminated or ester-terminated amide block, the ester content of the polyesteramide being from 20 to 80 wt.%, preferably from 30 to 70 wt.%, and the amide content being from 80 to 20 wt.%, preferably from 70 to 30 wt.%.

For the synthesis of the polyesteramides, it is preferable to use caprolactam or AH salt or mixtures thereof with butanediol and/or diethylene glycol and terephthalic acid (ester) and adipic acid (ester).

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The short blocks produced, consisting of amide units or ester units, are prepared from the monomers according to methods known in polymer chemistry, by selecting the monomeric composition. For example, a polyamide block having a molecular weight of 598 and with acid end groups can be prepared from 3 mol adipic acid and 2 mol hexamethylenediamine.

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Equally, a polyester block having a molecular weight of 490 can be prepared from 2 mol adipic acid and 3 mol butanediol. If these two blocks are now reacted with one another in stoichiometric ratio, one obtains polyesteramides of block construction, containing short amide segments and ester segments, which do not interfere with the biodegradation process.

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In the preparation of the short blocks and also of the polyesteramides, suitable catalysts can be used in order to catalyse the esterification or amidation reaction. These include, for example, titanium compounds for the esterifications and phosphorus compounds for the amidation reactions. These catalysts are in accordance with prior art. They must not, however, subsequently restrict the use of the degradable polymer in the compost and they must not interfere with the biodegradability. For this reason catalysts based on heavy metals such as antimony or lead, for example, are completely dispensed with.

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The polyesteramides prepared in this way are completely biodegradable and compostable according to DIN 54 900 and have very good mechanical properties.

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The capacity of a polymer to be decomposed by enzymes is termed enzymic degradability. Here, the bonds by which the structural units of the polymer are linked together are broken. The resulting breakdown products are the monomers of the polymer and its oligomers. The enzymic degradation of the polymer leads to a decrease

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in its molecular weight. Enzymic degradation differs from biodegradation in that it does not as a rule lead to naturally-occurring metabolites.

5 In principle, all enzymes which are capable of breaking the bonds present in the polymer can be used as enzymes which degrade the biodegradable polymers. In selecting the enzymes, care is to be taken to ensure that these are capable of rapidly and completely degrading the polymer. The degradation is carried out in an aqueous solution, which can be buffered. The pH can be between 3 and 11, is preferably between 5 and 9 and particularly preferably between 6 and 8. The temperature at which
10 the enzymic degradation is carried out can be between 5°C and 95°C, is preferably between 20°C and 70°C and particularly preferably between 30°C and 50°C.

The following are examples of buffers which can be used according to the invention: citrate, acetate, phosphate, formate, carbonate, tris(hydroxymethyl)aminomethane,
15 triethanolamine, imidazole, oxalate, tartrate, fumarate, maleate, phthalate, succinate, ethylenediamine, as well as mixtures of several of these. Preferably acetate, phosphate and citrate are used as buffers.

The procedure is to add the enzyme and polymer to the aqueous solution. The
20 biodegradable polymer can be added in the form of a film, sheet or granules. Mouldings can be added as an intact whole or can be comminuted. Coated or bonded materials, or materials in the case of which coatings have been applied or bonds produced using biodegradable polymers, such as, for example, paper or cardboard, as well as coated paper or coated cardboard, can be added either as an intact whole or in
25 comminuted form to the enzyme-containing solution.

The aqueous enzyme-containing solution can also be applied by spraying, or sprayed, onto the coating to be degraded or onto the moulding to be degraded.

30 The enzymes used can be lipolytic and/or proteolytic enzymes.

For the purpose of this invention, lipases, cutinases, esterases, phospholipases and lysophospholipases are referred to as lipolytic enzymes. The lipolytic enzymes

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originate preferably from microorganisms. They originate in particular from bacteria, fungi or yeasts. The lipolytic enzymes may also be of vegetable or animal origin.

For the purpose of this invention, proteases are referred to as proteolytic enzymes.
5 These originate preferably from bacteria of the genus *Bacillus*; proteases of the organisms *Bacillus alcalophilus* and *Bacillus lichheniformis* are particularly preferred. They may also originate from fungi or from plants.

The joint use of lipolytic and proteolytic enzymes as well as of lipolytic enzymes of
10 varying specificity, which can lead to synergistic effects, is according to the invention. The addition of metal ions such as, for example, sodium ions or calcium ions, which accelerate the enzymic degradability, is also according to the invention. The addition of auxiliary substances such as anionic or nonionic surfactants such as, for example, sec. alcoholethoxylates, is also according to the invention.

15 Compostability is the capacity of a polymeric material to be biodegraded during a composting process. For the polymeric material to be regarded as compostable, it has to be proved by means of standard methods that it can be biodegraded in a composting system and that compost of flawless quality can be produced (according to DIN 54
20 900).

The biodegradation of a material is a process which is caused by biological activity and which leads to naturally-occurring metabolic end products, with alteration of the chemical structure of the material (according to DIN 54 900).

25 A polymeric material is biodegradable if all organic constituents are subject to a complete biological degradation, which is determined by standard processes (according to DIN 54 900).

30 The mixtures according to the invention may contain in addition from 0 to 80 wt.% of conventional additives, for example, inorganic fillers and reinforcing materials (for example, glass fibres, carbon fibres) and mineral fillers (for example, talc, mica, chalk, kaolin, wollastonite, gypsum, quartz, dolomite and others), UV stabilisers,

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antioxidants, pigments, dye, nucleating agents, accelerators or inhibitors of crystallisation, flow-promoting agents, lubricants, mould release agents, flameproofing agents.

- 5 The polyestaramides according to the invention may further contain from 0.05 to 5 wt.%, preferably from 0.1 to 1 wt.%, of branching agents. These branching agents can be, for example, trifunctional alcohols, such as trimethylolpropane or glycerol, tetrafunctional alcohols such as pentaerythritol, trifunctional carboxylic acids such as citric acid or even tri- or tetrafunctional hydroxycarboxylic acids.

Examples**Example 1**

- 5 Preparation of a hydroxyl-terminated oligoester block having a molecular weight of 490

292 g (2 mol) adipic acid and 270 g (3 mol) butanediol are heated together at 250°C under nitrogen. After 1 hour a water jet vacuum is applied and after 2.5 hours, an oil
10 pump vacuum. Water is distilled off. After a polycondensation time of 4 hours, a colourless wax having a hydroxyl value of 21 is obtained.

Example 2

- 15 Preparation of an ester-terminated oligoester block having a molecular weight of 1038

696 g (4 mol) dimethyl adipate and 270 g (3 mol) butanediol are heated together at 250°C under nitrogen. After 1 hour a water jet vacuum is applied and after 2.5 hours,
an oil pump vacuum. Methanol is distilled off. After a polycondensation time of 4
20 hours, a colourless wax is obtained.

Example 3

- 25 Preparation of an ester-terminated amide block having a molecular weight of 626

522 g (3 mol) dimethyl adipate and 180 g (2 mol) hexamethylenediamine are heated together at 250°C under nitrogen. After 1 hour a water jet vacuum is applied and after 2.5 hours, an oil pump vacuum. Methanol is distilled off. After a polycondensation
time of 3 hours, a colourless wax is obtained.

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Example 4

Preparation of an amino-terminated amide block having a molecular weight of 568

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292 g (2 mol) adipic acid and 348 g (3 mol) hexamethylenediamine are heated together at 250°C under nitrogen. After 1 hour a water jet vacuum is applied and after 2.5 hours, an oil pump vacuum. Water is distilled off. After a polycondensation time of 3 hours, a
5 colourless wax is obtained.

Example 5

Preparation of a polyesteramide from the individual blocks

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626 g (1 mol) of an ester-terminated amide block as in Example 3 and 490 g (1 mol) of a hydroxyl-terminated ester block as in Example 1 are heated together at 190°C under nitrogen. After 1 hour a water jet vacuum is applied and after 2.5 hours, an oil pump vacuum. Methanol is distilled off. After a polycondensation time of 7 hours, a
15 colourless polymer having a melting point of 136°C is obtained. The polymer obtained has good mechanical properties and is biodegradable according to DIN 54 900.

Claims

1. Polyesteramides of block construction, have an amide structure or ester structure, which contain the following monomers:

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- aliphatic dialcohols or cycloaliphatic alcohols and/or
- aliphatic dicarboxylic acid, also in the form of its respective esters and/or

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- aromatic dicarboxylic acids, also in the form of their respective esters and/or

- hydroxycarboxylic acids, lactones and/or

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- aminoalcohols and/or

- cyclic lactams and/or

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- ω -aminocarboxylic acids and/or

- mixtures (1 : 1 salts) of dicarboxylic acids and diamines,

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the polyesteramides being obtainable by polycondensation of a hydroxyl-, acid- or ester-terminated ester block and of an amino acid-terminated or ester-terminated amide block, the ester content of the polyesteramide being between 20 and 80 wt.% and the amide content being 80 to 20 wt.%.

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2. Polyesteramides according to claim 1, which have been formed by polycondensation of a mixture of 2 or more hydroxyl-, acid- or ester-terminated ester blocks and a mixture of 2 or more of an amino-, acid- or ester-terminated amide blocks.

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3. Use of the polyestamide according to claims 1 and 2 for the production of sheets, injection-moulded articles, nonwoven fabrics, fibres or foams.
4. Films, sheets, injection-moulded articles, nonwoven fabrics, fibres and foams,
5 produced from polyestamides according to claims 1 and 2.

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