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- (71) **Applicant (for all designated States except US):** ETH ZÜRICH [CH/CH]; Raemistrasse 101, ETH transfer, CH-8092 Zürich (CH).
- (72) **Inventors; and**
- (75) **Inventors/Applicants (for US only):** GRÜTZMACHER, Hansjörg [DE/CH]; Rebbergstrasse 1d, CH-8157 Dielsdorf / ZH (CH). OTT, Timo [DE/CA]; 294 Besserer St., Ottawa, Ontario K1N 6B3 (CA).
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(54) **Title:** POLYMER NANOPARTICLES

(57) **Abstract:** The present invention relates to polymer nanoparticles with a low polydispersity and a photo-induced process for the preparation of such polymer nanoparticles. The invention further relates to novel photoinitiators suitable for carrying out said process.

### Polymer Nanoparticles

The present invention relates to polymer nanoparticles with a low polydispersity and a photo-induced process for the preparation of such polymer nanoparticles. The invention further relates to novel photoinitiators suitable for carrying out said process.

5 Polymer particles are widely used as coating, adhesive, ink and painting materials, for precision mold constructions and the manufacture of micro-sized materials. The unique properties of micro- and nanoscaled polymer particles with low polydispersities have meanwhile gained significant attention not only in the electronics industry, for example, in the manufacture of TFT and LCD displays, digital toners and e-paper, but also in the medical sector such as for drug delivery systems, diagnostic sensors, contrast agents and many other fields of industry.

Polymer nanoparticles are frequently synthesized by physical methods like evaporation of polymer solution droplets or by the direct synthesis of the nanoparticles using special polymerisation processes. The most common processes are radical polymerisations like suspension polymerizations and emulsion polymerizations.

15 Over the last decades, a vast number of radical polymerization processes were developed in order to achieve a better control over the polymerisation process and thus the properties of the resulting polymer nanoparticles.

S. Nozari et al. (*Macromolecules* **2005**, *38*, 10449) describes a RAFT (reversible addition fragmentation transfer) emulsion polymerization process for the preparation of polystyrene nanoparticles using dithioic acids as sur-iniferters, thereby obtaining polystyrene with an polydispersity index ( $M_w/M_n$ ), hereinafter also referred to as M-PDI, of 1.22 to 1.31, and a weight average molar mass of 110 to 170 kg/mol.

Emulsion polymerisations induced by X-ray radiation are described in S. Wang, X. Wang, Z. Zhang, *Eur. Polym. J.*, **2007**, *43*, 178).

25 Emulsion polymerisations induced by UV/Vis radiation are described in P. Kuo, N. Turro, *Macromolecules* **1987**, *20*, 1216-1221, wherein the formation of polystyrene nanoparticles having a M-PDI of 1.6 to 2.2 and a weight average molecular weight of 500 kg/mol or less.

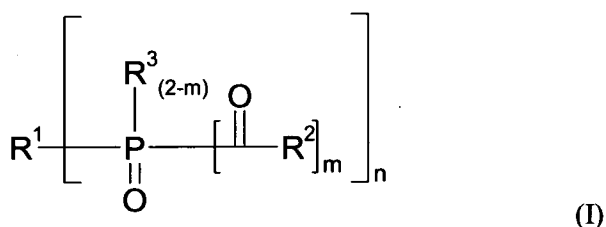
The industrial applicability of the processes described above is, however, significantly hampered due to the use of toxic, expensive, coloured or malodorous chemicals such as heavy metal salts, sulphur containing compounds and stable radicals such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO).

As a consequence, there is still a need for a process for the preparation of polymer nanoparticles having a low polydispersity while simultaneously allowing for the easy control of the particle size.

A process was now found for the preparation of polymer nanoparticles by photoinduced emulsion polymerization which comprises at least the steps of:

- 5 A) preparing an emulsion comprising at least one surfactant, a dispersed phase and a continuous phase, whereby the dispersed phase comprises one or more polymerizable monomers and the continuous phase comprises water and one or more photoinitiators;
- B) polymerizing one or more polymerizable monomers by exposing said emulsion to electromagnetic radiation having a wavelength sufficient to induce the generation of
- 10 radicals from one or more photoinitiators,

wherein the photoinitiators are selected from compounds of formula (I):



wherein

n is 1 or 2,

15 m is 1 or 2,

**R<sup>1</sup>, if n = 1** is C<sub>6</sub>-C<sub>14</sub>-aryl or heterocyclyl or

is C<sub>1</sub>-C<sub>18</sub>-alkoxy, -N(R<sup>4</sup>)<sub>2</sub>, C<sub>1</sub>-C<sub>18</sub>-alkyl, C<sub>2</sub>-C<sub>18</sub>-alkenyl, C<sub>7</sub>-C<sub>20</sub>-arylalkyl,

which is either not, once, twice or more than twice interrupted by non-successive functional groups selected from the group consisting of:

20 -O-, -S-, -SO<sub>2</sub>-, -SO-, -SO<sub>2</sub>NR<sup>4</sup>-, NR<sup>4</sup>SO<sub>2</sub>-, -NR<sup>4</sup>-, -N<sup>+</sup>(R<sup>4</sup>)<sub>2</sub>An<sup>-</sup>-, -CO-, -O(CO)-, (CO)O-, -O(CO)O-, -NR<sup>4</sup>(CO)NR<sup>4</sup>-, NR<sup>4</sup>(CO)-, -(CO)NR<sup>4</sup>-, -NR<sup>4</sup>(CO)O-, -O(CO)NR<sup>4</sup>-, -Si(R<sup>5</sup>)<sub>2</sub>-, -OSi(R<sup>5</sup>)<sub>2</sub>-, -OSi(R<sup>5</sup>)<sub>2</sub>O-, -Si(R<sup>5</sup>)<sub>2</sub>O-,

and which is either not, once, twice or more than twice interrupted by bivalent residues selected from the group consisting of heterocyclo-diyl, heterocyclo-diylum<sup>+</sup>An<sup>-</sup> and C<sub>6</sub>-C<sub>14</sub>-aryldiyl,

5 and which is not, additionally or alternatively either once, twice or more than twice substituted by substituents selected from the group consisting of:

halogen, cyano, azido, epoxy, C<sub>6</sub>-C<sub>14</sub>-aryl, C<sub>1</sub>-C<sub>8</sub>-alkyl, C<sub>1</sub>-C<sub>8</sub>-alkoxy, C<sub>2</sub>-C<sub>8</sub>-alkenyl, C<sub>1</sub>-C<sub>8</sub>-alkylthio, C<sub>7</sub>-C<sub>20</sub>-arylalkyl, hydroxy, -SO<sub>3</sub>M, -COOM, PO<sub>3</sub>M<sub>2</sub>, -PO(N(R<sup>5</sup>)<sub>2</sub>)<sub>2</sub>, PO(OR<sup>5</sup>)<sub>2</sub>, -SO<sub>2</sub>N(R<sup>4</sup>)<sub>2</sub>, -N(R<sup>4</sup>)<sub>2</sub>, -N<sup>+</sup>(R<sup>4</sup>)<sub>3</sub>An<sup>-</sup>, heterocyclylium<sup>+</sup>An<sup>-</sup>, -CO<sub>2</sub>N(R<sup>5</sup>)<sub>2</sub>, -COR<sup>4</sup>, -OCOR<sup>4</sup>, -NR<sup>4</sup>(CO)R<sup>5</sup>, -(CO)OR<sup>4</sup>, -NR<sup>4</sup>(CO)N(R<sup>4</sup>)<sub>2</sub>, -Si(OR<sup>5</sup>)<sub>y</sub>(R<sup>5</sup>)<sub>3-y</sub>, -OSi(OR<sup>5</sup>)<sub>y</sub>(R<sup>5</sup>)<sub>3-y</sub> with y = 1, 2 or 3,

10

**R<sup>1</sup>, if n = 2** is C<sub>6</sub>-C<sub>15</sub>-aryldiyl or

is C<sub>4</sub>-C<sub>18</sub>-alkanediyl, C<sub>4</sub>-C<sub>18</sub>-alkenediyl, C<sub>4</sub>-C<sub>18</sub>-alkinediyl,

which is either not, once, twice or more than twice interrupted by non-successive groups selected from the group consisting of:

15 -O-, -SO<sub>2</sub>-, -NR<sup>4</sup>-, -N<sup>+</sup>(R<sup>4</sup>)<sub>2</sub>An<sup>-</sup>, -CO-, -OCO-, -O(CO)O-, NR<sup>4</sup>(CO)-, -NR<sup>4</sup>(CO)O-, O(CO)NR<sup>4</sup>-, -NR<sup>4</sup>(CO)NR<sup>4</sup>-, C<sub>6</sub>-C<sub>15</sub>-aryl, heterocyclo-diyl and heterocyclo-diylum<sup>+</sup>An<sup>-</sup>,

and which is not, additionally or alternatively either once, twice or more than twice substituted by substituents selected from the group consisting of:

20 halogen, cyano, C<sub>6</sub>-C<sub>14</sub>-aryl, heterocyclyl, heterocyclo-diylum<sup>+</sup>An<sup>-</sup>, C<sub>1</sub>-C<sub>8</sub>-alkyl, C<sub>1</sub>-C<sub>8</sub>-alkoxy, C<sub>1</sub>-C<sub>8</sub>-alkylthio, -SO<sub>3</sub>M, -COOM, PO<sub>3</sub>M<sub>2</sub>, -N(R<sup>4</sup>)<sub>2</sub>, -N<sup>+</sup>(R<sup>4</sup>)<sub>3</sub>An<sup>-</sup>, -CO<sub>2</sub>N(R<sup>4</sup>)<sub>2</sub>, -OCOR<sup>4</sup>-, -O(CO)OR<sup>4</sup>-, NR<sup>4</sup>(CO)R<sup>5</sup>, -NR<sup>3</sup>(CO)OR<sup>5</sup>, O(CO)N(R<sup>4</sup>)<sub>2</sub>, -NR<sup>4</sup>(CO)N(R<sup>4</sup>)<sub>2</sub>,

25 or is bivalent bis(C<sub>6</sub>-C<sub>15</sub>)-aryl, which is either not or once interrupted by groups selected from the group consisting of:

-O-, -S-, C<sub>4</sub>-C<sub>18</sub>-alkanediyl, C<sub>4</sub>-C<sub>18</sub>-alkenediyl,

**R<sup>2</sup>** is C<sub>6</sub>-C<sub>14</sub>-aryl or heterocyclyl or

is C<sub>1</sub>-C<sub>18</sub>-alkyl, C<sub>2</sub>-C<sub>18</sub>-alkenyl, C<sub>7</sub>-C<sub>20</sub>-arylalkyl,

which is either not, once, twice or more than twice interrupted by non-successive functional groups selected from the group consisting of:

-O-, -NR<sup>4</sup>-, -N<sup>+</sup>(R<sup>4</sup>)<sub>2</sub>An<sup>-</sup>-, -CO-, -OCO-, -O(CO)O-, NR<sup>4</sup>(CO)-, -NR<sup>4</sup>(CO)O-, O(CO)NR<sup>4</sup>-, -NR<sup>4</sup>(CO)NR<sup>4</sup>-,

5 and which is either not, once, twice or more than twice interrupted by bivalent residues selected from the group consisting of heterocyclo-diyl, heterocyclo-diylum<sup>+</sup>An<sup>-</sup>, and C<sub>6</sub>-C<sub>14</sub>-aryldiyl,

and which is not, additionally or alternatively either once, twice or more than twice substituted by substituents selected from the group consisting of:

10 halogen, cyano, C<sub>6</sub>-C<sub>14</sub>-aryl; heterocyclyl, C<sub>1</sub>-C<sub>8</sub>-alkyl, C<sub>1</sub>-C<sub>8</sub>-alkoxy, C<sub>1</sub>-C<sub>8</sub>-alkylthio, C<sub>2</sub>-C<sub>8</sub>-alkenyl, C<sub>4</sub>-C<sub>15</sub>-arylalkyl, -COOM, -SO<sub>3</sub>M, -PO<sub>3</sub>M<sub>2</sub>, -SO<sub>2</sub>N(R<sup>4</sup>)<sub>2</sub>, -NR<sup>4</sup>SO<sub>2</sub>R<sup>5</sup>, -N(R<sup>4</sup>)<sub>2</sub>-, -N<sup>+</sup>(R<sup>4</sup>)<sub>3</sub>An<sup>-</sup>, -CO<sub>2</sub>N(R<sup>4</sup>)<sub>2</sub>-, -COR<sup>4</sup>-, -OCOR<sup>5</sup>, -O(CO)OR<sup>5</sup>, NR<sup>4</sup>(CO)R<sup>4</sup>, -NR<sup>4</sup>(CO)OR<sup>4</sup>, O(CO)N(R<sup>4</sup>)<sub>2</sub>, -NR<sup>4</sup>(CO)N(R<sup>4</sup>)<sub>2</sub>,

R<sup>3</sup> independently denotes a substituent as defined for R<sup>1</sup> if n is 1,

15 whereby

R<sup>4</sup> is independently selected from the group consisting of hydrogen, C<sub>1</sub>-C<sub>8</sub>-alkyl, C<sub>6</sub>-C<sub>14</sub>-aryl, C<sub>7</sub>-C<sub>15</sub>-arylalkyl and heterocyclyl or N(R<sup>4</sup>)<sub>2</sub> as a whole is a N-containing heterocycle, or N<sup>+</sup>(R<sup>4</sup>)<sub>2</sub>An<sup>-</sup> and N<sup>+</sup>(R<sup>4</sup>)<sub>3</sub>An<sup>-</sup> as a whole are or contain a cationic N-containing heterocycle with a counteranion,

20 R<sup>5</sup> is independently selected from the group consisting of C<sub>1</sub>-C<sub>8</sub>-alkyl, C<sub>6</sub>-C<sub>14</sub>-aryl, C<sub>7</sub>-C<sub>15</sub>-arylalkyl and heterocyclyl or N(R<sup>5</sup>)<sub>2</sub> as a whole is a N-containing heterocycle or N<sup>+</sup>(R<sup>5</sup>)<sub>2</sub>An<sup>-</sup> and N<sup>+</sup>(R<sup>5</sup>)<sub>3</sub>An<sup>-</sup> as a whole are or contain a cationic N-containing heterocycle with a counteranion,

M is hydrogen, or 1/q equivalent of an q-valent metal ion or is an ammonium ion or a primary, secondary, tertiary or quarternary organic ammonium ion or a guanidinium ion, and

An<sup>-</sup> is 1/p equivalent of a p-valent anion.

The compounds of formula (I) can be prepared according to or in analogy to the procedures disclosed in WO2005/014605; WO2006/056541 and WO2006/074983.

5 The scope of the invention encompasses all combinations of substituent definitions, parameters and illustrations set forth above and below, either in general or within areas of preference or preferred embodiments, with one another, i.e., also any combinations between the particular areas and areas of preference.

Whenever used herein the terms “including”, “e.g.”, “such as” and “like” are meant in the sense of “including but without being limited to” or “for example without limitation”, respectively.

10 The term “polymer nanoparticles” denotes polymer nanoparticles comprising at least 50 wt.-%, preferably at least 80 wt.-% and more preferably at least 90 wt.-% of a polymer and having an average particle size of 1 to 10.000 nm, preferably, 5 to 1.000 nm, more preferably 10 to 200 nm and even more preferably 10 to 100 nm.

In an embodiment the term “polymer nanoparticles” denotes polymer nanoparticles consisting of a polymer having an average particle size as defined above.

15 The average particle size as used herein is defined as being the particle size (z average) measured using dynamic light scattering (DLS), which is also known as photon correlation spectroscopy (PSC) or quasi-elastic light scattering (QELS). The particle size measured thereby is also frequently called hydrodynamic diameter and reflects how a particle diffuses within a fluid. The measured hydrodynamic diameter is equivalent to that of an ideal sphere having the same  
20 translational diffusion coefficient as the particle being measured. Since the surface structure may have a significant influence, the hydrodynamic diameter measured using DLS can be significantly larger than the true diameter measured e.g. by electron microscopy.

In Dynamic Light Scattering (DLS), the polydispersity index (PDI) reflects the width of the particle size distribution. It ranges from 0 to 1. A value of zero refers to an ideal suspension with no  
25 distribution in size. Distributions with PDI values of 0.1 or smaller are called monodisperse while dispersions with values between 0.1 and 0.3 are considered as having a narrow size distribution. Dispersions having a PDI larger than 0.5 are considered being polydisperse.

Results referred to herein were obtained using a Zetasizer 3000 of Malvern Instruments, Malvern, UK with a fixed scattering angle of 90°.

To distinguish the particle size PDI obtained by DLS from the polydispersity index reflecting the molecular mass distribution of a polymer sample ( $M_w/M_n$ ), the former is abbreviated as "DLS-PDI" and the latter as "M-PDI".

As used herein, and unless specifically stated otherwise, **C<sub>6</sub>-C<sub>14</sub>-aryl** denotes carbocyclic aromatic substituents, preferably phenyl, naphthyl, phenanthrenyl and anthracenyl, whereby said carbocyclic, aromatic substituents are unsubstituted or substituted by up to five identical or different substituents per cycle. For example and with preference, the substituents are selected from the group consisting of fluorine, bromine, chlorine, iodine, nitro, cyano, formyl or protected formyl, hydroxyl or protected hydroxyl, C<sub>1</sub>-C<sub>8</sub>-alkyl, C<sub>1</sub>-C<sub>8</sub>-haloalkyl, C<sub>1</sub>-C<sub>8</sub>-alkoxy, C<sub>1</sub>-C<sub>8</sub>-haloalkoxy, C<sub>6</sub>-C<sub>14</sub>-aryl, in particular phenyl and naphthyl, C<sub>7</sub>-C<sub>15</sub>-arylalkyl, in particular benzyl, di(C<sub>1</sub>-C<sub>8</sub>-alkyl)amino, (C<sub>1</sub>-C<sub>8</sub>-alkyl)amino, CO(C<sub>1</sub>-C<sub>8</sub>-alkyl), OCO(C<sub>1</sub>-C<sub>8</sub>-alkyl), NHCO(C<sub>1</sub>-C<sub>8</sub>-alkyl), N(C<sub>1</sub>-C<sub>8</sub>-alkyl)CO(C<sub>1</sub>-C<sub>8</sub>-alkyl), CO(C<sub>6</sub>-C<sub>14</sub>-aryl), OCO(C<sub>6</sub>-C<sub>14</sub>-aryl), NHCO(C<sub>6</sub>-C<sub>14</sub>-aryl), N(C<sub>1</sub>-C<sub>8</sub>-alkyl)CO(C<sub>6</sub>-C<sub>14</sub>-aryl), COO-(C<sub>1</sub>-C<sub>8</sub>-alkyl), COO-(C<sub>6</sub>-C<sub>14</sub>-aryl), CON(C<sub>1</sub>-C<sub>8</sub>-alkyl)<sub>2</sub> or CONH(C<sub>1</sub>-C<sub>8</sub>-alkyl), CO<sub>2</sub>M, CONH<sub>2</sub>, SO<sub>2</sub>NH<sub>2</sub>, SO<sub>2</sub>N(C<sub>1</sub>-C<sub>8</sub>-alkyl)<sub>2</sub>, SO<sub>3</sub>M and PO<sub>3</sub>M<sub>2</sub>.

In a preferred embodiment, the carbocyclic, aromatic substituents are unsubstituted or substituted by up to three identical or different substituents per cycle selected from the group consisting of fluorine, chlorine, cyano, C<sub>1</sub>-C<sub>8</sub>-alkyl, C<sub>1</sub>-C<sub>8</sub>-haloalkyl, C<sub>1</sub>-C<sub>8</sub>-alkoxy, C<sub>1</sub>-C<sub>8</sub>-haloalkoxy, C<sub>6</sub>-C<sub>14</sub>-aryl, in particular phenyl.

In a more preferred embodiment the carbocyclic, aromatic substituents are unsubstituted or substituted by up to three identical or different substituents per cycle selected from the group consisting of fluorine, C<sub>1</sub>-C<sub>8</sub>-alkyl, C<sub>1</sub>-C<sub>8</sub>-perfluoroalkyl, C<sub>1</sub>-C<sub>8</sub>-alkoxy, C<sub>1</sub>-C<sub>8</sub>-perfluoroalkoxy, and phenyl.

The definitions given above including their areas of preference also apply analogously to the aryl moiety of a **C<sub>7</sub>-C<sub>20</sub>-arylalkyl** substituent.

As used herein and unless specifically stated otherwise, **heterocyclyl** denotes heterocyclic aliphatic, aromatic or mixed aliphatic and aromatic substituents in which no, one, two or three skeleton atoms per cycle, but at least one skeleton atom in the entire cyclic system is a heteroatom selected from the group consisting of nitrogen, sulphur and oxygen which are unsubstituted or substituted by up to five identical or different substituents per cycle, whereby the substituents are selected from the same group as given above for carbocyclic aromatic substituents including the areas of preference.

Preferred heterocyclyl-substituents are pyridinyl, oxazolyl, thiophen-yl, benzofuranyl, benzothiophen-yl, dibenzofuranyl, dibenzothiophenyl, furanyl, indolyl, pyridazinyl, pyrazinyl, imidazolyl, pyrimidinyl and quinolinyl, either unsubstituted or substituted with up to three substituents selected from the group consisting of fluorine, C<sub>1</sub>-C<sub>8</sub>-alkyl, C<sub>1</sub>-C<sub>8</sub>-perfluoroalkyl, C<sub>1</sub>-C<sub>8</sub>-alkoxy, C<sub>1</sub>-C<sub>8</sub>-perfluoroalkoxy, and phenyl.

The definitions given above, including their areas of preference, also apply analogously to **heterocyclium** cations, the bivalent **heterocyclo-diyli** substituents and the bivalent **heterocyclo-dylium** cations.

Preferred heterocyclium cations are N-(C<sub>1</sub>-C<sub>8</sub>-alkyl)imidazolium or pyridinium cations.

10 Preferred **heterocyclo-dylium** cations are N,N-imidazol-dylium cations.

As used herein, and unless specifically stated otherwise, **protected formyl** is a formyl substituent which is protected by conversion to an aminal, acetal or a mixed aminal acetal, whereby the aminals, acetals and mixed aminal acetals are either acyclic or cyclic.

For example, and with preference, protected formyl is 1,1-(2,4-dioxycyclopentanediyli).

15 As used herein, and unless specifically stated otherwise, **protected hydroxyl** is a hydroxyl radical which is protected by conversion to a ketal, acetal or a mixed aminal acetal, whereby the aminals, acetals and mixed aminal acetals are either acyclic or cyclic. A specific example of protected hydroxyl is tetrahydropyranyl (O-THP).

20 As used herein, and unless specifically stated otherwise, **C<sub>1</sub>-C<sub>18</sub>-alkyl**, **C<sub>1</sub>-C<sub>18</sub>-alkanediyl**, **C<sub>1</sub>-C<sub>18</sub>-alkoxy**, **C<sub>2</sub>-C<sub>18</sub>-alkenyl**, **C<sub>2</sub>-C<sub>18</sub>-alkenediyl** and **C<sub>1</sub>-C<sub>18</sub>-alkinediyl** are a straight-chain, cyclic either in part or as a whole, branched or unbranched **C<sub>1</sub>-C<sub>18</sub>-alkyl**, **C<sub>1</sub>-C<sub>18</sub>-alkanediyl**, **C<sub>1</sub>-C<sub>18</sub>-alkoxy**, **C<sub>2</sub>-C<sub>18</sub>-alkenyl**, **C<sub>2</sub>-C<sub>18</sub>-alkenediyl** and **C<sub>1</sub>-C<sub>18</sub>-alkinediyl** substituents. The same applies to the alkandiyl moiety of an **C<sub>7</sub>-C<sub>20</sub>-arylalkyl** substituent.

25 Specific examples of C<sub>1</sub>-C<sub>4</sub>-alkyl are methyl, ethyl, n-propyl, isopropyl, n-butyl, tert-butyl. Additional examples for C<sub>1</sub>-C<sub>8</sub>-alkyl are n-pentyl, cyclohexyl, n-hexyl, n-heptyl, n-octyl, isooctyl. Additional examples for C<sub>1</sub>-C<sub>8</sub>-alkyl are C<sub>1</sub>-C<sub>18</sub>-alkyl norbornyl, adamantyl, n-decyl, n-dodecyl alkyl, n-hexadecyl, n-octadecyl.

Specific examples of C<sub>1</sub>-C<sub>8</sub>-alkanediyl-substituents are methylene, 1,1-ethylene, 1,2-ethylene, 1,1-propylene, 1,2-propylene, 1,3-propylene, 1,1-butylene, 1,2-butylene, 2,3-butylene and 1,4-butylene,



1,5-pentylene, 1,6-hexylene, 1,1-cyclohexylene, 1,4-cyclohexylene, 1,2-cyclohexylene and 1,8-octylene.

Specific examples of C<sub>1</sub>-C<sub>4</sub>-alkoxy-substituents are methoxy, ethoxy, isopropoxy, n-propoxy, n-butoxy and tert-butoxy. An additional example for C<sub>1</sub>-C<sub>8</sub>-alkoxy is cyclohexyloxy.

5 Specific examples of C<sub>2</sub>-C<sub>8</sub>-alkenyl- substituents are allyl, 3-propenyl and buten-2-yl.

As used hereinabove, C<sub>1</sub>-C<sub>8</sub>-haloalkyl and C<sub>1</sub>-C<sub>8</sub>-haloalkoxy are C<sub>1</sub>-C<sub>8</sub>-alkyl and C<sub>1</sub>-C<sub>8</sub>-alkoxy substituents which are once, more than once or fully substituted by halogen atoms. Substituents which are fully substituted by fluorine are referred to as C<sub>1</sub>-C<sub>8</sub>-perfluoroalkyl and C<sub>1</sub>-C<sub>8</sub>-perfluoroalkoxy, respectively.

10 Specific examples of C<sub>1</sub>-C<sub>8</sub>-haloalkyl-substituents are trifluoromethyl, 2,2,2-trifluoroethyl, chloromethyl, fluoromethyl, bromomethyl, 2-bromoethyl, 2-chloroethyl, nonafluorobutyl and n-perfluorooctyl.

In step A), an emulsion is prepared, whereby the emulsion comprises at least one surfactant, a dispersed phase and a continuous phase, whereby the dispersed phase comprises one or more polymerizable monomers and the continuous phase comprises water and one or more photoinitiators.

The preparation of the emulsion is typically effected by simply mixing the components and introducing mixing energy e.g. by standard agitators and/or static mixing elements, whereby the latter are particularly useful in flow-through reactors. Even though not typically necessary, the mixing can be supported by using high force dispersion devices such as, for example, ultrasound sonotrodes or high pressure homogenizers.

Step A), the preparation of the emulsion or step B) the polymerization or both steps A) and B) may either be performed batchwise or continuously.

The continuous phase comprises water and at least one photoinitiator and may further comprise water miscible solvents.

As used herein, the term water miscible organic solvent denotes organic solvents which are miscible with water in any ratio.

Suitable water miscible organic solvents include aliphatic alcohols, glycols, ethers, glycol ethers, pyrrolidines, N-alkylpyrrolidinones, N-alkyl pyrrolidones, polyethylene glycols, polypropylene

glycols, amides, carboxylic acids, esters, sulfoxides, sulfones, hydroxyether derivatives such as butyl carbitol or cellosolve, amino alcohols, ketones, and the like, as well as derivatives thereof and mixtures thereof, provided, however, that they are miscible with water in any ratio.

Specific examples include methanol, ethanol, propanol, dioxane, ethylene glycol, propylene glycol, diethylene glycol, glycerol, dipropylene glycol or mixtures thereof.

The addition of water miscible organic solvents might be useful in those cases where the used amount of photoinitiator is either insoluble or incompletely soluble in water or the water-surfactant mixture.

In an embodiment, the solubility of hydrophobic polymerizable monomers within the aqueous continuous phase is typically raised so that the reaction rate, the particle size and the average molecular weight can be influenced by the added amount of water miscible organic solvent.

In an embodiment, the addition of water miscible organic solvents allows the reaction temperature to be lowered significantly below the freezing point of water or the water-surfactant mixture.

In an embodiment, the continuous phase comprises less than 20 wt-% of water-miscible organic solvents, preferably less than 10 wt-%, more preferably less than 5 wt-% and even more preferably less than 2 wt-%. In one aspect of the invention the continuous phase does not contain water-miscible organic solvents.

In another embodiment, the solubility of hydrophilic polymerizable monomers within the aqueous continuous phase can optionally be lowered by adding soluble salts such as inorganic salts like sodium chloride and the like. The content of inorganic salts may then be for example 0,1 to 5 wt-%, preferably 0,1 to 1 wt-%.

In an embodiment, one or more photoinitiators of formula (I) are used, where in formula (I):

n is 1,

m is 2,

$R^1$  is C<sub>6</sub>-C<sub>14</sub>-aryl or heterocyclyl or

is C<sub>1</sub>-C<sub>18</sub>-alkyl, C<sub>2</sub>-C<sub>18</sub>-alkenyl, C<sub>7</sub>-C<sub>15</sub>-arylalkyl,

which is either not or once, twice or more than twice interrupted by non-successive functional groups selected from the group consisting of:

-O-, -NR<sup>4</sup>-, -N<sup>+</sup>(R<sup>4</sup>)<sub>2</sub>An<sup>-</sup>-, -CO-, -OCO-, NR<sup>4</sup>(CO)-, -(CO)NR<sup>4</sup>-,

and which is not, additionally or alternatively either once, twice or more than twice substituted by substituents selected from the group consisting of:

5 halogen, cyano, epoxy, C<sub>6</sub>-C<sub>14</sub>-aryl; C<sub>1</sub>-C<sub>8</sub>-alkyl, C<sub>1</sub>-C<sub>8</sub>-alkoxy, C<sub>2</sub>-C<sub>8</sub>-alkenyl, C<sub>4</sub>-C<sub>15</sub>-arylalkyl, hydroxy, -SO<sub>3</sub>M, -COOM, PO<sub>3</sub>M<sub>2</sub>, -PO(N(R<sup>5</sup>)<sub>2</sub>)<sub>2</sub>, -SO<sub>2</sub>N(R<sup>4</sup>)<sub>2</sub>, -N(R<sup>4</sup>)<sub>2</sub>, -N<sup>+</sup>(R<sup>4</sup>)<sub>3</sub>An<sup>-</sup>, heterocyclo-diylium<sup>+</sup>An<sup>-</sup>, -CO<sub>2</sub>N(R<sup>5</sup>)<sub>2</sub>, -COR<sup>4</sup>, -OCOR<sup>4</sup>, NR<sup>4</sup>(CO)R<sup>5</sup>,

R<sup>2</sup> is C<sub>6</sub>-C<sub>14</sub>-aryl or heterocyclyl or

is C<sub>1</sub>-C<sub>18</sub>-alkyl, C<sub>2</sub>-C<sub>18</sub>-alkenyl, C<sub>7</sub>-C<sub>15</sub>-arylalkyl,

10 which is either not, once, twice or more than twice interrupted by non-successive functional groups selected from the group consisting of:

-O-, -NR<sup>4</sup>-, -N<sup>+</sup>(R<sup>4</sup>)<sub>2</sub>An<sup>-</sup>-, -CO-, NR<sup>4</sup>(CO)-, -NR<sup>4</sup>(CO)O-, (CO)NR<sup>4</sup>-,

and which is not, additionally or alternatively either once, twice or more than twice substituted by substituents selected from the group consisting of:

15 halogen, cyano, C<sub>6</sub>-C<sub>14</sub>-aryl; heterocyclyl, C<sub>1</sub>-C<sub>8</sub>-alkyl, C<sub>1</sub>-C<sub>8</sub>-alkoxy, C<sub>1</sub>-C<sub>8</sub>-alkylthio, C<sub>2</sub>-C<sub>8</sub>-alkenyl, C<sub>4</sub>-C<sub>15</sub>-arylalkyl, -COOM, SO<sub>2</sub>N(R<sup>3</sup>)<sub>2</sub>-, N(R<sup>4</sup>)<sub>2</sub>-, -N<sup>+</sup>(R<sup>4</sup>)<sub>3</sub>An<sup>-</sup>, -CO<sub>2</sub>N(R<sup>4</sup>)<sub>2</sub>,

whereby

20 R<sup>4</sup> is independently selected from the group consisting hydrogen, C<sub>1</sub>-C<sub>8</sub>-alkyl, C<sub>6</sub>-C<sub>14</sub>-aryl, C<sub>7</sub>-C<sub>15</sub>-arylalkyl and heterocyclyl or N(R<sup>4</sup>)<sub>2</sub> as a whole is a N-containing heterocycle or N<sup>+</sup>(R<sup>4</sup>)<sub>2</sub>An<sup>-</sup> and N<sup>+</sup>(R<sup>4</sup>)<sub>3</sub>An<sup>-</sup> as a whole is or contains a cationic N-containing heterocycle with a counteranion,

25 R<sup>5</sup> is independently selected from the group consisting C<sub>1</sub>-C<sub>8</sub>-alkyl, C<sub>6</sub>-C<sub>14</sub>-aryl, C<sub>7</sub>-C<sub>15</sub>-arylalkyl and heterocyclyl or N(R<sup>5</sup>)<sub>2</sub> as a whole is a N-containing heterocycle or N<sup>+</sup>(R<sup>5</sup>)<sub>2</sub>An<sup>-</sup> and N<sup>+</sup>(R<sup>5</sup>)<sub>3</sub>An<sup>-</sup> as a whole is or contains a cationic N-containing heterocycle with a counteranion,

M is hydrogen, lithium, sodium, potassium, one half equivalent of calcium, zinc or iron (II), or one third equivalent of aluminium (III) or is an ammonium ion or a primary, secondary, tertiary or quaternary organic ammonium ion, and

An<sup>-</sup> is 1/p equivalent of an p-valent anion.

5 In an embodiment, one or more photoinitiators of formula (I) are used, where in formula (I):

n is 1,

m is 2,

R<sup>1</sup> is C<sub>1</sub>-C<sub>18</sub>-alkyl, C<sub>2</sub>-C<sub>18</sub>-alkenyl, C<sub>7</sub>-C<sub>20</sub>-arylalkyl,

10 which is either not or once, twice or more than twice interrupted by non-successive functional groups selected from the group consisting of:

-O-, -NR<sup>4</sup>-, -N<sup>+</sup>(R<sup>4</sup>)<sub>2</sub>An<sup>-</sup>, -NR<sup>4</sup>(CO)-, -(CO)NR<sup>4</sup>-,

and which is not, additionally or alternatively either once, twice or more than twice substituted by substituents selected from the group consisting of:

15 halogen, C<sub>6</sub>-C<sub>14</sub>-aryl; C<sub>1</sub>-C<sub>8</sub>-alkyl, C<sub>1</sub>-C<sub>8</sub>-alkoxy, C<sub>2</sub>-C<sub>8</sub>-alkenyl, hydroxy, -SO<sub>3</sub>M, -COOM, PO<sub>3</sub>M<sub>2</sub>, -PO(N(R<sup>5</sup>)<sub>2</sub>)<sub>2</sub>, -SO<sub>2</sub>N(R<sup>4</sup>)<sub>2</sub>, -N(R<sup>4</sup>)<sub>2</sub>, -N<sup>+</sup>(R<sup>4</sup>)<sub>3</sub>An<sup>-</sup>, heterocyclo-diylum<sup>+</sup>An<sup>-</sup>, -CO<sub>2</sub>N(R<sup>5</sup>)<sub>2</sub>,

R<sup>2</sup> is C<sub>6</sub>-C<sub>14</sub>-aryl,

whereby

20 R<sup>4</sup> is independently selected from the group consisting hydrogen, C<sub>1</sub>-C<sub>8</sub>-alkyl, C<sub>6</sub>-C<sub>14</sub>-aryl, C<sub>7</sub>-C<sub>15</sub>-arylalkyl and heterocyclyl or N(R<sup>4</sup>)<sub>2</sub> as a whole is a N-containing heterocycle or N<sup>+</sup>(R<sup>4</sup>)<sub>2</sub>An<sup>-</sup> and N<sup>+</sup>(R<sup>4</sup>)<sub>3</sub>An<sup>-</sup> as a whole is or contains a cationic N-containing heterocycle with a counteranion,

25 R<sup>5</sup> is independently selected from the group consisting C<sub>1</sub>-C<sub>8</sub>-alkyl, C<sub>6</sub>-C<sub>14</sub>-aryl, C<sub>7</sub>-C<sub>15</sub>-arylalkyl and heterocyclyl or where N(R<sup>5</sup>)<sub>2</sub> as a whole is a N-containing heterocycle or N<sup>+</sup>(R<sup>5</sup>)<sub>2</sub>An<sup>-</sup> and N<sup>+</sup>(R<sup>5</sup>)<sub>3</sub>An<sup>-</sup> as a whole is or contains a cationic N-containing heterocycle with a counteranion,

M is hydrogen, lithium, sodium, potassium, one half equivalent of calcium, zinc or iron (II), or one third equivalent of aluminium (III) or is an ammonium ion or a primary, secondary, tertiary or quaternary organic ammonium ion, and

5 An<sup>-</sup> is 1/p equivalent of a p-valent anion, preferably a halide, a carboxylate, C<sub>1</sub>-C<sub>8</sub>-alkylsulfate, C<sub>6</sub>-C<sub>14</sub>-arylsulfate, hexafluorophosphate, tetrafluoroborate, dihydrogenphosphate, one half equivalent of sulphate or hydrogenphosphate.

In a preferred embodiment of the invention, one or more photoinitiators of formula (I) are used, where in formula (I):

n is 1,

10 m is 2,

R<sup>1</sup> is C<sub>1</sub>-C<sub>18</sub>-alkyl,

which is either not or once, twice or more than twice interrupted by non-successive functional groups selected from the group consisting of:

-O-, -NR<sup>4</sup>-, -N<sup>+</sup>(R<sup>4</sup>)<sub>2</sub>An<sup>-</sup>,

15 and which is not, additionally or alternatively either once, twice or more than twice substituted by substituents selected from the group consisting of:

halogen, C<sub>1</sub>-C<sub>8</sub>-alkoxy, hydroxy, -SO<sub>3</sub>M, -COOM, PO<sub>3</sub>M<sub>2</sub>, SO<sub>2</sub>N(R<sup>4</sup>)<sub>2</sub>, -N(R<sup>4</sup>)<sub>2</sub>, -N<sup>+</sup>(R<sup>4</sup>)<sub>3</sub>An<sup>-</sup>, -CO<sub>2</sub>N(R<sup>4</sup>)<sub>2</sub>, C<sub>1</sub>-C<sub>8</sub>-alkylsulfate,

R<sup>2</sup> is C<sub>6</sub>-C<sub>14</sub>-aryl,

20 whereby

R<sup>4</sup> is independently selected from the group consisting hydrogen, C<sub>1</sub>-C<sub>8</sub>-alkyl, C<sub>6</sub>-C<sub>14</sub>-aryl, C<sub>7</sub>-C<sub>15</sub>-arylalkyl and heterocyclyl or N(R<sup>4</sup>)<sub>2</sub> as a whole is a N-containing heterocycle or N<sup>+</sup>(R<sup>4</sup>)<sub>2</sub>An<sup>-</sup> and N<sup>+</sup>(R<sup>4</sup>)<sub>3</sub>An<sup>-</sup> as a whole is or contains a cationic N-containing heterocycle with a counteranion,

25 M is hydrogen, lithium, sodium, potassium, one half equivalent of calcium, zinc or iron (II), or one third equivalent of aluminium (III) or is an ammonium ion or a primary, secondary, tertiary or quaternary organic ammonium ion, and

An<sup>-</sup> is 1/p equivalent of an p-valent anion, preferably a halide, a carboxylate, C<sub>1</sub>-C<sub>8</sub>-alkylsulfate, C<sub>6</sub>-C<sub>14</sub>-arylsulfate, hexafluorophosphate, tetrafluoroborate, dihydrogenphosphate, one half equivalent of sulphate or hydrogenphosphate.

5 In another preferred embodiment, one or more photoinitiators of formula (I) are used, where in formula (I):

n is 1,

m is 2,

R<sup>1</sup> is C<sub>1</sub>-C<sub>8</sub>-alkyl,

10 which is either not or once, twice or more than twice interrupted by non-successive functional groups selected from the group consisting of:

-O-, -NR<sup>4</sup>-, -N<sup>+</sup>(R<sup>4</sup>)<sub>2</sub>An<sup>-</sup>, preferably those containing one to ten polyethyleneglycolether groups [-OCH<sub>2</sub>CH<sub>2</sub>]<sub>x</sub>-,

and which additionally or alternatively are either once, twice or more than twice substituted by substituents selected from the group consisting of:

15 hydroxy, -SO<sub>3</sub>M, -COOM, PO<sub>3</sub>M<sub>2</sub>, -N(R<sup>4</sup>)<sub>2</sub>, -N<sup>+</sup>(R<sup>4</sup>)<sub>3</sub>An<sup>-</sup>, heterocyclium<sup>+</sup>An<sup>-</sup>,

R<sup>2</sup> is C<sub>6</sub>-C<sub>14</sub>-aryl, preferably mesityl or 2,6-dimethoxyphenyl,

whereby

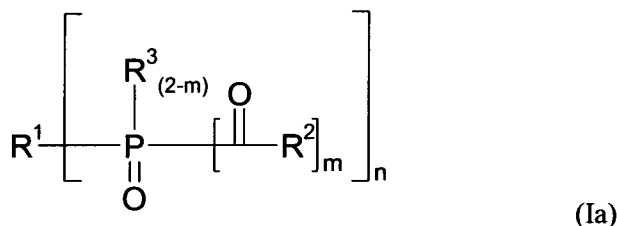
20 R<sup>4</sup> is independently selected from the group consisting hydrogen, C<sub>1</sub>-C<sub>8</sub>-alkyl, C<sub>6</sub>-C<sub>14</sub>-aryl, C<sub>7</sub>-C<sub>15</sub>-arylalkyl and heterocyclyl or N(R<sup>4</sup>)<sub>2</sub> as a whole is a N-containing heterocycle or N<sup>+</sup>(R<sup>4</sup>)<sub>2</sub>An<sup>-</sup> and N<sup>+</sup>(R<sup>4</sup>)<sub>3</sub>An<sup>-</sup> as a whole is or contains a cationic N-containing heterocycle with a counteranion,

M is hydrogen, lithium, sodium, potassium, one half equivalent of calcium or zinc or is an ammonium ion or a primary, secondary, tertiary or quaternary organic ammonium ion, and

25 An<sup>-</sup> is 1/p equivalent of a p-valent anion, preferably a halide, a carboxylate, C<sub>1</sub>-C<sub>8</sub>-alkylsulfate, C<sub>6</sub>-C<sub>14</sub>-arylsulfate, hexafluorophosphate, tetrafluoroborate, dihydrogenphosphate, one half equivalent of sulphate or hydrogenphosphate.

Particularly suitable for the process according to the invention are water-soluble photoinitiators. Some of the aforementioned photoinitiators of formula (I) are novel.

Therefore, one further aspect of the invention relates to novel photoinitiators of formula (Ia):



5 wherein

$n$ ,  $m$ ,  $\text{R}^1$  to  $\text{R}^5$  and  $\text{An}^-$  have the meaning given above including their areas of preference, provided, however, that the molecule contains at least one functional group or substituent selected from the group consisting of:

$-\text{SO}_3\text{M}$ ,  $-\text{COOM}$ ,  $\text{PO}_3\text{M}_2$ ,  $-\text{N}^+(\text{R}^4)_3\text{An}^-$ , heterocyclium $^+\text{An}^-$ .

10 wherein

$\text{M}$  is  $1/q$  equivalent of an  $q$ -valent metal ion or is an ammonium ion or a primary, secondary, tertiary or quarternary organic ammonium ion or a guanidinium ion.

Most preferred photoinitiators of formula (Ia) are those where in formula (Ia):

$n$  is 1,

15  $m$  is 2,

$\text{R}^1$  is  $\text{C}_1$ - $\text{C}_8$ -alkyl which is either once, twice or more than twice substituted by substituents selected from the group consisting of:

$-\text{SO}_3\text{M}$ ,  $-\text{COOM}$ ,  $\text{PO}_3\text{M}_2$ ,  $-\text{N}^+(\text{R}^4)_3\text{An}^-$  and heterocyclium $^+\text{An}^-$ , and

$\text{R}^2$  is mesityl or 2,6-dimethoxyphenyl,

20 whereby

$\text{R}^4$  is independently selected from the group consisting of hydrogen and  $\text{C}_1$ - $\text{C}_8$ -alkyl,

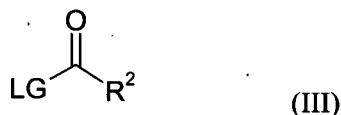
M is lithium, sodium or potassium, or is an ammonium ion or a primary, secondary, tertiary or quarternary organic ammonium ion, and

An<sup>-</sup> is a halide, a carboxylate, a C<sub>1</sub>-C<sub>8</sub>-alkylsulfate, a C<sub>6</sub>-C<sub>14</sub>-arylsulfate, hexafluorophosphate, tetrafluoroborate, dihydrogenphosphate or one half equivalent of sulphate or hydrogenphosphate.

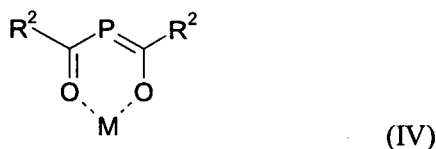
The compounds of formula (Ia) can be prepared analogous to the procedures disclosed in WO2005/014605; WO2006/056541 and WO2006/074983.

For example and preferably, the compounds of formula (Ia) are prepared by the steps of:

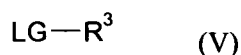
- A) contacting elemental phosphorous with a alkali or alkaline earth metal optionally in the presence of a catalyst or an activator in a solvent to obtain metal phosphides M<sub>3</sub>P, wherein M is an alkali or alkaline earth metal or to obtain alkali metal polyphosphides or alkaline earth metal polyphosphides;
- B) optionally adding a proton source, optionally in the presence of a catalyst or an activator to obtain metal dihydrogen phosphides MPH<sub>2</sub> which may depending on the proton source exist as complexes;
- C) acylating with:
- two equivalents of acid halides of formula (III)



to obtain compounds of formula (IV)

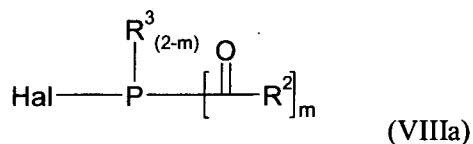


- or with one equivalent of acid halides of formula (III)
- and one compound of formula (V)









and

G) reacting the compounds of formula (VIIIa) with compounds of formulae (IXa) or (IXb)

H—R

5 wherein R is C<sub>1</sub>-C<sub>18</sub>-alkoxy or -N(R<sup>4</sup>)<sub>2</sub>

optionally in the presence of a base

whereby

R<sup>2</sup> to R<sup>4</sup>, n and m have the same meaning and areas of preference as given above for formula (Ia) and Hal is Halogen, preferably chlorine, bromine or iodine.

10 Halogen releasing compounds include e.g. hexachloroethane.

In an embodiment steps F) and G) are performed simultaneously.

It is known to one skilled in the art, that for some of the substitution patterns mentioned above, standard protection and deprotection techniques might have to be applied in order to enhance the chemicals yield of the compounds.

15 The compounds of formula (Ia) may be further functionalized by standard operations such as alkylations, nucleophilic substitutions, protonations with acids, deprotonations with bases, optionally followed by ion exchange and the like in order to obtain other compounds of formula (Ia).

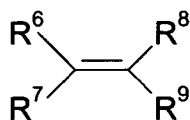
Further details are given in the examples.

20 The compounds of formulae (VIII) and (VIIIa) are also one aspect of the invention.

The emulsion further contains one or more polymerizable monomers.

As used herein, the term polymerizable monomer encompasses all monomers which can be polymerized in a radical polymerization.

Preferred polymerizable monomers are those of formula (II):



(II)

wherein

**R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup> and R<sup>9</sup>** are independently of one another selected from the group consisting of:

5 C<sub>1</sub>-C<sub>18</sub>-alkoxy, C<sub>1</sub>-C<sub>18</sub>-alkyl, C<sub>2</sub>-C<sub>18</sub>-alkenyl, C<sub>7</sub>-C<sub>15</sub>-arylalkyl

which is either not, once, twice or more than twice interrupted by non-successive functional groups selected from the group consisting of:

-O-, -CO-, -OCO-, -O(CO)O-, NR<sup>4</sup>(CO)-, -NR<sup>4</sup>(CO)O-, -O(CO)NR<sup>4</sup>-,  
-(CO)NR<sup>4</sup>-, -NR<sup>4</sup>(CO)NR<sup>4</sup>-, -Si(R<sup>5</sup>)<sub>2</sub>-, -OSi(R<sup>5</sup>)<sub>2</sub>-, -OSi(R<sup>5</sup>)<sub>2</sub>O-, -Si(R<sup>5</sup>)<sub>2</sub>O-

10 and which is either not, once, twice or more than twice interrupted by bivalent residues selected from the group consisting of heterocyclo-diyl and C<sub>6</sub>-C<sub>14</sub>-aryldiyl,

and which is not, additionally or alternatively either once, twice or more than twice substituted by substituents selected from the group consisting of:

15 halogen, cyano, epoxy, C<sub>6</sub>-C<sub>14</sub>-aryl; heterocyclyl, C<sub>1</sub>-C<sub>8</sub>-alkyl, C<sub>1</sub>-C<sub>8</sub>-alkoxy, C<sub>1</sub>-C<sub>8</sub>-alkylthio, C<sub>2</sub>-C<sub>8</sub>-alkenyl, C<sub>4</sub>-C<sub>15</sub>-arylalkyl, hydroxy, -SO<sub>2</sub>N(R<sup>4</sup>)<sub>2</sub>, NR<sup>4</sup>SO<sub>2</sub>-R<sup>5</sup>, -N(R<sup>4</sup>)<sub>2</sub>, -CO<sub>2</sub>N(R<sup>5</sup>)<sub>2</sub>, -COR<sup>4</sup>, -OCOR<sup>4</sup>, -O(CO)OR<sup>4</sup>, NR<sup>4</sup>(CO)R<sup>5</sup>, -NR<sup>4</sup>(CO)OR<sup>5</sup>, O(CO)N(R<sup>4</sup>)<sub>2</sub>, -NR<sup>4</sup>(CO)N(R<sup>4</sup>)<sub>2</sub>, -OSi(OR<sup>5</sup>)<sub>y-3</sub>(R<sup>5</sup>)<sub>y</sub>, -Si(OR<sup>5</sup>)<sub>y-3</sub>(R<sup>5</sup>)<sub>y</sub> where y is 1, 2 or 3.

20

Examples of preferred polymerizable monomers include:

- Mono(meth)acrylates, such as methyl-, ethyl-, butyl-, 2-ethylhexyl- and 2-hydroxyethyl acrylate, isobornyl acrylate gl;
  - other unsaturated carboxylic acid esters such as C<sub>1</sub>-C<sub>8</sub>-alkylesters of crotonic acid, maleic acid, fumaric acid, itaconic acid, cinnamic acid and unsaturated fatty acids such as linolenic
- 25

acid or oleic acid. glycidylacrylate, glycidylmethacrylate and methyl and ethyl methacrylate, acrylonitrile;

- poly(meth)acrylates such as ethylene glycol diacrylate, 1,6-hexanediol diacrylate, propylene glycol diacrylate, dipropylene glycol diacrylate, tripropylene glycol diacrylate, 5 neopentyl glycol diacrylate, hexamethylene glycol diacrylate and bis-phenol-A diacrylate, 4,4'-bis(2-acryloyloxyethoxy)diphenylpropane, trimethylolpropane tri-acrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, vinyl acrylate, divinyl- benzene, divinyl succinate, diallyl phthalate, triallyl phosphate, triallyl isocyanurate, tris- (hydroxyethyl) isocyanurate triacrylate (Sartomer 368; from Cray Valley) and tris(2- 10 acryloyl- ethyl) isocyanurate, ethyleneglycoldivinylether, diethyleneglycoldivinylether, triethylene-glycoldivinylether, polyethyleneglycol-mono-(meth)acrylate, polyethylene-glycol-di-(meth)acrylate;
- other crosslinking olefins such as divinyl-benzene;
- vinyl esters, such as vinyl acetate;
- 15 ● vinyl ethers, such as isobutyl vinyl ether;
- styrenes such as styrene and styrene substituted by C<sub>1</sub>-C<sub>8</sub>-alkyl- or halogen or sulfonic acid salts at the aromatic ring;
- siloxanes such as trimethoxyvinylsilane, triethoxyvinylsilane; and
- monoalkenes and polyalkenes like isobutene, butadiene, isoprene.

20 More preferred polymerizable monomers are styrene, para-methyl-styrene, sodium 4-vinyl-benzosulfonate, butylmethacrylate, butylacrylate, acrylonitrile, glycidylacrylate, and glycidylmethacrylate or mixtures thereof.

In an embodiment, the polymerizable monomer or the mixture of polymerizable monomers is used in an amount that the content of the polymerizable monomer or the mixture of polymerizable 25 monomers in the continuous phase is less than 50 g/l, preferably less than 25 g/l, more preferably less than 10 g/l and even more preferably less than 2 g/l.

In an embodiment, the polymerizable monomer or the mixture of polymerizable monomers is selected from those resulting in polymer nanoparticles having a glass transition temperature or a melting point or melting range higher than the polymerization temperature in order to avoid 30 immediate agglomeration.

The weight ratio of photoinitiator to polymerizable monomer is typically between 1:5 and 1:100.000, preferably between 1: 10 and 1:10.000 and more preferably 1:50 to 1:1,000.

5 In step A), the photoinitiator may be either added completely or partially. If in step A) the photoinitiator is added partially, the rest can be added during step B) either batchwise or continuously.

The emulsion further comprises at least one surfactant. Suitable surfactants are, for example, non-ionic, cationic or anionic or amphoteric surfactants.

10 Preferred surfactants are anionic surfactants such as C<sub>6</sub>-C<sub>24</sub>-alkyl sulfonates, C<sub>6</sub>-C<sub>24</sub>-perfluoroalkyl sulfonates C<sub>6</sub>-C<sub>24</sub>-alkyl ether sulfonates, C<sub>7</sub>-C<sub>24</sub>-aryl alkyl sulfonates, C<sub>6</sub>-C<sub>24</sub>-alkyl aryl sulfonates, C<sub>1</sub>-C<sub>24</sub>-alkyl succinates, C<sub>1</sub>-C<sub>24</sub>-alkyl sulfo succinates, N-(C<sub>1</sub>-C<sub>24</sub>-alkyl)-sarkosinate, acyltaurates, C<sub>6</sub>-C<sub>24</sub>-perfluoroalkyl carboxylates, C<sub>6</sub>-C<sub>24</sub>-alkyl phosphates, C<sub>6</sub>-C<sub>24</sub>-alkyl ether phosphates, C<sub>6</sub>-C<sub>24</sub>-alkyl ether carboxylates, in particular the alkali metal, ammonium-, and organic ammonium salts of the aforementioned compounds and cationic surfactants such as quarternary ammonium salts or pyridinium salts.

15 In an embodiment, at least one surfactant is selected from the group consisting of sodium lauryl sulfonate, ammonium lauryl sulfonate, sodium lauryl ether sulfonate, ammonium lauryl ether sulfonate, sodium lauryl sarkosinate, sodium oleyl succinate, sodium dodecylbenzene sulfonate, triethanolamine dodecyl benzene sulphate, cetyltrimethylammonium bromide, cetylpyridinium chloride, polyethoxylated tallow amine, benzalkonium chloride and benzethonium chloride.

20 The weight ratio of surfactant and the continuous phase is typically between 1:10.000 and 1:10, preferably between 1:1.000 and 1:50, whereby the amount should be at least equal or higher than the critical micelle concentration (CMC) in the emulsion. The CMC is defined as being the lowest concentration of surfactant at which micelle formation is observed and which is dependant on the nature of the surfactant used.

25 The weight ratio of the aqueous continuous phase and the dispersed phase depends on the surface energy and the phase inversion point but is typically between 1:2 and 500:1, preferably, between 1.5:1 and 20:1.

In step B), the emulsion of step A) is exposed to electromagnetic radiation having a wavelength sufficient to induce the generation of radicals from the photoinitiator.

30 Upon exposure to said electromagnetic radiation, the photoinitiator molecules typically undergo excitation to the singlet state, electron-spin reversal to the triplet state and defragmentation thereby

forming at least two radicals. At least some of these radicals are capable of initiating a radical polymerization of the polymerizable monomers.

For the photoinitiators according to formula I, the radical formation is typically induced by exposure to electromagnetic radiation having a wavelength of below 500 nm, preferably below 450 nm, more preferably in the range of 200 to 450 nm, even more preferably in the range of 300 to 440 nm.

As a consequence, suitable sources of electromagnetic radiation having a wavelength sufficient to induce the generation of radicals from the photoinitiator include excimer lasers such as KrF and XeF-lasers; UV lamps like medium-pressure, super-high-pressure, high-pressure and low-pressure mercury lamps which can be undoped or doped e.g. with gallium iodide, thallium iodide or other metal halides; blue or white LEDs; concentrated, direct or indirect sunlight; xenon or xenon mercury arc lamps such as continuous-output xenon short- or long-arc lamps, xenon or xenon mercury flash lamps or other flash lamps; microwave-excited metal vapour lamps; excimer lamps, superactinic fluorescent tubes; fluorescent lamps; and noble gas incandescent lamps.

The determination of a suitable reaction temperature range during polymerization depends on the composition of the aqueous continuous phase, the composition of the dispersed phase and the reaction pressure since freezing or boiling in the emulsion should be avoided.

A typical and preferred reaction temperature range to carry out the polymerization according to step B) is from -30°C to 120°C, preferably from -10 to 80°C and even more preferably from 0 to 40°C.

A typical and preferred reaction pressure range to carry out the polymerization according to step B) is from 100 hPa to 10 Mpa, preferably from 500 hPa to 1 MPa and even more preferably from 800 hPa to 1,2 MPa. Most preferably the reaction is carried out under ambient pressure.

The pH value of the aqueous continuous phase is typically in the range of 3 to 10, preferably in the range of 5 to 9 calculated on standard conditions. If compounds of formula (I) are used which bear carboxylic acid groups, a pH value above the pKa value of the respective compound of formula (I) is preferred.

The exposure to electromagnetic radiation depends on the intensity but typically can, for example, last for 1s to 24 h, preferably for 10s to 3h.

In an embodiment, the amount of electromagnetic radiation having a wavelength sufficient to induce the generation of radicals is from 10 J/l to 500kJ/l of the emulsion, preferably 100 J/l to 50 kJ/l.

5 After the exposure to electromagnetic radiation, the reaction might either continue or not, depending on the remaining polymerizable monomers in the emulsion. In those cases where the polymerization is not finished after the exposure to electromagnetic radiation ends, the reaction mixture is either reacted further e.g. for 1 min to 10h or terminated immediately of after e.g. 1 min to 10h by adding radical scavengers such as hydroquinones, diphenyldisulfides, phenothiazine and the like.

10 In an embodiment, the polymerization is terminated after consumption of 60 to 99 wt-% of the polymerizable monomers, preferably after consumption of 65 to 90 wt.-%.

In an embodiment the residual polymerizable monomers are removed from the resulting dispersion by standard stripping or distillation techniques.

15 In an embodiment, the process might be carried out using a batch reactor or a flow-through reactor, whereby the reactors allow the irradiation of the emulsion contained therein with electromagnetic radiation.

The polymer nanoparticles are obtained via the process according to the invention as an aqueous suspension.

20 The main advantage of the process according to the invention is that it allows the efficient synthesis of polymer particles in the nanometer to micrometer range. Unprecedented control over the dispersity of the size and the molecular weight distribution can be achieved. Furthermore, the molecular weight of the individual polymer chains is typically very high.

The polymer nanoparticles obtained typically have a M-PDI of 1.00 to 1.50, preferably a M-PDI of 1.02 to 1.40.

25 The polymer nanoparticles further typically have a DLS-PDI of 0.05 to 0.50, preferably a DLS-PDI of 0.10 to 0.30.

The molecular weight of the polymer chains within the polymer nanoparticles typically have a weight average molecular mass of more than 500 kg/mol to 5,000 kg/mol, preferably 1,000 kg/mol to 5,000 kg/mol.

Therefore, an embodiment relates to polymer nanoparticles having a DLS-PDI of 0.05 to 0.50, preferably 0.10 to 0.30 and a M-PDI of 1.00 to 1.50, preferably 1.02 to 1.40 and/or a weight average molecular mass of more than 500 kg/mol to 5,000 kg/mol, preferably 1,000 kg/mol to 5,000 kg/mol.

5 In an embodiment, polymer suspensions comprise 0,001 to 50 wt-%, preferably 0,001 to 25 wt-% and even more preferably 0.5 to 20 wt-% of the aforementioned polymer nanoparticles.

The polymer nanoparticles can be concentrated in or isolated from the dispersions using standard techniques well known to those skilled in the art. For example, inorganic salts or solutions thereof are added to the suspension and the resulting mixture can be subjected to centrifugation,  
10 sedimentation, filtration or other separation processes of a like nature.

In an embodiment, the concentration or isolation is performed by nano- or microfiltration using membranes.

In an embodiment, the aforementioned polymer suspensions or polymer nanoparticles can be used, for example, in coating, adhesive, ink, and painting materials, precision mold constructions, in the  
15 manufacture of electronic articles, for drug delivery systems, diagnostic sensors and contrast agents.

A further aspect of the invention therefore relates to coatings, adhesives, inks, and painting materials, precision mold constructions, electronic articles, drug delivery systems, diagnostic sensors and contrast agents comprising the polymer nanoparticles according to the invention.

20 The invention is further illustrated by the examples without being limited thereby.



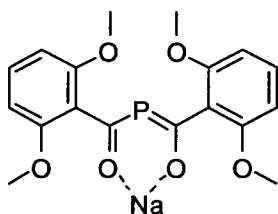
**Examples:****I Preparation of photoinitiators and their precursor materials****1) Preparation of sodium bis(mesitoyl)phosphide**

In a 100 mL thick-walled Schlenk flask equipped with a teflon screw cap, sodium (1.73 g, 0.075 mmol, 3 eq.) and red phosphorus (0.78 g, 0.025 mmol, 1 eq.) were put together under inert conditions. A glass covered magnetic stirrer was added and 20 mL of ammonia were condensed into the flask, by cooling with dry ice/ acetone to -78°C. Subsequently, dimethoxyethane (dme) (20 mL) was added and the flask was closed and warmed up to room temperature. After 90 min, stirring at room temperature a change in colour from blue to dark yellow was observed and after another 30 min, the colour became intensively yellow. The pressure in the reaction vessel was 7 to 8 bar. The reaction mixture was cooled down to -40°C. The Schlenk flask, which had now a pressure of 1 bar, was opened and *tert*-butanol (3.71 g, 0.05 mol, 2 eq.) was added. The reaction mixture was warmed up to room temperature over a period of two hours. Finally, the solvent was completely removed in vacuo at room temperature. The remaining oil was dissolved in dme (40 mL). Mesitoyl chloride (9.15 g, 0.05 mol, 2 eq.) was added dropwise.

- i): Isolation of the product under dry conditions: The reaction mixture was stirred for one hour at room temperature, the precipitate of sodium chloride was removed by filtration and the solvent was evaporated in vacuo. The pure microcrystalline product can be obtained by dissolving the sodium bis(mesitoyl)phosphide in dme and precipitation with n-hexane (Yield: 5.89 g, 67.7 %).
- ii). Working up with degassed water: The reaction mixture was mixed with 100 mL degassed, distilled water. After stirring the solution until the sodium chloride was completely dissolved, the reaction mixture was extracted three times with 50 mL of toluene. After removing the toluene in vacuo, the pure product remains. It can contain small amounts of water, which can be completely removed by azeotropic distillation with toluene. The product is dissolved in toluene and the solvent is removed in vacuo afterwards again. This procedure has to be repeated two or three times. The yield is the same as for procedure a).

m.p.: 208°C (Decomposition).

<sup>31</sup>P NMR (101.25 MHz):  $\delta$  = 84.1 ppm (br.).

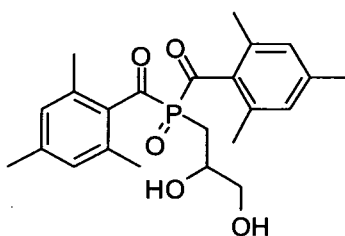
2) Preparation of sodium bis(2,6-dimethoxybenzoyl)phosphide

5

NaPH<sub>2</sub> x 2 NaO<sup>t</sup>Bu (0.846 g, 3.41 mmol, 1 eq.) was dissolved in dme (6 mL) and cooled in an ice water bath to 0°C. 2,6-dimethoxybenzoyl chloride (1.37 g, 6.82 mmol, 2 eq.) dissolved in dme (8 mL) was added dropwise to the solution. After 1 hour of stirring at room temperature the solvent was removed in vacuo to yield a yellow powder of sodium bis(2,6-dimethoxy-benzoyl)phosphide (Yield: 87 %, 1.14 g, 2.97 mmol).

10

<sup>31</sup>P{<sup>1</sup>H}-NMR (121.5 MHz, d<sup>8</sup>-thf): δ = 91.0 (s).

3) Preparation of ((2,3-dihydroxypropyl)phosphoryl)bis(mesitylmethanone)

15

Sodium bis(mesityl)phosphide of example 1 (250 mg, 0.72 mmol, 1 eq.) was dissolved in thf (5 mL). 1-Bromo-2,3-propanediol (111.6 mg, 0.063 mL, 0.72 mmol, 1 eq.) was added and the solution was stirred over night. The white precipitate was filtered off. The thf was removed in vacuo and the phosphane was dissolved in ethanol (5 mL). Hydrogen peroxide (10%) (0.244 mL, 0.72 mmol, 1 eq.) was added and the solution was stirred over night. Diethyl ether (5 mL) was added and the solution was washed with sodium hydrogen carbonate solution (2%) and brine. After drying with sodium sulfate, the solvent was evaporated. A pale yellow product was obtained (Yield: 64 %, 0.46 mmol, 191.5 mg).

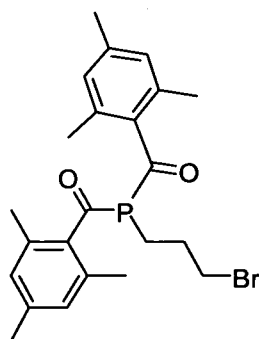
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25

<sup>31</sup>P NMR (121.5 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 26.4 (t, J = 16.8 Hz)

4) Preparation of ((3-bromopropyl)phosphinediyl)bis(mesitylmethanone)

5



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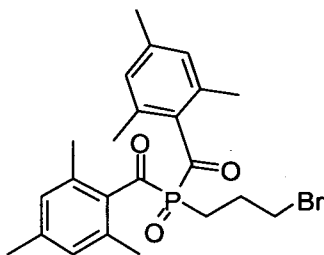
Sodium bis(mesityl)phosphide of example 1 (1.00 g, 2.88 mmol, 1 eq.) was dissolved in toluene (5.00 mL). This solution was added dropwise in a cooled (ice bath) solution of 1,3-dibromopropane (0.028 mL, 0.056 g, 28.8 mmol, 10 eq.) in thf (5.00 mL). Then the reaction mixture was stirred for 24 hours at 50°C to complete the reaction. A white precipitate of sodium bromide was formed. After removing the sodium bromide by filtration, the solution was evaporated in vacuo. The remaining yellow oil was dissolved in diethyl ether and washed with an aqueous and degassed ammonium chloride solution (5%). After the ether solution had been dried with sodium sulfate it was evaporated in vacuum at room temperature and dried in high vacuum for 4 hours to remove the excess of 1,3-dibromopropane. (Yield: 1.16 g, 2.59 mmol, 90%).

15

$^{31}\text{P}$  NMR: (121.5 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 50.8$  (t,  $J = 9.6$  Hz).

5) Preparation of ((3-bromopropyl)phosphoryl)bis(mesitylmethanone)

20



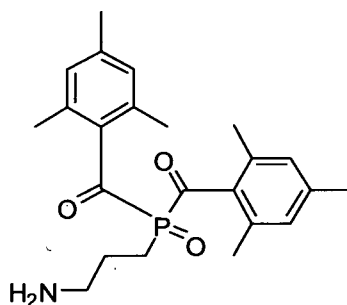
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((3-bromopropyl)phosphinediyl)bis(mesitylmethanone) of example 4 (1.16 g, 2.59 mmol, 1 eq.) was dissolved in toluene (5 mL) and hydrogen peroxide (10%) (8.88 mL, 2.59 mmol, 1 eq.) was added. The reaction mixture was stirred at 40°C for 12 hours. Afterwards diethylether (50 mL) were added and the solution was washed with twice sodium hydrogencarbonate (2%) solution, once

with brine and finally dried with magnesium sulfate. After removing the solvent in vacuo at room temperature, the pure product was obtained as a yellow oil (Yield: 0.97 g, 2.10 mmol).

$^{31}\text{P}$  NMR (121.5 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 25.83$  (t,  $J = 9.7$  Hz).

5      6) Preparation of ((3-aminopropyl)phosphoryl)bis(mesitylmethanone)



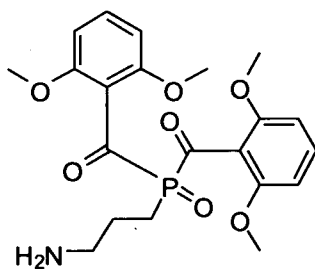
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Sodium bis(mesityl)phosphide of example 1 (22.8 mg, 0.065 mmol, 1 eq.) was dissolved in dme (2 mL). 3-Bromopropylammonium bromide (14 mg, 0.065 mmol, 1 eq.) was added at room temperature. After 15 minutes of stirring, the solvent was removed in vacuo at room temperature and replaced by 2 mL ethanol. With a microlitre syringe hydrogen peroxide (30 %) (0.008 mL, 0.065 mmol, 1 eq.) was added slowly. The solution was stirred for 30 minutes. Subsequently, the solvent was removed in vacuo. The product was dissolved in diethylether (2 mL), washed with brine and dried with sodium sulfate. After filtration and evaporation of the diethylether, the pure product was obtained (Yield not determined).

15

$^{31}\text{P}\{^1\text{H}\}$ -NMR (121.5 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 23.1$  (s).

20      7) Preparation of 3-(bis(2,6-dimethoxybenzoyl)phosphino)propylamine



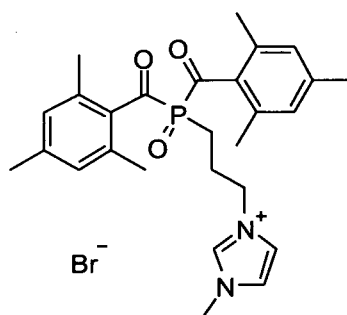
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Sodium bis(2,6-dimethoxybenzoyl)phosphide of example 2 (25 mg (0.065 mmol, 1 eq.) was dissolved in dme (2 mL). 3-Bromopropylamine hydrobromide (14 mg, 0.065 mmol, 1 eq.) was

added at room temperature. After stirring the reaction mixture for 15 minutes, the solvent was removed in vacuo at room temperature and replaced by ethanol (2 mL). With a microlitre syringe hydrogen peroxide (30 %) (0.008 ml, 0.065 mmol, 1 eq.) was added slowly and the solution was stirred for 30 minutes. Subsequently, the solvent was removed in vacuo. The residue was dissolved in diethylether (2 mL) and washed with brine and dried with sodium sulfate. After filtration and evaporation of the diethylether the pure product was obtained.

$^{31}\text{P}\{^1\text{H}\}$  NMR (121.5 MHz,  $\text{d}^8\text{-thf}$ ):  $\delta = 24.1$  (s).

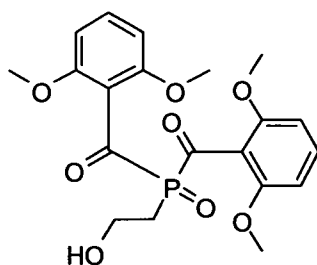
8) Preparation of 3-(3-(bis(2,4,6-trimethylbenzoyl)phosphoryl)propyl)-1-methyl-1H-imidazol-3-ium bromide



15 ((3-Bromopropyl)-phosphoryl) bis(mesitylmethanone) of example 5 (825 mg, 1.78 mmol, 1 eq.) and methylimidazol (0.15 mL, 155 mg, 1.89 mmol, 1.06 eq.) were dissolved in toluene (2 mL). The solution was stirred for 24 h at 50°C. A yellow precipitate was formed. The solution was decanted and the yellow solid was washed three times with 2 mL toluene. The microcrystalline product was dried for two hours in vacuo.

20  $^{31}\text{P}$  NMR (101.25 MHz,  $\text{D}_2\text{O}$ ):  $\delta = 23.1$  (br.)

9) Preparation of bis(2,6-dimethoxybenzoyl)hydroxyethylphosphanoxide

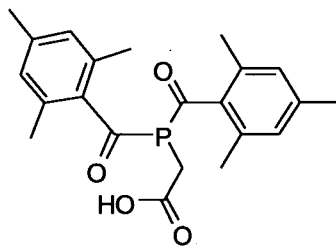


25

Sodium bis(2,6-dimethoxybenzoyl)phosphide of example 2 (25 mg, 0.065 mmol, 1 eq.) was dissolved in dme (2 mL). With a microlitre syringe 2-bromoethanol (0.005 ml, 0.065 mmol, 1 eq.) was added at room temperature. After stirring the reaction mixture for 15 minutes, the solvent was removed in vacuo at room temperature and replaced by ethanol (2 mL). To this solution hydrogen peroxide (30 %) (0.008 ml, 0.065 mmol, 1 eq.) was added slowly with a microlitre syringe. The solution was stirred for 5 minutes. Subsequently, the solvent was removed in vacuo (Yield: 76 %, 0.05 mmol, 20.85 mg).

$^{31}\text{P}$  NMR (101.3 MHz,  $\text{d}^8\text{-thf}$ ):  $\delta = 26.47$  (br.).

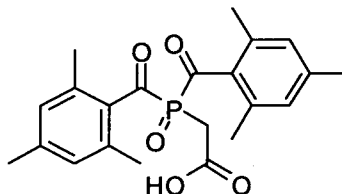
10 10) Preparation of 2-(bis(2,4,6-trimethylbenzoyl)phosphino)acetic acid



15 Sodium bis(mesityl)phosphide of example 1 (1.00 g, 2.88 mmol, 1 eq.) was dissolved in thf (5.00 mL). Bromoacetic acid (0.40 g, 2.88 mmol, 1 eq.) was dissolved in thf (5.00 mL). The solutions were put together and stirred for 24 hours at room temperature. A white precipitate of sodium bromide was formed. After removing the sodium bromide by filtration, the solution was evaporated in vacuo. The remaining yellow oil was dissolved in diethyl ether and washed with an aqueous and degassed ammonium chloride solution (5%). After the ether solution was dried with sodium sulfate, the solvent was evaporated in vacuum at room temperature and dried in high vacuum for 4 hours. (Yield: 0.96 g, 2.51 mmol, 87%)

$^{31}\text{P}$  NMR (101.3 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 46.7$ .

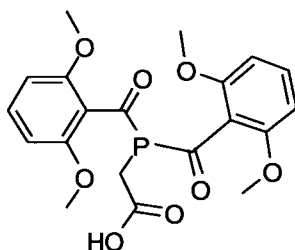
11) Preparation of 2-(bis(2,4,6-trimethylbenzoyl)phosphoryl)acetic acid (BAPO-acetic acid)



5 2-(Bis(2,4,6-trimethylbenzoyl)phosphino)-acetic acid of example 10 (1.00 g, 2.60 mmol, 1 eq.) was dissolved in degassed ethanol (5.00 mL) and hydrogen peroxide (30%) (0.29 mL, 2.60 mmol, 1 eq.) was added. The solution was stirred at 40°C for one hour. The ethanol was removed in vacuo at room temperature. A white crystalline powder was obtained, which can be easily recrystallised from 40°C warm water (Yield: Quantitative).

10  $^{31}\text{P}$  NMR (121.5 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 19.6$  (t,  $J = 10.9$  Hz).

12) Preparation of 2-(bis(2,6-dimethoxybenzoyl)phosphino)acetic acid ( $^{\text{MeO}}$ BAP acetic acid)



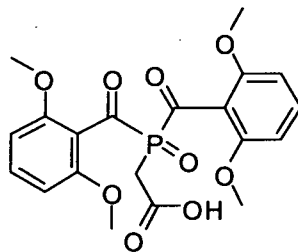
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Sodium bis(2,6-dimethoxybenzoyl)phosphide of example 2 (100 mg, 0.26 mmol, 1 eq.) was dissolved in dme (5 mL), bromoacetic acid (36 mg, 0.26 mmol, 1 eq.) was dissolved in dme (2 mL) and added to this solution at room temperature. After stirring the reaction mixture for 2 hours, the solvent was removed in vacuo at room temperature (Yield: not determined).

20

$^{31}\text{P}\{^1\text{H}\}$ -NMR (101.3 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 49.2$  (s)

13) Preparation of 2-(bis(2,6-dimethoxybenzoyl)phosphoryl)acetic acid (<sup>MeO</sup>BAPO-acetic acid)



5

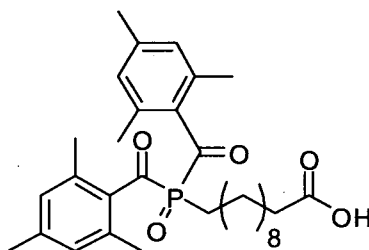
To a solution of <sup>MeO</sup>BAP-acetic acid of example 12 (109 mg, 0.26 mmol, 1 eq.) in ethanol (4 mL), hydrogen peroxide (30 %) (0.03 ml, 0.26 mmol, 1 eq.) was added slowly. The reaction mixture was stirred for 30 minutes. Subsequently, the solvent was removed in vacuo and the <sup>MeO</sup>BAPO-acetic acid was once again dissolved in ethanol. After filtration of the sodium bromide the solvent was evaporated in vacuo to yield crystalline <sup>MeO</sup>BAPO-acetic acid (Yield: 78 %, 88 mg, 0.20 mmol).

10

<sup>31</sup>P{<sup>1</sup>H}-NMR (121.5 MHz, d<sup>8</sup>-thf): δ = 22.2 (s).

14) Preparation of 11-(bis(2,4,6-trimethylbenzoyl)phosphoryl)undecanoic acid (BAPO-undecanoic acid)

15



In a 20 mL Schlenk flask sodium bis(mesityl)phosphide of example 1 (251.9 mg, 0.724 mmol, 1 eq.) was dissolved in thf (5.00 mL). 11-bromo-undecanoic acid (197.8 mg, 0.72 mmol, 1 eq.) was added and the solution was stirred for two days at 40°C. The white precipitate of sodium bromide was filtered off and the solvent of the yellow filtrate was removed in vacuo at room temperature. The phosphane remains as a yellow oil (<sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>, 81.0 MHz): δ = 51.5). After solving the phosphane in ethanol, hydrogen peroxide (10%) (0.24 g, 0.72 mmol, 1 eq.) was added and the solution was stirred for 40 minutes at 40°C. The ethanol was evaporated in vacuo at room temperature and the solid pale yellow product was dried in high vacuum (Yield: 312.3 mg, 0.594 mmol, 82%).

20

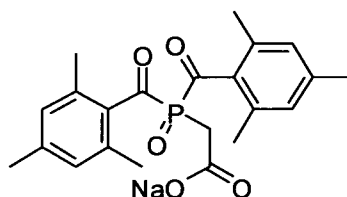
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$^{31}\text{P}$  NMR (121.5 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 18.12$  (t,  $J_{\text{CP}} = 9.8$  Hz).

UV/Vis (acetonitrile): 284 nm (max.), 311 nm (max.), 384 nm (max.)

5 15) Preparation of sodium 2-(bis(2,4,6-trimethylbenzoyl)phosphoryl)acetate (Na-BAPO-acetate)

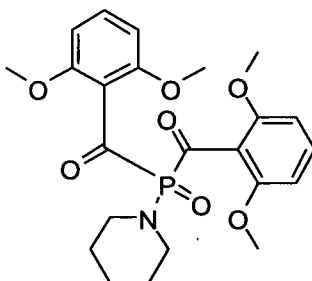


10 BAPO-acetic acid of example 11 (0.1 g, 0.25 mmol, 1 eq.) was suspended in distilled water (2 mL) and sodium hydrogencarbonate (21.0 mg, 0.25 mmol, 1 eq.) were added. A clear pale yellow solution was obtained. After removing the water in vacuo at room temperature, a pale yellow crystalline powder was isolated (Yield: quantitative). The same procedure can be performed to synthesise other alkali salts of BAPO-acetic acid from carbonates or hydrogencarbonates. (e.g. with  
15 potassium hydrogen carbonate, or lithium carbonate).

$^{31}\text{P}$  NMR (121.5 MHz,  $\text{D}_2\text{O}$ ):  $\delta = 23.6$  (t,  $J = 10.8$  Hz).

16) Preparation of bis(2,6-dimethoxybenzoyl)-N-piperidinylphosphanoxide

20



25

Sodium bis(2,6-dimethoxybenzoyl)phosphide of example 2 (200 mg, 0.52 mmol, 1 eq.) was dissolved in thf (5 mL). Acetic acid (0.03 mL, 0.52 mmol, 1 eq.) was added at room temperature. After stirring the reaction mixture for 2 hours, the solvent was removed in vacuo at room temperature. 2-Propanol (10 mL) was added and the solution was stirred at 70°C under atmospheric

conditions for 80 hours. The solvent was replaced with dichloromethane (5 mL). To this solution triethylamine (0.07 mL, 0.52 mmol, 1 eq.) and piperidine (0.05 mL, 0.52 mmol, 1 eq.) were added. Finally, the reaction mixture was cooled down to 0°C with an ice-bath and a solution of hexachloroethane (107 mg, 0.52 mmol, 1 eq.) in dichloromethane (5 mL) was added dropwise. The solution was stirred for 2 hours at 0°C. Subsequently, the solvent was removed in vacuo (Yield: 41%, 0.21 mmol, 96.9 mg).

$^{31}\text{P}$  NMR (101.3 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = -4.7$  (s).

## II) Photoinitiated Emulsion Polymerization

### 17) Synthesis of poly(vinylacetate) particles

In a Schlenk flask under exclusion of oxygen, 3 mL of a 10% aqueous degassed solution of sodium dodecylsulfate (SDS), 6 mL of degassed and deionised water, 1 mL of an 1% aqueous solution of Na-BAPO-acetate of example 15 and 2 mL of vinylacetate (purification by filtration over MP Alumina N, activity 1, degassed) were mixed. After 5 min. of vigorous stirring (stirrer: RCT Basic, IKA Labortechnik, stage 6) the resulting emulsion was irradiated for 10 min. with a medium pressure mercury lamp (TQ 150 in a DURAN 50 glass mantel, UV-Consulting Peschl) to give a latex. The sample was stirred for another 24 h under an atmosphere of argon and under exclusion of light. Subsequently, small portion of the latex were removed for the determination of the particle size and the solid content. For the light scattering measurements, 0.1 mL of latex was diluted with 5 mL water. For the determination of the solid content, 1 mL of sample solution was given onto sea sand (carefully dried at 130 °C in a drying oven) in a Petri dish. Subsequently, the sample was kept at 110 °C for 24 h in a drying oven under vacuum (Vacucell, MMM Medcenter GmbH) to remove all volatiles (solvents, unreacted monomer).

In order to isolate the polymer in substance, an aqueous saturated sodium chloride solution was added to the latex. The polymer was isolated by centrifugation (10 min. at 25'000 rpm in a 3K 30 Sigma centrifuge). This procedure was repeated three times to yield a white powder.

Analytic Results:

Dynamic Light Scattering (DLS) (after dilution with water):

Z-average: 35 nm

DLS-PDI=0.16

Solid content: 13.8 % (71 % conversion).

18) Synthesis of poly(acrylic acid butyl ester) particles

In a Schlenk flask under exclusion of oxygen, 2 mL of a 10% aqueous degassed solution of sodium dodecylsulfate (SDS), 7 mL of degassed and deionised water, 1 mL of an 1% aqueous solution of Na-BAPO-acetate of example 15 and 2 mL of acrylic acid butyl ester (purification by filtration over MP Alumina N, activity 1, degassed) were mixed. After 5 min. of vigorous stirring (stirrer: RCT Basic, IKA Labortechnik, stage 6) the resulting emulsion was irradiated for 10 min. with a medium pressure mercury lamp (TQ 150 in a DURAN 50 glass mantel, UV-Consulting Peschl) to give a latex. The sample was stirred for another 24 h under an atmosphere of argon and under exclusion of light. Subsequently, small portion of the latex were removed for the determination of the particle size and the solid content. For the light scattering measurements, 0.1 mL of latex was diluted with 5 mL water. For the determination of the solid content, 1 mL of sample solution was given onto sea sand (carefully dried at 130 °C in a drying oven) in a Petri dish. Subsequently, the sample was kept at 110 °C for 24 h in a drying oven under vacuum (Vacucell, MMM Medcenter GmbH) to remove all volatiles (solvents, unreacted monomer).

In order to isolate the polymer in substance, an aqueous saturated sodium chloride solution was added to the latex. The polymer was isolated by centrifugation (10 min. at 25'000 rpm in a 3K 30 Sigma centrifuge). This procedure was repeated three times to yield a white powder.

Analytic Results:

20 Dynamic Light Scattering (DLS) (after dilution with water):

Z-average: 42 nm

DLS-PDI = 0.12

Solid content: 15.7 % (92 % conversion).

25 19) Synthesis of poly(para-methylstyrene)particles

In a Schlenk flask under exclusion of oxygen, 50 mg sodium dodecylsulfate (SDS), 10 mL of degassed and deionised water, 0.5 mL of an 1% aqueous solution of Na-BAPO-acetate of example 15 and 3 mL of para-methylstyrene (purification by filtration over MP Alumina N, activity 1, degassed) were mixed. After 5 min. of vigorous stirring (stirrer: RCT Basic, IKA Labortechnik,

stage 6) the resulting emulsion was irradiated for 10 min. with a medium pressure mercury lamp (TQ 150 in a DURAN 50 glass mantel, UV-Consulting Peschl) to give a latex. The sample was stirred for another 24 h under an atmosphere of argon and under exclusion of light. Subsequently, small portion of the latex were removed for the determination of the particle size and the solid content. For the light scattering measurements, 0.1 mL of latex was diluted with 5 mL water. For the determination of the solid content, 1 mL of sample solution was given onto sea sand (carefully dried at 130 °C in a drying oven) in a Petri dish. Subsequently, the sample was kept at 110 °C for 24 h in a drying oven under vacuum (Vacucell, MMM Medcenter GmbH) to remove all volatiles (solvents, unreacted monomer).

10 In order to isolate the polymer in substance, a saturated sodium chloride solution in methanol was added to the latex. The polymer was isolated by centrifugation (25'000 rpm in a 3K 30 Sigma centrifuge). This procedure was repeated three times to yield a white powder.

Analytic Results:

Dynamic Light Scattering (DLS) (after dilution with water):

15 Z-average: 59 nm

DLS-PDI = 0.28

Solid content: 16.0 % (89 % conversion).

#### 20) Synthesis of copolymer particles from styrene/sodium 4-vinyl-benzosulfonate

20 In a Schlenk flask under exclusion of oxygen, 100 mg of sodium 4-vinyl-benzosulfonate, 2 mL of a 10% aqueous degassed solution of sodium dodecylsulfate (SDS), 8 mL of degassed and deionised water, 1 mL of an 1% aqueous solution of Na-BAPO-acetate of example 15 and 2 mL of styrene (purification by filtration over MP Alumina N, activity 1, degassed) were mixed. After 5 min. of vigorous stirring (stirrer: RCT Basic, IKA Labortechnik, stage 6) the resulting emulsion was irradiated for 10 min. with a medium pressure mercury lamp (TQ 150 in a DURAN 50 glass mantel, UV-Consulting Peschl) to give a latex. The sample was stirred for another 24 h under an atmosphere of argon and under exclusion of light. Subsequently, small portion of the latex were removed for the determination of the particle size and the solid content. For the light scattering measurements, 0.1 mL of latex was diluted with 5 mL water. For the determination of the solid content, 1 mL of sample solution was given onto sea sand (carefully dried at 130 °C in a drying

25

30

oven) in a Petri dish. Subsequently, the sample was kept at 110 °C for 24 h in a drying oven under vacuum (Vacucell, MMM Medcenter GmbH) to remove all volatiles (solvents, unreacted monomer).

5 In order to isolate the polymer in substance, a saturated sodium chloride solution in methanol was added to the latex. The polymer was isolated by centrifugation (10 min. at 25'000 rpm in a 3K 30 Sigma centrifuge). This procedure was repeated three times to yield a white powder.

Analytic Results:

Dynamic Light Scattering (DLS) (after dilution with water):

Z-average: 29 nm

10 DLS-PDI=0.15

Solid content: 14.6 % (74 % conversion).

#### 21) Synthesis of copolymer particles from styrene/methacrylic acid butyl ester

15 In a Schlenk flask under exclusion of oxygen, 4 mL of a 10% aqueous degassed solution of sodium dodecylsulfate (SDS), 7 mL of degassed and deionised water, 1 mL of an 1% aqueous solution of Na-BAPO-acetate of example 15, 1.2 mL of styrene (purification by filtration over MP Alumina N, activity 1, degassed), and 0.8 mL of methacrylic acid butyl ester (purification by filtration over MP Alumina N, activity 1, degassed) were mixed. After 5 min. of vigorous stirring (stirrer: RCT Basic, IKA Labortechnik, stage 6) the resulting emulsion was irradiated for 10 min.  
20 with a medium pressure mercury lamp (TQ 150 in a DURAN 50 glass mantel, UV-Consulting Peschl) to give a latex. The sample was stirred for another 24 h under an atmosphere of argon and under exclusion of light. Subsequently, small portion of the latex were removed for the determination of the particle size and the solid content. For the light scattering measurements, 0.1 mL of latex was diluted with 5 mL water. For the determination of the solid content, 1 mL of  
25 sample solution was given onto sea sand (carefully dried at 130 °C in a drying oven) in a Petri dish. Subsequently, the sample was kept at 110 °C for 24 h in a drying oven under vacuum (Vacucell, MMM Medcenter GmbH) to remove all volatiles (solvents, unreacted monomer).

30 In order to isolate the polymer in substance, an aqueous saturated sodium chloride solution was added to the latex. The polymer was isolated by centrifugation (10 min. at 25'000 rpm in a 3K 30 Sigma centrifuge). This procedure was repeated three times to yield a white powder.

Analytic Results:

Dynamic Light Scattering (DLS) (after dilution with water):

Z-average: 22 nm

DLS-PDI = 0.15

5 Solid content: 15.5 % (87 % conversion).

## 22) Synthesis of copolymer particles from styrene/acrylonitrile

10 In a Schlenk flask under exclusion of oxygen, 2 mL of a 10% aqueous degassed solution of sodium dodecylsulfate (SDS), 9 mL of degassed and deionised water, 1 mL of an 1% aqueous solution of Na-BAPO-acetate of example 15, 1.6 mL of styrene (purification by filtration over MP Alumina N, activity 1, degassed), and 0.4 mL of acrylonitrile (purification by filtration over MP Alumina N, activity 1, degassed) were mixed. After 5 min. of vigorous stirring (stirrer: RCT Basic, IKA Labortechnik, stage 6) the resulting emulsion was irradiated for 10 min. with a medium pressure mercury lamp (TQ 150 in a DURAN 50 glass mantel, UV-Consulting Peschl) to give a  
15 latex. The sample was stirred for another 24 h under an atmosphere of argon and under exclusion of light. Subsequently, small portion of the latex were removed for the determination of the particle size and the solid content. For the light scattering measurements, 0.1 mL of latex was diluted with 5 mL water. For the determination of the solid content, 1 mL of sample solution was given onto sea sand (carefully dried at 130 °C in a drying oven) in a Petri dish. Subsequently the sample was kept  
20 at 110 °C for 24 h in a drying oven under vacuum (Vacucell, MMM Medcenter GmbH) to remove all volatiles (solvents, unreacted monomer).

In order to isolate the polymer in substance, an aqueous saturated sodium chloride solution was added to the latex. The polymer was isolated by centrifugation (10 min. 25'000 rpm in a 3K 30 Sigma centrifuge). This procedure was repeated three times to yield a white powder.

25 Analytic Results:

Dynamic Light Scattering (DLS) (after dilution with water):

Z-average: 46 nm

DLS-PDI = 0.12; Solid content: 10.0 % (58 % conversion).

23) Synthesis of copolymer particles from styrene/ methacrylic acid glycidyl ester

In a Schlenk flask under exclusion of oxygen, 20 mg of Na-BAPO-acetate of example 15, 200 mg of sodium dodecylsulfate (SDS), 12 mL of degassed and deionised water, 1.5 mL of styrene (purification by filtration over MP Alumina N, activity 1, degassed), and 0.5 mL of methacrylacid glycidyl ester (purification by filtration over MP Alumina N, activity 1, degassed) were mixed. After 5 min. of vigorous stirring (stirrer: RCT Basic, IKA Labortechnik, stage 6) the resulting emulsion was irradiated for 10 min. with a medium pressure mercury lamp (TQ 150 in a DURAN 50 glass mantel, UV-Consulting Peschl) to give a latex. The sample was stirred for another 24 h under an atmosphere of argon and under exclusion of light. Subsequently, small portion of the latex were removed for the determination of the particle size and the solid content. For the light scattering measurements, 0.1 mL of latex was diluted with 5 mL water. For the determination of the solid content, 1 mL of sample solution was given onto sea sand (carefully dried at 130 °C in a drying oven) in a Petri dish. Subsequently the sample was kept at 110 °C for 24 h in a drying oven under vacuum (Vacucell, MMM Medcenter GmbH) to remove all volatiles.

In order to isolate the polymer in substance, an aqueous saturated sodium chloride solution was added to the latex. The polymer was isolated by centrifugation (10 min. at 25'000 rpm in a 3K 30 Sigma centrifuge). This procedure was repeated three times to yield a white powder.

## Analytic Results:

## Dynamic Light Scattering (DLS) (after dilution with water):

Z-average: 35 nm

DLS-PDI = 0.12

Solid content: 12.7 % (95 % conversion).

24) Synthesis of poly(styrene) particles with cetyltrimethylammonium bromide (CTAB)

In a Schlenk flask under exclusion of oxygen 12 mg Na-BAPO-acetate of example 15, 380 mg of cetyltrimethylammonium bromide (CTAB), 30 mL of degassed and deionised water, and 5 mL of styrene (distilled under reduced pressure, degassed) were mixed. After 5 min. of vigorous stirring (stirrer: RCT Basic, IKA Labortechnik, stage 6) the resulting emulsion was irradiated for 30 min. with a medium pressure mercury lamp (TQ 150 in a DURAN 50 glass mantel, UV-Consulting Peschl) to give a latex. The sample was stirred for another 24 h under an atmosphere of argon and

under exclusion of light. Subsequently, small portion of the latex were removed for the determination of the particle size and the solid content. For the light scattering measurements, 0.1 mL of latex was diluted with 5 mL water. For the determination of the solid content, 1 mL of sample solution was given onto sea sand (carefully dried at 130 °C in a drying oven) in a Petri dish.  
5 Subsequently, the sample was kept at 110 °C for 24 h in a drying oven under vacuum (Vacucell, MMM Medcenter GmbH) to remove all volatiles (solvents, unreacted monomer).

In order to isolate the polymer in substance, an aqueous saturated sodium chloride solution was added to the latex. The polymer was isolated by centrifugation (10 min. at 25'000 rpm in a 3K 30 Sigma centrifuge). This procedure was repeated three times to yield a white powder.

10 Analytic Results:

Dynamic Light Scattering (DLS) (after dilution with water):

Z-average: 63 nm

DLS-PDI = 0.18

Solid content: 9.2 % (71 % conversion).

15

#### 25) to 27) Synthesis of poly(styrene) particles in the presence of sodium dodecylsulfate, SDS

All examples were made according to the following procedure:

Sodium dodecylsulfate (SDS), styrene (10 g), degassed water (33.5 g) and Na-BAPO-acetate of example 15 were mixed. The reaction mixture was stirred vigorously and exposed to irradiation of  
20 a medium pressure mercury lamp (TQ 150 in a DURAN 50 glass mantle, UV-Consulting Peschl).

#### 25) Comparison of particle size and polymerisation time (with late quenching)

To study the effect of the irradiation time on the particle size, samples were taken out of the reaction mixture continuously during irradiation. Said samples were put in a flask under argon  
25 atmosphere and stirred in the dark for 72 hours minus the irradiation time. After 72 h, the reaction was quenched by adding one drop of an aqueous hydroquinone solution (1%).



SDS: 100mg, Na-BAPO-acetate of example 15: 20 mg

Result: After about one hour of irradiation the yield exceeded 90%, the particle size increased continuously from around 65 nm after 30 min to about 110 nm after 3 h of irradiation.

5     26) Comparison of particle size and polymerisation time (with immediate quenching)

To study the effect of the irradiation time on the particle size, samples were taken out of the reaction mixture continuously during irradiation. Said samples were immediately quenched by adding one drop of an aqueous hydroquinone solution (1%).

SDS: 100mg, Na-BAPO-acetate of example 15: 20 mg

10    Result: After about one hour of irradiation the yield exceeded 90%, the particle size was quite constant in the range of around 65 nm to about 70 nm during 3 h of irradiation.

27) Effect of photoinitiator concentration

15    To study the effect of the photoinitiator concentration on the particle size, the reaction mixture was irradiated for 10 min, after which the reaction was immediately quenched with hydroquinone.

SDS: 100mg, Na-BAPO-acetate of example 15: from 0.1 mg to 20 mg

Result: For 1 to 10 mg of photoinitiator the particle size was at a constant level of about 48 nm; for higher concentrations the particle size decreases constantly to reach around 30 nm at 20 mg of photoinitiator, for 0.1 mg of photoinitiator an initial particle size of 50 nm was observed.

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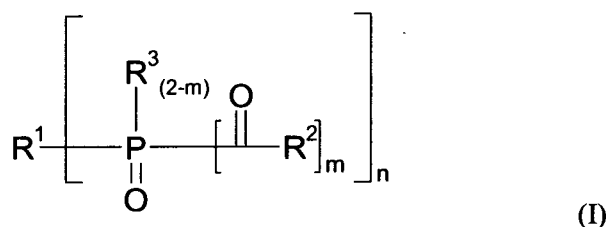
**Claims:**

1. A process for the preparation of polymer nanoparticles by photoinduced emulsion polymerization which comprises at least the steps of:

5 A) preparing an emulsion comprising at least one surfactant, a dispersed phase and a continuous phase, whereby the dispersed phase comprises one or more polymerizable monomers and the continuous phase comprises water and one or more photoinitiators;

B) polymerizing one or more polymerizable monomers by exposing said emulsion to electromagnetic radiation having a wavelength sufficient to induce the generation of radicals from one or more photoinitiators,

10 wherein the photoinitiators are selected from compounds of formula (I):



wherein

n is 1 or 2,

m is 1 or 2,

15 **R<sup>1</sup>, if n = 1** is C<sub>6</sub>-C<sub>14</sub>-aryl or heterocyclyl or

is C<sub>1</sub>-C<sub>18</sub>-alkoxy, -N(R<sup>4</sup>)<sub>2</sub>, C<sub>1</sub>-C<sub>18</sub>-alkyl, C<sub>2</sub>-C<sub>18</sub>-alkenyl, C<sub>7</sub>-C<sub>20</sub>-arylalkyl,

which is either not, once, twice or more than twice interrupted by non-successive functional groups selected from the group consisting of:

20 -O-, -S-, -SO<sub>2</sub>-, -SO-, -SO<sub>2</sub>NR<sup>4</sup>-, NR<sup>4</sup>SO<sub>2</sub>-, -NR<sup>4</sup>-, -N<sup>+</sup>(R<sup>4</sup>)<sub>2</sub>An<sup>-</sup>-, -CO-, -O(CO)-, (CO)O-, -O(CO)O-, -NR<sup>4</sup>(CO)NR<sup>4</sup>-, NR<sup>4</sup>(CO)-, -(CO)NR<sup>4</sup>-, -NR<sup>4</sup>(CO)O-, -O(CO)NR<sup>4</sup>-, -Si(R<sup>5</sup>)<sub>2</sub>-, -OSi(R<sup>5</sup>)<sub>2</sub>-, -OSi(R<sup>5</sup>)<sub>2</sub>O-, -Si(R<sup>5</sup>)<sub>2</sub>O-,

and which is either not, once, twice or more than twice interrupted by bivalent residues selected from the group consisting of heterocyclo-diyl, heterocyclo-dylium<sup>+</sup>An<sup>-</sup> and C<sub>6</sub>-C<sub>14</sub>-aryldiyl,

and which is not, additionally or alternatively either once, twice or more than twice substituted by substituents selected from the group consisting of:

5 halogen, cyano, azido, epoxy, C<sub>6</sub>-C<sub>14</sub>-aryl, C<sub>1</sub>-C<sub>8</sub>-alkyl, C<sub>1</sub>-C<sub>8</sub>-alkoxy, C<sub>2</sub>-C<sub>8</sub>-alkenyl, C<sub>1</sub>-C<sub>8</sub>-alkylthio, C<sub>7</sub>-C<sub>20</sub>-arylalkyl, hydroxy, -SO<sub>3</sub>M, -COOM, PO<sub>3</sub>M<sub>2</sub>, -PO(N(R<sup>5</sup>)<sub>2</sub>)<sub>2</sub>, PO(OR<sup>5</sup>)<sub>2</sub>, -SO<sub>2</sub>N(R<sup>4</sup>)<sub>2</sub>, -N(R<sup>4</sup>)<sub>2</sub>, -N<sup>+</sup>(R<sup>4</sup>)<sub>3</sub>An<sup>-</sup>, heterocyclylium<sup>+</sup>An<sup>-</sup>, -CO<sub>2</sub>N(R<sup>5</sup>)<sub>2</sub>, -COR<sup>4</sup>, -OCOR<sup>4</sup>, -NR<sup>4</sup>(CO)R<sup>5</sup>, -(CO)OR<sup>4</sup>, -NR<sup>4</sup>(CO)N(R<sup>4</sup>)<sub>2</sub>, -Si(OR<sup>5</sup>)<sub>y</sub>(R<sup>5</sup>)<sub>3-y</sub>, -OSi(OR<sup>5</sup>)<sub>y</sub>(R<sup>5</sup>)<sub>3-y</sub> with y = 1, 2 or 3,

**R<sup>1</sup>, if n = 2** is C<sub>6</sub>-C<sub>15</sub>-aryldiyl or

is C<sub>4</sub>-C<sub>18</sub>-alkanediyl, C<sub>4</sub>-C<sub>18</sub>-alkenediyl, C<sub>4</sub>-C<sub>18</sub>-alkinediyl,

10 which is either not, once, twice or more than twice interrupted by non-successive groups selected from the group consisting of:

-O-, -SO<sub>2</sub>-, -NR<sup>4</sup>-, -N<sup>+</sup>(R<sup>4</sup>)<sub>2</sub>An<sup>-</sup>, -CO-, -OCO-, -O(CO)O-, NR<sup>4</sup>(CO)-, -NR<sup>4</sup>(CO)O-, O(CO)NR<sup>4</sup>-, -NR<sup>4</sup>(CO)NR<sup>4</sup>-, C<sub>6</sub>-C<sub>15</sub>-aryl, heterocyclo-diyl and heterocyclo-dylium<sup>+</sup>An<sup>-</sup>,

15 and which is not, additionally or alternatively either once, twice or more than twice substituted by substituents selected from the group consisting of:

halogen, cyano, C<sub>6</sub>-C<sub>14</sub>-aryl, heterocyclyl, heterocyclo-dylium<sup>+</sup>An<sup>-</sup>, C<sub>1</sub>-C<sub>8</sub>-alkyl, C<sub>1</sub>-C<sub>8</sub>-alkoxy, C<sub>1</sub>-C<sub>8</sub>-alkylthio, -SO<sub>3</sub>M, -COOM, PO<sub>3</sub>M<sub>2</sub>, -N(R<sup>4</sup>)<sub>2</sub>, -N<sup>+</sup>(R<sup>4</sup>)<sub>3</sub>An<sup>-</sup>, -CO<sub>2</sub>N(R<sup>4</sup>)<sub>2</sub>, -OCOR<sup>4</sup>-, -O(CO)OR<sup>4</sup>-, NR<sup>4</sup>(CO)R<sup>5</sup>, -NR<sup>3</sup>(CO)OR<sup>5</sup>, O(CO)N(R<sup>4</sup>)<sub>2</sub>, -NR<sup>4</sup>(CO)N(R<sup>4</sup>)<sub>2</sub>,

20 or is bivalent bis(C<sub>6</sub>-C<sub>15</sub>)-aryl, which is either not or once interrupted by groups selected from the group consisting of:

-O-, -S-, C<sub>4</sub>-C<sub>18</sub>-alkanediyl, C<sub>4</sub>-C<sub>18</sub>-alkenediyl,

**R<sup>2</sup>** is C<sub>6</sub>-C<sub>14</sub>-aryl or heterocyclyl or

is C<sub>1</sub>-C<sub>18</sub>-alkyl, C<sub>2</sub>-C<sub>18</sub>-alkenyl, C<sub>7</sub>-C<sub>20</sub>-arylalkyl,

25 which is either not, once, twice or more than twice interrupted by non-successive functional groups selected from the group consisting of:

-O-, -NR<sup>4</sup>-, -N<sup>+</sup>(R<sup>4</sup>)<sub>2</sub>An<sup>-</sup>, -CO-, -OCO-, -O(CO)O-, NR<sup>4</sup>(CO)-, -NR<sup>4</sup>(CO)O-, O(CO)NR<sup>4</sup>-, -NR<sup>4</sup>(CO)NR<sup>4</sup>-,

and which is either not, once, twice or more than twice interrupted by bivalent residues selected from the group consisting of heterocyclo-diyl, heterocyclo-dylium<sup>+</sup>An<sup>-</sup>, and C<sub>6</sub>-C<sub>14</sub>-aryldiyl,

5 and which is not, additionally or alternatively either once, twice or more than twice substituted by substituents selected from the group consisting of:

halogen, cyano, C<sub>6</sub>-C<sub>14</sub>-aryl; heterocyclyl, C<sub>1</sub>-C<sub>8</sub>-alkyl, C<sub>1</sub>-C<sub>8</sub>-alkoxy, C<sub>1</sub>-C<sub>8</sub>-alkylthio, C<sub>2</sub>-C<sub>8</sub>-alkenyl, C<sub>4</sub>-C<sub>15</sub>-arylalkyl, -COOM, -SO<sub>3</sub>M, -PO<sub>3</sub>M<sub>2</sub>, -SO<sub>2</sub>N(R<sup>4</sup>)<sub>2</sub>, -NR<sup>4</sup>SO<sub>2</sub>R<sup>5</sup>, -N(R<sup>4</sup>)<sub>2</sub><sup>-</sup>, -N<sup>+</sup>(R<sup>4</sup>)<sub>3</sub>An<sup>-</sup>, -CO<sub>2</sub>N(R<sup>4</sup>)<sub>2</sub>, -COR<sup>4</sup>, -OCOR<sup>5</sup>, -O(CO)OR<sup>5</sup>, NR<sup>4</sup>(CO)R<sup>4</sup>, -NR<sup>4</sup>(CO)OR<sup>4</sup>, O(CO)N(R<sup>4</sup>)<sub>2</sub>, -NR<sup>4</sup>(CO)N(R<sup>4</sup>)<sub>2</sub>,

10 **R<sup>3</sup>** independently denotes a substituent as defined for R<sup>1</sup> if n is 1,

whereby

**R<sup>4</sup>** is independently selected from the group consisting of hydrogen, C<sub>1</sub>-C<sub>8</sub>-alkyl, C<sub>6</sub>-C<sub>14</sub>-aryl, C<sub>7</sub>-C<sub>15</sub>-arylalkyl and heterocyclyl or N(R<sup>4</sup>)<sub>2</sub> as a whole is a N-containing heterocycle, or N<sup>+</sup>(R<sup>4</sup>)<sub>2</sub>An<sup>-</sup> and N<sup>+</sup>(R<sup>4</sup>)<sub>3</sub>An<sup>-</sup> as a whole are or contain a cationic N-containing heterocycle with a counteranion,

15

**R<sup>5</sup>** is independently selected from the group consisting of C<sub>1</sub>-C<sub>8</sub>-alkyl, C<sub>6</sub>-C<sub>14</sub>-aryl, C<sub>7</sub>-C<sub>15</sub>-arylalkyl and heterocyclyl or N(R<sup>5</sup>)<sub>2</sub> as a whole is a N-containing heterocycle or N<sup>+</sup>(R<sup>5</sup>)<sub>2</sub>An<sup>-</sup> and N<sup>+</sup>(R<sup>5</sup>)<sub>3</sub>An<sup>-</sup> as a whole are or contain a cationic N-containing heterocycle with a counteranion,

20 **M** is hydrogen, or 1/q equivalent of an q-valent metal ion or is an ammonium ion or a primary, secondary, tertiary or quaternary organic ammonium ion or a guanidinium ion, and

An<sup>-</sup> is 1/p equivalent of a p-valent anion.

2. A process according to claim 1, wherein in formula (I):

25 **n** is 1,

**m** is 2,

**R<sup>1</sup>** is C<sub>1</sub>-C<sub>18</sub>-alkyl,

which is either not or once, twice or more than twice interrupted by non-successive functional groups selected from the group consisting of:

-O-, -NR<sup>4</sup>-, -N<sup>+</sup>(R<sup>4</sup>)<sub>2</sub>An<sup>-</sup>,

5 and which is not, additionally or alternatively either once, twice or more than twice substituted by substituents selected from the group consisting of:

halogen, C<sub>1</sub>-C<sub>8</sub>-alkoxy, hydroxy, -SO<sub>3</sub>M, -COOM, PO<sub>3</sub>M<sub>2</sub>, SO<sub>2</sub>N(R<sup>4</sup>)<sub>2</sub>, -N(R<sup>4</sup>)<sub>2</sub>, -N<sup>+</sup>(R<sup>4</sup>)<sub>3</sub>An<sup>-</sup>, -CO<sub>2</sub>N(R<sup>4</sup>)<sub>2</sub>, C<sub>1</sub>-C<sub>8</sub>-alkylsulfate,

R<sup>2</sup> is C<sub>6</sub>-C<sub>14</sub>-aryl,

whereby

10 R<sup>4</sup> is independently selected from the group consisting hydrogen, C<sub>1</sub>-C<sub>8</sub>-alkyl, C<sub>6</sub>-C<sub>14</sub>-aryl, C<sub>7</sub>-C<sub>15</sub>-arylalkyl and heterocyclyl or N(R<sup>4</sup>)<sub>2</sub> as a whole is a N-containing heterocycle or N<sup>+</sup>(R<sup>4</sup>)<sub>2</sub>An<sup>-</sup> and N<sup>+</sup>(R<sup>4</sup>)<sub>3</sub>An<sup>-</sup> as a whole is or contains a cationic N-containing heterocycle with a counteranion,

15 M is hydrogen, lithium, sodium, potassium, one half equivalent of calcium, zinc or iron (II), or one third equivalent of aluminium (III) or is an ammonium ion or a primary, secondary, tertiary or quaternary organic ammonium ion, and

An<sup>-</sup> is 1/p equivalent of a p-valent anion:

3. A process according to claim 1 or 2, wherein in formula (I):

n is 1,

20 m is 2,

R<sup>1</sup> is C<sub>1</sub>-C<sub>8</sub>-alkyl,

which is either not or once, twice or more than twice interrupted by non-successive functional groups selected from the group consisting of:

25 -O-, -NR<sup>4</sup>-, -N<sup>+</sup>(R<sup>4</sup>)<sub>2</sub>An<sup>-</sup>, preferably those containing one to ten polyethylene glycol ether groups [-OCH<sub>2</sub>CH<sub>2</sub>]<sub>x</sub>-,

and which additionally or alternatively are either once, twice or more than twice substituted by substituents selected from the group consisting of:

hydroxy,  $-\text{SO}_3\text{M}$ ,  $-\text{COOM}$ ,  $\text{PO}_3\text{M}_2$ ,  $-\text{N}(\text{R}^4)_2$ ,  $-\text{N}^+(\text{R}^4)_3\text{An}^-$ , heterocyclylium $^+\text{An}^-$ ,

$\text{R}^2$  is  $\text{C}_6\text{-C}_{14}$ -aryl, preferably mesityl or 2,6-dimethoxyphenyl,

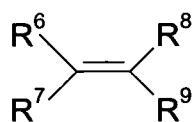
5 whereby

$\text{R}^4$  is independently selected from the group consisting hydrogen,  $\text{C}_1\text{-C}_8$ -alkyl,  $\text{C}_6\text{-C}_{14}$ -aryl,  $\text{C}_7\text{-C}_{15}$ -arylalkyl and heterocyclyl or  $\text{N}(\text{R}^4)_2$  as a whole is a N-containing heterocycle or  $\text{N}^+(\text{R}^4)_2\text{An}^-$  and  $\text{N}^+(\text{R}^4)_3\text{An}^-$  as a whole is or contains a cationic N-containing heterocycle with a counteranion,

10  $\text{M}$  is hydrogen, lithium, sodium, potassium, one half equivalent of calcium or zinc or is an ammonium ion or a primary, secondary, tertiary or quaternary organic ammonium ion, and

$\text{An}^-$  is 1/p equivalent of a p-valent anion.

4. A process according to one of claims 1 to 3, wherein steps A) and B) are performed
- 15 continuously.
5. A process according to one of claims 1 to 4, wherein the continuous phase further comprises water miscible solvents.
6. A process according to one of claims 1 to 5, wherein the polymerizable monomers are those of formula (II):



(II)

20

wherein

$\text{R}^6$ ,  $\text{R}^7$ ,  $\text{R}^8$  and  $\text{R}^9$  are independently of one another selected from the group consisting of:

$\text{C}_1\text{-C}_{18}$ -alkoxy,  $\text{C}_1\text{-C}_{18}$ -alkyl,  $\text{C}_2\text{-C}_{18}$ -alkenyl,  $\text{C}_7\text{-C}_{15}$ -arylalkyl

25

which is either not, once, twice or more than twice interrupted by non-successive functional groups selected from the group consisting of:

-O-, -CO-, -OCO-, -O(CO)O-,  $\text{NR}^4(\text{CO})$ -,  $\text{-NR}^4(\text{CO})\text{O-}$ ,  $\text{-O(CO)NR}^4$ -,  $\text{-(CO)NR}^4$ -,  
 $\text{NR}^4(\text{CO)NR}^4$ -,  $\text{-Si(R}^5)_2$ -,  $\text{-OSi(R}^5)_2$ -,  $\text{-OSi(R}^5)_2\text{O-}$ ,  $\text{-Si(R}^5)_2\text{O-}$

and which is either not, once, twice or more than twice interrupted by bivalent residues selected from the group consisting of heterocyclo-diyl and  $\text{C}_6$ - $\text{C}_{14}$ -aryldiyl,

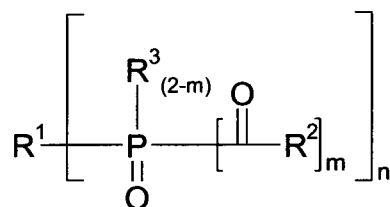
5 and which is not, additionally or alternatively either once, twice or more than twice substituted by substituents selected from the group consisting of:

halogen, cyano, epoxy,  $\text{C}_6$ - $\text{C}_{14}$ -aryl; heterocyclyl,  $\text{C}_1$ - $\text{C}_8$ -alkyl,  $\text{C}_1$ - $\text{C}_8$ -alkoxy,  $\text{C}_1$ - $\text{C}_8$ -alkylthio,  $\text{C}_2$ - $\text{C}_8$ -alkenyl,  $\text{C}_4$ - $\text{C}_{15}$ -arylalkyl, hydroxy,  $\text{-SO}_2\text{N(R}^4)_2$ ,  $\text{NR}^4\text{SO}_2\text{-R}^5$ ,  $\text{-N(R}^4)_2$ ,  $\text{-CO}_2\text{N(R}^5)_2$ ,  $\text{-COR}^4$ ,  $\text{-OCOR}^4$ ,  $\text{-O(CO)OR}^4$ ,  $\text{NR}^4(\text{CO)R}^5$ ,  $\text{-NR}^4(\text{CO)OR}^5$ ,  $\text{O(CO)N(R}^4)_2$ ,  
 10  $\text{NR}^4(\text{CO)N(R}^4)_2$ ,  $\text{-OSi(OR}^5)_{y-3}(\text{R}^5)_y$ ,  $\text{-Si(OR}^5)_{y-3}(\text{R}^5)_y$ , where y is 1, 2 or 3.

7. A process according to one of claims 1 to 6, wherein the weight ratio of photoinitiator to polymerizable monomer is between 1:5 and 1:100.000.

8. A process according to one of claims 1 to 7, wherein the amount of electromagnetic radiation having a wavelength sufficient to induce the generation of radicals is from 10 J to  
 15 500 kJ per liter of the emulsion.

9. Compounds of formula (Ia):



(Ia)

wherein

n, m,  $\text{R}^1$  to  $\text{R}^5$ , and  $\text{An}^-$  have the meaning set forth in claim 1 for formula (I)

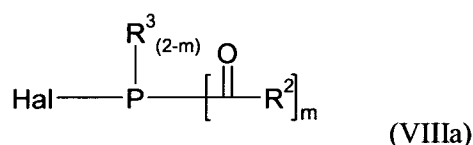
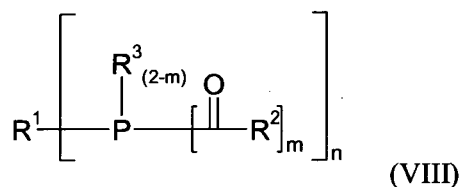
20 whereby the molecule contains at least one functional group or substituent selected from the group consisting of:

$\text{-SO}_3\text{M}$ ,  $\text{-COOM}$ ,  $\text{PO}_3\text{M}_2$ ,  $\text{-N}^+(\text{R}^4)_3\text{An}^-$ , heterocyclylium $^+\text{An}^-$

wherein

M is 1/q equivalent of a q-valent metal ion or is an ammonium ion or a primary, secondary, tertiary or quaternary organic ammonium ion or a guanidinium ion.

10. Compounds of formulae (VIII) and (VIIIa)



wherein

n, m, R<sup>1</sup> to R<sup>5</sup>, and An<sup>-</sup> have the meaning set forth in claim 1 for formula (I)

whereby the molecules contain at least one functional group or substituent selected from the group consisting of:

-SO<sub>3</sub>M, -COOM, PO<sub>3</sub>M<sub>2</sub>, -N<sup>+</sup>(R<sup>4</sup>)<sub>3</sub>An<sup>-</sup>, heterocyclylium<sup>+</sup>An<sup>-</sup>

wherein

M is 1/q equivalent of a q-valent metal ion or is an ammonium ion or a primary, secondary, tertiary or quaternary organic ammonium ion or a guanidinium ion

and wherein

Hal is a halogen.

11. Polymer nanoparticles obtainable by a process according to one or more of claims 1 to 8.

12. Polymer nanoparticles having an average particle size of 1 to 10.000 nm, an M-PDI (M<sub>w</sub>/M<sub>n</sub>) of 1.00 to 1.50 and a DLS-PDI of 0.10 to 0.50.

13. Polymer suspension comprising 0,001 to 50 wt of polymer nanoparticles according to claims 11 or 12.



14. Use of polymer suspensions according to claim 13 or polymer nanoparticles according to claims 11 or 12 in coating, adhesive, ink, and painting materials, precision mold constructions, in the manufacture of electronic articles, for drug delivery systems, diagnostic sensors and contrast agents.
- 5 15. Coatings, adhesives, inks, and painting materials, precision mold constructions, electronic articles, drug delivery systems, diagnostic sensors and contrast agents comprising polymer nanoparticles according to claims 11 or 12.

**INTERNATIONAL SEARCH REPORT**

International application No  
PCT/CH2010/000103

**A. CLASSIFICATION OF SUBJECT MATTER**  
 INV. C08F2/24 C08F2/50 C07F9/53  
 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 C07F

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 practical, search terms used)  
 EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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Y	paragraphs [0362] - [0381], [0436], [0498], [0500], [0503]; claim 2	1-8, 11-15
X	WO 03/019295 A1 (CIBA SC HOLDING AG [CH]; WOLF JEAN-PIERRE [CH]; HUG GEBHARD [CH]) 6 March 2003 (2003-03-06)	9,10
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Y	paragraphs [0183] - [0186]; claims 1,8,11	1-8, 11-15
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Further documents are listed in the continuation of Box C.       See patent family annex.

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"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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search	Date of mailing of the international search report
22 June 2010	01/07/2010

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  Queste, Sébastien
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International application No  
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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Y	claim 1 page 7, lines 9-25 page 8, lines 24-25	1-8, 11-15
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