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(54) Title: BLOCK COPOLYMERS AS SOIL RELEASE AGENTS IN LAUNDRY PROCESSES

(57) Abstract: The present invention relates to block copolymers which have been prepared by controlled free radical polymerization, the use of said block copolymers as soil release agents in laundry processes and a process to produce said block copolymers. Further aspects of the invention area method for easier releasing soil from textiles in laundry processes and detergent containing said block copolymers.

Block copolymers as soil release agents in laundry processes

Description

5 The present invention relates to block copolymers which have been prepared by controlled free radical polymerization, the use of said block copolymers as soil release agents in laundry processes and a process to produce said block copolymers. Further aspects of the invention are a method for easier releasing soil from textiles in laundry processes and detergent containing said block copolymers.

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In customary household washing methods, the problem exists that some types of soil and dirt are difficult to remove from textiles when using suboptimal detergent formulations and/or low wash temperatures, because these soils and dirt are strongly attached to the fiber surface or are strongly absorbed inside the fibers.

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The use of several agents as soil release agents in laundry processes is known. Examples are carboxymethyl cellulose or anionic derivatives of polymers from terephthalic acid and polyethylene glycol (see e.g. E. Smulders in "Laundry Detergents" Wiley-VCH Verlag GmbH, 2002, page 88). Regarding soil release agents it is often assumed that these are deposited and accumulated on the fiber surface during laundry washing, thereby modifying the surface properties of the fibers. Soil and dirt that is subsequently deposited onto this modified fiber surface is easier released in a subsequent washing cycle. In PCT/EP2012/071020 (not published yet) the use of one or more comb or block copolymers as soil antiredeposition agents and soil release agents in aqueous laundry processes has been described.

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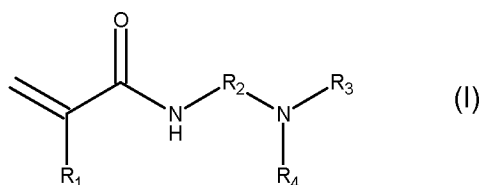
The objective of the present invention is to provide block copolymers for use as soil release agents in laundry processes. A further object is to provide liquid and powder detergent compositions suitable for that use.

30 It has now been found, surprisingly, that the mentioned objectives can be met to a great extent by block copolymers obtainable by controlled free radical polymerization, analogous transesterification of the block copolymer and optionally quaternization of the obtained block copolymer.

35 One aspect of the invention is a block copolymer obtainable by a process comprising the steps of

- a) polymerizing a C₁-C₁₀ alkyl ester of acrylic or methacrylic acid with controlled free radical polymerization;
- b) polymerizing the polymer of step a) with controlled free radical polymerization with
 - (i) one or more monomers according to the following formula (I):

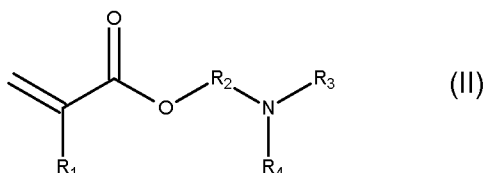
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wherein R_1 is hydrogen or C_{1-10} alkyl, R_2 is C_{1-20} alkyl and R_3 and R_4 are independently linear or branched C_1-C_{22} alkyl; or

(ii) one or more monomers according to the following formula (II):

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wherein R_1 is hydrogen or C_{1-10} alkyl, R_2 is C_{1-20} alkyl and R_3 and R_4 are independently linear or branched C_1-C_{22} alkyl; or

(iii) a mixture of monomers according to formula (I) and (II);

(iv) and optionally with styrene or 4-Vinylpyridine to form a block copolymer;

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c) modifying the block copolymer of step b) in a polymer analogous transesterification reaction with a primary or secondary alcohol;

d) optionally quaternizing of the block copolymer of step c).

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Any controlled free radical polymerization known in the art can be used to prepare the block copolymers of the present invention. Examples for controlled free radical polymerizations are atom transfer radical polymerization (see US 2004/0204556), nitroxide-mediated radical polymerization (see WO2006/0074969) or reversible addition-fragmentation chain transfer polymerization (see US6855840).

25

It has been found that the controlled free radical polymerisation (CFRP) is a tool for the preparation of block copolymers according to the present invention. The combination of CFRP with subsequent post-modification of the stabilizing block allows enlarging the possible groups that can be used in the above mentioned detergent applications. With one CFRP-process a large row of different polymer materials becomes available. Block and comb copolymers prepared in

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such a two step reaction are, for example, described in WO 2006/0074969.

Controlled free radical polymerization using alkoxyamines or stable nitroxyl radicals is a well known technique and has been described extensively in the last twenty years.

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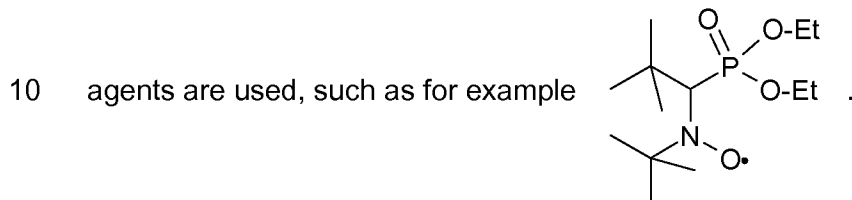
For example US 4,581,429 discloses a free radical polymerization process which controls the growth of polymer chains to produce short chain or oligomeric homopolymers and copolymers. The process employs an initiator having the formula (in part) $R'R''N-O-X$, where X is a free radical species capable of polymerizing unsaturated monomers and the radical $R'R''N-O\bullet$ is terminating the growing oligomer/polymer.

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US 5,322,912 discloses a polymerization process using a free radical initiator, a polymerizable monomer compound and a stable free radical agent of the basic structure R'R''N-O• for the synthesis of homopolymers and block copolymers which are terminated by the nitroxyl radical.

- 5 More recently further nitroxyl radicals and nitroxyl ethers have been described. WO 98/13392 for example describes open chain alkoxyamine compounds, which have a symmetrical substitution pattern and are derived from NO gas or from nitroso compounds.

WO 96/24620 describes a polymerization process in which very specific stable free radical



WO 98/30601 discloses specific nitroxyls based on imidazolidinons.

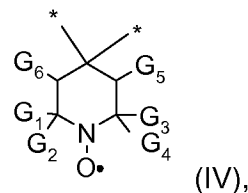
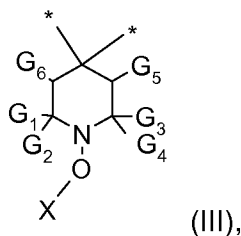
WO 98/44008 discloses specific nitroxyls based on morpholinones, piperazinones and piperazindiones.

- 15 These prior art nitroxyl radicals and nitroxyl ethers are all suitable for the instant invention. Thus, in a preferred embodiment, nitroxyl radicals and nitroxyl ethers are used in the process to prepare the block copolymers according to the present invention.

- 20 The nitroxylethers and nitroxyl radicals suitable for the invention are principally known from US 4,581,429 or EP-A-621 878. Particularly useful are the open chain compounds described in WO 98/13392, WO 99/03894 and WO 00/07981, the piperidine derivatives described in WO 99/67298, GB 2335190 and GB 2 361 235 or the heterocyclic compounds described in GB 2342649 and WO 96/24620. Recently further nitroxyl radicals and nitroxyl ethers have been
- 25 described in WO 02/48205, WO02/48109 and WO 02/100831.

Also suitable are the compounds described by Hawker et al, Chem. Commun., 2001, 823-824. Some compounds are commercially available or can be prepared according to the aforementioned documents.

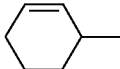
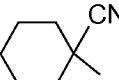
- For example, the structural element of the alkoxyamine, >N-O-X is a structural element of
- 30 formula (III) and the structural element of the stable nitroxyl radical, $\text{>N-O}\cdot$ is a structural element of formula (IV)



wherein

G₁, G₂, G₃, G₄ are independently C₁-C₆ alkyl or G₁ and G₂ or G₃ and G₄, or G₁ and G₂ and G₃ and G₄ together form a C₅-C₁₂ cycloalkyl group;

- 5 G₅, G₆ independently are H, C₁-C₁₈ alkyl, phenyl, naphthyl or a group COOC₁-C₁₈ alkyl;
X is selected from the group consisting of -CH₂-phenyl, CH₃CH-phenyl, (CH₃)₂C-phenyl, (C₅-

C₆cycloalkyl)₂CCN, (CH₃)₂CCN, , , -CH₂CH=CH₂, CH₃CH-CH=CH₂ (C₁-

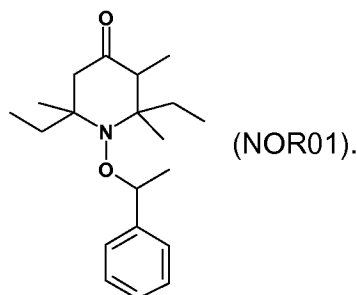
C₄alkyl)CR₂₀-C(O)-phenyl, (C₁-C₄)alkyl-CR₂₀-C(O)-(C₁-C₄)alkoxy, (C₁-C₄)alkyl-CR₂₀-C(O)-(C₁-C₄)alkyl, (C₁-C₄)alkyl-CR₂₀-C(O)-N-di(C₁-C₄)alkyl, (C₁-C₄)alkyl-CR₂₀-C(O)-NH(C₁-C₄)alkyl, (C₁-C₄)alkyl-CR₂₀-C(O)-NH₂, wherein R₂₀ is hydrogen or (C₁-C₄)alkyl and

- 10

* denotes a valence.

In a very specific embodiment of the present invention the alkoxyamine used for the controlled free radical polymerization is a compound of formula NOR01.

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Preferably the alkoxyamine compound is used in an amount from 0.01 mol-% to 30 mol-%, more preferably in an amount of from 0.1 mol-% to 20 mol-% and most preferred in an amount of from 0.1 mol-% to 10 mol-% based on the monomer.

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Because CFRP is a "living" polymerization, it can be started and stopped practically at will. Furthermore, the polymer product retains the functional alkoxyamine group allowing a continuation of the polymerization in a living matter. Thus, once the first monomer is consumed in the initial polymerizing step a second monomer can then be added to form a second block on the growing polymer chain in a second polymerization step. Therefore it is possible to carry out additional polymerizations with the same or different monomer(s) to prepare multi-block copolymers.

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Furthermore, since this is a radical polymerization, blocks can be prepared in essentially any order. One is not necessarily restricted to preparing block copolymers where the sequential polymerizing steps must flow from the least stabilized polymer intermediate to the most stabilized

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polymer intermediate, such as is the case in ionic polymerization. Thus, it is possible to prepare a multi-block copolymer in which a polyacrylonitrile or a poly(meth)acrylate block is prepared first and then a styrene block is attached thereto.

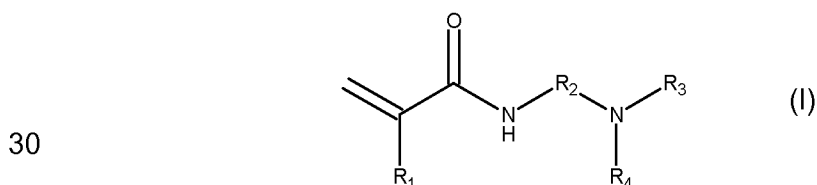
- 5 Furthermore, there is no linking group required for joining the different blocks of the present block copolymer. One can simply add successive monomers to form successive blocks. The blocks might be separated by a tapered zone, in which monomers of both the previous and continued block are present in different ratios.
- 10 A plurality of specifically designed polymers and copolymers are accessible such as star and graft (co)polymers as described, inter alia, by C. J. Hawker in *Angew. Chemie*, 1995, 107, pages 1623-1627, dendrimers as described by K. Matyaszewski et al. in *Macromolecules* 1996, Vol 29, No. 12, pages 4167-4171, graft (co)polymers as described by C. J. Hawker et al. in *Macromol. Chem. Phys.* 198, 155-166(1997), random copolymers as described by C. J. Hawker in
- 15 *Macromolecules* 1996, 29, 2686-2688, or diblock and triblock copolymers as described by N. A. Listigovers in *Macromolecules* 1996, 29, 8992-8993.

The block copolymer of the present invention may be prepared by using different combinations of monomers.

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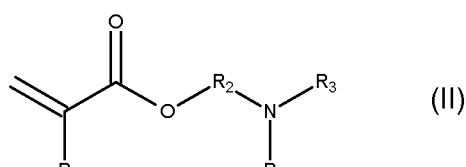
In a preferred embodiment, the block copolymer has been prepared in step a) from n-butylacrylate.

- 25 In a preferred embodiment, the block copolymer has been prepared in step a) from a C₁-C₁₀ alkyl ester of acrylic or methacrylic acid, preferably n-butylacrylate, and from one or more monomers according to the following formula (I) in step b):



- wherein R₁ is hydrogen or C₁₋₁₀ alkyl, R₂ is C₁₋₂₀ alkyl and R₃ and R₄ are independently linear or branched C₁-C₂₂ alkyl and optionally with styrene or 4-Vinylpyridine. In a more preferred embodiment, R₁ is hydrogen or methyl, R₂ is C₁₋₃ alkyl and R₃ and R₄ are independently linear or branched C₁-C₂₂ alkyl and optionally and optionally with styrene or 4-Vinylpyridine.
- 35

- In another preferred embodiment, the block copolymer has been prepared in step a) from a C₁-C₁₀ alkyl ester of acrylic or methacrylic acid, preferably n-butylacrylate, and from one or more monomers according to the following formula (II) in step b):
- 40



5 wherein R₁ is hydrogen or C₁₋₁₀ alkyl, R₂ is C₁₋₂₀ alkyl and R₃ and R₄ are independently linear or branched C_{1-C22} alkyl and optionally with styrene or 4-Vinylpyridine. In a more preferred embodiment, R₁ is hydrogen or methyl, R₂ is C₁₋₃ alkyl and R₃ and R₄ are independently linear or
10 branched C_{1-C22} alkyl and optionally with styrene or 4-Vinylpyridine.

10 Another preferred embodiment is the block copolymer that has been prepared in step a) from a C_{1-C10} alkyl ester of acrylic or methacrylic acid, preferably n-butylacrylate, and from a mixture of monomers according to formula (I) and (II) in step b) and optionally with styrene or 4-
15 Vinylpyridine.

15 In a further preferred embodiment, the monomer of step b) to be polymerized with polymers of a C_{1-C10} alkyl ester of acrylic or methacrylic acid, preferably n-butylacrylate, prepared in step a) is preferably selected from the group consisting of dialkylaminopropyl methacrylate, dialkylaminopropyl acrylate, 2-(dialkylamino)ethyl methacrylate, 2-(dialkylamino)ethyl acrylate, dialkylaminopropyl methacrylamide, dialkylaminopropyl acrylamide, 2-(dialkylamino)ethyl acrylamide
20 and 2-(dialkylamino)ethyl methacrylamide.

In another preferred embodiment, the monomer of step b) to be polymerized with polymers of a C_{1-C10} alkyl ester of acrylic or methacrylic acid, preferably n-butylacrylate, prepared in step a) is preferably selected from the group consisting of dimethylaminopropyl methacrylate, dimethylaminopropyl acrylate, 2-(dimethylamino)ethyl methacrylate, 2-(dimethylamino)ethyl acrylate, dimethylaminopropyl acrylamide, dimethylaminopropyl methacrylamide, 2-(dimethylamino)ethyl acrylamide and 2-(dimethylamino)ethyl methacrylamide.
25

30 In a more preferred embodiment, the monomer of step a) is n-butylacrylate and wherein the monomer of step b) is 2-(dimethylamino)ethyl methacrylate or dimethylaminopropyl methacrylamide.

In a further preferred embodiment, the monomer according to formula (I) in step b) is not 3-
35 dimethylaminopropylmethylacrylamide.

In a further embodiment, optionally styrene or 4-Vinylpyridine is added to the monomers of step b) as defined above. In a preferred embodiment, styrene or 4-Vinylpyridine is added to the monomers of step b) as defined above.

40 In a preferred embodiment, the monomers of step a) are present in the range of from 10 to 200 repeating units, more preferably in the range of from 30 to 100 repeating units.

In another preferred embodiment, the monomers of step b) in accordance with formula (I) and (II) as defined above are present in the range of from 1 to 100 repeating units, more preferably in the range of from 5 to 50 repeating units.

- 5 In a further preferred embodiment, styrene or 4-Vinylpyridine are present in the range of from 0 to 20 repeating units, more preferably in the range of from 1 to 20 repeating units or even more preferably in the range of from 1 to 10 repeating units.

10 The polydispersity (PDI) of a sample is defined as weight average molecular weight M_w divided by number average molecular weight M_n and gives an indication on how narrow a distribution is.

In a preferred embodiment, the block copolymer of the present invention has a polydispersity, PDI from 1.0 to 2.5. More preferably, the block copolymer of the present invention has a PDI from 1.1 to 2.0.

15 In another preferred embodiment, the block copolymer of the invention has amphiphilic properties.

20 When the controlled free radical polymerization is carried out with a nitroxyl radical an initiating radical source is additionally necessary for preparing the block copolymer of the invention. This radical source initiator is preferably an azo compound, a peroxide, perester or a hydroperoxide.

Specific preferred radical sources are 2,2'-azobisisobutyronitrile, 2,2'-azobis(2-methylbutyronitrile), 2,2'-azobis(2,4-dimethylvaleronitrile), 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile), 1,1'-azobis(1-cyclohexanecarbonitrile), 2,2'-azobis(isobutyramide) dihydrate, 2-phenylazo-2,4-dimethyl-4-methoxyvaleronitrile, dimethyl-2,2'-azobisisobutyrate, 2-(carbamoylethyl)isobutyronitrile, 2,2'-azobis(2,4,4-trimethylpentane), 2,2'-azobis(2-methylpropane), 2,2'-azobis(N,N'-dimethyleneisobutyramidine), free base or hydrochloride, 2,2'-azobis(2-amidinopropane), free base or hydrochloride, 2,2'-azobis{2-methyl-N-[1,1-bis(hydroxymethyl)ethyl]propionamide} or 2,2'-azobis{2-methyl-N-[1,1-bis(hydroxymethyl)-2-hydroxyethyl]propionamide; acetyl cyclohexane sulphonyl peroxide, diisopropyl peroxy dicarbonate, t-amyl perneodecanoate, t-butyl perneodecanoate, t-butyl perpivalate, t-amylperpivalate, bis(2,4-dichlorobenzoyl)peroxide, diisononoyl peroxide, didecanoyl peroxide, dioctanoyl peroxide, dilauroyl peroxide, bis(2-methylbenzoyl) peroxide, disuccinic acid peroxide, diacetyl peroxide, 35 dibenzoyl peroxide, t-butyl per 2-ethylhexanoate, bis-(4-chlorobenzoyl)-peroxide, t-butyl perisobutyrate, t-butyl permaleinate, 1,1-bis(t-butylperoxy)3,5,5-trimethylcyclohexane, 1,1-bis(t-butylperoxy)cyclohexane, t-butyl peroxy isopropyl carbonate, t-butyl perisononaoate, 2,5-dimethylhexane 2,5-dibenzoate, t-butyl peracetate, t-amyl perbenzoate, t-butyl perbenzoate, 2,2-bis(t-butylperoxy) butane, 2,2 bis(t-butylperoxy) propane, dicumyl peroxide, 2,5-dimethylhexane-2,5-di-t-butylperoxide, 3-t-butylperoxy 3-phenylphthalide, di-t-amyl peroxide, α , 40 α' -bis(t-butylperoxy isopropyl) benzene, 3,5-bis(t-butylperoxy)3,5-dimethyl 1,2-dioxolane, di-t-butyl peroxide, 2,5-dimethylhexyne-2,5-di-t-butylperoxide, 3,3,6,6,9,9-hexamethyl 1,2,4,5-

tetraoxa cyclononane, p-menthane hydroperoxide, pinane hydroperoxide, diisopropylbenzene mono- α -hydroperoxide, cumene hydroperoxide or t-butyl hydroperoxide.

5 The radical source is preferably present in an amount of from 0.01 mol-% to 30 mol-%, more preferred in an amount of from 0.1 mol-% to 20 mol-% and most preferred in an amount of from 0.5 mol-% to 10 mol-% based on the monomer.

10 In a preferred embodiment of the invention, the molar ratio of the radical source to the nitroxyl radical may be from 1:10 to 10:1, preferably from 1:5 to 5:1 and more preferably from 1:2 to 2:1.

The reaction conditions for the CFRP step a) are widely described in the documents listed above. In general the polymerization temperature is between 60 and 180° C at normal pressure and the reaction time may vary from 30 minutes to 20 hours.

15 The reaction conditions for the CFRP step b) are widely described in the documents listed above. In general the polymerization temperature is between 60 and 180° C at normal pressure and the reaction time may vary from 30 minutes to 20 hours.

20 In a preferred embodiment, the primary or secondary alcohol to be used in the transesterification of step c) is an ethoxylate of formula (A) $R_A-[O-CH_2-CH_2-]_n-OH$ (A) wherein R_A is saturated or unsaturated, linear or branched chain alkyl with 1–22 carbon atoms, or alkylaryl or dialkylaryl with up to 24 carbon atoms and n is 1 to 150;

a polydimethylsilicone oligomer of formula (B) $R_B-\left[\begin{array}{c} CH_3 \\ | \\ Si-O \\ | \\ CH_3 \end{array} \right]_n-R'-CH_2-OH$ (B)

25 wherein R_B is C_1 - C_{18} alkyl, phenyl or C_7 - C_{15} alkyl; n is 1 to 50 and R' is a linking group with 1 to 20 carbon atoms;

a partly or fully fluorinated primary alcohol; or

a C_8 to C_{60} alkyl linear or branched primary or secondary alcohol.

30 In the term alkylaryl, aryl means phenyl or naphthyl and alkyl is preferably C_1 - C_{20} linear or branched alkyl.

The term aralkyl means $-(C_1-C_7\text{alkyl})-C_6H_5$ or $-(C_1-C_3\text{alkyl})-C_{10}H_7$.

35 In a specifically preferred embodiment, the alcohol used in the process to prepare the block polymers of the present invention is a partly or fully fluorinated primary alcohol. Examples of commercial fluorinated alcohol mixtures are: Zonyl BA®, Zonyl BA-L®, Zonyl BA-LD®, Zonyl BA-N® from Du Pont or fluorinated polyoxetane alcohols from Omnova Solutions Inc.

In a more preferred embodiment, the primary alcohol of step b) used in the process to prepare the block copolymer of the invention is an ethoxylate of formula (A):

$R_A-[O-CH_2-CH_2-]_n-OH$ (A)

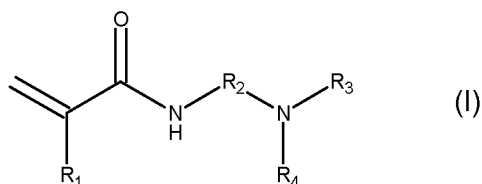
40 wherein R_A is saturated or unsaturated, linear or branched chain alkyl with 1–22 carbon atoms and n is 1 to 150.

In a most preferred embodiment, the primary alcohol is methoxy polyethylene glycol.

In accordance with the present invention, the block copolymers of the present invention described above can be quaternized in step d) by methods known in the art. Quaternization is carried out with cooking or without cooking (at room temperature) of the mixture comprising the block copolymer, the quaternization agent, and optionally solvent or water, as described e.g. in *Macromolecules* 1996, 29, 3416-3420. In a preferred embodiment, the block copolymer has a quaternization degree of 0 to 99%. In a more preferred embodiment, the block copolymer has a quaternization degree of 0 to 80%. In an even more preferred embodiment, the block copolymer has a quaternization degree of 20 to 80%. In a most preferred embodiment, the block copolymer has a quaternization degree of 20%, 50% or 80%. The quaternization degree can be determined via the reduction of amine number by titration. For instance, a quaternization degree of 20% means that the amine number is 20% reduced.

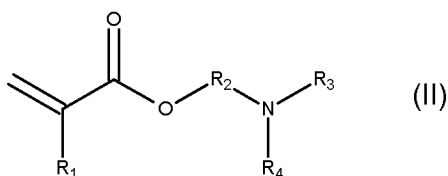
In a further embodiment, the block copolymer may be obtainable by using poly ethylene glycol monoethylether (MPEG) acrylate, siloxane acrylate, siloxane methacrylate, fluorinated acrylate, fluorinated methacrylate, C16/C18 alkyl acrylate in step a) of the process and thereby no analogous transesterification will be required after step b). Thus, another aspect of the invention is a block copolymer obtainable by a process comprising the steps of

- a) polymerizing a MPEG acrylate, siloxane acrylate, siloxane methacrylate, fluorinated acrylate, fluorinated methacrylate, C16/C18 alkyl acrylate with controlled free radical polymerization;
- b) polymerizing the polymer of step a) with controlled free radical polymerization with
 - (i) one or more monomers according to the following formula (I):



wherein R₁ is hydrogen or C₁₋₁₀ alkyl, R₂ is C₁₋₂₀ alkyl and R₃ and R₄ are independently linear or branched C_{1-C22} alkyl; or

- (ii) one or more monomers according to the following formula (II):



wherein R_1 is hydrogen or C_{1-10} alkyl, R_2 is C_{1-20} alkyl and R_3 and R_4 are independently linear or branched C_1-C_{22} alkyl; or

(iii) a mixture of monomers according to formula (I) and (II);

(iv) and optionally with styrene or 4-Vinylpyridine,

5 to form a block copolymer;

c) optionally quaternizing of the block copolymer of step b).

The preferred embodiments described above also apply to this block copolymer.

10 One other aspect of the present invention is a process as described above for the preparation of the block copolymer of the present invention.

A further aspect of the invention relates to the use of the block copolymer of the present invention as soil release agent in aqueous laundry processes.

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Typically the aqueous laundry process is a domestic laundry process.

For example the textile may be made from polyester, polyacrylate, cotton, wool, polyamide or mixtures thereof; preferably it is made from cotton.

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Another aspect of the invention is a method for soil release from textiles during an aqueous laundry process, which method comprises applying a block copolymer which is obtainable by, preferably which has been obtained by, a process comprising the steps of

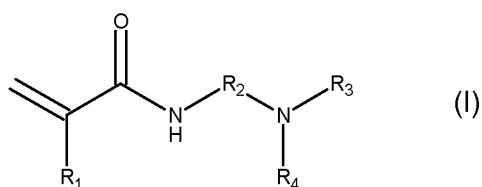
a) polymerizing a C_1-C_{10} alkyl ester of acrylic or methacrylic acid with controlled free radical polymerization;

25

b) polymerizing the polymer of step a) with controlled free radical polymerization with

(i) one or more monomers according to the following formula (I):

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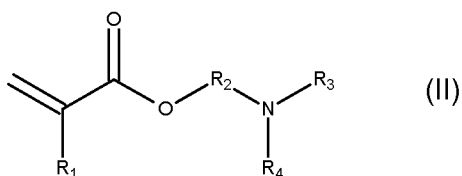


wherein R_1 is hydrogen or C_{1-10} alkyl, R_2 is C_{1-20} alkyl and R_3 and R_4 are independently linear or branched C_1-C_{22} alkyl; or

35

(ii) one or more monomers according to the following formula (II):

40



wherein R₁ is hydrogen or C₁₋₁₀ alkyl, R₂ is C₁₋₂₀ alkyl and R₃ and R₄ are independently linear or branched C_{1-C22} alkyl; or

(iii) a mixture of monomers according to formula (I) and (II);

(iv) and optionally with styrene or 4-Vinylpyridine,

5 to form a block copolymer;

c) modifying the block copolymer of step b) in a polymer analogous transesterification reaction with a primary or secondary alcohol; and

d) optionally quaternizing of the block copolymer of step c).

10 In a further embodiment, a method for soil release from textiles during an aqueous laundry process can be a method which comprises applying a block copolymer which has been prepared by using MPEG acrylate, siloxane acrylate, siloxane methacrylate, fluorinated acrylate, fluorinated methacrylate, C16/C18 alkyl acrylate in step a) of the process and thereby no step c), i.e. an analogous transesterification will be required after step b.)

15 When the block copolymer is used as part of a detergent it preferably is present in an amount of from 0.01 % by weight to 5 % by weight, based on the weight of the total detergent composition.

20 Also an aspect of the invention is a detergent comprising block copolymer according to the invention or a block copolymer which is obtainable by, preferably which has been obtained by, a process according to the invention, as disclosed above, in an amount of from 0.01 % by weight to 5 % by weight, preferably from 0.1 % by weight to 2 % by weight, based on the weight of the total detergent composition

25 The detergent according to the invention can be, for example, a bleach-containing heavy-duty detergent, a detergent for delicate textiles, or a detergent for colored goods. It can be solid, such as a powder, granulate, or tablet, or liquid, such as a structured (i.e. turbid) or unstructured (i.e. clear) liquid detergent based on water and/or one or more of organic solvents.

30 The detergent will normally include at least one surfactant which may be anionic, cationic, nonionic or amphoteric.

35 The anionic surfactant can be, for example, a sulfate, sulfonate or carboxylate surfactant or a mixture thereof. Preference is given to alkylbenzenesulfonates, alkyl sulfates, alkyl ether sulfates, olefin sulfonates, fatty acid salts, alkyl and alkenyl ether carboxylates or to an α -sulfonic fatty acid salt or an ester thereof.

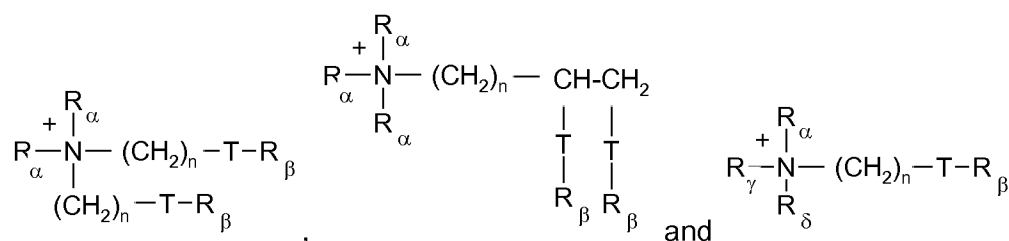
40 Preferred sulfonates are, for example, alkylbenzenesulfonates having from 10 to 20 carbon atoms in the alkyl radical, alkyl sulfates having from 8 to 18 carbon atoms in the alkyl radical, alkyl ether sulfates having from 8 to 18 carbon atoms in the alkyl radical, and fatty acid salts derived from palm oil or tallow and having from 8 to 18 carbon atoms in the alkyl moiety. The average molar number of ethylene oxide units added to the alkyl ether sulfates is from 1 to 20, preferably

from 1 to 10. The cation in the anionic surfactants is preferably an alkaline metal cation, especially sodium or potassium, more especially sodium. Preferred carboxylates are alkali metal sarcosinates of formula $R_{19}'\text{-CON}(R_{20}')\text{CH}_2\text{COOM}_1$ wherein R_{19}' is $C_9\text{-}C_{17}$ alkyl or $C_9\text{-}C_{17}$ alkenyl, R_{20}' is $C_1\text{-}C_4$ alkyl and M_1 is an alkali metal, especially sodium.

5 The non-ionic surfactant may be, for example, a primary or secondary alcohol ethoxylate, especially a $C_8\text{-}C_{20}$ aliphatic alcohol ethoxylated with an average of from 1 to 20 mol of ethylene oxide per alcohol group. Preference is given to primary and secondary $C_{10}\text{-}C_{15}$ aliphatic alcohols ethoxylated with an average of from 1 to 10 mol of ethylene oxide per alcohol group. Non-ethoxylated non-ionic surfactants, for example alkylpolyglycosides, glycerol monoethers and polyhydroxyamides (glucamide), may likewise be used.

15 In addition to or instead of anionic and/or non-ionic surfactants the composition may contain cationic surfactants. Possible cationic surfactants include all common cationic surface-active compounds, especially surfactants having a textile softening effect.

Non-limiting examples of cationic surfactants are given in the formulas below:



20 wherein
 each radical R_α is independent of the others C_{1-6} -alkyl-, -alkenyl- or -hydroxyalkyl; each radical R_β is independent of the others C_{8-28} -alkyl- or alkenyl;
 R_γ is R_α or $(\text{CH}_2)_n\text{-T-R}_\beta$;
 25 R_δ is R_α or R_β or $(\text{CH}_2)_n\text{-T-R}_\beta$; $T = \text{-CH}_2\text{-}$, -O-CO- or -CO-O- and
 n is between 0 and 5.

30 Preferred cationic surfactants include hydroxyalkyl-trialkyl-ammonium-compounds, especially C_{12-18} alkyl(hydroxyethyl)dimethylammonium compounds, and especially preferred the corresponding chloride salts.

Detergents of the present invention may contain up to 15 wt-%, for example between 0.5 wt-% and 15 wt-% of the cationic surfactant, based on the total weight of the composition.

35 The total amount of surfactants is preferably from 1 to 50 wt-%, especially from 1 to 40 wt-% and more especially from 1 to 30 wt-% of the detergent.

As builder substance there come into consideration, for example, alkali metal phosphates, especially tripolyphosphates, carbonates and hydrogen carbonates, especially their sodium salts, silicates, aluminum silicates, polycarboxylates, polycarboxylic acids, organic phosphonates, aminoalkylenepoly(alkylenephosphonates) and mixtures of such compounds.

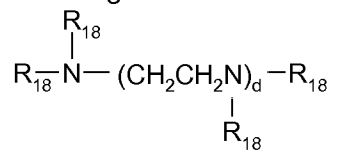
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Silicates that are especially suitable are sodium salts of crystalline layered silicates of the formula $\text{NaHSi}_t\text{O}_{2t+1} \cdot p\text{H}_2\text{O}$ or $\text{Na}_2\text{Si}_t\text{O}_{2t+1} \cdot p\text{H}_2\text{O}$ wherein t is a number from 1.9 to 4 and p is a number from 0 to 20.

10 Among the aluminum silicates, preference is given to those commercially available under the names zeolite A, B, X and HS, and also to mixtures comprising two or more of such components. Special preference is given to zeolite A.

15 Among the polycarboxylates, preference is given to polyhydroxycarboxylates, especially citrates, and acrylates, and also to copolymers thereof with maleic anhydride. Preferred polycarboxylic acids are nitrilotriacetic acid, ethylenediaminetetraacetic acid and ethylenediamine disuccinate either in racemic form or in the enantiomerically pure (S,S) form.

20 Phosphonates or aminoalkylenepoly(alkylenephosphonates) that are especially suitable are alkali metal salts of 1-hydroxyethane-1,1-diphosphonic acid, nitrilotris(methylenephosphonic acid), ethylenediaminetetramethylenephosphonic acid and diethylenetriaminepenta-methylenephosphonic acid, and also salts thereof. Also preferred polyphosphonates have the following formula



25 wherein

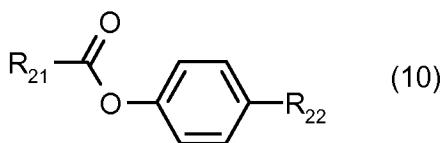
R_{18} is $\text{CH}_2\text{PO}_3\text{H}_2$ or a water soluble salt thereof and d is an integer of the value 0, 1, 2 or 3.

Especially preferred are the polyphosphonates wherein b is an integer of the value of 1.

30 As bleach component, which preferably is a peroxide bleach, there come into consideration hydrogen peroxide and compounds capable of yielding hydrogen peroxide in aqueous solutions, for example, the organic and inorganic peroxides known in the literature and available commercially that may bleach textile materials at conventional washing temperatures, for example at a temperature in the range of from 10 to 95°C. Preferably, however, inorganic peroxides are used,
35 for example persulfates, perborates, percarbonates and/or persilicates.

Peroxide bleach compounds may be utilized alone or in conjunction with a peroxyacid bleach precursor and/or a bleach catalyst. Peroxy acids precursors are often referred to as bleach activators. Suitable bleach activators include the bleach activators, that carry O- and/or N-acyl
40 groups and/or unsubstituted or substituted benzoyl groups. Preference is given to polyacylated

alkylenediamines, especially tetraacetylenediamine (TAED); acylated glycolurils, especially tetraacetyl glycol urea (TAGU), N,N-diacetyl-N,N-dimethylurea (DDU); sodium-4-benzoyloxy benzene sulphonate (SBOBS); sodium-1-methyl-2-benzoyloxy benzene-4-sulphonate; sodium-4-methyl-3-benzoyloxy benzoate; trimethyl ammonium toluoyloxy-benzene sulphonate; acylated triazine derivatives, especially 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine (DADHT); compounds of formula (6):



wherein R₂₂ is a sulfonate group, a carboxylic acid group or a carboxylate group, and wherein R₂₁ is linear or branched (C₇-C₁₅)alkyl, especially activators known under the names SNOBS, SLOBS and DOBA; nitrile compounds that form perimine acids with peroxides also come into consideration as bleach activators. These bleach activators may be used in an amount of up to 12 wt-%, preferably from 2-10 wt-% based on the total weight of the composition.

It is also possible to use bleach catalysts, which are commonly known, for example transition metal complexes as disclosed in EP 1194514, EP 1383857 or WO04/007657.

Further bleach catalysts are disclosed in: US 2001044401, EP 0458397, WO 9606154, EP 1038946, EP 0900264, EP 0909809, EP 1001009, WO 9965905, WO 0248301, WO 0060045, WO 02077145, WO 0185717, WO 0164826, EP 0923635, DE 19639603, DE102007017654, DE102007017657, DE102007017656, US 20030060388, EP 0918840B1, EP 1174491A2, EP 0805794B1, WO 9707192A1, US 6235695B1, EP 0912690B1, EP 832969B1, US 6479450B1, WO 9933947A1, WO 0032731A1, WO 03054128A1, DE102004003710, EP 1083730, EP 1148117, EP 1445305, US 6476996, EP 0877078, EP 0869171, EP 0783035, EP 0761809 and EP 1520910. If desired a bleach catalyst may be combined with a peroxyacid bleach precursor.

The detergent may comprise one or more optical brighteners, for example from the classes bis-triazinylamino-stilbenedisulfonic acid, bis-triazolyl-stilbenedisulfonic acid, bis-styryl-biphenyl or bis-benzofuranyl-biphenyl, α bis-benzoxalyl derivative, bis-benzimidazolyl derivative or coumarin derivative or a pyrazoline derivative.

The compositions may furthermore comprise one or more further additives. Such additives are, for example, dirt-suspending agents, for example sodium carboxymethylcellulose; pH regulators, for example alkali metal or alkaline earth metal silicates; foam regulators, for example soap; salts for adjusting the spray drying and the granulating properties, for example sodium sulfate; perfumes; and also, if appropriate, antistatics and softening agents such as, for example, smectite; pigments; and/or toning agents. These constituents should especially be stable to any bleaching agent, if such is employed.

If such auxiliaries are used they normally are added in a total amount of from 0.1 - 20 wt-%, preferably from 0.5 - 10 wt-%, especially from 0.5 - 5 wt-%, based on the total weight of the detergent.

- 5 Furthermore, the detergent may optionally also comprise enzymes. Enzymes can be added for the purpose of stain removal. The enzymes usually improve the action on stains caused by protein or starch, such as, for example, blood, milk, grass or fruit juices. Preferred enzymes are cellulases and proteases, especially proteases. Cellulases are enzymes that react with cellulose and its derivatives and hydrolyse them to form glucose, cellobiose and cellooligosaccharides.
- 10 Cellulases remove dirt and, in addition, have the effect of enhancing the soft handle of the fabric.

Examples of customary enzymes include, but are by no means limited to, the following: proteases as described in US 6,242 405, column 14, lines 21 to 32;

- 15 lipases as described in US 6,242,405, column 14, lines 33 to 46;
amylases as described in US 6,242,405, column 14, lines 47 to 56; and
cellulases as described in US 6,242,405, column 14, lines 57 to 64;
Commercially available detergent proteases, such as Alcalase[®], Esperase[®], Everlase[®], Savinase[®], Kannase[®] and Durazym[®], sold e.g. by NOVOZYMES A/S;
- 20 Commercially available detergent amylases, such as Termamyl[®], Duramyl[®], Stainzyme[®], Natalase[®], Ban[®] and Fungamyl[®], sold e.g. by NOVOZYMES A/S;
Commercially available detergent cellulases, such as Celluzyme[®], Carezyme[®] and Endolase[®], sold e.g. by NOVOZYMES A/S;
- 25 Commercially available detergent lipases, such as Lipolase[®], Lipolase Ultra[®] and Lipoprime[®], sold e.g. by NOVOZYMES A/S;
Suitable mannanases, such as Mannanaway[®], sold by NOVOZYMES A/S.

- The enzymes, when used, may be present in a total amount of from 0.01 to 5 wt-%, especially from 0.05 to 5 wt-% and more especially from 0.1 to 4 wt-%, based on the total weight of the detergent.
- 30

- Further preferred ingredients in a detergent according to the invention are dye-fixing agents and/or polymers which, during the washing of textiles, prevent staining caused by dyes in the washing liquor that have been released from the textiles under the washing conditions. Such
- 35 polymers are preferably polyvinylpyrrolidones, polyvinylimidazoles or polyvinylpyridine-N-oxides, which may have been modified by the incorporation of anionic or cationic substituents, especially those having a molecular weight in the range of from 5000 to 60 000, more especially from 10 000 to 50 000. If such polymers are used, they are usually used in a total amount of from 0.01 to 5 wt-%, especially from 0.05 to 5 wt-%, more especially from 0.1 to 2 wt-%, based on
- 40 the total weight of the detergent formulation. Preferred polymers are those mentioned in WO-A-02/02865 (see especially page 1, last paragraph and page 2, first paragraph) and those in WO-A-04/05688.

It is also possible to employ a block copolymer according to the invention or obtainable by a process according to the invention in combination with a conventional soil-release polymer obtainable from dicarboxylic acid and optionally polymeric diol, in order to further enhance the cleaning power of laundry detergents when washing fabrics. In the context of a detergent according to the invention, such combinations are also possible. The known polyester soil-release polymers that can be additionally incorporated or used include copolyesters of dicarboxylic acids, for example adipic acid, phthalic acid, terephthalic acid or sulfoisophthalic acid, with diols, for example ethylene glycol or propylene glycol, and optionally polydiols, for example polyethylene glycol or polypropylene glycol.

The detergent according to the invention may also optionally contain one or more heavy metal chelating agents, such as hydroxyethyldiphosphonate (HEDP). More generally, chelating agents suitable for use herein can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures thereof. Other suitable chelating agents for use herein are the commercial DEQUEST series, and chelants from Nalco, Inc. Aminocarboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexacetates, diethylenetriamine-pentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts thereof and mixtures thereof. Aminophosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates). Further biodegradable sequestrants are, for example, aminoacid acetates, such as Trilon M (BASF) and Disolvine GL (AKZO), as well as asparaginic acid derivatives, such as Baypure CX. Preferably, the aminophosphonates do not contain alkyl or alkenyl groups with more than about 6 carbon atoms. A highly preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"). If utilized, such chelating agents or transition-metal selective sequestrants will generally comprise from about 0.001 wt-% to about 10 wt-%, more preferably from about 0.05 wt-% to about 1 wt-% of the laundry detergent compositions herein.

A preferred detergent according to the invention may additionally contain a dispersant polymer. When present, a dispersant polymer is typically at levels in the range from 0 wt-% to about 25 wt-%, preferably from about 0.5 wt-% to about 20 wt-%, more preferably from about 1 wt-% to about 8 wt-% of the detergent.

Suitable polymers are preferably at least partially neutralized or alkali metal, ammonium or substituted ammonium (e.g., mono-, di- or triethanolammonium) salts of polycarboxylic acids. The alkali metal, especially sodium salts are most preferred. While the molecular weight of the polymer can vary over a wide range, it preferably is from about 1,000 to about 500,000, more preferably is from about 1,000 to about 250,000.

Unsaturated monomeric acids that can be polymerized to form suitable dispersant polymers include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalononic acid. The presence of monomeric segments containing no carboxylate radicals such as methyl vinyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 50 wt-% of the dispersant polymer.

Copolymers of acrylamide and acrylate having a molecular weight of from about 3,000 to about 100,000, preferably from about 4,000 to about 20,000, and an acrylamide content of less than about 50 wt-%, preferably less than about 20 wt-% of the dispersant polymer can also be used. Most preferably, such dispersant polymer has a molecular weight of from about 4,000 to about 20,000 and an acrylamide content of from about 0 wt-% to about 15 wt-%, based on the total weight of the polymer.

Particularly preferred dispersant polymers are low molecular weight modified polyacrylate copolymers. Such copolymers contain as monomer units: a) from about 90 wt-% to about 10 wt-%, preferably from about 80 wt-% to about 20 wt-% acrylic acid or its salts and b) from about 10 wt-% to about 90 wt-%, preferably from about 20 wt-% to about 80 wt-% of a substituted acrylic monomer or its salt and have the general formula:

$-\text{[C(R}_a\text{)C(R}_b\text{)(C(O)OR}_c\text{)]}$ wherein the apparently unfilled valencies are in fact occupied by hydrogen and at least one of the substituents R_a , R_b , or R_c , preferably R_a or R_b , is a 1 to 4 carbon alkyl or hydroxyalkyl group; R_a or R_b can be a hydrogen and R_c can be a hydrogen or alkali metal salt. Most preferred is a substituted acrylic monomer wherein R_a is methyl, R_b is hydrogen, and R_c is sodium.

A suitable low molecular weight polyacrylate dispersant polymer preferably has a molecular weight of less than about 15,000, preferably from about 500 to about 10,000, most preferably from about 1,000 to about 5,000. The most preferred polyacrylate copolymer for use herein has a molecular weight of about 3,500 and is the fully neutralized form of the polymer comprising about 70 wt-% acrylic acid and about 30 wt-% methacrylic acid.

Other dispersant polymers useful herein include the polyethylene glycols and polypropylene glycols having a molecular weight of from about 950 to about 30,000.

Yet other dispersant polymers useful herein include the cellulose sulfate esters such as cellulose acetate sulfate, cellulose sulfate, hydroxyethyl cellulose sulfate, methylcellulose sulfate, and hydroxypropylcellulose sulfate. Sodium cellulose sulfate is the most preferred polymer of this group.

Other suitable dispersant polymers are the carboxylated polysaccharides, particularly starches, celluloses and alginates.

Yet another group of acceptable dispersants are the organic dispersant polymers, such as poly-aspartate.

5 Organic solvents that can be used in a detergent according to the invention, especially when the latter are in liquid or paste form, include alcohols having from 1 to 4 carbon atoms, especially methanol, ethanol, isopropanol and tert-butanol, diols having from 2 to 4 carbon atoms, especially ethylene glycol and propylene glycol, and mixtures thereof, and the ethers derivable from the mentioned classes of compound. Such water-miscible solvents are present in the cleaning formulations according to the invention preferably in amounts not exceeding 20 wt-%, especially
10 in amounts of from 1 wt-% to 15 wt-%.

The detergent formulations can take a variety of physical forms such as, for example, powder granules, tablets (tabs), gel and liquid. Examples thereof include, *inter alia*, conventional high-performance detergent powders, supercompact high-performance detergent powders, conventional heavy duty liquid detergents, highly concentrated gels and tabs.
15

The detergent may also be in the form of an aqueous liquid containing from 5 wt-% to 90 wt-%, preferably from 10 wt-% to 70 wt-%, of water, or in the form of a non-aqueous liquid containing no more than 5 wt-%, preferably from 0 wt-% to 1 wt-% of water. Non-aqueous liquid detergent formulations may comprise other solvents as carriers. Low molecular weight primary or secondary alcohols, for example methanol, ethanol, propanol and isopropanol, are suitable for that purpose. The solubilising surfactant used is preferably a monohydroxy alcohol but polyols, such as those containing from 2 to 6 carbon atoms and from 2 to 6 hydroxy groups (e.g., 1,3-propanediol, ethylene glycol, glycerol and 1,2-propanediol) can also be used. Such carriers are usually used in a total amount of from 5 wt-% to 90 wt-%, preferably from 10 wt-% to 50 wt-%, based on the total weight of the detergent formulation. The detergent formulations can also be used in so-called "unit liquid dose" form.
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25

The definitions and preferences given above apply equally for all aspects of the invention.
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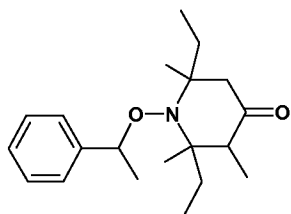
The following examples illustrate the invention.

Abbreviations and Reagents:

GPC: gel permeation chromatography
35 PS-Standard: polystyrene standards for GPC calibration
mbar = millibar
THF: tetrahydrofurane
n-BA: n-butylacrylate
MPEG500 (poly ethylene glycol monomethylether with Mn of 500 g/mol, obtainable from the company Clariant)
40 MPEG1000 (poly ethylene glycol monomethylether with Mn of 1000 g/mol, obtainable from the company Clariant)

quat: quaternized

NOR 01: polymerization regulator, which is prepared according to GB 2335190.



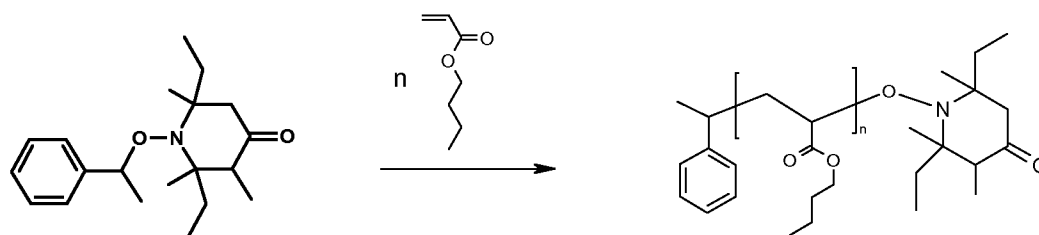
NOR 01

- 5 The transesterification proceeds at random. It should, however, be noted that the abbreviated names e.g. poly(n-BA-co-MPEG500A) of Example 1, do not mention the end groups on both sides of the polymer, i.e. the 1-phenyl-ethyl group and the NOR fragment. The designation -co- in the abbreviated names indicates that the monomers formally constituting the polymer, in this example n-BA and MPEG500-acrylate, are present at random.
- 10 The designation -b-, as shown in example 1, of poly(n-BA-b-DMAPMA-co-STY), means that the polymer consists of two defined blocks, the first of n-BA monomer units and the second block of random copolymer of DMAPMA monomer units and STY means styrene.

Examples

15

A) Preparation of the block copolymers

Example A: Synthesis of a linear polymer poly(n-BA)

10 In a 2000 ml flask, 302.8 g of n-butylacrylate (nBA) and 15.0 g of NOR 1 were mixed. The mixture was stirred at room temperature and inerted for 1 h by a nitrogen stream. The temperature was increased from 25 to 115°C and the reaction medium was reacted at 115°C under a nitrogen atmosphere until the solid content reached 20%. Then, the internal temperature was increased from 115°C to 125°C and a dosage of further 605.6 g of n-butylacrylate was added during 120 minutes. The reaction medium was stirred under a nitrogen stream at 125°C until the solid content reached the target value of 50%. Residual monomers and solvents were distilled off at 70°C under vacuum (GPC: THF, PS-Standard, Mn = 9,500 g/mol, PDI = 1.20).

Example B1: Synthesis of a block copolymer poly(n-BA-b-DMAPMA-co-STY)

15
20 In a 500 ml flask equipped with a magnetic stirring bar and a distillation column 102 g of poly(n-BA) according to Example A and 44 g of dimethylaminopropyl methacrylamide (DMAPMA) and 4.5 g styrene were loaded. The mixture was heated under N₂ gas to 145°C. The reaction was terminated after 4.5 hours and non-reacted monomer DMAPMA was distilled off under vacuum. Finally, 127 g high viscous block copolymer was obtained (GPC: THF, PS-standard, Mn=10,500 g/mol, PDI=1.30).

Example B2: Synthesis of a block copolymer poly(n-BA-b-DMAEMA-co-STY)

25
30 In a 500 ml flask equipped with a magnetic stirring bar and distillation column 100 g of poly(n-BA) according to Example A and 50 g of 2-(dimethylamino)ethyl methacrylate (DMAEMA) and 5 g styrene were loaded. The mixture was heated under N₂ gas to 145°C. The reaction was terminated after 4 hours and non-reacted monomer DMAEMA was distilled off under vacuum. Finally, 133 g high viscous block copolymer was obtained (GPC: THF, PS-standard, Mn=11,000 g/mol, PDI=1.33).

Example 1: Synthesis of poly(n-BA-co-MPEG500A-b-DMAPMA-co-STY)

Transesterification with MPEG500 40wt%

35 In a 100 ml flask equipped with an overhead propeller stirrer and a distillation column with dry ice acetone cooling 60.0 g of poly(n-BA-b-DMAPMA-co-STY) according to Example B1 and 40 g of MPEG500 (Mn = 500 g/mol) were added and dried by degasing at 80°C for 60 min at 50 mbar. The clear reaction mass in the flask was heated to 135°C. Two portions of 100 mg of Lithium tert-butoxide were added during 5 hours at 130-135°C. The formed n-butanol was distilled

off at reduced pressure (10 mbar). Finally, a brownish viscous liquid was obtained (GPC: THF, PS-standard, Mn=12,800 g/mol, PDI=1.55).

Example 2: Synthesis of poly(n-BA-co-MPEG500A-b-DMAEMA-co-STY)

5 Transesterification with MPEG500 40wt%

In a 100 ml flask equipped with an overhead propeller stirrer and a distillation column with dry ice acetone cooling 60 g of poly(n-BA-b-DMAEMA-co-STY) according to Example B2 and 40 g of MPEG500 (Mn = 500 g/mol) were added and dried by degasing at 80°C for 60 min at 50 mbar. The clear reaction mass in the flask was heated to 135°C. One portion of 1.3 g of titanium (IV) butoxide was added during 5 hours at 130-135°C. The formed n-butanol was distilled off at reduced pressure (10 mbar). Finally, a brownish viscous liquid was obtained (GPC: THF, PS-standard, Mn=12,500 g/mol, PDI=1.50).

Example 3: Synthesis of poly(n-BA-co-MPEG500A-b-DMAEMA-co-STY)

15 Transesterification with MPEG500 55wt%

In a 100 ml flask equipped with an overhead propeller stirrer and a distillation column with dry ice acetone cooling 45 g of poly(n-BA-b-DMAEMA-co-STY) according to Example B2 and 55 g of MPEG500 (Mn = 500 g/mol) were added and dried by degasing at 80°C for 60 min at 50 mbar. The clear reaction mass in the flask was heated to 135°C. One portion of 1.3 g of titanium (IV) butoxide was added during 5 hours at 130-135°C. The formed n-butanol was distilled off at reduced pressure (10 mbar). Finally, a brownish viscous liquid was obtained (GPC: THF, PS-standard, Mn=13,000 g/mol, PDI=1.52).

Example 4: Synthesis of poly(n-BA-co-MPEG1000A-b-DMAEMA-co-STY)

25 Transesterification with MPEG1000 40wt%

In a 100 ml flask equipped with an overhead propeller stirrer and a distillation column with dry ice acetone cooling 60 g of poly(n-BA-b-DMAEMA-co-STY) according to Example B2 and 40 g of MPEG1000 (Mn = 1000 g/mol) were added and dried by degasing at 80°C for 60 min at 50 mbar. The clear reaction mass in the flask was heated to 135°C. One portion of 1.3 g of titanium (IV) butoxide was added during 5 hours at 130-135°C. The formed n-butanol was distilled off at reduced pressure (10 mbar). Finally, a brownish viscous liquid was obtained (GPC: THF, PS-standard, Mn=13,000 g/mol, PDI=1.52).

Example 5: Quaternization with ethylbromide (20% quat.) of block copolymer poly(n-BA-co-MPEG500A-b-DMAPMA-co-STY) according to Example 1

35 In a 100 ml flask equipped with an overhead propeller stirrer, 20 g of poly(n-BA-co-MPEG500A-b-DMAPMA-co-STY) according to Example 1 were dissolved in 30 g of water, and 0.31 g of ethylbromide (quaternization agent) was added at room temperature. The clear solution was stirred for 3 hours at 40°C and further 3 hours at 60°, and subsequently cooked under vacuum (50 mbar) for 1 hour. Finally, a brownish viscous soil release polymer solution was obtained (40 wt% active) (GPC: THF, PS-standard, Mn=13,200 g/mol, PDI=1.56).

Examples 6 to 16: Quaternization of block copolymers according to Examples 2 to 4

In analogous way as described for the synthesis of poly(n-BA-co-MPEG500A-b-DMAPMA[quat⁺]-co-STY) (see Example 5), Examples 6 to 16 were prepared. The results and the reaction conditions are summarized in Table 1. Examples 6 to 8: Block copolymer of Example 2 quat. with ethylbromide 20%, 50% and 80%; Examples 9 and 10: Block copolymer of Examples 3 and 4 quat. with ethylbromide 20%; Examples 11 to 16: Block copolymer of Example 2 quat. with different quat. agents

Table 1: Quaternization of block copolymers according to Examples 2 to 4

Examples	Block copolymer (Example/amount in g)	Quaternization agent (amount in g)	Conditions	Mn (g/mol)	PDI
6	Example 2 20 g	Ethylbromide 0.50 g	3 h at 40°C, 3 h at 60°C, 1 h at 60°C (50 mbar)	13,100	1.56
7	Example 2 20 g	Ethylbromide 1.25 g	3 h at 40°C, 3 h at 60°C, 1 h at 60°C (50 mbar)	13,500	1.54
8	Example 2 20 g	Ethylbromide 2.00 g	3 h at 40°C, 3 h at 60°C, 1 h at 60°C (50 mbar)	13,800	1.57
9	Example 3 20 g	Ethylbromide 0.38 g	3 h at 40°C, 3 h at 60°C, 1 h at 60°C (50 mbar)	13,900	1.58
10	Example 4 20 g	Ethylbromide 0.50 g	3 h at 40°C, 3 h at 60°C, 1 h at 60°C (50 mbar)	14,100	1.58
11	Example 2 20 g	Propyliodide 0.79 g	3 h at 60°C, 3 h at 90°C, 1 h at 90°C (50 mbar)	13,500	1.57
12	Example 2 20 g	2-chlorobenzylchloride 0.81 g	6h at 60°C	14,200	1.60
13	Example 2 20 g	Glycidol 0.34 g	6 h at 70°C	13,800	1.58
14	Example 2	p-toluenesulfonic	2 h at 70°C	13,100	1.52

	20 g	acid monohydrate 0.79 g			
15	Example 2 20 g	1,4-butane sultone 0.58 g	6 h at 80°C	13,900	1.60
16	Example 2 20 g	Diethyl sulfate 0.70 g	6 h at 80°C	13,300	1.57

B) Application Examples

5 Example 17: Testing of soil release effect of the block copolymers of the invention in liquid detergents

Washing machine: Miele W 918 Novotronic®

Washing temperature: 20 °C

Liquor volume: 17 l

10 Water hardness: 16°dH (German hardness degree)

Ballast textiles: Clean laundry (Pillow, tricot, dish towels); 3.5 kg including the test textiles

15 The laundry including the cotton and polyester test textiles was washed three times with a wash liquor comprising 75 ml of either detergent E1 or V1 (see composition in Table 2) according to the conditions given above. After the washing process, the laundry was air-dried.

Table 2: Detergent composition [wt-%]:

	V1	E1
C ₁₂₋₁₄ -fatty alcohol with 7 EO	7	7
C ₁₂₋₁₈ -fatty acid, Na-salt	10	10
Boric acid	4	4
Citric acid	2	2
Propanediol	6	6
NaOH	3	3
Protease	0,6	0,6
Amylase	0,1	0,1
Block copolymer of Examples 1 to 16	-	1.5
H ₂ O	ad 100	

20 Subsequently, the test textiles were soiled with standardized fat/pigment stains (A: Make-up; B: Lipstick; C: sebum) and the stained test textiles were kept for 7 days at room temperature. The test textiles, together with the ballast textiles, were then washed with the wash liquors comprising the same detergent V1 or E1 (again in an amount of 75 ml) under the conditions given

above. The CIE brightness Y of the test textiles was measured with a DATA-COLOR Spectra Flash SF500 remission spectrometer.

In Table 3 the performance results are shown (mean value of brightness Y of 6 washing procedures). A significant increase in Y of the stained test textiles was observed when using wash liquors comprising detergents with the block copolymers of the invention (E1). Thus, detergents comprising block copolymers of the invention (E1) have a significantly increased washing performance as compared to a detergent without such polymer (V1) as can be derived from Table 3.

10

Table 3: Performance results

Detergent	Make-up on cotton	Lipstick on cotton	Sebum on cotton	Lipstick on polyester
V1	40,0	39,4	39,5	41,2
E1-polymer 1	43,0	42,1	43,0	43,0
E1-polymer 2	47,4	46,2	47,5	47,0
E1-polymer 3	44,1	44,5	45,6	45,1
E1-polymer 4	45,6	44,3	43,2	45,0
E1-polymer 5	42,8	43,9	45,8	44,1
E1-polymer 6	46,3	46,3	47,0	46,2
E1-polymer 7	45,1	45,0	45,1	45,6
E1-polymer 8	44,9	44,8	44,9	45,1
E1-polymer 9	43,8	42,1	43,5	44,8
E1-polymer 10	42,8	42,6	43,8	43,9
E1-polymer 11	44,9	45,8	45,0	46,1
E1-polymer 12	45,0	45,2	44,5	46,1
E1-polymer 13	45,1	44,8	44,2	44,6
E1-polymer 14	44,8	45,0	44,8	45,6
E1-polymer 15	45,6	45,6	46,2	45,8
E1-polymer 16	44,2	45,1	44,6	44,7

Example 18: Testing of soil release effect of the block copolymers of the invention in powder detergents

15

Example 17 was repeated by substituting the detergents V1 and E1, respectively, by the powder detergents V2 and E2 (see composition in Table 4), which were used in amounts of 75 g per wash liquor.

Table 4: Detergent composition [wt-%]:

	V2	E2
C ₁₂₋₁₈ -fatty alcohol with 7 EO	2	2
C ₁₂₋₁₈ -fatty alcohol sulfate with 7 EO, sodium salt	1,5	1,5

Linear alkylbenzol sulfonate, sodium salt	10	10
Sodium carbonate	20	20
Sodium hydrogen carbonate	6,5	6,5
Sodium disilicate	4	4
Sodium percarbonate	17	17
TAED	4	4
Polyacrylates, sodium salt	3	3
carboxymethylcellulose	1	1
Sodium phosphoante	1	1
Sodium sulfate	25	25
Mix of enzymes	1	1
Block copolymer of Examples 1 to 16	-	1.5

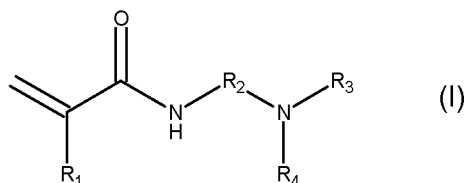
In Table 5 the performance results are shown (mean value of brightness Y of 6 washing procedures). A significant increase in Y of the stained test textiles was observed when using wash liquors comprising detergents with the block copolymers of the invention (E2). Thus, detergents comprising block copolymers of the invention (E2) have a significantly increased washing performance as compared to a detergent without such polymer (V2) as can be derived from Table 5.

Table 5: Performance results of powder detergent (with selected polymers only)

	Make-up on cotton	Lipstick on cotton	Sebum on cotton	Lipstick on polyester
V2	46,2	44,8	47,8	49,0
E2-polymer 2	52,6	51,7	51,8	52,2
E2-polymer 6	51,5	51,7	50,5	51,9
E2-polymer 7	51,2	49,2	51,0	50,1
E2-polymer 8	50,7	47,9	50,7	49,8
E2-polymer 15	49,8	47,6	50,9	51,0

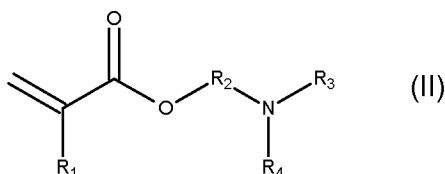
Claims

1. A block copolymer obtainable by a process comprising the steps of
- a) polymerizing a C₁-C₁₀ alkyl ester of acrylic or methacrylic acid with controlled free radical polymerization;
- b) polymerizing the polymer of step a) with controlled free radical polymerization with
- (i) one or more monomers according to the following formula (I):



wherein R₁ is hydrogen or C₁₋₁₀ alkyl, R₂ is C₁₋₂₀ alkylene and R₃ and R₄ are independently linear or branched C₁-C₂₂ alkyl; or

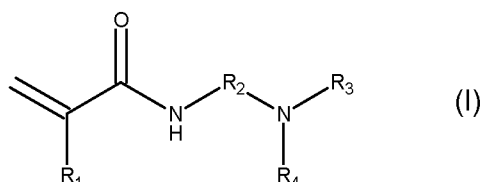
- (ii) one or more monomers according to the following formula (II):



wherein R₁ is hydrogen or C₁₋₁₀ alkyl, R₂ is C₁₋₂₀ alkylene and R₃ and R₄ are independently linear or branched C₁-C₂₂ alkyl; or

- (iii) a mixture of monomers according to formula (I) and (II);
- (iv) and optionally with styrene or 4-Vinylpyridine, to form a block copolymer;
- c) modifying the block copolymer of step b) in a polymer analogous transesterification reaction with a primary or secondary alcohol; and
- d) optionally quaternizing of the block copolymer of step c).

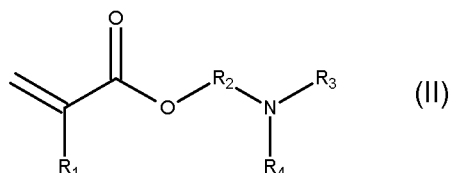
2. A block copolymer obtainable by a process comprising the steps of
- a) polymerizing a MPEG acrylate, siloxane acrylate, siloxane methacrylate, fluorinated acrylate, fluorinated methacrylate, C₁₆/C₁₈ alkyl acrylate with controlled free radical polymerization;
- b) polymerizing the polymer of step a) with controlled free radical polymerization with
- (i) one or more monomers according to the following formula (I):



wherein R_1 is hydrogen or C_{1-10} alkyl, R_2 is C_{1-20} alkyl and R_3 and R_4 are independently linear or branched C_1-C_{22} alkyl; or

(ii) one or more monomers according to the following formula (II):

5



10

wherein R_1 is hydrogen or C_{1-10} alkyl, R_2 is C_{1-20} alkyl and R_3 and R_4 are independently linear or branched C_1-C_{22} alkyl; or

(iii) a mixture of monomers according to formula (I) and (II);

(iv) and optionally with styrene or 4-Vinylpyridine, to form a block copolymer;

15

c) optionally quaternizing of the block copolymer of step b).

3. The block copolymer according to claim 1 or 2, wherein the block copolymer has a quaternization degree of 0 to 99%.

20

4. The block copolymer according to any one of claims 1 to 3, wherein styrene or 4-Vinylpyridine are present in the range of from 0 to 20 repeating units.

5. The block copolymer according to any one of claims 1 to 4, wherein the block copolymer has a polydispersity index PDI from 1.0 to 2.5.

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6. The block copolymer according to any one of claims 1 and 3 to 5, wherein the block copolymer has been prepared in step a) from n-butylacrylate.

30

7. The block copolymer according to any one of claims 1 to 6, wherein the monomer of step b) is selected from the group consisting of dimethylaminopropyl methacrylate, dimethylaminopropyl acrylate, 2-(dimethylamino)ethyl methacrylate, 2-(dimethylamino)ethyl acrylate, dimethylaminopropyl acrylamide, dimethylaminopropyl methacrylamide, 2-(dimethylamino)ethyl acrylamide and 2-(dimethylamino)ethyl methacrylamide.

35

8. The block copolymer according to claims 1 and 3 to 7, wherein the monomer of step a) is n-butylacrylate and wherein the monomer of step b) is 2-(dimethylamino)ethyl methacrylate or dimethylaminopropyl methacrylamide.

40

9. The block copolymer according to any one of claims 1 and 3 to 8, wherein the primary or secondary alcohol in step c) is selected from the group consisting of:

a) an ethoxylate of formula (A) $R_A-[O-CH_2-CH_2]_n-OH$ (A)

wherein R_A is saturated or unsaturated, linear or branched chain alkyl with 1 to 22 carbon atoms, or alkylaryl or dialkylaryl with up to 24 carbon atoms and n is 1 to 150;

- b) a polydimethylsilicone oligomer of formula (B)
- $$R_B \left[\begin{array}{c} \text{CH}_3 \\ | \\ \text{---Si---O---} \\ | \\ \text{CH}_3 \end{array} \right]_n \text{R}'\text{---CH}_2\text{---OH}$$

5 (B)
wherein R_B is C_1 - C_{18} alkyl, phenyl or C_7 - C_{15} aralkyl; n is 1 to 50 and R' is a linking group with 1 to 20 carbon atoms;

- c) a partly or fully fluorinated primary alcohol; or
d) a C_8 to C_{60} alkyl linear or branched primary or secondary alcohol.

10 10. The block copolymer according to claim 9, wherein the primary or secondary alcohol is methoxy poly(ethylene glycol).

11. A process as defined in any one of claims 1 to 10.

15 12. Use of the block copolymer according to any one of claims 1 to 10 as soil release agent in aqueous laundry processes.

20 13. Detergent comprising a block copolymer according to any one of claims 1 to 10.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/055226

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F293/00 C08F8/14 C11D3/37
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
C08F C11D
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2009/151235 A1 (SCANLON EUGENE [US] ET AL) 18 June 2009 (2009-06-18) paragraphs [0056], [0057]; claims 1-8; examples 17-22	1-11
X	WO 2008/006723 A1 (CIBA SC HOLDING AG [CH]; SCHELLENBERG CARSTEN [DE]; AUSCHRA CLEMENS [D] 17 January 2008 (2008-01-17) claims 1-13; examples A35, A36	1-11
X	WO 2006/074969 A1 (CIBA SC HOLDING AG [CH]; KNISCHKA RALF [DE]; ECKSTEIN ERNST [DE]; AUSC) 20 July 2006 (2006-07-20) claims 1-16; examples A14, A15	1-11
	-/--	

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
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Date of the actual completion of the international search 15 May 2014	Date of mailing of the international search report 21/05/2014
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Madalinski, Maciej

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/055226

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2012/000992 A1 (BASF SE [DE]; DABBOUS RAPHAEL [CH]; ONCLIN STEFFEN [DE]; ROEMLING HART) 5 January 2012 (2012-01-05) page 12, line 39 - page 13, line 4; example 29 -----	1-11

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/EP2014/055226

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2009151235	A1	18-06-2009	EP 2235146 A1 06-10-2010
			KR 20100093567 A 25-08-2010
			US 2009151235 A1 18-06-2009
			WO 2009077396 A1 25-06-2009

WO 2008006723	A1	17-01-2008	CN 101490620 A 22-07-2009
			EP 2038704 A1 25-03-2009
			JP 5425623 B2 26-02-2014
			JP 2009543145 A 03-12-2009
			KR 20090034376 A 07-04-2009
			TW 200813149 A 16-03-2008
			US 2009186285 A1 23-07-2009
			WO 2008006723 A1 17-01-2008

WO 2006074969	A1	20-07-2006	BR PI0606305 A2 16-06-2009
			CN 101103049 A 09-01-2008
			EP 1861429 A1 05-12-2007
			JP 5225689 B2 03-07-2013
			JP 2008527130 A 24-07-2008
			KR 20070099646 A 09-10-2007
			US 2009221739 A1 03-09-2009
			US 2011224375 A1 15-09-2011
			US 2013059964 A1 07-03-2013
			WO 2006074969 A1 20-07-2006

WO 2012000992	A1	05-01-2012	CN 102958993 A 06-03-2013
			EP 2588520 A1 08-05-2013
			JP 2013530288 A 25-07-2013
			US 2013144011 A1 06-06-2013
			WO 2012000992 A1 05-01-2012
