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(54) Title: PROCESS FOR THE MODIFICATION OF POLYMERS, IN PARTICULAR POLYMER NANOPARTICLES

(57) Abstract: The present invention relates to a highly efficient and ultra fast process for the photo-initiated preparation of polymers by polymerization using photoinitiators comprising a phosphorous oxide or -sulfide group and modification of said polymers. In particular the invention relates to an ultra fast process for the photo-initiated preparation of latices comprising polymer nanoparticles by heterophase polymerization using photoinitiators comprising a phosphorous oxide or -sulfide group and their modification. In another aspect, the invention relates to polymers and polymer nanoparticles obtainable by said process.



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Process for the modification of polymers, in particular polymer nanoparticles

The present invention relates to a highly efficient process for the photo-initiated preparation of polymers by polymerization using photoinitiators comprising a phosphorous oxide or –sulfide group and modification of said polymers. In particular the invention relates to an ultra fast process for the photo-initiated preparation of latices comprising polymer nanoparticles by heterophase polymerization using photoinitiators comprising a phosphorous oxide or –sulfide group and their modification. In another aspect, the invention relates to polymers and polymer nanoparticles obtainable by said process.

Polymers, in particular latices or polymer particles obtained therefrom are widely used as coatings, adhesives, ink and painting materials, for precision mold constructions and the manufacture of micro-sized materials.

For the latter, the unique properties of micro- and nanoscaled polymer particles with specific properties such as defined molecular weight distributions and polydispersities have meanwhile gained further 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, in particular for commercially important polymers such as polystyrene and poly(meth)acrylates, by direct synthesis of nanoparticles using special polymerisation processes. The most common processes are heterophase polymerisations, in particular thermally or photo-initiated emulsion polymerizations.

Over the last decades, efforts were made to develop heterophase polymerization processes and/or post polymerisation modifications in order to achieve a better control over molecular weight distribution, particle size of primary polymer nanoparticles, the crosslinking behaviour of polymers or polymer nanoparticles or the introduction of polymer end groups.

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

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 weight average molecular weight of 500 kg/mol or less is disclosed.

In T. Ott, Dissertation ETH Zürich No. 18055, 2008, Chapter 6, batch emulsion polymerisations induced by photofragmentation of bisacylphosphines are investigated in detail. However, high monomer conversion typically requires irradiation times of more than 2 hours.

5 A. Chemtob et al. disclose a batch process (in a cuvette) for the preparation of latices comprising copolymers by irradiating a miniemulsion of nanodroplets comprising acrylic acid, butylacrylate and methylmethacrylate encapsulating high amounts (4 wt.-%) of a hydrophobic photoinitiator of the BAPO type (BAPO = bisacylphosphine oxide).

10 In WO 2005/042591 A a process for preparing polymers with defined end group functionalities is disclosed which comprises polymerizing monomers in a heterophase medium and in the presence of a water-soluble photoinitiator system bearing said desired end group. The end group is deliberated as starter radical for chain propagation upon photofragmentation of the photoinitiator.

A major disadvantage is the use of methylene blue or other coloured and/or toxic compounds and the low variability of end groups.

15 In EP 1 300 427 A a process for preparing hot melt adhesives is disclosed which comprises polymerisation of acrylates in the presence of common photoinitiators and control agents such as thioesters, trithiocarbonates or dithioesters in order to provide enhanced crosslinking ability upon UV-irradiation.

A major disadvantage is the use of high amounts of different compounds necessary to achieve the desired properties.

20 As a consequence, there is still a need for a process for the efficient and easily controllable post-polymerization modification of polymers, in particular of latices or polymer nanoparticles.

A process was now found for the preparation of modified polymers by photo-initiated polymerization which comprises at least the steps of:

A) preparing a polymerization medium comprising at least

- 25
- one or more photoinitiators comprising at least one phosphorous oxide (P=O) or phosphorous sulfide (P=S) group and
 - one or more polymerizable monomers
- and

- B) polymerizing the one or more polymerizable monomers by irradiating said polymerization medium with electromagnetic radiation having a wavelength sufficient to induce the generation of radicals to obtain a polymer
- 5 C) modifying the polymer obtained in step B) by irradiating said polymer with electromagnetic radiation having a wavelength sufficient to induce the generation of radicals from said polymer in the presence of at least one modifying agent.

In one embodiment the process encompasses a process for the preparation of modified polymer nanoparticles formed by photo-initiated heterophase polymerization which comprises at least the steps of:

- 10 A) preparing a heterophase medium comprising at least a dispersed phase and a continuous phase and at least
- one or more surfactants
 - one or more photoinitiators
 - one or more polymerizable monomers
- 15 and
- B) polymerizing the one or more polymerizable monomers by irradiating said heterophase medium with electromagnetic radiation having a wavelength sufficient to induce the generation of radicals to obtain latices comprising polymer nanoparticles
- 20 whereby the photoinitiators are selected from compounds comprising at least one phosphorous oxide (P=O) or phosphorous sulfide (P=S) group and
- C) modifying the latices or polymer nanoparticles obtained in step B) by irradiating said latices or polymer nanoparticles with electromagnetic radiation having a wavelength sufficient to induce the generation of radicals from said latices or polymer nanoparticles in the presence of at least one modifying agent.

25 The scope of the invention encompasses all combinations of substituent definitions, parameters, features and illustrations set forth above and below, either in general or within areas of preference or preferred or alternative embodiments, with one another.

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

The terms "latex" and "latices" denote suspensions, preferably aqueous suspensions, comprising polymer nanoparticles 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.

5 The term "polymer nanoparticles" denotes polymer nanoparticles comprising for example at least 10 wt.-%, preferably at least 50 wt.-%, more preferably at least 80 wt.-% and even more preferably at least 90 wt.-% of a polymer, and even more preferably consisting of a polymer.

10 The average particle size as used herein is defined as being the particle size 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 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.

15 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 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 as polydisperse.

20 Particle sizes referred to herein were obtained using a Nicomp particle sizer (PSS Santa Barbara, USA, model 370) at 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".

25 **The polymerization medium**

The polymerization according to step B) can be effected in any manner known to those skilled in the art which means for example either as bulk or solution polymerization or as heterophase polymerization in a heterophase medium.

30 If the polymerization is carried out as bulk or solution polymerization the polymerization medium comprises at least one or more photoinitiators comprising at least one phosphorous oxide (P=O) or

phosphorous sulfide (P=S) group and one or more polymerizable monomers as defined and specified in the sections "the photoinitiators" and "the polymerizable polymers" hereinbelow.

In this case the one or more photoinitiators are for example mixed with the one or more polymerizable polymers and polymerized in step B) as described in the section "the polymerization conditions" hereinbelow.

Where solution polymerization is employed the polymerization medium comprises at least one or more photoinitiators comprising at least one phosphorous oxide (P=O) or phosphorous sulfide (P=S) group, one or more polymerizable monomers as defined and specified in the sections "the photoinitiators" and "the polymerizable polymers" hereinbelow and at least one solvent.

In this case the weight ratio of solvent to polymerizable monomer in the polymerization medium is typically of from 1:100 to 100:1, preferably of from 1: 5 to 50:1 and more preferably of from 1:1 to 5:1.

As solvents, all compounds capable of dissolving the polymerizable monomers in the intended amounts can be used and which are not radically polymerizable and thus virtually inert under the reaction conditions employed.

Examples of solvents include

- ethers like for example alkylenglycol ethers such as ethyleneglycoldimethyl- or diethylether, tetrahydrofurane, diethylether, 1,4-dioxane and tert.-butylmethylether,
- aromatic and aliphatic hydrocarbons like petrolethers, pentane, hexane, cyclohexane, heptane, benzene, toluene and xylenes, #
- halogenated aromatic and aliphatic hydrocarbons like chlorobenzene, dichlorobenzenes, chloromethane or dichloromethane, nitriles like
- nitriles such as acetonitrile, propanitrile or benzonitrile
- esters and amides such as dimethylformamide, dimethylacetamide, N-methylpyrrolidone, acetic acid methyl- and ethylester

In one embodiment the type and amount of solvent is chosen so that the polymer formed during polymerization is kept in solution to 80 wt.-% or more, preferably 90 wt.-% or more and even more preferably 95 wt.-% or more.

5 In another embodiment, the type and amount of solvent is chosen so that the polymer formed during polymerization precipitates from the solution in an amount of 50 wt.-% or more, preferably 75 wt.-% or more and even more preferably 90 wt.-% or more.

The weight ratio of photoinitiator to polymerizable monomer in the polymerization medium is typically of from 1:1 to 1:100'000, preferably between 1:5 and 1:100'000, preferably between 1: 10 and 1:10'000 and more preferably 1:50 to 1:2'000.

10 In another embodiment, where bulk or solution polymerization are applied the weight ratio of photoinitiator to polymerizable monomer in the polymerization medium is typically of from 5:1 to 1:10'000, preferably of from 2:1 to 1:5'000, more preferably of from 1: 1 to 1:1'000 and even more preferably of from 1:2 to 1:500.

The heterophase medium

15 In one embodiment, in steps A) and B) a heterophase medium is employed. In step A), a heterophase medium comprising at least a dispersed phase and a continuous phase is then prepared, whereby the heterophase medium further comprises one or more surfactants, one or more polymerizable monomers and one or more photoinitiators comprising at least one phosphorous oxide (P=O) or phosphorous sulfide (P=S) group.

20 As used herein, the term "heterophase medium comprising at least a dispersed phase and a continuous phase" includes any type of medium comprising at least two phases forming an interface between the continuous phase and the dispersed phase. This includes suspensions and emulsions of any type referred to in the literature such as classical emulsions, microemulsions and miniemulsions. The preparation of emulsions in step A) is preferred.

25 It is apparent to those skilled in the art, that upon performance of step B) the heterophase medium may undergo a transition e.g. from an emulsion to a suspension.

The heterophase medium prepared in step A) may either comprise one or more solid phases or not.

In one embodiment, the heterophase medium comprises solid materials within the ranges given above which are intended to be encapsulated by the polymers formed during polymerization.

Such solid materials may comprise inorganic compounds or organic compounds which are either not or not completely soluble in the heterophase medium.

5 In one embodiment, the heterophase medium prepared in step A1) comprises a solids content of from more than 0 to 50 wt.-%, preferably of from more than 0 to 25 wt.-%, more preferably of from more than 0 wt.-% to 10 wt.-% and even more preferably of from more than 0 wt.-% to 2 wt.-%.

10 In one embodiment, the heterophase medium comprises at least two liquid organic phases or a liquid aqueous phase and a liquid organic phase, whereby in a preferred embodiment the liquid aqueous phase represents the continuous phase and the liquid organic phase represents the dispersed phase.

In one embodiment, an aqueous phase, in particular an aqueous continuous phase comprises water and either at least one water miscible organic solvent or not.

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

15 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, ethers such as tetrahydrofuran and dioxane, ketones, and the like, as well as derivatives thereof and mixtures thereof, provided, however, that they are
20 miscible with water in any ratio.

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

25 The addition of water miscible organic solvents might be useful in those cases where low polymerization temperatures shall be employed or where the partition of the photoinitiator between the phases or the monomer solubility in the phases shall be adjusted.

In addition to that 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.

30 Furthermore, the addition of water miscible organic solvents allows the reaction temperature to be lowered significantly below the freezing point of water or an aqueous phase.

In an embodiment, the aqueous phase, in particular the aqueous continuous phase comprises either 0 wt.-%, or from more than 0 to 20 wt.-% of water-miscible organic solvents.

5 If water miscible solvents are employed, their content in an aqueous phase, in particular an aqueous continuous phase is preferably more than 0 to 10 wt.-%, more preferably more than 0 to 5 wt.-% and even more preferably more than 0 to 2 wt.-%.

In another embodiment, the solubility of hydrophilic polymerizable monomers within the aqueous continuous phase can optionally be lowered by dissolving salts such as inorganic salts like sodium chloride and the like. The content of salts may in this case amount to for example more than 0 to 5 wt.-%, preferably from 0.1 to 3 wt.-%.

10 If water is applied as dispersed or preferably continuous phase, the pH value of the aqueous phase is typically in the range of 3 to 10, preferably in the range of 5 to 9 measured or calculated on standard conditions.

The preparation of the heterophase medium is typically effected by simply mixing the components by standard mixing elements such as agitators, static mixers or combinations thereof such as rotor-
15 stator mixers. 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.

In an embodiment, the mixing results in a number average droplet size of below 100 μm , preferably between 5 and 50 μm as measured by light microscopy imaging.

20 The preparation of the heterophase medium in step A) may either be performed batchwise or continuously, whereby, in a preferred embodiment, the continuous preparation is preferred.

The heterophase medium comprises one or more surfactants. Suitable surfactants are, for example, non-ionic, cationic or anionic or amphoteric surfactants.

25 Anionic surfactants include C_6 - C_{24} -alkyl sulfonates which are either not or once substituted by C_6 to C_{14} aryl, C_6 - C_{24} -fluoroalkyl sulfonates, C_6 - C_{18} -alkyl ether sulfonates, C_6 - C_{14} -aryl sulfonates, C_1 - C_{24} -alkyl succinates, C_1 - C_{24} -alkyl sulfo succinates, N-(C_1 - C_{24} -alkyl)-sarkosinates, acyltaurates, C_6 - C_{24} -perfluoroalkyl carboxylates, C_6 - C_{24} -alkyl phosphates, C_6 - C_{24} -alkyl ether phosphates, C_6 - C_{24} -alkyl ether carboxylates, in particular the alkali metal, ammonium-, and organic ammonium salts of the aforementioned compounds.

30 Cationic surfactants include quaternary ammonium salts or pyridinium salts.

Non-ionic surfactants include polymeric surfactants of the block and graft copolymer type such as triblock copolymers commercially available and commonly known as pluronics (BASF SE) and synperonics (ICI) comprising two blocks of poly(ethylene)oxide and one intermediate poly(propyleneoxide) block or “inverse pluronics” and “inverse synperonics” comprising two blocks of poly(propyleneoxide) and one intermediate poly(ethylene)oxide block. Non-ionic surfactants further include homopolymers of ethyleneoxide and propyleneoxide and ethoxylated and/or propoxylated sugars, phenols or hydroxyl fatty acids. Non-ionic surfactants further include statistical polymers such as those disclosed in WO 2005/070979 A.

In one 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 (SDS), triethanolamine dodecyl benzene sulphate, cetyltrimethylammonium bromide, cetylpyridinium chloride, polyethoxylated tallow amine, benzalkonium chloride and benzethonium chloride.

In one embodiment one or more photoinitiators may themselves serve as a surfactant if comprising C₆-C₂₄-alkyl which are either not or once substituted by C₆ to C₁₄ aryl, C₆-C₂₄-fluoroalkyl or C₆-C₂₄-alkyl ether substituents.

The weight ratio of surfactant and the continuous phase is typically between 1:10'000 and 1:5, preferably between 1:100 and 1:20, whereby the amount should be at least equal or higher than the critical micelle concentration (CMC) in the heterophase medium. 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 and the heterophase medium employed.

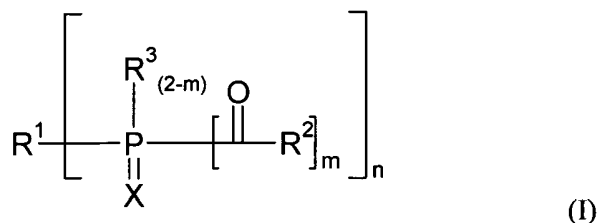
In a preferred embodiment, the amount of surfactant employed is at least four times, preferably at least eight times and more preferably at least twelve times higher than the CMC.

The weight ratio of the 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.

The photoinitiators

The polymerization medium, in particular the heterophase medium further comprises one or more photoinitiators comprising at least one phosphorous oxide (P=O) or phosphorous sulfide (P=S) group.

Preferred photoinitiators are those of formula (I):



wherein

n is 1 or 2 or a higher integer,

5 m is 0, 1 or 2,

X is sulphur or oxygen

R¹, if n = 1 is C₆-C₁₄-aryl or C₃-C₁₄- heterocyclyl or

is C₁-C₁₈-alkoxy, -N(R⁴)₂, C₁-C₁₈-alkyl, C₂-C₁₈-alkenyl or C₂-C₁₈-alkinyl

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

-O-, -S-, -SO₂-, -SO-, -SO₂NR⁴-, NR⁴SO₂-, -NR⁴-, -N⁺(R⁴)₂An⁻-, -CO-, -O(CO)-, (CO)O-, -O(CO)O-, -NR⁴(CO)NR⁴-, NR⁴(CO)-, -(CO)NR⁴-, -NR⁴(CO)O-, -O(CO)NR⁴-, -Si(R⁵)₂-, -OSi(R⁵)₂-, -OSi(R⁵)₂O-, -Si(R⁵)₂O-,

15 and which is either not, once, twice or more than twice interrupted by bivalent residues selected from the group consisting of C₃-C₁₄-heterocyclo-diyl, C₃-C₁₄-heterocyclo-dylium⁺An⁻ and C₆-C₁₄-aryldiyl,

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, azido, vicinal oxo (forming epoxides), vicinal NR⁵ (forming aziridins), C₆-C₁₄-aryl, C₁-C₈-alkoxy, C₁-C₈-alkylthio, hydroxy, -SO₃M, -COOM, PO₃M₂, -PO(N(R⁵)₂)₂, PO(OR⁵)₂, -SO₂N(R⁴)₂, -N(R⁴)₂, -N⁺(R⁴)₃An⁻, C₃-C₁₄-heterocyclylium⁺An⁻, -CO₂N(R⁴)₂, -COR⁴, -OCOR⁴, -NR⁴(CO)R⁵, -(CO)OR⁴, -NR⁴(CO)N(R⁴)₂, NR⁴SO₂R⁴, -Si(OR⁵)_y(R⁵)_(3-y), -OSi(OR⁵)_y(R⁵)_(3-y) with y = 1, 2 or 3,

R¹, if n = 2 is C₆-C₁₅-aryldiyl or C₃-C₁₄- heterocyclo-diyl

is C₁-C₁₈-alkanediyl, C₂-C₁₈-alkenediyl or C₂-C₁₈-alkinediyl,

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

5 -O-, -S-, -SO₂-, -SO-, -SO₂NR⁴-, NR⁴SO₂-, -NR⁴-, -N⁺(R⁴)₂An⁻-, -CO-, -O(CO)-, (CO)O-, -O(CO)O-, -NR⁴(CO)NR⁴-, NR⁴(CO)-, -(CO)NR⁴-, -NR⁴(CO)O-, -O(CO)NR⁴-, -Si(R⁵)₂-, -OSi(R⁵)₂-, -OSi(R⁵)₂O-, -Si(R⁵)₂O-,

and which is either not, once, twice or more than twice interrupted by bivalent residues selected from the group consisting of C₃-C₁₄-heterocyclo-diyl, C₃-C₁₄- heterocyclo-dylium⁺An⁻ and C₆-C₁₄-aryldiyl,

10

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, azido, vicinal oxo (forming epoxides), vicinal NR⁵ (forming aziridins), C₆-C₁₄-aryl, C₁-C₈-alkoxy, C₁-C₈-alkylthio, hydroxy, -SO₃M, -COOM, PO₃M₂, -PO(N(R⁵))₂, PO(OR⁵)₂, -SO₂N(R⁴)₂, -N(R⁴)₂, -N⁺(R⁴)₃An⁻, C₃-C₁₄- heterocyclylium⁺An⁻, -CO₂N(R⁴)₂, -COR⁴, -OCOR⁴, -NR⁴(CO)R⁵, -(CO)OR⁴, -NR⁴(CO)N(R⁴)₂, NR⁴SO₂R⁴, -Si(OR⁵)_y(R⁵)_(3-y), -OSi(OR⁵)_y(R⁵)_(3-y) with y = 1, 2 or 3,

or is bivalent bis(C₆-C₁₅)-aryl, which is either not or once interrupted by groups selected from the group consisting of:

20

-O-, -S-, -SO₂-, -SO-, C₄-C₁₈-alkanediyl, C₂-C₁₈-alkenediyl,

R¹, if n is an integer larger than 2

is a polymeric backbone having n binding sites to residues of formula (I) given in brackets labelled with n

25

R² is C₆-C₁₄-aryl or C₃-C₁₄-heterocyclyl or

is C₁-C₁₈-alkyl, C₂-C₁₈-alkenyl or C₂-C₁₈-alkinyl,

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

-O-, -NR⁴-, -N⁺(R⁴)₂An⁻-, -CO-, -OCO-, -O(CO)O-, NR⁴(CO)-, -NR⁴(CO)O-, O(CO)NR⁴-, -NR⁴(CO)NR⁴-,

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⁺An⁻, and C₆-C₁₄-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, hydroxy, protected hydroxyl, C₆-C₁₄-aryl; C₃-C₁₄-heterocyclyl, C₁-C₈-alkoxy, C₁-C₈-alkylthio, C₂-C₈-alkenyl, -COOM, -SO₃M, -PO₃M₂, -SO₂N(R⁴)₂, -NR⁴SO₂R⁵, -N(R⁴)₂-, -N⁺(R⁴)₃An⁻-, -CO₂N(R⁴)₂-, -COR⁴-, -OCOR⁵, -O(CO)OR⁵, NR⁴(CO)R⁴, -NR⁴(CO)OR⁴, O(CO)N(R⁴)₂-, -NR⁴(CO)N(R⁴)₂,

15 whereby in case of m = 2 the two substituents R² are different or identical, preferably identical or jointly are C₆-C₁₅-aryldiyl, C₃-C₁₄-heterocyclo-diyl, C₁-C₁₈-alkanediyl, C₂-C₁₈-alkenediyl or C₂-C₁₈-alkinediyl,

R³ independently denotes a substituent as defined for R¹ if n is 1,

whereby

20 R⁴ is independently selected from the group consisting of hydrogen, C₁-C₈-alkyl, C₆-C₁₄-aryl and C₃-C₁₄-heterocyclyl or N(R⁴)₂ as a whole is a N-containing C₃-C₁₄-heterocycle, or N⁺(R⁴)₂An⁻ and N⁺(R⁴)₃An⁻ as a whole are or contain a N-containing C₃-C₁₄-heterocyclyl substituent with a counteranion,

25 R⁵ is independently selected from the group consisting of C₁-C₈-alkyl, C₆-C₁₄-aryl and C₃-C₁₄-heterocyclyl or N(R⁵)₂ as a whole is a N-containing C₃-C₁₄-heterocycle, or N⁺(R⁵)₂An⁻ and N⁺(R⁵)₃An⁻ as a whole are or contain a N-containing C₃-C₁₄-heterocyclyl substituent with a counteranion,

30 M is hydrogen, or 1/q equivalent of an q-valent metal ion or is a C₃-C₁₄-heterocyclylum cation, an ammonium ion or a primary, secondary, tertiary or quarternary organic ammonium ion or a guanidinium ion or an organic guanidinium ion

An^- is $1/p$ equivalent of a p -valent anion.

The compounds of formula (I) are known and can be prepared according to or in analogy to methods known to those skilled in the art.

For compounds wherein m is 1 or 2 preparation procedures are disclosed in WO2005/014605; 5 WO2006/056541, WO2006/074983 and in T. Ott, Dissertation ETH Zürich No. 18055, 2008, whereby the latter in particular discloses compounds wherein R^1 is a polymeric backbone. These compounds are incorporated herein by reference.

In a preferred embodiment, one or more photoinitiators of formula (I) are used, whereby in formula (I) X denotes oxygen.

10 In an embodiment, one or more photoinitiators of formula (I) are used, whereby in formula (I) X denotes oxygen and n is 1 or 2.

In an embodiment, one or more photoinitiators of formula (I) are used, whereby in formula (I) X denotes oxygen and n is 1 or 2 and m is 1 or 2.

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

15 X is oxygen

n is 1,

m is 0, 1 or 2, preferably 1 or 2

R^1 is C_6 - C_{14} -aryl or C_3 - C_{14} -heterocyclyl or

is C_1 - C_{18} -alkyl or C_2 - C_{18} -alkenyl,

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

$-O-$, $-NR^4-$, $-N^+(R^4)_2An^-$, $-CO-$, $-OCO-$, $NR^4(CO)-$, $-(CO)NR^4-$,

and which is not, additionally or alternatively, preferably alternatively either not, once, twice or more than twice, preferably not or once, preferably once substituted 25 by substituents selected from the group consisting of:

halogen, cyano, vicinal oxo (forming epoxides), vicinal NR^5 (forming aziridins), $\text{C}_6\text{-C}_{14}\text{-aryl}$; $\text{C}_1\text{-C}_8\text{-alkoxy}$, $\text{C}_2\text{-C}_8\text{-alkenyl}$, hydroxy, $-\text{SO}_3\text{M}$, $-\text{COOM}$, PO_3M_2 , $-\text{PO}(\text{N}(\text{R}^5)_2)_2$, $-\text{SO}_2\text{N}(\text{R}^4)_2$, $-\text{N}(\text{R}^4)_2$, $-\text{N}^+(\text{R}^4)_3\text{An}^-$, $\text{C}_3\text{-C}_{14}\text{-heterocyclo-diylium}^+\text{An}^-$, $-\text{CO}_2\text{N}(\text{R}^4)_2$, $-\text{COR}^4$, $-\text{OCOR}^4$, $\text{NR}^4(\text{CO})\text{R}^5$,

5 R^2 is $\text{C}_6\text{-C}_{14}\text{-aryl}$ or $\text{C}_3\text{-C}_{14}\text{-heterocyclyl}$ or

is $\text{C}_1\text{-C}_{18}\text{-alkyl}$ or $\text{C}_2\text{-C}_{18}\text{-alkenyl}$

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

$-\text{O}-$, $-\text{NR}^4-$, $-\text{N}^+(\text{R}^4)_2\text{An}^-$, $-\text{CO}-$, $\text{NR}^4(\text{CO})-$, $-\text{NR}^4(\text{CO})\text{O}-$, $(\text{CO})\text{NR}^4-$,

10 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, hydroxyl, $\text{C}_6\text{-C}_{14}\text{-aryl}$; $\text{C}_3\text{-C}_{14}\text{-heterocyclyl}$, $\text{C}_1\text{-C}_8\text{-alkylthio}$, $\text{C}_2\text{-C}_8\text{-alkenyl}$, $-\text{COOM}$, $\text{SO}_2\text{N}(\text{R}^4)_2$, $\text{N}(\text{R}^4)_2$, $-\text{N}^+(\text{R}^4)_3\text{An}^-$, $-\text{CO}_2\text{N}(\text{R}^4)_2$,

15 whereby in case of $m = 2$ the two substituents R^2 are different or identical, preferably identical or jointly are $\text{C}_6\text{-C}_{15}\text{-aryldiyl}$ or $\text{C}_1\text{-C}_{18}\text{-alkanediyl}$

R^3 independently denotes a substituent as defined for R^1 directly above,

whereby

20 R^4 is independently selected from the group consisting of halogen, $\text{C}_1\text{-C}_8\text{-alkyl}$, $\text{C}_6\text{-C}_{14}\text{-aryl}$ and $\text{C}_3\text{-C}_{14}\text{-heterocyclyl}$ or $\text{N}(\text{R}^4)_2$ as a whole is a N-containing $\text{C}_3\text{-C}_{14}\text{-heterocycle}$, or $\text{N}^+(\text{R}^4)_2\text{An}^-$ and $\text{N}^+(\text{R}^4)_3\text{An}^-$ as a whole are or contain a N-containing $\text{C}_3\text{-C}_{14}\text{-heterocyclyl}$ substituent with a counteranion,

25 R^5 is independently selected from the group consisting $\text{C}_1\text{-C}_8\text{-alkyl}$, $\text{C}_6\text{-C}_{14}\text{-aryl}$ and $\text{C}_3\text{-C}_{14}\text{-heterocyclyl}$ or $\text{N}(\text{R}^5)_2$ as a whole is a N-containing $\text{C}_3\text{-C}_{14}\text{-heterocycle}$, or $\text{N}^+(\text{R}^5)_2\text{An}^-$ and $\text{N}^+(\text{R}^5)_3\text{An}^-$ as a whole are or contain a N-containing $\text{C}_3\text{-C}_{14}\text{-heterocyclyl}$ substituent with a counteranion,

M is hydrogen, or $1/q$ equivalent of an q -valent metal ion or is a $\text{C}_3\text{-C}_{14}\text{-heterocyclium}$ cation, an ammonium ion or a primary, secondary, tertiary or quarternary organic ammonium ion or a guanidinium ion or an organic

guanidinium ion, preferably hydrogen, lithium, sodium, potassium, one half equivalent of calcium, zinc or iron (II), or one third equivalent of aluminium (III) or a C₃-C₁₄-heterocyclylium cation or an ammonium ion or a primary, secondary, tertiary or quarternary organic ammonium ion, and

5 An⁻ is 1/p equivalent of a p-valent anion.

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

X is oxygen

n is 1,

m is 1 or 2

10 **R¹ and R³** are independently of each other

C₆-C₁₄-aryl or C₃-C₁₄-heterocyclyl or

are C₁-C₁₈-alkyl or C₂-C₁₈-alkenyl

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

15 -O-, -NR⁴-, -NR⁴(CO)-, -(CO)NR⁴-,

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

20 chloro, fluoro, cyano, hydroxy, C₆-C₁₄-aryl; C₁-C₈-alkoxy, -SO₃M, -COOM, PO₃M₂, -PO(N(R⁵)₂)₂, -SO₂N(R⁴)₂, -N(R⁴)₂, -N⁺(R⁴)₃An⁻, C₃-C₁₄-heterocyclo-
diylium⁺An⁻, -CO₂N(R⁴)₂, -COR⁴, -(CO)OR⁴, -OCOR⁴, NR⁴(CO)R⁵,

R² is C₆-C₁₄-aryl, whereby in case of m = 2 the two substituents R² are different or identical, preferably identical or jointly are C₆-C₁₅-aryldiyl or C₁-C₁₈-alkanediyl, whereby preferably R² is C₆-C₁₄-aryl.

25 whereby

- R^4 is independently selected from the group consisting of hydrogen, C_1 - C_8 -alkyl, C_6 - C_{14} -aryl and C_3 - C_{14} -heterocyclyl or $N(R^4)_2$ as a whole is a N-containing C_3 - C_{14} -heterocycle, or $N^+(R^4)_2An^-$ and $N^+(R^4)_3An^-$ as a whole are or contain a N-containing C_3 - C_{14} -heterocyclyl substituent with a counteranion,
- 5 R^5 is independently selected from the group consisting C_1 - C_8 -alkyl, C_6 - C_{14} -aryl and C_3 - C_{14} -heterocyclyl or $N(R^5)_2$ as a whole is a N-containing C_3 - C_{14} -heterocycle, or $N^+(R^5)_2An^-$ and $N^+(R^5)_3An^-$ as a whole are or contain a N-containing C_3 - C_{14} -heterocyclyl substituent with a counteranion,
- 10 M is hydrogen, or $1/q$ equivalent of an q -valent metal ion or is a C_3 - C_{14} -heterocyclium cation, an ammonium ion or a primary, secondary, tertiary or quarternary organic ammonium ion or a guanidinium ion or an organic guanidinium ion, preferably hydrogen, lithium, sodium, potassium, one half equivalent of calcium, zinc or iron (II), or one third equivalent of aluminium (III) or a C_3 - C_{14} -heterocyclium cation or an ammonium ion or a primary, secondary, tertiary or quarternary organic ammonium ion, and whereby hydrogen, lithium, sodium and potassium are even more preferred and
- 15 An^- is $1/p$ equivalent of a p -valent anion, preferably chloride, a carboxylate, C_1 - C_8 -alkylsulfate, C_6 - C_{14} -arylsulfate, hexafluorophosphate, tetrafluoroborate, dihydrogenphosphate, one half equivalent of sulphate or hydrogenphosphate.
- 20 In an embodiment of the invention, one or more photoinitiators of formula (I) are used, where in formula (I):
- X is oxygen
- n is 1,
- m is 1 or 2,
- 25 R^1 and R^3 are independently of each other C_6 - C_{14} -aryl or
are C_1 - C_{18} -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- or $-NR^4$,

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

5 chloro, fluoro, C₁-C₈-alkoxy, hydroxy, -SO₃M, -COOM, PO₃M₂, SO₂N(R⁴)₂, -N(R⁴)₂, -N⁺(R⁴)₃An⁻, -CO₂N(R⁴)₂,

R² is C₆-C₁₄-aryl,

whereby in case of m = 2 the two substituents R² are different or identical, preferably identical or jointly are C₆-C₁₅-aryldiyl or C₁-C₁₈-alkanediyl, whereby preferably R² is C₆-C₁₄-aryl.

10 whereby

R⁴ is independently selected from the group consisting of C₁-C₈-alkyl, C₆-C₁₄-aryl and C₃-C₁₄-heterocyclyl or N(R⁴)₂ as a whole is a N-containing C₃-C₁₄-heterocycle, or N⁺(R⁴)₂An⁻ and N⁺(R⁴)₃An⁻ as a whole are or contain a N-containing C₃-C₁₄-heterocyclyl substituent with a counteranion,

15 M is hydrogen, or 1/q equivalent of an q-valent metal ion or is a C₃-C₁₄-heterocyclium cation, an ammonium ion or a primary, secondary, tertiary or quarternary organic ammonium ion or a guanidinium ion or an organic guanidinium ion, preferably hydrogen, lithium, sodium, potassium, one half equivalent of calcium, zinc or iron (II), or one third equivalent of aluminium (III)
20 or a C₃-C₁₄-heterocyclium cation or an ammonium ion or a primary, secondary, tertiary or quarternary organic ammonium ion, and whereby hydrogen, lithium, sodium and potassium are even more preferred and whereby hydrogen, lithium, sodium and potassium are even more preferred and

25 An⁻ is 1/p equivalent of a p-valent anion, preferably chloride, a C₁-C₈-alkyl carboxylate, C₁-C₈-alkylsulfate, C₆-C₁₄-arylsulfate, hexafluorophosphate, tetrafluoroborate, dihydrogenphosphate, one half equivalent of sulphate or hydrogenphosphate.

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

X is oxygen

30 n is 1,

m is 1 or 2,

R¹ and R³ are different or identical and are C₆-C₁₄-aryl or

are C₁-C₁₈-alkyl,

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

-O-, -NR⁴-, preferably in case of -O- to form polyethyleneglycolether groups [-CH₂CH₂-O]_x-H, [-CH₂CH₂-O]_(x-1)-CH₃ or [-CH₂CH₂-O]_(x-1)-CH₂CH₃ with x being an integer from 1 to 8

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

chloro, fluoro, hydroxy, -SO₃M, -COOM, -CON(R⁴)₂, -N(R⁴)₂, -N⁺(R⁴)₃An⁻, heterocyclylium⁺An⁻, preferably -COOM, more preferably once by COOM and

15 **R²** is C₆-C₁₄-aryl, preferably 2,4,6-trimethylphenyl (mesityl) or 2,6-dimethoxyphenyl, whereby in case of m = 2 the substituents R² are different or identical, preferably identical, more preferably identically are 2,4,6-trimethylphenyl or 2,6-dimethoxyphenyl, even more preferably 2,4,6-trimethylphenyl

whereby

20 **R⁴** is independently selected from the group consisting of hydrogen, C₁-C₈-alkyl, C₆-C₁₄-aryl and C₃-C₁₄-heterocyclyl or N(R⁴)₂ as a whole is a N-containing C₃-C₁₄-heterocycle, or N⁺(R⁴)₂An⁻ and N⁺(R⁴)₃An⁻ as a whole are or contain a N-containing C₃-C₁₄-heterocyclyl substituent with a counteranion,

25 **M** is hydrogen, or 1/q equivalent of an q-valent metal ion or is a C₃-C₁₄-heterocyclylium cation, an ammonium ion or a primary, secondary, tertiary or quarternary organic ammonium ion or a guanidinium ion or an organic guanidinium ion, preferably hydrogen, lithium, sodium, potassium, one half equivalent of calcium, zinc or iron (II), or one third equivalent of aluminium (III) or a C₃-C₁₄-heterocyclylium cation or an ammonium ion or a primary, secondary, tertiary or quarternary organic ammonium ion, and whereby hydrogen, lithium, sodium and potassium are even more preferred and

30

An⁻ is 1/p equivalent of a p-valent anion, preferably chloride, a C₁-C₈-alkyl carboxylate, C₁-C₈-alkylsulfate, C₆-C₁₄-arylsulfate, hexafluorophosphate, tetrafluoroborate, dihydrogenphosphate, one half equivalent of sulphate or hydrogenphosphate.

Particular preferred photoinitiators of formula (I) are:

5

2-(bis(2,4,6-trimethylbenzoyl)phosphoryl)acetic acid (hereinafter also referred to as BAPO-AA) and its salts, in particular its sodium and potassium salts, (2-(2-(2-methoxyethoxy)ethoxy)ethyl)-(bis(2,4,6-trimethylbenzoyl)-phosphineoxide, 2,4,6-trimethylbenzoyl-diphenylphosphineoxide (hereinafter also referred to as MAPO, which is commercially available as Lucirin TPO from BASF SE) and bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide (which is commercially available as Irgacure ® 819 from BASF SE).

10

15

In one embodiment for the process according to the invention water-soluble photoinitiators of formula (I) are employed if a polymerization medium, in particular a heterophase medium, comprising an aqueous phase is used. As used herein "water-soluble" means a solubility of a photoinitiator in water at 25°C of at least 0.5 g per 1000 g of water.

20

25

As used herein, and unless specifically stated otherwise, C₆-C₁₄-aryl denotes carbocyclic aromatic substituents having six to fourteen carbon atoms within the aromatic system as such, i.e. without carbon atoms of substituents, preferably phenyl (C₆), naphthyl (C₁₀), phenanthrenyl and anthracenyl (each C₁₄), 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 fluoro, bromo, chloro, iodo, nitro, cyano, formyl or protected formyl, hydroxyl or protected hydroxyl, C₁-C₈-alkyl, C₁-C₈-haloalkyl, C₁-C₈-alkoxy, C₁-C₈-haloalkoxy, C₆-C₁₄-aryl, in particular phenyl and naphthyl, di(C₁-C₈-alkyl)amino, (C₁-C₈-alkyl)amino, CO(C₁-C₈-alkyl), OCO(C₁-C₈-alkyl), NHCO(C₁-C₈-alkyl), N(C₁-C₈-alkyl)CO(C₁-C₈-alkyl), CO(C₆-C₁₄-aryl), OCO(C₆-C₁₄-aryl), NHCO(C₆-C₁₄-aryl), N(C₁-C₈-alkyl)CO(C₆-C₁₄-aryl), COO-(C₁-C₈-alkyl), COO-(C₆-C₁₄-aryl), CON(C₁-C₈-alkyl)₂ or CONH(C₁-C₈-alkyl), CO₂M, CONH₂, SO₂NH₂, SO₂N(C₁-C₈-alkyl)₂, SO₃M and PO₃M₂.

30

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 fluoro, chloro, cyano, C₁-C₈-alkyl, C₁-C₈-haloalkyl, C₁-C₈-alkoxy, C₁-C₈-haloalkoxy, C₆-C₁₄-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, C₁-C₈-alkyl, C₁-C₈-perfluoroalkyl, C₁-C₈-alkoxy, C₁-C₈-perfluoroalkoxy, and phenyl.

5 Most preferred carbocyclic, aromatic substituents are phenyl, 2,4,6-trimethylphenyl and 2,6-dimethoxyphenyl

The definitions given above including their areas of preference also apply analogously to C₆-C₁₄-aryl-diyl substituents.

10 As used herein and unless specifically stated otherwise, **C₃-C₁₄-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 and whereby the entire cyclic system as such, i.e. without carbon atoms of substituents, comprises three to fourteen carbon atoms and whereby the heterocyclic aliphatic, aromatic or mixed aliphatic and aromatic substituents are
15 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,
20 imidazolyl, pyrimidinyl and quinolinyl, either unsubstituted or substituted with up to three substituents selected from the group consisting of fluorine, C₁-C₈-alkyl, C₁-C₈-perfluoroalkyl, C₁-C₈-alkoxy, C₁-C₈-perfluoroalkoxy, and phenyl.

The definitions given above, including their areas of preference, also apply analogously to **C₃-C₁₄-heterocyclium cations**, the bivalent **C₃-C₁₄-heterocyclo-diyl** substituents and the bivalent **C₃-C₁₄-heterocyclo-diylum cations**.
25

Preferred C₃-C₁₄-heterocyclium cations are N-(C₁-C₈-alkyl)imidazolium or pyridinium cations.

Preferred C₃-C₁₄-heterocyclo-diylum cations are N, N-imidazol-diylum 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
30 aminals, acetals and mixed aminal acetals are either acyclic or cyclic.

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

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 aminor acetal, whereby the aminorals, acetals and mixed aminor acetals are either acyclic or cyclic. A specific example of protected hydroxyl is tetrahydropyranyl (O-THP).

As used herein, and unless specifically stated otherwise, **C₁-C₁₈-alkyl**, **C₁-C₁₈-alkanediyl**, **C₁-C₁₈-alkoxy**, **C₁-C₈-alkylthio**, **C₂-C₁₈-alkenyl**, **C₂-C₁₈-alkenediyl** and **C₁-C₁₈-alkinediyl** are a straight-chain, cyclic either in part or as a whole, branched or unbranched alkyl, alkanediyl, alkoxy, alkylthio, alkenyl, alkenediyl and alkinediyl substituents having the given number of carbon atoms in the substituent as such, i.e. without carbon atoms of further, optionally present substituents or carbon atoms of functions interrupting the aforementioned substituents. As an example, a benzyl substituent represents a C₁-alkyl substituent substituted by phenyl.

The same analogously applies to C₁-C₈, C₁-C₂₄ and C₆-C₂₄-alkyl, C₂-C₁₈-alkanediyl, C₃-C₁₈-alkanetriyl, C₄-C₁₈-alkanetetrayl, C₂-C₁₈-alkenediyl, C₃-C₁₈-alkenetriyl, C₄-C₁₈-alkenetrayl and C₂-C₁₈-alkinediyl substituents.

Haloalkyl or haloalkoxy substituents denote alkyl or alkoxy substituents with the given number of carbon atoms which are once or more than once, preferably fully substituted by halogen.

Fluoroalkyl or fluoroalkoxy substituents denote alkyl or alkoxy substituents with the given number of carbon atoms which are once or more than once, preferably fully substituted by fluorine.

Perfluoroalkyl or perfluoroalkoxy substituents denote alkyl or alkoxy substituents with the given number of carbon atoms which are fully substituted by fluorine.

Specific examples of C₁-C₈-alkyl are methyl, ethyl, n-propyl, isopropyl, n-butyl, tert-butyl, n-pentyl, cyclohexyl, n-hexyl, n-heptyl, n-octyl and isoctyl. Additional examples for C₁-C₁₈-alkyl are norbornyl, adamantyl, n-decyl, n-dodecyl alkyl, n-hexadecyl, n-octadecyl.

Specific examples of C₁-C₁₈-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, 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 C₁-C₈-alkoxy-substituents are methoxy, ethoxy, isopropoxy, n-propoxy, n-butoxy, tert-butoxy and cyclohexyloxy.

Specific examples of C₂-C₁₈-alkenyl- substituents are allyl, 3-propenyl and buten-2-yl.

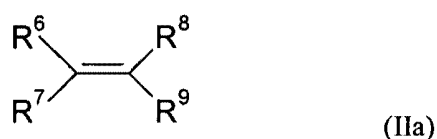
Specific examples of C₂-C₁₈-alkynyl- substituents are ethynyl, and 1,3-propynyl.

Polymerizable monomers

The polymerization medium, in particular the heterophase medium further comprises one or more polymerizable monomers.

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

Preferred polymerizable monomers are selected from the group consisting of those of formula (IIa):



wherein

10 R⁶, R⁷, R⁸ and R⁹ are independently of one another selected from the group consisting of:
hydrogen, cyano, fluorine, chlorine, bromine, iodine, C₆-C₁₄-aryl, C₃-C₁₄-heterocyclyl, C₁-C₁₈-alkoxy, C₁-C₁₈-alkyl, C₂-C₁₈-alkenyl and C₂-C₁₈-alkynyl

15 • which is either directly bound to the double bond depicted in formula (IIa) or in case of C₆-C₁₄-aryl, C₃-C₁₄-heterocyclyl, C₁-C₁₈-alkyl, C₂-C₁₈-alkenyl and C₂-C₁₈-alkynyl alternatively via a functional group selected from the group consisting of:

20 -CO-, -OCO-, -O(CO)O-, NR⁴(CO)-, -NR⁴(CO)O-, -O(CO)NR⁴-,
-(CO)NR⁴-, -NR⁴(CO)NR⁴-, -Si(R⁵)₂-, -OSi(R⁵)₂-, -OSi(R⁵)₂O-, -
Si(R⁵)₂O-

and

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

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

5

- and which is additionally or alternatively either not, once, twice or more than twice, preferably not, or once interrupted by bivalent residues selected from the group consisting of C_3 - C_{14} -heterocyclo-diyl and C_6 - C_{14} -aryldiyl,

10

- 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, vicinal oxo (forming epoxides), vicinal NR^5 (forming aziridins), C_6 - C_{14} -aryl; C_3 - C_{14} -heterocyclyl, C_1 - C_8 -alkylthio, hydroxy, $-\text{SO}_2\text{N}(\text{R}^4)_2$, $\text{NR}^4\text{SO}_2\text{R}^5$, $-\text{N}(\text{R}^4)_2$, $-\text{CO}_2\text{N}(\text{R}^4)_2$, $-\text{COR}^4$, $-\text{OCOR}^4$, $-\text{O}(\text{CO})\text{OR}^4$, $\text{NR}^4(\text{CO})\text{R}^5$, $-\text{NR}^4(\text{CO})\text{OR}^5$, $\text{O}(\text{CO})\text{N}(\text{R}^4)_2$, $-\text{NR}^4(\text{CO})\text{N}(\text{R}^4)_2$, $-\text{OSi}(\text{OR}^5)_{y-3}(\text{R}^5)_y$, $-\text{Si}(\text{OR}^5)_{y-3}(\text{R}^5)_y$ where y is 1, 2 or 3.

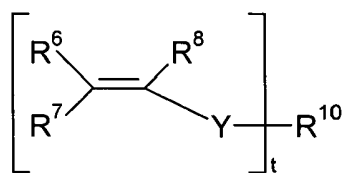
or wherein

two residues of R^6 , R^7 , R^8 and R^9 together are C_2 - C_{18} -alkanediyl or C_3 - C_{18} -alkenediyl.

20

Preferred polymerizable monomers of formula (IIa) are selected from the group consisting of those wherein at two or three, preferably three of the substituents R^6 , R^7 , R^8 and R^9 are hydrogen.

Preferred polymerizable monomers further include those of formula (IIb):



(IIb)

wherein

R^6 , R^7 and R^8

have the same meaning given above for formula (IIa)

25

or wherein

two residues of R^6 , R^7 and R^8 together are C_2 - C_{18} -alkanediyl or C_3 - C_{18} -alkenediyl

and wherein

t is an integer from 2 to 4 and

5 Y is missing such that R^{10} is directly bound to the double bond depicted in formula (IIb) or is -CO- or -(CO)O-

R^{10} is a t-valent residue selected from the group consisting of C_2 - C_{18} -alkanediyl (t=2), C_3 - C_{18} -alkanetriyl (t=3), C_4 - C_{18} -alkanetetrayl (t=4), C_2 - C_{18} -alkenediyl (t=2), C_3 - C_{18} -alkenetriyl (t=3), C_4 - C_{18} -alkenetetrayl (t=4), C_2 - C_{18} -alkinediyl (t=2), C_6 - C_{14} -aryldiyl (t=2) and C_3 - C_{14} -heterocyclodiyl (t=2).

10 Preferred polymerizable monomers of formula (IIb) are selected from the group consisting of those wherein at two or three, preferably three of the substituents R^6 , R^7 , R^8 and R^9 are hydrogen.

Examples of preferred polymerizable monomers include:

Monoolefins such as

- 15 • Acrylic acid and methacrylic acid and their respective esters, amides and nitriles, such as methyl-, ethyl-, n-butyl-, glycidyl-, 2-ethylhexyl- and 2-hydroxyethyl acrylate, acrylamide, N-isopropylacrylamide and acrylonitrile, and methyl-, ethyl-, n-butyl-, glycidyl-, 2-ethylhexyl-, 2-hydroxyethyl and isobornyl methacrylate; methacrylamide, N-isopropylmethacrylamide and methacrylonitrile;
- 20 • other unsaturated carboxylic acids and their respective esters such crotonic acid, maleic acid, fumaric acid, itaconic acid, cinnamic acid and unsaturated fatty acids such as linolenic acid or oleic acid and the respective C_1 - C_8 -alkyl esters of the aforementioned acids and where applicable C_1 - C_8 -alkyl diesters;
- vinyl ethers, such as ethyl vinyl ether and isobutyl vinyl ether;
- vinyl esters, such as vinyl acetate;
- 25 • vinyl aromatic compounds such as vinylpyridine, styrene and styrene substituted by C_1 - C_8 -alkyl- or halogen or sulfonic acid salts at the aromatic ring, preferably styrene, 2-, 3- and 4-methylstyrene, 2-, 3- and 4-bromomethylstyrene, 2-, 3- and 4-chlorostyrene and p-methoxystyrene;

- siloxanes such as trimethoxyvinylsilane, triethoxyvinylsilane.

and multiolefins such as

- poly(meth)acrylates such as ethylene glycol diacrylate, 1,6-hexanediol diacrylate, propylene glycol diacrylate, dipropylene glycol diacrylate, tripropylene glycol diacrylate, 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, polyethyleneglycol-mono-acrylate, polyethylene-glycol-di-acrylate, ethylene glycol dimethacrylate, 1,6-hexanediol dimethacrylate, propylene glycol dimethacrylate, dipropylene glycol dimethacrylate, tripropylene glycol dimethacrylate, neopentyl glycol dimethacrylate, hexamethylene glycol dimethacrylate and bis- phenol-A dimethacrylate, 4,4'-bis(2-methacryloyloxyethoxy)diphenylpropane, trimethylolpropane tri-methacrylate, pentaerythritol trimethacrylate, pentaerythritol tetramethacrylate, vinyl methacrylate, polyethyleneglycol-mono-methacrylate, polyethylene-glycol-di-methacrylate;
- other multiolefins such as butadiene, isoprene, chloroprene, 2,4-dimethylbutadiene, cyclopentadiene, methylcyclopentadiene, cyclohexadiene, divinyl-benzene, 1-vinyl-cyclohexadiene, norbornadiene, 2-isopropenylnorbornene, 2-vinyl-norbornene, diisopropenylbenzene, divinyltoluene, divinylxylene and C₁ to C₂₀ alkyl-substituted derivatives of the aforementioned divinylaromatic multiolefins, divinyl succinate, diallyl phthalate, triallyl phosphate, triallyl isocyanurate, tris- (hydroxyethyl) isocyanurate triacrylate (Sartomer 368; from Cray Valley) and tris(2-acryloyl- ethyl) isocyanurate, ethyleneglycoldivinylether, diethyleneglycoldivinylether, triethylene-glycoldivinylether

and any mixture of the aforementioned monoolefins and/or multiolefins.

In an embodiment, monoolefins or mixtures of monoolefins of formula (IIa), preferably those monoolefins explicitly mentioned above are used, whereby butadiene, isoprene, chloroprene, methyl-, ethyl-, n-butyl- and 2-ethylhexylacrylate and methyl-, ethyl-, n-butyl- and 2-ethylhexylmethacrylate, acrylamide, acrylonitrile, vinylpyridine, styrene and styrene substituted by C₁-C₈-alkyl- or halogen or sulfonic acid salts at the aromatic ring, preferably styrene, 2-, 3- and 4-methylstyrene, 2-, 3- and 4- bromomethylstyrene, 2-, 3- and 4-chlorostyrene and p-methoxystyrene and any mixture of the aforementioned monoolefins are particularly preferred.

In an embodiment, where an aqueous phase is employed in step A) and B), in particular as dispersed phase or continuous phase, preferably as continuous phase, in a heterophase

polymerization, 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 monomers dissolved in the said aqueous 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.

- 5 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. This helps to avoid immediate agglomeration.

10 The weight ratio of photoinitiator to polymerizable monomer in the heterophase medium is typically of from 1:1 to 1:100'000, preferably between 1:5 and 1:100'000, preferably between 1: 10 and 1:10'000 and more preferably 1:50 to 1:2'000.

In one embodiment, the heterophase medium comprises a continuous aqueous phase and a dispersed organic phase, whereby the organic phase comprises the one or more polymerizable monomers.

- 15 In another embodiment, if heterophase polymerization is applied in step B), the heterophase medium comprises a continuous aqueous phase and a dispersed organic phase, whereby the content of polymerizable monomer within the dispersed organic phase is 20 to 100 wt.-%, preferably 90 to 100 wt.-% and more preferably 98 to 100 wt.-% of one or more polymerizable monomers whereby surfactants are not counted as being part of the organic phase.

- 20 Generally, in step A), the photoinitiator may be either added partially or preferably completely. If in step A) the photoinitiator is added partially, the rest can be added during step B) either batchwise or continuously.

The polymerization conditions

- 25 In step B), the one or more polymerizable monomers present in the polymerization medium, in particular in the heterophase medium are polymerized by irradiating said polymerization medium, in particular in the heterophase medium, with electromagnetic radiation having a wavelength sufficient to induce the generation of radicals.

This includes wavelengths sufficient to induce the generation of radicals from

- at least the one or more photoinitiators employed and optionally

- at least one reaction product of radicals generated from said one or more photoinitiators with said one or more polymerizable monomers, preferably at least one reaction product of radicals comprising at least one phosphorous oxide (P=O) or phosphorous sulfide (P=S) group with said one or more polymerizable monomers or
- preferably from both of the aforementioned sources of radicals

It is apparent to those skilled in the art, that the electromagnetic radiation sufficient to induce the generation of radicals is dependant on the exact structure of the photoinitiator and/or the reaction product of radicals generated from the photoinitiator with the polymerizable monomers but can easily determined by performing very few and commonly known simple measurements, tests or experiments.

Such tests include UV-Vis spectroscopy and radical scavenger experiments known to those skilled in the art.

As a consequence, and in order to carry out the process according to the invention one may either adapt the photoinitiators employed to a given source of electromagnetic radiation or vice versa.

With the photoinitiators used herein generation of radicals of any type mentioned above is typically induced by irradiation with electromagnetic radiation having a wavelength of below 500 nm, preferably below 480 nm, more preferably in the range of 200 to 480 nm, even more preferably in the range of 280 to 480 nm.

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

Preferred sources are UV lamps like low-pressure, medium-pressure, high-pressure and super-high-pressure mercury lamps which can be undoped or doped e.g. with gallium iodide, thallium iodide or other metal halides; blue, violet-blue or UV-LEDs, xenon or xenon mercury arc lamps such as continuous-output xenon short- or long-arc lamps.

In an embodiment, multichromatic sources of electromagnetic radiation are used to generate radicals.

As used herein a multichromatic sources of electromagnetic radiation denotes a source emitting electromagnetic radiation having more than one relative emission maxima (also known as emission bands) preferably more than one relative emission maxima within the wavelength ranges disclosed above.

The irradiation time of the polymerization medium, in particular the heterophase medium may vary depending on the intensity of irradiance and its penetration depth within the polymerization medium, in particular the heterophase medium, but typically is for example in the range of from 5 min to 24 h.

In a highly preferred embodiment, irradiation of the polymerization medium, in particular the heterophase medium is effected in such a manner, that the ratio of the irradiated surface of the polymerization medium, in particular the heterophase medium and its volume (SVR) is at least 200 m^{-1} , preferably at least 600 m^{-1} , in a more preferred embodiment at least 1000 m^{-1} , in an even more preferred embodiment at least 1500 m^{-1} .

Figures 1, 2 and 3 depict the examples given below, which are not intended to limit the spatial design of devices allowing the described SVR.

A ratio of the irradiated surface of the polymerization medium (PM), in particular the heterophase medium (HM) and its volume of at least 200 m^{-1} is for example achieved by irradiation of the surface (S) of a thin film of polymerization medium, in particular the heterophase medium (HM) having a uniform layer thickness (L) of 5 mm (see figure 1).

A ratio of the irradiated surface of the polymerization medium, in particular the heterophase medium and its volume of at least 200 m^{-1} is for example also achieved by irradiation of the surface of a polymerization medium (PM), in particular the heterophase medium (HM) confined

- in a transparent round tube having a inner radius (r) of 5 mm if irradiated from one direction (in this case the irradiated surface S is $\pi \cdot r \cdot l$, the volume $\pi \cdot r^2 \cdot l$ with l being the length of the irradiated tube or the irradiated part thereof) (see figure 2 in which the dashed part of the surface is not irradiated) or
- in a transparent round tube having a inner radius (r) of 10 mm if irradiated from two opposite directions (in this case the irradiated surface is the whole inner surface of $2\pi \cdot r \cdot l$,

the volume is $\pi \cdot r^2 \cdot l$ with l being the length of the irradiated tube or the irradiated part thereof) (see figure 3).

Surprisingly it was found that irradiation in the spatial dimensions described above tremendously increases polymerization rates and, where heterophase polymerization is applied, also molecular weights of the polymer chains within the latices.

In one embodiment, in particular where heterophase polymerization is applied, the irradiation is effected in a transparent tube, tubing or channel having an effective diameter of 5 mm or less, for example 0.1 to 5 mm, preferably 2 mm or less, for example 0.1 to 2 mm and more preferably 1 mm or less, for example 0.1 to 1 mm.

As used herein, the effective diameter of a tube, tubing or channel, which is typically circular, but also might deviate from circular shape, is understood as the diameter of a circular tube, tubing or channel having the same cross sectional area.

In one embodiment, in particular where bulk or solution polymerization, preferably bulk polymerization is applied, the irradiation is effected by irradiating a thin film of polymerization medium having a layer thickness of 5 mm or less, for example 0.001 to 5 mm, preferably 2 mm or less, for example 0.001 to 2 mm and more preferably 1 mm or less, for example 0.001 to 1 mm. Low layer thicknesses can for example be achieved by spin coating.

In this preferred embodiment of the invention the irradiation time of the polymerization medium, in particular the heterophase medium is therefore typically for example in the range of from 1 s to 30 min, preferably from 5s to 15 min and even more preferably from 10 s to 3 min. Longer exposure times than 30 min typically do not positively affect the monomer conversion.

In this embodiment of the invention the irradiance with electromagnetic radiation sufficient to induce the generation of radicals is effected at average intensities of at least 50 W per square meter of irradiated surface of the polymerization medium, in particular the heterophase medium (50 W/m²), preferably at least 100 W/m² and more preferably from 200 W/m² to 50 kW/ m² and even more preferably from 200 W/m² to 10 kW/ m².

In a preferred embodiment irradiance is effected with electromagnetic radiation having a wavelength of below 500 nm at average intensities of at least 50 W per square meter of irradiated surface of the polymerization medium, in particular the heterophase medium (50 W/m²), preferably at least 100 W/m² and more preferably from 200 W/m² to 50 kW/ m² and even more preferably

from 200 W/m^2 to 10 kW/m^2 . In this embodiment the SVR is preferably at least 600 m^{-1} , in a more preferred embodiment at least 1000 m^{-1} , in an even more preferred embodiment at least 1500 m^{-1} .

5 In an embodiment irradiance is effected with electromagnetic radiation having a wavelength of below 480 nm at average intensities of at least 50 W per square meter of irradiated surface of the polymerization medium, in particular the heterophase medium (50 W/m^2), preferably at least 100 W/m^2 and more preferably from 200 W/m^2 to 50 kW/m^2 and even more preferably from 200 W/m^2 to 10 kW/m^2 . In this embodiment the SVR is preferably at least 600 m^{-1} , in a more preferred embodiment at least 1000 m^{-1} , in an even more preferred embodiment at least 1500 m^{-1} .

10 In a preferred embodiment irradiance is effected with electromagnetic radiation having a wavelength in the range of 280 to 480 nm at average intensities of at least 200 W per square meter of irradiated surface of the polymerization medium, in particular the heterophase medium (50 W/m^2), preferably at least 100 W/m^2 and more preferably from 200 W/m^2 to 50 kW/m^2 and even more preferably from 200 W/m^2 to 10 kW/m^2 . In this embodiment the SVR is preferably at least 600 m^{-1} , in a more preferred embodiment at least 1000 m^{-1} , in an even more preferred embodiment at least 1500 m^{-1} .

In a preferred embodiment step B) is carried out

- with a SVR of at least 600 m^{-1} , preferably at least 1000 m^{-1} , in an even more preferred embodiment at least 1500 m^{-1}
- an irradiance with electromagnetic radiation having a wavelength of below 500 nm at average intensities of at least 50 W per square meter of irradiated surface of the polymerization medium, in particular the heterophase medium (50 W/m^2), preferably at least 100 W/m^2 and more preferably from 200 W/m^2 to 50 kW/m^2 and even more preferably from 200 W/m^2 to 10 kW/m^2
- for 1 s to 30 min , preferably from 5 s to 15 min and even more preferably from 10 s to 3 min .

In another preferred embodiment step B) is carried out

- with a SVR of at least 1000 m^{-1} , in an even more preferred embodiment at least 1500 m^{-1}
- an irradiance with electromagnetic radiation having a wavelength of below 480 nm at average intensities of at least 50 W per square meter of irradiated surface of the polymerization medium, in particular the heterophase medium (50 W/m^2), preferably at

least 100 W/m^2 and more preferably from 200 W/m^2 to 50 kW/m^2 and even more preferably from 200 W/m^2 to 10 kW/m^2

- for 5s to 15 min and even more preferably from 10 s to 3 min.

In another preferred embodiment step B) is carried out with

- 5
- with a SVR of at least 1000 m^{-1} , in an even more preferred embodiment at least 1500 m^{-1}
 - an irradiance with electromagnetic radiation having a wavelength in the range of 280 to 480 nm at average intensities of at least 50 W per square meter of irradiated surface of the polymerization medium, in particular the heterophase medium (50 W/m^2), preferably at least 100 W/m^2 and more preferably from 200 W/m^2 to 50 kW/m^2 and even more
- 10
- for 5s to 15 min and even more preferably from 10 s to 3 min.

The determination of a suitable reaction temperature range during polymerization depends on the composition of the polymerization medium, for example where a heterophase medium is employed on the composition of the continuous phase, the composition of the dispersed phase and the reaction pressure since freezing or boiling in the polymerization medium should be avoided, in particular when the continuous phase or the dispersed phase, preferably the continuous phase is an aqueous phase within a heterophase medium..

15

Generally, 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 50°C .

20

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.

In an embodiment, the polymerization carried out such that a monomer conversion of 60 to 100 wt-% of the polymerizable monomers is achieved, preferably 90 to 100 wt-%.

25 Step B) can be carried out batchwise or continuously, preferably continuously, whereby step B) is more preferably carried out continuously using a flow-through reactor if a heterophase medium is applied.

In those embodiments where a flow-through reactor is employed, the flow rate is adjusted to an average flow velocity of 0.005 to 1 m/s, preferably 0.01 to 0.5 m/s.

In an embodiment, where a heterophase medium is employed, the latices 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.

5 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.

Typically, the average particle sizes experimentally obtained are in the range of from 30 to 150 nm as measured by Dynamic Light Scattering (DLS) using a Nicomp particle sizer (PSS Santa Barbara, USA, model 370) at a fixed scattering angle of 90°.

10 The latices comprising polymer nanoparticles obtained typically have an M-PDI of 1.1 to 20, preferably an M-PDI of 2 to 10.

The latices comprising polymer nanoparticles further typically have a very low DLS-PDI of 0.05 to 0.40, preferably a DLS-PDI of 0.08 to 0.20. Step C) might directly be carried out after performance of step B).

15 In another embodiment, residual polymerizable monomers, if present at all (see above) are removed from the resulting polymer or dispersion by standard stripping or distillation techniques.

In still another embodiment, in particular where solution or heterophase polymerization was applied in step B) the polymer or polymer nanoparticles can be concentrated in or isolated from the polymerized medium or the latices using standard techniques well known to those skilled in the art and subsequently directly or after re-dispersion employed in step C).

20 Where solution or bulk polymerization was applied in step B) the preparation of modified nanoparticles can be effected by first preparing a solution of the polymer or taking the solution obtained via solution polymerization and adding the solution to a solvent or a solvent to the polymer solution, wherein the solvent or the polymer is only sparingly soluble which leads in a manner known per se to formation of latices, in particular if additional surfactants and/or high shear forces are applied. The original solvent of the polymer solution can for example be removed via standard techniques such as distillation.

25 In one embodiment the polymer obtained in step B) is purified before its employment in step C). The purification can be effected for example by precipitation, dialysis or any other manner known to those skilled in the art.

30

To concentrate or isolate the polymer nanoparticles inorganic salts or solutions thereof are for example added to the suspension and the resulting mixture is subjected to centrifugation, sedimentation, filtration or other separation processes of a like nature.

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

In step C) the polymers, in particular the latices or polymer nanoparticles obtained in step B) are modified by irradiating said polymers, in particular the latices or polymer nanoparticles, with electromagnetic radiation having a wavelength sufficient to induce the generation of radicals from said polymers and in particular from said latices or polymer nanoparticles in the presence of at least
10 one modifying agent.

Surprisingly, said modification does not require additional photoinitiators for example those of formula (I) or additional photoinitiators known to those skilled in the art since the polymers, in particular the latices and the polymer nanoparticles, obtained according in step B) were found to act as photoinitiators themselves. Therefore, in one embodiment step C) is carried out without
15 additional photoinitiators, in particular without additional photoinitiators of formula (I) and in another embodiment in absence of photoinitiators of formula (I).

As used herein a modifying agent is any compound that is able to react with radicals generated by irradiation of the polymers, in particular of the latices or polymer nanoparticles obtained in step B).

20 For example, the modifying agent or the modifying agents are added to the polymer obtained in step B) before carrying out step C).

In one embodiment, polymerizable monomers as defined above are used as modifying agents, whereby in a preferred embodiment the polymerizable monomers used in step C) are different from those taken in step A) and B).

25 If monoolefins or conjugated diolefins are employed as polymerizable monomers in step C) blockcopolymers are obtained.

If multiolefins, in particular non-conjugated crosslinkers are employed as polymerizable monomers in step C) crosslinked polymers are obtained.

If mono- or multiolefins carrying functional groups are employed telechelic polymers or functionalized blockcopolymers can be obtained.

30 Examples of such mono- or multiolefins carrying functional groups include

- hydroxyfunctionalized (meth)acrylates such as 3-hydroxypropyl(meth)acrylate, 3,4-dihydroxybutylmono(meth)acrylate, 2-hydroxyethyl(meth)acrylate, 4-Hydroxybutyl(meth)acrylate, 2-Hydroxypropyl(meth)acrylate and 2,5-dimethyl-1,6-hexandiolmono(meth)acrylate.
- 5 • aminofunctionalized (meth)acrylates such as 2-dimethylaminoethyl-(meth)acrylate (DMAEMA), 2-diethylaminoethyl-(meth)acrylate (DEAEMA), 2-tert-butylaminoethyl-(meth)acrylate (t-BAEMA), 2-dimethylaminoethyl-acrylate (DMAEA), 2-diethylaminoethyl-acrylate (DEAEA), 2-tert-butylaminoethyl-acrylate (t-BAEA), 3-dimethylaminopropyl-methacrylamide (DMPMA) and 3-dimethylaminopropyl-10 acrylamide (DMPAA)
- unsaturated functionalized (meth)acrylates such as allyl(meth)acrylate
- epoxy functionalized (meth)acrylates such as glycidyl(meth)acrylate.
- carboxylic acid functionalized (meth)acrylates such as tert-butyl(meth)acrylate which may be subjected to saponification or thermal degradation to obtain carboxylic acid groups
- 15 • silicon functionalized (meth)acrylates such as 3-methacryloxypropyltrimethoxysilane.

In one embodiment, radical scavengers are used as modifying agents. In this case, chain degradation occurs which lowers the average molecular weight of the polymer, in particular of the latex.

20 For the irradiation in step C) the same conditions may be applied in any aspect as described for step B) whether in general or within areas of preference.

Step C) may be repeated once or more for example to obtain tri- or multiblockcopolymers if different monoolefins or conjugated diolefins are employed as polymerizable monomers in every repeat of step C) .

Mechanistic aspects

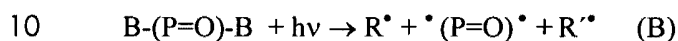
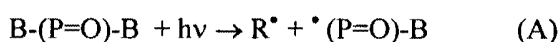
25 In order to provide a better understanding of the invention, some mechanistic aspects are discussed, which, however, in no way shall be binding or be deemed as limiting feature.

The mechanism of classical photoinitiated polymerizations in particular heterophase polymerizations such as aqueous emulsion polymerization is rather well understood. The parameters that influence the reaction have been determined, including the relative influences of

monomer, initiator, temperature and reaction time on the resulting polymer molecular weight and other features.

5 Upon exposure to electromagnetic radiation, the photoinitiators used herein undergo excitation to the singlet state, electron-spin reversal to the triplet state and fragmentation thereby forming at least two radicals.

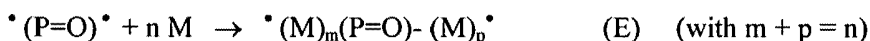
A possible explanation for generation of radicals in step B) or C) in particular the avalanche-like generation of radicals when using high SVRs is given below using a photoinitiator of the bisacylphosphine oxide (BAPO) type as an example



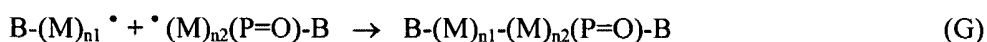
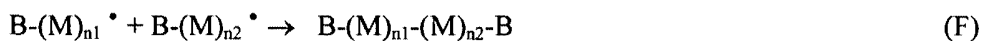
Residues B denote two acyl substituents of the photoinitiator, the third substituent was omitted for clarity. However, radical formation and reaction may, depending on its nature, occur in the same manner as discussed for B.

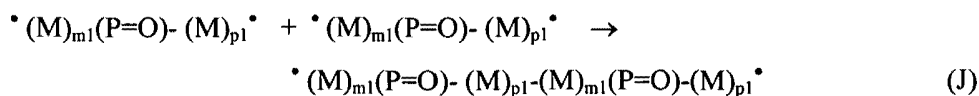
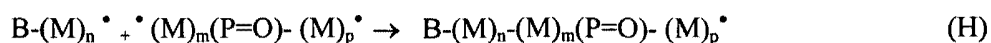
15 "hv" denotes electromagnetic radiation having a wavelength sufficient to induce the generation of the radicals depicted in the respective formulae.

After initial fragmentation of the photoinitiator, the polymerization is then started and propagated by reaction of the radicals formed according to equations (A) and (B) with n molecules of polymerizable monomer M.



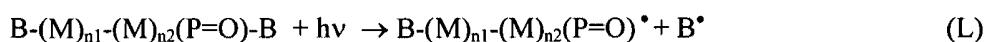
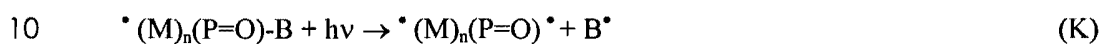
25 Termination occurs inter alia by radical combinations which limit the rate of conversion by lowering the number of free radicals present in the reaction mixture. Such termination reactions by radical combination include e.g.



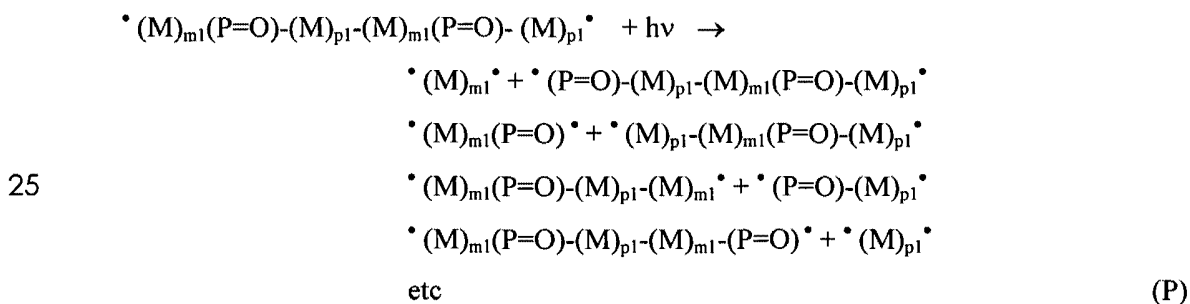
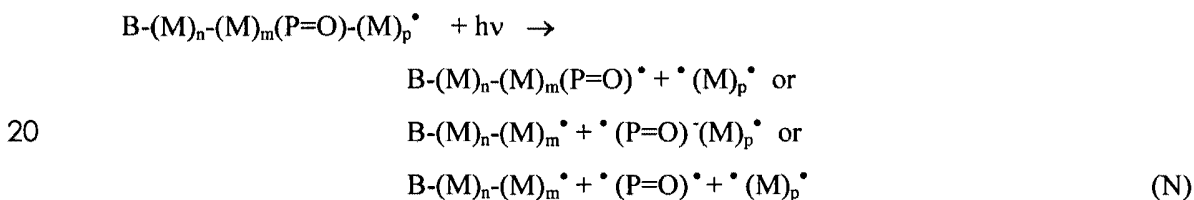
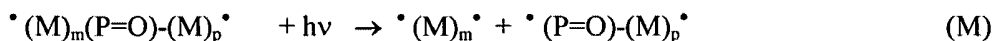


5 According to equations (E), (H) and (J) incorporation of a phosphine oxide containing moiety into the growing polymer chain occurs.

The polymers formed according to equations (D) and (G) under irradiation can undergo further scission of an acyl substituent resulting in the formation of further radicals:



15 Under the irradiation conditions with high SVRs the dramatic increase in reaction rate is proposed to be caused by further fast fragmentation of polymer chains resulting for example from reactions according to equations (E), (H) and (J)



The radicals so generated may further react with monomers M in analogy to the propagation reactions depicted in equations (C), (D) and (E).

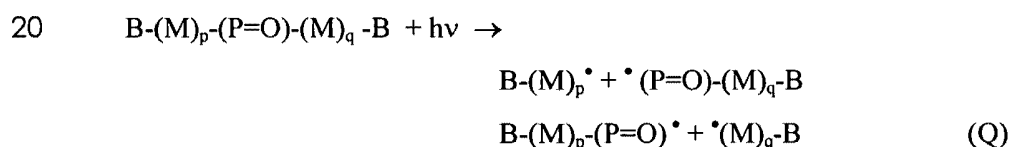
30 For heterophase polymerizations, a commonly used descriptor of radical heterophase polymerization is the average number of radicals per particle (\bar{n}). This value depends on particle

size and concentration, the rates of initiator decomposition, and radical entry into and exit out of particles. Classical emulsion polymerization of polystyrene and other polymers for example produces particles of less than 100 nm diameter, each of which contain, on average, one half radical per particle ($\bar{n} = 0.5$). Such reactions are said to conform to so-called zero-one kinetics, where each particle contains either one or no growing radical (see Ugelstad, J., Mork, P. C. & Aasen, J. O. Kinetics of Emulsion Polymerization. *J. Polym. Sci., A: Pol. Chem.* **5**, 2281-2288 (1967)). As will be shown in the examples, the repeated chain scission and avalanche-like radical generation discussed above leads to average number of radicals per particle (\bar{n}) of up to 30, which explains the ultra fast reaction rates and high molecular weights observed.

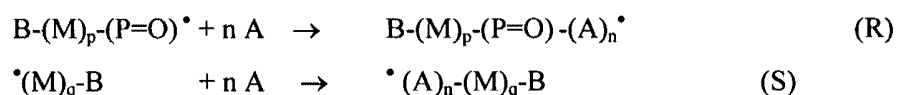
10 In one embodiment of the invention, therefore, the generation of radicals of at least one reaction product of radicals generated from the one or more photoinitiators with the one or more polymerizable monomers occurs via scission of a phosphorous-carbon-bond of reaction products comprising a phosphorous oxide (P=O) or phosphorous sulphide (P=S) group.

15 In case photoinitiators of formula (I) are employed in which m is 1 or 2, and in particular 2, the radical generation of at least one reaction product of said radicals with said one or more polymerizable monomers is preferably meant to denote a radical generation other than by scission of a phosphorous-carbon bond between the (X=P) and the (C=O)-R² group.

In step C), the polymer chains finally formed in step B) are under irradiation fragmented again to form radicals as for example shown in equation (Q):



25 In the presence of a modifying agent representing for example a further monomer A blockcopolymers are formed:



30 Analogously, crosslinked polymers are obtainable if the modifying agent is a crosslinker, chain fragmentation is effected if the modifying agent is a radical scavenger.

Devices suitable to perform steps B) and C)

The process can be carried out using every type of device designed to carry out step B) and / or step C) and optionally but preferably also step A) under the conditions described hereinabove.

This includes photoreactors known to those skilled in the art having irradiation zones and in particular those with dimensions to allow irradiation in with the prescribed SVR.

5 Suitable types of photoreactors include rising or falling film photoreactors and flow-through reactors, in particular microfluidic devices in particular if solution polymerization or heterophase polymerization is applied.

10 Bulk polymerizations are typically performed batchwise. Flow-through reactors may be any device comprising in flow direction an inlet, at least one irradiation zone comprising a wall material transparent to the electromagnetic radiation employed such as simple tubes, tubings or hoses and an outlet as well as means to convey the polymerization medium, in particular the heterophase medium from the inlet via the at least one exposure zone to the outlet such as pumps. In particular the at least one irradiation zone has a SVR of 200 m^{-1} , preferably at least 600 m^{-1} , more preferably at least 1000 m^{-1} and even more preferably at least 1500 m^{-1} .

15 Suitable wall material transparent to the electromagnetic radiation generating radicals include polyolefins such as fluorinated polyolefins such as fluorinated poly(ethylene-co-propylene), hereinafter also denoted as FEP, and polytetrafluoroethylene, polyesters (including polycarbonates), polyacrylates, polyurethanes and glass such as quartz glass, borax containing glasses and other glasses which are at least partially transparent to the electromagnetic radiation
20 employed.

Examples of suitable flow-through reactors include the flow-through reactors disclosed in US2008/013537, US2003/0118486 and US2003/0042126.

In a preferred the flow-through reactors further comprise at least one mixing device to carry out step A) which is in flow direction arranged before the at least one exposure zone.

25 Said mixing zones may be equipped with the standard mixing elements mentioned above. In a preferred embodiment the mixing zone comprises static mixing elements such as slit type mixers.

Figures 4 and 5 further illustrate suitable devices to carry out the invention.

Figure 4 is an exemplary, simplified flow diagram of a process according to the invention using a flow through reactor 1.

The feeding system comprises a storage tank **2a** for the monomers to be polymerized and a storage tank **2b** for water **W**, surfactant **SUR** and photoinitiator **PI**. Feed stream controller comprising conveying means **3a** and **3b** are employed to feed the monomers **M**, water **W**, surfactant **SUR** and photoinitiator **PI** via lines **4a** and **4b** through a mixing device **5** to form a heterophase medium **HM**. The heterophase medium **HM** is then fed via feed line **6** further to irradiation zone **7** which is irradiated by a source of electromagnetic radiation **8** powered by power source **9** and shielded by a filter **10** through the UV transparent wall material **11**. Cooling of the heterophase medium **HM** is effected by cooling means **12**. After leaving the exposure zone **7** the resulting latex comprising polymer nanoparticles **L** is transferred via exit line **13** to collection tank **14** for further workup or storage.

Figure 5 is an exemplary, detailed cross sectional view of a flow-through reactor used to carry out the experiments:

The combined feed streams comprising water **W**, surfactant **SUR**, photoinitiator **PI** and monomer **M**, are fed to mixing device **5** to form the heterophase medium **HM**. Via feed line **6** the heterophase medium **HM** is, in flow direction **F**, further conveyed to irradiation zone **7** and exits the flow-through reactor **1** via exit line **13**. Feed line **6**, irradiation zone **7** and exit line **13** are designed as a tube from a single piece of a UV transparent wall material **11**.

Emulsion **E** takes place inside the mixing device **5** typically resulting in a main drop size of below 100 μm . Relaxing and spontaneous emulsification **SE** occurs after passing the mixing device **5** in feed line **6** and typically leads to sub- μm drops.

Irradiation is effected in three zones: In reaction zones **RZ1** and **RZ2**, where irradiation is carried out without cooling and in the main reaction zone **MRZ**, where irradiation is carried out by cooling means **12**. The total irradiation zone **TIZ** consists of **RZ1**, **RZ2** and **MRZ**.

The outflow zone **OF** is exit line **13**.

It is evident that the device described above is also suitable to perform step C). In one embodiment two reactors are connected in series to perform steps A), B) and C) continuously.

Products and other aspects of the invention

As a result of the polymerization of step B) polymers, in particular latices comprising nanoparticles are obtained which are further modified in step C).

In an embodiment, the aforementioned modified polymers and in particular the modified latices or polymer nanoparticles can be used, for example, in coatings, adhesives such as adhesives for laminated glass, inks, painting materials, precision mold constructions, in the manufacture of electronic articles, for drug delivery systems, diagnostic sensors and contrast agents.

5 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 modified polymers and in particular the modified polymer nanoparticles obtained according to the process described herein.

10 One important achievement is that the polymers obtained according to step B) simultaneously serve as a building block and as photoinitiator in step C). therefore the invention further encompasses the use of polymers comprising phosphorous oxide or phosphorous sulfide groups in the main polymer chain as photoinitiators.

15 In one embodiment, the invention relates to polymers having at least one phosphorous oxide or phosphorous sulfide group within the main polymer chain per 10'000 repeating units derived from the monomer or monomers employed in step B), preferably per 1'000 repeating units, more preferably per 100 repeating units and the use of aforementioned polymers as photoinitiators.

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

Examples:**I General Materials and Methods**

The water used throughout was purified using a Seral purification system (PURELAB Plus) or an Integra UV plus (SG Reinstwassersysteme) system with a conductivity of $0.06 \mu\text{S cm}^{-1}$. Sodium dodecyl sulfate (SDS) (Roth) was used as surfactant, unless stated otherwise, and was used as received. The monomers were distilled under reduced pressure and stored refrigerated prior to use. The water-soluble photo-initiator 2-(bis(2,4,6-trimethylbenzoyl)phosphoryl)acetic acid sodium salt (BAPO-AA-Na) was prepared as described in: T. Ott, Dissertation ETH Zürich No. 18055, 2008. 2,4,6-Trimethylbenzoyl-diphenylphosphineoxide (Lucirin TPO, MAPO) and bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide (Irgacure ® 819) were obtained from BASF SE, Germany.

The continuous flow-through reactor

A microfluidic device as shown in Figures 4 and 5 was used as continuous flow reactor (1) for photoinitiated emulsion polymerization.

The feeding system consisted of two gas-tight syringes (2a, 2b), one 2.5 mL syringe for the monomer (M) and a 10 mL syringe for the aqueous phase containing water (W) photoinitiator (PI) and sodium dodecylsulfate (SUR). Two syringe pumps (3a, 3b) were used to feed the reagents through a micromixer (5) and to convey the emulsion formed therein (HM) further through the feed line (6), irradiation zone (7) and exit line (13) to a collection flask (14). The emulsion (HM) was prepared in a countercurrent micromixer (5) (SSIMM) with an inlet channel inner diameter of $45 \mu\text{m}$ and an outlet channel inner diameter of $30 \mu\text{m}$. For this micromixer and a 4 mL/min flow rate, the monomer droplet size distribution was quite broad, however, also droplets below $1 \mu\text{m}$ were formed as was confirmed by light microscopy.

The feed line (6), the exposure zone (7), and the exit line (13) was commonly formed by a tube of fluorinated poly(ethylene-co-propylene) (FEP), a UV transparent material (12) with an outer diameter of 1.590 mm and an inner diameter of 0.762 mm .

A medium pressure mercury lamp with an arc length of 27.9 cm (450 W, Hanovia) was used as a source of electromagnetic radiation (8, 9), shielded by a 1 mm thick pyrex glass filter (10).

The medium pressure mercury lamp was placed inside a quartz cooling jacket (12) and the FEP tube was wound around this set-up to form the irradiation zone (7).

The average irradiation intensity, calculated on the hemispherical surface of the heterophase medium within the FEP tube i.e. also including adsorption of the quartz cooling jacket, the FEP tube and the pyrex filter) was:

168 W/m² at 578.0 nm, 201 W/m² at 546.1 nm 144 W/m² at 435.8 nm, 75 W/m² at 404.5 nm, 147
5 W/m² at 366.0 nm, 10 W/m² at 334.1 nm, 41 W/m² at 313.0 nm, 15 W/m² at 302.5 nm, 6 W/m² at
296.7 nm and 1 W/m² at 289.4 nm.

Therefore the irradiation intensity for the electromagnetic radiation having a wavelength of below 500 nm or below 480 nm or in the range of 200 to 480 nm or in the range of 280 to 480 nm was in each case 439 W/m².

10 The temperature in the tube during the reaction was in the range from 25 to 30°C, based on temperature measurements taken between the quartz cooling jacket (12) and the tube (7).

Volumes:

Total FEP tube volume was 2.7 mL.

15 **E:** emulsification takes place inside the micro-mixer resulting in a main drop size of below 100 μm. The mixing system used is a Standard Slit Interdigital Micro Mixer (SSIMM), and is made of 15 lamellae each with a height of 200 μm, width of 45 μm, and outflow width of 30 μm.

SE: relaxing and spontaneous emulsification after micro-mixer typically into sub-μm drops.

20 **RZ1, 2:** irradiation zones, irradiation without cooling.

MRZ: main irradiation zone, wound around cooler,

TIZ (total irradiation zone) = RZ1 + MRZ + RZ2 = 2.432 mL

OF: outflow zone

25 The SVR of the TIZ was calculated to be 2625 m⁻¹.

Flow rates and residence times

Flow rates of 4 mL/min, 2 mL/min, and 1 mL/min were employed leading to residence times in the total irradiation zone (TIZ) and thus irradiation times of 36 s, 72 s and 144 s respectively

30 Latex Characterization

Samples were purified for further characterization by repeated reprecipitation from tetrahydrofurane in methanol followed by intense washing with distilled water.

Solid content was determined using a HR73 Halogen Moisture Analyzer (Mettler Toledo). Average particle size (intensity-weighted diameter) was determined with a Nicomp particle sizer (PSS Santa Barbara, USA, model 370) at a fixed scattering angle of 90°.

5 Molecular weight distributions (MWD) were determined by gel permeation chromatography (GPC) and were used to calculate weight and the number of average molecular weight polymers (Mw, Mn). GPC was carried out by injecting 100 μ L polymer solutions (solvent tetrahydrofuran (THF)) through a Teflon-filter with a mesh size of 450 nm into a Thermo Separation Products set-up equipped with ultra violet (UV) (TSP UV1000), and refractive index (RI) (Shodex RI-71) detectors in THF at 30 °C with a flow rate of 1 mL/min. A column set was employed, which consisted of 10 three 300 x 8 mm columns filled with a MZ-SDplus spherical polystyrene gel (average particle size 5 μ m), with pore sizes of 10³, 10⁵, and 10⁶ Å, respectively. Average molecular weights, and number of average molecular weight polymers (Mw and, Mn) were calculated based on polystyrene standards (between 500 and 2·10⁶ g mol⁻¹ from PSS, Mainz, Germany).

II Photoinitiated heterophase polymerization

15 Synthesis of latices according to steps A) and B)

All examples were made according to the following procedure: Sodium dodecylsulfate (SDS), the monomer (2.5 g), degassed water (10.0 g) and the photoinitiator (PI) were fed into and conveyed through the reactor and irradiated. The temperature during irradiation was 25°C for all examples.

Example 1:

20 Monomer: styrene

Photoinitiator: 2,4,6-trimethylbenzoyl-diphenylphosphineoxide (MAPO)

Ex.	SDS [mg]	PI [mg]	Irradiation time [s]	Flow rate (μ L/min)	DLS [nm]	Solid content [%]	Yield [%]
1	300	10	36	4000	61	12	62

Examples 2 to 5:

25 Monomer: styrene

Photoinitiator: 2-(bis(2,4,6-trimethylbenzoyl)phosphoryl)acetic acid sodium salt (BAPO-AA-Na)

Ex.	SDS [mg]	PI [mg]	Irradiation time [s]	Flow rate ($\mu\text{L}/\text{min}$)	DLS [nm]	Solid content [%]	Yield [%]
2	200	10	36	4000	51	15	79
3	300	10	36	4000	45	19	100
4	400	10	36	4000	38	20	100
5	500	10	36	4000	45	19	100

III Modification of polymer nanoparticles

Examples 6 and 7

5 The latices obtained according to examples 1 (to result in example 6) and 3 (to result in example 7) were purified by extensive dialysis, however retaining colloidal stability. Then, the latices were swollen with butylmethacrylate (BMA) overnight while gently stirring only the latex phase with a magnetic stir bar. Formation of macroscopic droplets of BMA was avoided. A latex sample (2 mL) was collected carefully from the bottom of the vial with a pipette in order not to drag swelling agent. The swollen particles were placed in a 6 mL glass flask and irradiated for 2 h while the flask was gently shaken. The latex was characterized to determine the solids content, average particle size, and molecular weight distribution.

10 The results are illustrated in figures 6 and 7.

The latex according to example 6 (thin dashed lines) and the latex according to example 7 in BMA emulsion (thin solid lines). The molecular weight distribution of the starting polymer is given in bold dashed lines (example 1) and bold solid lines (example 3) respectively.

15 The molecular weight distribution (MWD) of the modified polymers were determined by size exclusion chromatography (SEC). A significant change in molecular weight distribution (MWD) occurs after irradiation in either case as can be seen in figure 7.

20 Furthermore, FT-IR spectroscopic analyses of the latices of examples 1 and 3 and of the modified polymers after performing step C) in figure 6 demonstrate that an IR absorption of the carbonyl stretching frequency (*) appears proving that photo-induced modification of the latices yielded blockcopolymers of styrene and BMA.

25 As a control, styrene and BMA were irradiated for two hours but did not polymerize in the absence of the latices of examples 1 and 3.

IV Photoinitiated bulk polymerization

Examples 8 and 9

Synthesis of unmodified polymers according to steps A) and B)

5 A polymerization medium consisting of styrene and bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide were bulk polymerized in a weight ratio of 250:1 (example 8) and 2.5:1 (example 9) by irradiating it with the following light source: Osram, L18 W, light color 840, lumilux, cool white.

Curves 1 and 2 of fig. 8 show the unmodified precursor polymer produced in examples 8 and 9 via bulk polymerization.

10 It is apparent that increasing the photoinitiator concentration by a factor of 100 shifted the distribution maximum into the low molecular weight region (Fig. 8, curve 2 compared to curve 1).

V Modification of polymers obtained via photoinitiated bulk polymerization

Example 10

15 The polymer obtained in example 9 was used as photoinitiator and building block simultaneously.

Prior to use the polymer was carefully purified by repeated reprecipitation from methanol so that no residual bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide (Irgacure® 819) was detectable by ³¹P-NMR.

20 20 g of water, 600 mg of SDS and 0.5 g of the purified polymer dissolved in 4 g of styrene were then irradiated at ambient temperature with the same light source used in example 9 in the flow through reactor. The molecular weight distribution of the modified polymer obtained thereby is shown in curve 3 of fig. 8.

Example 11

25 10 wt.-% of the polymer obtained in example 9 were purified as described in example 10 and dissolved in vinylacetate. The resulting solution was spread between a microscopy slide and a cover glass resulting in a uniform layer thickness of about 0.1 mm. The solution was then irradiated through the cover glass using the light source of examples 8 and 9.

Example 12 (for comparison)

Instead of the purified polymer obtained in example 9 the same amount of a thermally polymerized polystyrene was used. All other conditions were the same as in example 11.

Example 13 (for comparison)

5 Instead of the purified polymer obtained in example 9 the same amount of a thermally polymerized polystyrene was used. Additionally, 0.5 wt.-% of bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide (Irgacure® 819) based on n-butylacrylate was added. All other conditions were the same as in example 11.

Results of Examples 11, 12, 13

10 The onset of the polymerization in example 11 could be followed visually by the occurrence of a slight turbidity due to starting microphase separation of the block copolymer layer between the glasses (see fig 9, two pictures on the left side)

Contrary thereto, the solution employed in example 12 stayed transparent, for example 13 a strongly turbid layer was formed (see fig 9, upper right side) indicating strong scattering effects at phase boundaries of the much larger regions where the homopolymers (polystyrene and polybutylacrylate) demix (see fig 9, lower right side).

15

The light microscopy images of fig. 9 were taken using a Keyence VHX100 microscope under oblique illumination in transmission mode of the polymer film between the glass slides. The bars indicate 100 μm .

20 Both, the polystyrene-polybutylacrylate block copolymer obtained in example 11 and the polystyrene polybutylacrylate homopolymer mixture obtained in example 13 glued both glass slides together, whereas the cover glass on the non-reactive solution of polystyrene in butylacrylate without initiator could be easily removed.

Example 14

25 10 wt.-% of the polymer obtained in example 9 were purified as described in example 10 and dissolved in vinylacetate in a glass beaker. The resulting solution was then irradiated through the transparent walls using the light source of examples 8 and 9.

An elastic piece of a polystyrene-polyvinylacetate block copolymer was obtained having the shape of the beaker. The existence of a block copolymer was proven by adding glacial acetic acid which

is a selective solvent for poly(vinyl acetate). A dispersion was formed indicating the known stabilization of the “insoluble” polystyrene blocks by the “soluble” polyvinylacetate blocks.

In contrast, adding glacial acetic acid to a mixture of polystyrene and polyvinylacetate homopolymers resulted in a transparent solution polyvinylacetate with free floating chunks of polystyrene.

5

Example 15

The sequence of letters ‘SRG’ was phototyped through a PTFE stencil using a 50 wt.-% solution of the polymer obtained in example 9 purified as described in example 10 in a styrene-butylacrylate mixture (3:2 g/g) with a small amount of a yellow dye. The result is shown in fig. 10

10

5 **Claims:**

1. A process for the preparation of modified polymers by photo-initiated polymerization which comprises at least the steps of:

A) preparing a polymerization medium comprising at least

- one or more photoinitiators comprising at least one phosphorous oxide (P=O) or phosphorous sulfide (P=S) group and
- one or more polymerizable monomers

and

B) polymerizing the one or more polymerizable monomers by irradiating said polymerization medium with electromagnetic radiation having a wavelength sufficient to induce the generation of radicals to obtain a polymer

C) modifying the polymer obtained in step B) by irradiating said polymer with electromagnetic radiation having a wavelength sufficient to induce the generation of radicals from said polymer in the presence of at least one modifying agent.

2. The process according to claim 1, wherein step B) is carried out as bulk or solution polymerization or as heterophase polymerization in a heterophase medium.

3. The process according to claim 3, wherein modified latices or modified polymer nanoparticles are formed by photo-initiated heterophase polymerization by at least the steps of:

A) preparing a heterophase medium comprising at least a dispersed phase and a continuous phase and at least

- one or more surfactants
- one or more photoinitiators
- one or more polymerizable monomers and

and

B) polymerizing the one or more polymerizable monomers by irradiating said heterophase medium with electromagnetic radiation having a wavelength sufficient to induce the generation of radicals to obtain latices comprising polymer nanoparticles

5 whereby the photoinitiators are selected from compounds comprising at least one phosphorous oxide (P=O) or phosphorous sulfide (P=S) group and

C) modifying the latices or polymer nanoparticles obtained in step B) by irradiating said latices or polymer nanoparticles with electromagnetic radiation having a wavelength sufficient to induce the generation of radicals from said latices or
10 polymer nanoparticles in the presence of at least one modifying agent.

4. The process according to claim 3, wherein the heterophase medium is an emulsion.

5. The process according to claim 3 or 4, wherein the heterophase medium is an emulsion comprising an aqueous continuous phase and an organic dispersed phase.

6. The process according to anyone of claims 3 to 5, wherein the heterophase medium
15 prepared in step A) comprises a solids content of from more than 0 to 50 wt.-%, preferably of from more than 0 to 25 wt.-%, more preferably of from more than 0 wt.-% to 10 wt.-% and even more preferably of from more than 0 wt.-% to 2 wt.-%.

7. The process according to claim 5, wherein the aqueous phase comprises either 0 wt.-%, or from more than 0 to 20 wt.-% of water-miscible organic solvents.

8. The process according to claim 5 or 7, wherein the aqueous phase comprises salts.
20

9. The process according to anyone of claims 5 or 7 to 8, wherein the pH value of the aqueous phase is typically in the range of 3 to 10, preferably in the range of 5 to 9 measured at standard conditions.

10. The process according to anyone of claims 1 to 9, wherein step A) is carried out
25 continuously.

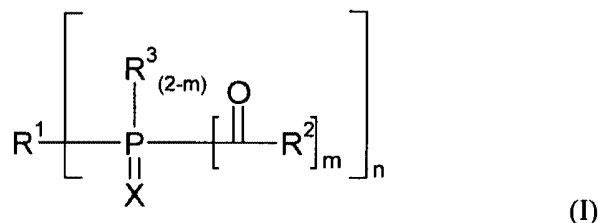
11. The process according to anyone of claims 3 to 10, wherein the heterophase medium comprises non-ionic, cationic, anionic or amphoteric surfactants.

12. The process according to anyone of claims 3 to 11, wherein the weight ratio of surfactant and the continuous phase is between 1:10'000 and 1:5 and preferably between 1:100 and

1:20, whereby the amount is at least equal or higher than the critical micelle concentration in the heterophase medium.

13. The process according to anyone of claims 1 to 12, wherein the photoinitiators are selected from compounds of formula (I):

5



wherein

n is 1 or 2 or a higher integer,

m is 0, 1 or 2,

10 X is sulphur or oxygen

R¹, if n = 1 is C₆-C₁₄-aryl or C₃-C₁₄- heterocyclyl or

is C₁-C₁₈-alkoxy, -N(R⁴)₂, C₁-C₁₈-alkyl, C₂-C₁₈-alkenyl or C₂-C₁₈-alkinyl

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

15 -O-, -S-, -SO₂-, -SO-, -SO₂NR⁴-, NR⁴SO₂-, -NR⁴-, -N⁺(R⁴)₂An⁻-, -CO-, -O(CO)-, (CO)O-, -O(CO)O-, -NR⁴(CO)NR⁴-, NR⁴(CO)-, -(CO)NR⁴-, -NR⁴(CO)O-, -O(CO)NR⁴-, -Si(R⁵)₂-, -OSi(R⁵)₂-, -OSi(R⁵)₂O-, -Si(R⁵)₂O-,

and which is either not, once, twice or more than twice interrupted by bivalent residues selected from the group consisting of C₃-C₁₄-heterocyclo-diyl, C₃-C₁₄- heterocyclo-dylium⁺An⁻ and C₆-C₁₄-aryldiyl,

20

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, vicinal oxo (forming epoxides), vicinal NR⁵ (forming aziridins), C₆-C₁₄-aryl, C₁-C₈-alkoxy, C₁-C₈-alkylthio, hydroxy, -SO₃M, -COOM, PO₃M₂, -PO(N(R⁵)₂)₂, PO(OR⁵)₂, -SO₂N(R⁴)₂, -N(R⁴)₂, -N⁺(R⁴)₃An⁻, C₃-C₁₄-heterocyclylium⁺An⁻, -CO₂N(R⁴)₂, -COR⁴, -OCOR⁴, -NR⁴(CO)R⁵, -(CO)OR⁴, -NR⁴(CO)N(R⁴)₂, NR⁴SO₂R⁴, -Si(OR⁵)_y(R⁵)_(3-y), -OSi(OR⁵)_y(R⁵)_(3-y) with y = 1, 2 or 3,

5

R¹, if n = 2 is C₆-C₁₅-aryldiyl or C₃-C₁₄- heterocyclo-diyl

is C₁-C₁₈-alkanediyl, C₂-C₁₈-alkenediyl or C₂-C₁₈-alkinediyl,

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

10

-O-, -S-, -SO₂-, -SO-, -SO₂NR⁴-, NR⁴SO₂-, -NR⁴-, -N⁺(R⁴)₂An⁻, -CO-, -O(CO)-, (CO)O-, -O(CO)O-, -NR⁴(CO)NR⁴-, NR⁴(CO)-, -(CO)NR⁴-, -NR⁴(CO)O-, -O(CO)NR⁴-, -Si(R⁵)₂-, -OSi(R⁵)₂-, -OSi(R⁵)₂O-, -Si(R⁵)₂O-,

and which is either not, once, twice or more than twice interrupted by bivalent residues selected from the group consisting of C₃-C₁₄-heterocyclo-diyl, C₃-C₁₄- heterocyclo-dylium⁺An⁻ and C₆-C₁₄-aryldiyl,

15

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, azido, vicinal oxo (forming epoxides), vicinal NR⁵ (forming aziridins), C₆-C₁₄-aryl, C₁-C₈-alkoxy, C₁-C₈-alkylthio, hydroxy, -SO₃M, -COOM, PO₃M₂, -PO(N(R⁵)₂)₂, PO(OR⁵)₂, -SO₂N(R⁴)₂, -N(R⁴)₂, -N⁺(R⁴)₃An⁻, C₃-C₁₄-heterocyclylium⁺An⁻, -CO₂N(R⁴)₂, -COR⁴, -OCOR⁴, -NR⁴(CO)R⁵, -(CO)OR⁴, -NR⁴(CO)N(R⁴)₂, NR⁴SO₂R⁴, -Si(OR⁵)_y(R⁵)_(3-y), -OSi(OR⁵)_y(R⁵)_(3-y) with y = 1, 2 or 3,

25

or is bivalent bis(C₆-C₁₅)-aryl, which is either not or once interrupted by groups selected from the group consisting of:

-O-, -S-, -SO₂-, -SO-, C₄-C₁₈-alkanediyl, C₂-C₁₈-alkenediyl,

R¹, if n is an integer larger than 2

is a polymeric backbone having n binding sites to residues of formula (I) given in brackets labelled with n

R^2 is C_6-C_{14} -aryl or C_3-C_{14} -heterocyclyl or

is C_1-C_{18} -alkyl, C_2-C_{18} -alkenyl or C_2-C_{18} -alkinyl,

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

-O-, $-NR^4$ -, $-N^+(R^4)_2An^-$ -, -CO-, -OCO-, -O(CO)O-, $NR^4(CO)$ -, $-NR^4(CO)O$ -, $O(CO)NR^4$ -, $-NR^4(CO)NR^4$ -,

10 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 $^+An^-$, and C_6-C_{14} -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, hydroxy, protected hydroxyl, C_6-C_{14} -aryl; C_3-C_{14} -heterocyclyl, C_1-C_8 -alkoxy, C_1-C_8 -alkylthio, C_2-C_8 -alkenyl, -COOM, - SO_3M , $-PO_3M_2$, $-SO_2N(R^4)_2$, $-NR^4SO_2R^5$, $-N(R^4)_2$ -, $-N^+(R^4)_3An^-$ -, $CO_2N(R^4)_2$, $-COR^4$ -, $-OCOR^5$, $-O(CO)OR^5$, $NR^4(CO)R^4$, $-NR^4(CO)OR^4$, $O(CO)N(R^4)_2$, $-NR^4(CO)N(R^4)_2$,

20 whereby in case of $m = 2$ the two substituents R^2 are different or identical, preferably identical or jointly are C_6-C_{15} -aryldiyl, C_3-C_{14} - heterocyclo-diyl, C_1-C_{18} -alkanediyl, C_2-C_{18} -alkenediyl or C_2-C_{18} -alkinediyl,

R^3 independently denotes a substituent as defined for R^1 if n is 1,

whereby

25 R^4 is independently selected from the group consisting of hydrogen, C_1-C_8 -alkyl, C_6-C_{14} -aryl and C_3-C_{14} -heterocyclyl or $N(R^4)_2$ as a whole is a N-containing C_3-C_{14} -heterocycle, or $N^+(R^4)_2An^-$ and $N^+(R^4)_3An^-$ as a whole are or contain a N-containing C_3-C_{14} -heterocyclyl substituent with a counteranion,

- R^5 is independently selected from the group consisting of C_1 - C_8 -alkyl, C_6 - C_{14} -aryl and C_3 - C_{14} -heterocyclyl or $N(R^5)_2$ as a whole is a N-containing C_3 - C_{14} -heterocycle, or $N^+(R^5)_2An^-$ and $N^+(R^5)_3An^-$ as a whole are or contain a N-containing C_3 - C_{14} -heterocyclyl substituent with a counteranion,
- 5 M is hydrogen, or $1/q$ equivalent of an q -valent metal ion or is a C_3 - C_{14} -heterocyclylum cation, an ammonium ion or a primary, secondary, tertiary or quarternary organic ammonium ion or a guanidinium ion or an organic guanidinium ion
- An^- is $1/p$ equivalent of a p -valent anion.
- 10 14. The process according to anyone of claims 1 to 13, wherein the photoinitiators are selected from compounds of formula (I) wherein
- X is oxygen
- n is 1,
- m is 1 or 2,
- 15 R^1 and R^3 are independently of each other C_6 - C_{14} -aryl or
- are C_1 - C_{18} -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- or $-NR^4-$,
- 20 and which is not, additionally or alternatively, preferably alternatively either not, once, twice or more than twice, preferably not or once, preferably once substituted by substituents selected from the group consisting of:
- 25 chloro, fluoro, C_1 - C_8 -alkoxy, hydroxy, $-SO_3M$, $-COOM$, PO_3M_2 , $SO_2N(R^4)_2$, $-N(R^4)_2$, $-N^+(R^4)_3An^-$, $-CO_2N(R^4)_2$,
- R^2 is C_6 - C_{14} -aryl, whereby in case of $m = 2$ the substituents R^2 are different or identical, preferably identical

whereby

R^4 is independently selected from the group consisting of C_1 - C_8 -alkyl, C_6 - C_{14} -aryl and C_3 - C_{14} -heterocyclyl or $N(R^4)_2$ as a whole is a N-containing C_3 - C_{14} -heterocycle, or $N^+(R^4)_2An^-$ and $N^+(R^4)_3An^-$ as a whole are or contain a N-containing C_3 - C_{14} -heterocyclyl substituent with a counteranion,

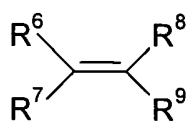
M is hydrogen, or $1/q$ equivalent of an q -valent metal ion or is a C_3 - C_{14} -heterocyclylum cation, an ammonium ion or a primary, secondary, tertiary or quaternary organic ammonium ion or a guanidinium ion or an organic guanidinium ion, preferably hydrogen, lithium, sodium, potassium, one half equivalent of calcium, zinc or iron (II), or one third equivalent of aluminium (III) or a C_3 - C_{14} -heterocyclylum cation or an ammonium ion or a primary, secondary, tertiary or quaternary organic ammonium ion, and whereby hydrogen, lithium, sodium and potassium are even more preferred and whereby hydrogen, lithium, sodium and potassium are even more preferred and

An^- is $1/p$ equivalent of a p -valent anion, preferably chloride, a C_1 - C_8 -alkyl carboxylate, C_1 - C_8 -alkylsulfate, C_6 - C_{14} -arylsulfate, hexafluorophosphate, tetrafluoroborate, dihydrogenphosphate, one half equivalent of sulphate or hydrogenphosphate.

15. The process according to anyone of claims 1 to 14, wherein the photoinitiators are selected from the following compounds:

2-(bis(2,4,6-trimethylbenzoyl)phosphoryl)acetic acid and its salts, in particular its sodium and potassium salts, (2-(2-(2-methoxyethoxy)ethoxy)ethyl)- (bis(2,4,6-trimethylbenzoyl)-phosphineoxide, 2,4,6-trimethylbenzoyl-diphenylphosphineoxide and bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide.

16. The process according to anyone of claims 1 to 15, wherein the polymerizable monomers are selected of the group consisting of compounds of formulae (IIa) and (IIb):



(IIa)

wherein

R^6 , R^7 , R^8 and R^9 are independently of one another selected from the group consisting of:

hydrogen, C_6 - C_{14} -aryl, C_3 - C_{14} -heterocyclyl, C_1 - C_{18} -alkoxy, C_1 - C_{18} -alkyl, C_2 - C_{18} -alkenyl and C_2 - C_{18} -alkinyl

- which is either directly bound to the double bond depicted in formula (IIa) or in case of C_6 - C_{14} -aryl, C_3 - C_{14} -heterocyclyl, C_1 - C_{18} -alkyl, C_2 - C_{18} -alkenyl and C_2 - C_{18} -alkinyl alternatively via a functional group selected from the group consisting of:

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

and

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

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

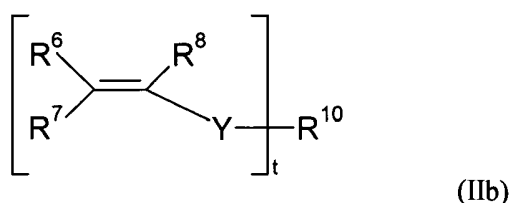
- and which is additionally or alternatively either not, once, twice or more than twice, preferably not, or once interrupted by bivalent residues selected from the group consisting of C_3 - C_{14} -heterocyclo-diyl and C_6 - C_{14} -aryldiyl,

- 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, vicinal oxo (forming epoxides), vicinal NR^5 (forming aziridins), C_6 - C_{14} -aryl; C_3 - C_{14} -heterocyclyl, C_1 - C_8 -alkylthio, hydroxy, $-\text{SO}_2\text{N}(\text{R}^4)_2$, $\text{NR}^4\text{SO}_2\text{R}^5$, $-\text{N}(\text{R}^4)_2$, $-\text{CO}_2\text{N}(\text{R}^4)_2$, $-\text{COR}^4$, $-\text{OCOR}^4$, $-\text{O}(\text{CO})\text{OR}^4$, $\text{NR}^4(\text{CO})\text{R}^5$, $-\text{NR}^4(\text{CO})\text{OR}^5$,

$O(CO)N(R^4)_2$, $-NR^4(CO)N(R^4)_2$, $-OSi(OR^5)_{y-3}(R^5)_y$, $-Si(OR^5)_{y-3}(R^5)_y$ where y is 1, 2 or 3.

or wherein two residues of R^6 , R^7 , R^8 and R^9 together are C_2 - C_{18} -alkanediyl or C_3 - C_{18} -alkenediyl



wherein

R^6 , R^7 and R^8 have the same meaning given above for formula (IIa)

or wherein

two residues of R^6 , R^7 and R^8 together are C_2 - C_{18} -alkanediyl or C_3 - C_{18} -alkenediyl

10 and wherein

t is an integer from 2 to 4 and

Y is missing such that R^{10} is directly bound to the double bond depicted in formula (IIb) or is $-CO-$ or $-(CO)O-$ and

15 R^{10} is a t-valent residue selected from the group consisting of C_2 - C_{18} -alkanediyl (t=2), C_3 - C_{18} -alkanetriyl (t=3), C_4 - C_{18} -alkanetetrayl (t=4), C_2 - C_{18} -alkenediyl (t=2), C_3 - C_{18} -alkenetriyl (t=3), C_4 - C_{18} -alkenetetrayl (t=4), C_2 - C_{18} -alkinediyl (t=2), C_6 - C_{14} -aryldiyl (t=2) and C_3 - C_{14} -heterocyclodiyl (t=2).

17. The process according to anyone of claims 1 to 16, wherein the polymerizable monomers are selected of the group consisting of:

20

- Methyl-, ethyl-, n-butyl-, glycidyl-, 2-ethylhexyl- and 2-hydroxyethyl acrylate, acrylamide, N-isopropylacrylamide and acrylonitrile, and methyl-, ethyl-, n-butyl-, glycidyl-, 2-ethylhexyl-, 2-hydroxyethyl and isobornyl methacrylate; methacrylamide, N-isopropylmethacrylamide and methacrylonitrile;

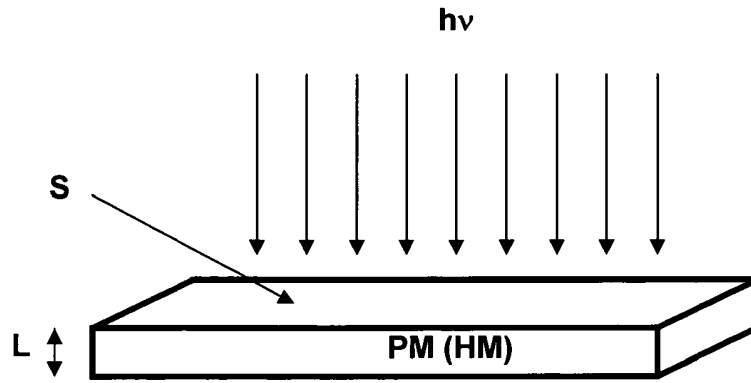
- crotonic acid, maleic acid, fumaric acid, itaconic acid, cinnamic acid and linolenic acid or oleic acid and the respective C₁-C₈-alkyl esters of the aforementioned acids and where applicable C₁-C₈-alkyl diesters;
 - ethyl vinyl ether and isobutyl vinyl ether;
 - 5 • vinyl acetate;
 - vinylpyridine, styrene and styrene substituted by C₁-C₈-alkyl- or halogen or sulfonic acid salts at the aromatic ring
 - trimethoxyvinylsilane, triethoxyvinylsilane.
 - ethylene glycol diacrylate, 1,6-hexanediol diacrylate, propylene glycol diacrylate, 10 dipropylene glycol diacrylate, tripropylene glycol diacrylate, 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, polyethyleneglycol-mono-acrylate, polyethylene-glycol-di-acrylate, ethylene glycol 15 dimethacrylate, 1,6-hexanediol dimethacrylate, propylene glycol dimethacrylate, dipropylene glycol dimethacrylate, tripropylene glycol dimethacrylate, neopentyl glycol dimethacrylate, hexamethylene glycol dimethacrylate and bis- phenol-A dimethacrylate, 4,4'-bis(2-methacryloyloxyethoxy)diphenylpropane, trimethylolpropane tri-methacrylate, pentaerythritol trimethacrylate, pentaerythritol 20 tetramethacrylate, vinyl methacrylate, polyethyleneglycol-mono-methacrylate, polyethylene-glycol-di-methacrylate;
 - butadiene, isoprene, chloroprene, 2,4-dimethylbutadiene, cyclopentadiene, methylcyclopentadiene, cyclohexadiene, divinyl-benzene, 1-vinyl-cyclohexadiene, norbornadiene, 2-isopropenylnorbornene, 2-vinyl-norbornene, 25 diisopropenylbenzene, divinyltoluene, divinylxylene and C₁ to C₂₀ alkyl-substituted derivatives of the aforementioned divinylaromatic multiolefins, divinyl succinate, diallyl phthalate, triallyl phosphate, triallyl isocyanurate, tris- (hydroxyethyl) isocyanurate triacrylate (Sartomer 368; from Cray Valley) and tris(2-acryloyl-ethyl) isocyanurate, ethyleneglycoldivinylether, diethyleneglycoldivinylether, 30 triethylene-glycoldivinylether
- and any mixture of the aforementioned monoolefins and/or multiolefins.

18. The process according to anyone of claims 1 to 17, wherein in step B) or step C), preferably in both steps B) and C), the irradiation of the polymerization medium, in particular the heterophase medium is effected in such a manner that the ratio of the irradiated surface of the polymerization medium, in particular the heterophase medium and its volume is at least 600 m^{-1} , preferably at least 1000 m^{-1} and more preferably at least 1500 m^{-1} .
19. The process according to anyone of claims 1 to 18, wherein in step B) or step C), preferably in both steps B) and C), the irradiation is effected with electromagnetic radiation having a wavelength of below 500 nm, preferably below 480 nm, and more preferably in the range of 200 to 480 nm and even more preferably in the range of 280 to 480 nm.
20. The process according to anyone of claims 1 to 19, wherein irradiation is effected at average intensities of at least 50 W per square meter of irradiated surface of the polymerization medium, in particular the heterophase medium (50 W/m^2), preferably at least 100 W/m^2 and more preferably from 200 W/m^2 to 50 kW/m^2 .
21. The process according to anyone of claims 1 to 20, wherein irradiation is effected with irradiation times of from 1s to 30 min, in particular from 5s to 15 min and more particularly from 10 s to 3 min.
22. The process according to anyone of claims 1 to 21, wherein step B) or step C), preferably both steps B) and C) are carried out continuously, preferably in a flow-through reactor.
23. The process according to anyone of claims 1 to 22, wherein the modifying agents is selected from polymerizable monomers according to claims 16 and 17 or radical scavengers.
24. The process according to anyone of claims 1 to 23, wherein the modifying agents are selected from polymerizable monomers according to claims 16 and 17 and differ from those polymerizable monomers employed in steps A) and B).
25. The process according to anyone of claims 1 to 24, wherein the weight ratio of photoinitiator to polymerizable monomer in the polymerization medium is of from 1:1 to 1:100'000, preferably between 1:5 and 1:100'000, preferably between 1: 10 and 1:10'000 and more preferably 1:50 to 1:2'000.
26. The process according to anyone of claims 1 to 25, wherein the weight ratio of photoinitiator to polymerizable monomer in the polymerization medium is of from 1:1 to

1:100'000, preferably between 1:5 and 1:100'000, preferably between 1: 10 and 1:10'000 and more preferably 1:50 to 1:2'000.

- 5 27. The process according to anyone of claims 1 to 26, wherein the modified polymers a blockcopolymers, crosslinked polymers, telechelic polymers or functionalized blockcopolymers.
28. The modified polymers obtainable by a process according to anyone of claims 1 to 27.
- 10 29. Polymers having at least one phosphorous oxide or phosphorous sulfide group within the main polymer chain per 10'000 repeating units derived from the monomer or monomers employed in the polymerization, preferably per 1'000 repeating units, more preferably per 100 repeating units.
30. Use of polymers comprising phosphorous oxide or phosphorous sulfide groups in the main polymer chain as photoinitiators.
31. Use according to claim 30, wherein the polymers are those according to claim 29 or those obtained in step B) or step C) of a process according to anyone of claims 1 to 27.
- 15 32. Coatings, adhesives, inks, painting materials, precision mold constructions, electronic articles, drug delivery systems, diagnostic sensors and contrast agents comprising modified polymers and in particular the modified latices or polymer nanoparticles prepared according to a process according to anyone of claims 1 to 27.

Fig 1/10



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Fig 2/10

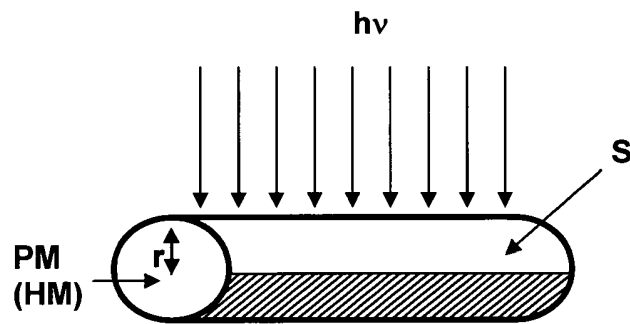


Fig 3/10

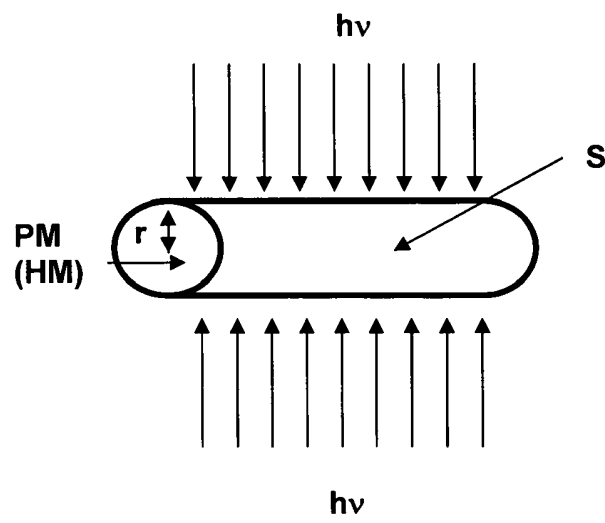


Fig 4/10

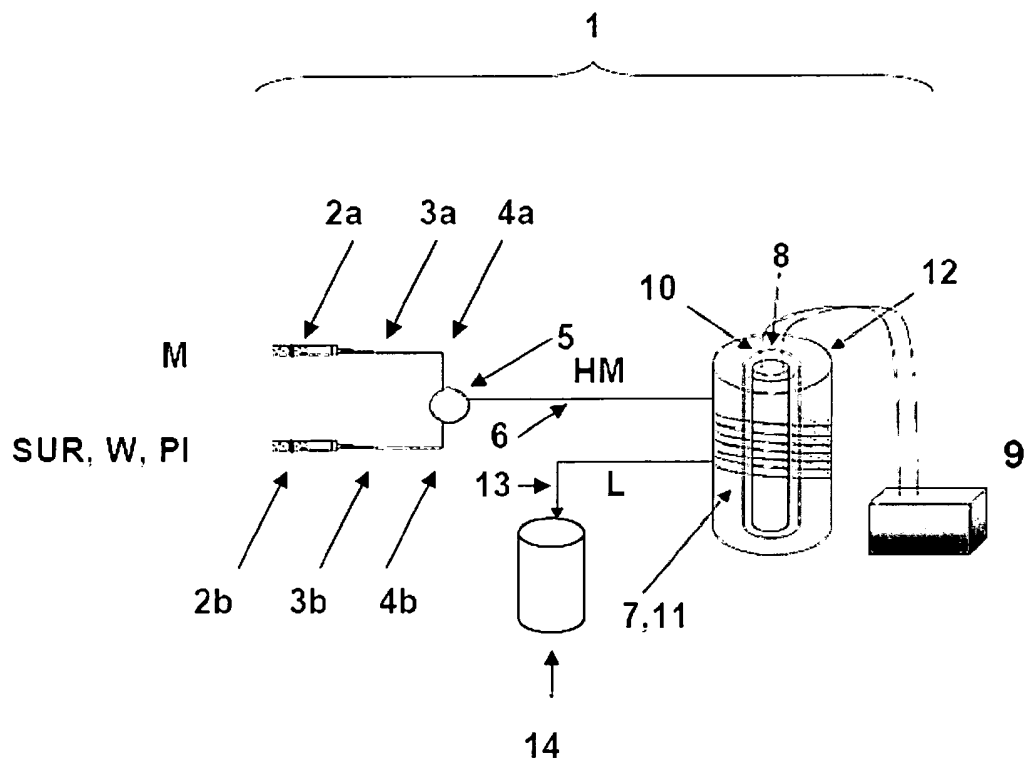


Fig 5/10

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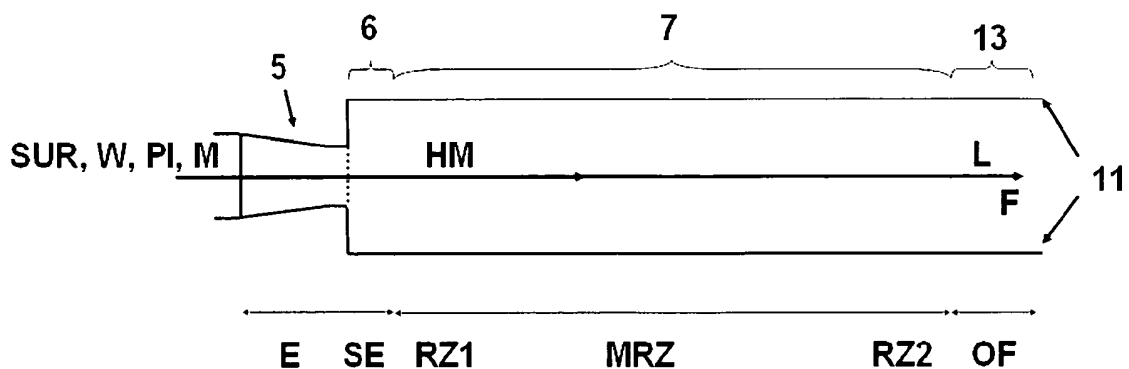
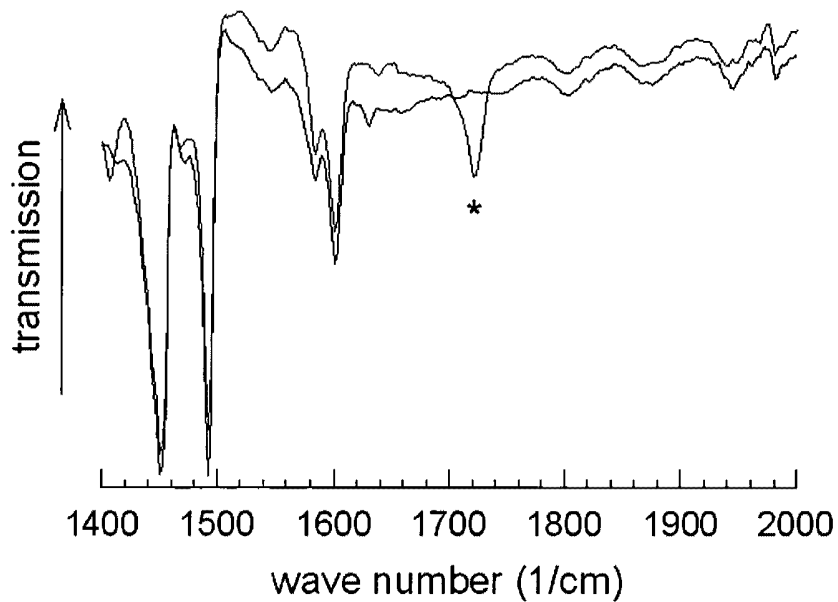


Fig 6/10



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Fig 7/10

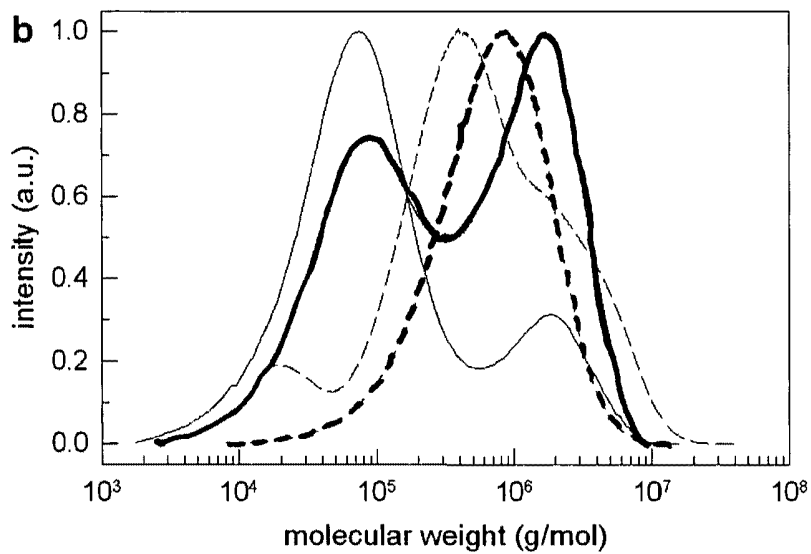


Fig 8/10

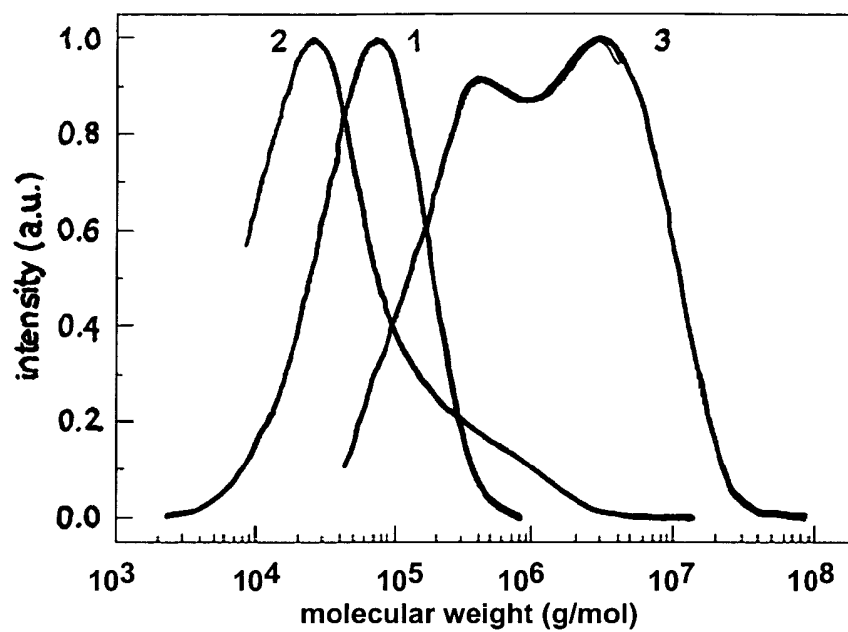
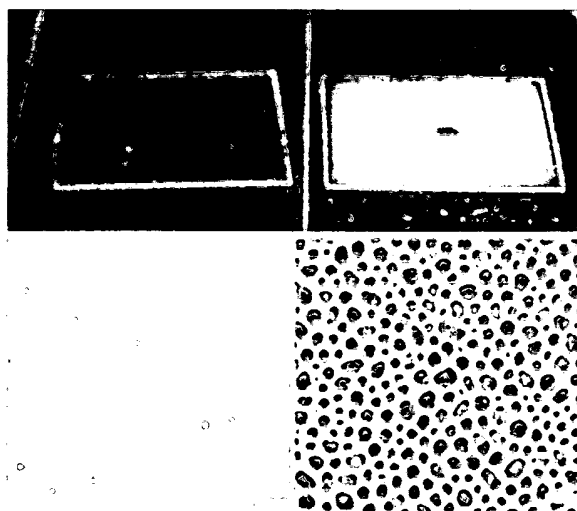


Fig 9/10



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Fig 10/10



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/005205

<p>A. CLASSIFICATION OF SUBJECT MATTER INV. C08F2/24 C08F2/48 C08F12/08 C08F212/08 B82Y40/00 C08F8/40 ADD. According to International Patent Classification (IPC) or to both national classification and IPC</p>								
<p>B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C08F B82Y 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</p>								
<p>C. DOCUMENTS CONSIDERED TO BE RELEVANT</p> <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>X,P</td> <td> WO 2011/003772 A1 (BASF SE [DE]; GRUETZMACHER HANSJOERG [CH]; OTT TIMO [DE]; DIETLIKER KU) 13 January 2011 (2011-01-13) page 1, line 3 - page 6, line 30; examples 1-A9 page 19, line 1 - line 18 page 23, line 10 - line 19 page 22, line 18 - line 20; claims 9,10 page 20, line 1 - line 9 page 28, line 33 - page 29, line 25 ----- -/-- </td> <td>1-32</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X,P	WO 2011/003772 A1 (BASF SE [DE]; GRUETZMACHER HANSJOERG [CH]; OTT TIMO [DE]; DIETLIKER KU) 13 January 2011 (2011-01-13) page 1, line 3 - page 6, line 30; examples 1-A9 page 19, line 1 - line 18 page 23, line 10 - line 19 page 22, line 18 - line 20; claims 9,10 page 20, line 1 - line 9 page 28, line 33 - page 29, line 25 ----- -/--	1-32
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.						
X,P	WO 2011/003772 A1 (BASF SE [DE]; GRUETZMACHER HANSJOERG [CH]; OTT TIMO [DE]; DIETLIKER KU) 13 January 2011 (2011-01-13) page 1, line 3 - page 6, line 30; examples 1-A9 page 19, line 1 - line 18 page 23, line 10 - line 19 page 22, line 18 - line 20; claims 9,10 page 20, line 1 - line 9 page 28, line 33 - page 29, line 25 ----- -/--	1-32						
<p><input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.</p>								
<p>* Special categories of cited documents :</p> <table border="0"> <tr> <td style="vertical-align: top;"> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </td> <td style="vertical-align: top;"> <p>"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</p> <p>"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</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </td> </tr> </table>			<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"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</p> <p>"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</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>				
<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"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</p> <p>"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</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>							
<p>Date of the actual completion of the international search 11 January 2012</p>		<p>Date of mailing of the international search report 02/02/2012</p>						
<p>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</p>		<p>Authorized officer Gold, Josef</p>						

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2011/005205

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>ANONYMOUS: "Novel applications for acylphosphine-oxides", RESEARCH DISCLOSURE, MASON PUBLICATIONS, HAMPSHIRE, GB, vol. 350, no. 77, 1 June 1993 (1993-06-01) , XP007119143, ISSN: 0374-4353 page 1 - page 3</p> <p style="text-align: center;">-----</p>	1-32

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2011/005205

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2011003772 A1	13-01-2011	TW 201111399 A	01-04-2011
		WO 2011003772 A1	13-01-2011
