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(54) Title: ULTRA FAST PROCESS FOR THE PREPARATION OF POLYMER NANOPARTICLES

(57) Abstract: The present invention relates to a highly efficient and 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, in another aspect, latices and polymer nanoparticles obtainable by said process. The invention further relates to the use of particular photoinitiators comprising a phosphorous oxide or -sulfide group suitable for performing said process.

Ultra fast process for the preparation of polymer nanoparticles

The present invention relates to a highly efficient and 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, in another aspect, latices and polymer nanoparticles obtainable by said process. The invention further relates to the use of particular photoinitiators comprising a phosphorous oxide or –sulfide group suitable for performing said process.

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

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.

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).

However, due to their long reaction times and/or limited throughputs the aforementioned processes are not industrially applicable or commercially attractive.

As a consequence, there is still a need for a process for the efficient and easily controllable preparation of latices comprising polymer nanoparticles.

A process was now found for the preparation of polymer latices by photo-initiated heterophase polymerization which comprises 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

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

whereby

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

whereby

- the irradiation of the heterophase medium is effected in such a manner that the ratio of the irradiated surface of the heterophase medium and its volume is at least 200 m^{-1}.

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”, 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.

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.-% even and more preferably at least 90 wt.-% of a polymer, and even more preferably consisting of a polymer.

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.

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.

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”.

The heterophase medium

In step A), a heterophase medium comprising at least a dispersed phase and a continuous phase is 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.

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.

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 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.-%.

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.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.

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 tetrahydrofurane and dioxane, ketones, and the like, as well as derivatives thereof and mixtures thereof, provided, however, that they are miscible with water in any ratio.

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

The addition of water miscible organic solvents might be useful in those cases where 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.

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.

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.-%.

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-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.

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,anionic or amphoteric surfactants.

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.

Cationic surfactants include quarternary 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 C_6-C_{24}-alkyl which are either not or once substituted by C_6 to C_{14} aryl, C_6-C_{24}-fluoroalkyl or C_6-C_{24}-alkyl ether substituents.

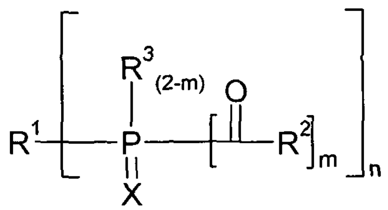
The weight ratio of surfactant and the continuous phase is typically between 1:10'000 and 1:5, preferably between 1:100 and 1:20, whereby the amount should be at least equal or higher than the critical micelle concentration (CMC) in the heterophase medium. The CMC is defined as being the lowest concentration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



(I)

wherein

n is 1 or 2 or a higher integer,

m is 0, 1 or 2,

X is sulphur or oxygen

R^1, if n = 1 is C_6-C_{14}-aryl or C_3-C_{14}- heterocyclyl or

is C_1-C_{18}-alkoxy, -$N(R^4)_2$, C_1-C_{18}-alkyl, C_2-C_{18}-alkenyl or C_2-C_{18}-alkinyl

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

-O-, -S-, $-SO_2-$, -SO-, $-SO_2NR^4-$, NR^4SO_2-, $-NR^4-$, $-N^+(R^4)_2An^--$, -CO-, -O(CO)-, (CO)O-, -O(CO)O-, $-NR^4(CO)NR^4-$, $NR^4(CO)-$, $-(CO)NR^4-$, $-NR^4(CO)O-$, $-O(CO)NR^4-$, $-Si(R^5)_2-$, $-OSi(R^5)_2-$, $-OSi(R^5)_2O-$, $-Si(R^5)_2O-$,

and which is either not, once, twice or more than twice interrupted by bivalent residues selected from the group consisting of C_3-C_{14}-heterocyclo-diyl, C_3-C_{14}-heterocyclo-diylium$^+$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:

halogen, cyano, azido, vicinal oxo (forming epoxides), vicinal NR^5 (forming aziridins), C_6-C_{14}-aryl, C_1-C_8-alkoxy, C_1-C_8-alkylthio, hydroxy, $-SO_3M$, -COOM, PO_3M_2, $-PO(N(R^5)_2)_2$, $PO(OR^5)_2$, $-SO_2N(R^4)_2$, $-N(R^4)_2$, $-N^+(R^4)_3An^-$, C_3-C_{14}-heterocyclylium$^+$An$^-$, $-CO_2N(R^4)_2$, $-COR^4$, $-OCOR^4$, $-NR^4(CO)R^5$, $-(CO)OR^4$, $-NR^4(CO)N(R^4)_2$, $NR^4SO_2R^4$, $-Si(OR^5)_y(R^5)_{(3-y)}$, $-OSi(OR^5)_y(R^5)_{(3-y)}$ with y = 1, 2 or 3,

R^1, if n = 2 is C_6-C_{15}-aryldiyl or C_3-C_{14}- heterocyclo-diyl

is C_1-C_{18}-alkanediyl, C_2-C_{18}-alkenediyl or C_2-C_{18}-alkinediyl,

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

-O-, -S-, $-SO_2-$, -SO-, $-SO_2NR^4-$, NR^4SO_2-, $-NR^4-$, $-N^+(R^4)_2An^--$, -CO-, -O(CO)-, (CO)O-, -O(CO)O-, $-NR^4(CO)NR^4-$, $NR^4(CO)-$, $-(CO)NR^4-$, $-NR^4(CO)O-$, $-O(CO)NR^4-$, $-Si(R^5)_2-$, $-OSi(R^5)_2-$, $-OSi(R^5)_2O-$, $-Si(R^5)_2O-$,

and which is either not, once, twice or more than twice interrupted by bivalent residues selected from the group consisting of C_3-C_{14}-heterocyclo-diyl, C_3-C_{14}-heterocyclo-diylium$^+$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:

halogen, cyano, azido, vicinal oxo (forming epoxides), vicinal NR^5 (forming aziridins), C_6-C_{14}-aryl, C_1-C_8-alkoxy, C_1-C_8-alkylthio, hydroxy, $-SO_3M$, -COOM, PO_3M_2, $-PO(N(R^5)_2)_2$, $PO(OR^5)_2$, $-SO_2N(R^4)_2$, $-N(R^4)_2$, $-N^+(R^4)_3An^-$, C_3-C_{14}-heterocyclylium$^+$An$^-$, $-CO_2N(R^4)_2$, $-COR^4$, $-OCOR^4$, $-NR^4(CO)R^5$, $-(CO)OR^4$,

$-NR^4(CO)N(R^4)_2$, $NR^4SO_2R^4$, $-Si(OR^5)_y(R^5)_{(3-y)}$, $-OSi(OR^5)_y(R^5)_{(3-y)}$ with y = 1, 2 or 3,

or is bivalent bis(C_6-C_{15})-aryl, which is either not or once interrupted by groups selected from the group consisting of:

-O-, -S-, $-SO_2-$, -SO-, C_4-C_{18}-alkanediyl, C_2-C_{18}-alkenediyl,

R^1, 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,

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-*, $O(CO)NR^4$-, $-NR^4(CO)NR^4$-,

and which is either not, once, twice or more than twice interrupted by bivalent residues selected from the group consisting of heterocyclo-diyl, heterocyclo-diylium$^+An^-$, 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:

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, $-SO_3M$, $-PO_3M_2$, $-SO_2N(R^4)_2$, $-NR^4SO_2R^5$, $-N(R^4)_2$-, $-N^+(R^4)_3An^-$. $-CO_2N(R^4)_2$, $-COR^4$-, $-OCOR^5$, $-O(CO)OR^5$, $NR^4(CO)R^4$, $-NR^4(CO)OR^4$, $O(CO)N(R^4)_2$, $-NR^4(CO)N(R^4)_2$,

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

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,

M is hydrogen, or 1/q equivalent of an q-valent metal ion or is a C_3-C_{14}-heterocyclylium 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; 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.

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):

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,

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 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_1-C_8-alkoxy, C_2-C_8-alkenyl, hydroxy, $-SO_3M$, -COOM, PO_3M_2, -$PO(N(R^5)_2)_2$, $-SO_2N(R^4)_2$, $-N(R^4)_2$, $-N^+(R^4)_3An^-$, C_3-C_{14}-heterocyclo-diylium$^+An^-$, -$CO_2N(R^4)_2$, $-COR^4$, $-OCOR^4$, $NR^4(CO)R^5$,

R^2 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

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-, $NR^4(CO)$-, $-NR^4(CO)O-$, $(CO)NR^4-$,

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, C_6-C_{14}-aryl; C_3-C_{14}-heterocyclyl, C_1-C_8-alkylthio, C_2-C_8-alkenyl, -COOM, $SO_2N(R^4)_2$-, $N(R^4)_2$-, $-N^+(R^4)_3An^-$, $-CO_2N(R^4)_2$,

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 or C_1-C_{18}-alkanediyl

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

R^4	is independently selected from the group consisting of halogen, 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 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,
M	is hydrogen, or 1/q equivalent of an q-valent metal ion or is a C_3-C_{14}-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 C_3-C_{14}-heterocyclylium cation or an ammonium ion or a primary, secondary, tertiary or quarternary organic ammonium ion, and
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

R^1 and R^3 are independently of each other

C_6-C_{14}-aryl or C_3-C_{14}-heterocyclyl or

are C_1-C_{18}-alkyl or C_2-C_{18}-alkenyl

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

-O-, $-NR^4-$, $-NR^4(CO)-$, $-(CO)NR^4-$, and which is not, additionally or alternatively, preferably alternatively either not, once, twice or more than twice, preferably not or once, preferably once substituted by substituents selected from the group consisting of:

chloro, fluoro, cyano, hydroxy, C_6-C_{14}-aryl; C_1-C_8-alkoxy, $-SO_3M$, -COOM, PO_3M_2, $-PO(N(R^5)_2)_2$, $-SO_2N(R^4)_2$, $-N(R^4)_2$, $-N^+(R^4)_3An^-$, C_3-C_{14}-heterocyclo-diylium$^+An^-$, $-CO_2N(R^4)_2$, $-COR^4$, $-(CO)OR^4$, $-OCOR^4$, $NR^4(CO)R^5$,

R^2 is C_6-C_{14}-aryl, 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 or C_1-C_{18}-alkanediyl, whereby preferably R^2 is C_6-C_{14}-aryl.

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,

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,

M is hydrogen, or 1/q equivalent of an q-valent metal ion or is a C_3-C_{14}-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 C_3-C_{14}-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

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.

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,

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:

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 two substituents R^2 are different or identical, preferably identical or jointly are C_6-C_{15}-aryldiyl or C_1-C_{18}-alkanediyl, whereby preferably R^2 is C_6-C_{14}-aryl.

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}-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 C_3-C_{14}-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 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.

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,

R^1 and R^3 are different or identical and are 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-, $-NR^4-$, preferably in case of -O- to form polyethyleneglycolether groups $[-CH_2CH_2-O]_x-H$, $[-CH_2CH_2-O]_{(x-1)}-CH_3$ or $[-CH_2CH_2-O]_{(x-1)}-CH_2CH_3$ with x being an integer from 1 to 8

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, $-SO_3M$, -COOM, $-CON(R^4)_2$, $-N(R^4)_2$, $-N^+(R^4)_3An^-$, heterocyclylium$^+An^-$, preferably –COOM, more preferably once by COOM and

R^2 is C_6-C_{14}-aryl, preferably 2,4,6-trimethylphenyl (mesityl) or 2,6-dimethoxyphenyl, whereby in case of m = 2 the substituents R^2 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

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,

M is hydrogen, or 1/q equivalent of an q-valent metal ion or is a C_3-C_{14}-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 C_3-C_{14}-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

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.

Particulary preferred photoinitiators of formula (I) are:

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 and 2,4,6-trimethylbenzoyl-diphenylphosphineoxide (hereinafter also referred to as MAPO, which is commercially available as Lucirin TPO from BASF SE).

In one embodiment for the process according to the invention water-soluble photoinitiators of formula (I) are employed if the heterophase medium comprises an aqueous phase. 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.

As used herein, and unless specifically stated otherwise, ***C_6-C_{14}*-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 (C_6), naphthyl (C_{10}), phenanthrenyl and anthracenyl (each C_{14}), 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, C_1-C_8-alkyl, C_1-C_8-haloalkyl, C_1-C_8-alkoxy, C_1-C_8-haloalkoxy, C_6-C_{14}-aryl, in particular phenyl and naphthyl, di(C_1-C_8-alkyl)amino, (C_1-C_8-alkyl)amino, CO(C_1-C_8-alkyl), OCO(C_1-C_8-alkyl), NHCO(C_1-C_8-alkyl), N(C_1-C_8-alkyl)CO(C_1-C_8-alkyl), CO(C_6-C_{14}-aryl), OCO(C_6-C_{14}-aryl), NHCO(C_6-C_{14}-aryl), N(C_1-C_8-alkyl)CO(C_6-C_{14}-aryl), COO-(C_1-C_8-alkyl), COO-(C_6-C_{14}-aryl), CON(C_1-C_8-alkyl)$_2$ or CONH(C_1-C_8-alkyl), CO_2M, $CONH_2$, SO_2NH_2, $SO_2N(C_1$-C_8-alkyl$)_2$, SO_3M and PO_3M_2.

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, C_1-C_8-alkyl, C_1-C_8-haloalkyl, C_1-C_8-alkoxy, C_1-C_8-haloalkoxy, C_6-C_{14}-aryl, in particular phenyl.

In a more preferred embodiment the carbocyclic, aromatic substituents are unsubstituted or substituted by up to three identical or different substituents per cycle selected from the group consisting of fluorine, C_1-C_8-alkyl, C_1-C_8-perfluoroalkyl, C_1-C_8-alkoxy, C_1-C_8-perfluoroalkoxy, and phenyl.

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 C_6-C_{14}-aryl-diyl substituents.

As used herein and unless specifically stated otherwise, **C_3-C_{14}-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 unsubstituted or substituted by up to five identical or different substituents per cycle, whereby the substituents are selected from the same group as given above for carbocyclic aromatic substituents including the areas of preference.

Preferred heterocyclyl-substituents are pyridinyl, oxazolyl, thiophen-yl, benzofuranyl, benzothiophen-yl, dibenzofuranyl, dibenzothiophenyl, furanyl, indolyl, pyridazinyl, pyrazinyl, imidazolyl, pyrimidinyl and quinolinyl, either unsubstituted or substituted with up to three substituents selected from the group consisting of fluorine, C_1-C_8-alkyl, C_1-C_8-perfluoroalkyl, C_1-C_8-alkoxy, C_1-C_8-perfluoroalkoxy, and phenyl.

The definitions given above, including their areas of preference, also apply analogously to **C_3-C_{14}-heterocyclylium cations**, the bivalent **C_3-C_{14}-heterocyclo-diyl** substituents and the bivalent **C_3-C_{14}-heterocyclo-diylium cations**.

Preferred C_3-C_{14}-heterocyclylium cations are N-(C_1-C_8-alkyl)imidazolium or pyridinium cations.

Preferred C_3-C_{14}-heterocyclo-diylium cations are N, N-imidazol-diylium cations.

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

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

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

As used herein, and unless specifically stated otherwise, **C_1-C_{18}-alkyl, C_1-C_{18}-alkanediyl, C_1-C_{18}-alkoxy, C_1-C_8-alkylthio, C_2-C_{18}-alkenyl, C_2-C_{18}-alkenediyl** and **C_1-C_{18}-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 C_1-alkyl substituent substituted by phenyl.

The same analogously applies to C_1-C_8, C_1-C_{24} and C_6-C_{24}-alkyl, C_2-C_{18}-alkanediyl, C_3-C_{18}-alkanetriyl C_4-C_{18}-alkanetetrayl, C_2-C_{18}-alkenediyl, C_3-C_{18}-alkenetriyl, C_4-C_{18}-alkenetetrayl and C_2-C_{18}-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.

Alkyl ether substituents denote alkyl substituents with the given number of carbon atoms which are at least once interrupted by -O- and either not or additionally substituted at ω-terminal position by hydroxy.

Specific examples of C_1-C_8-alkyl are methyl, ethyl, n-propyl, isopropyl, n-butyl, tert-butyl, n-pentyl, cyclohexyl, n-hexyl, n-heptyl, n-octyl and isooctyl. Additional examples for C_1-C_{18}-alkyl are norbornyl, adamantyl, n-decyl, n-dodecyl alkyl, n-hexadecyl, n-octadecyl.

Specific examples of C_1-C_{18}-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 C_1-C_8-alkoxy-substituents are methoxy, ethoxy, isopropoxy, n-propoxy, n-butoxy, tert-butoxy and cyclohexyloxy.

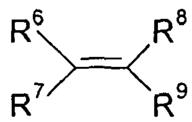
Specific examples of C_2-C_{18}-alkenyl- substituents are allyl, 3-propenyl and buten-2-yl.

Specific examples of C_2-C_{18}-alkinyl- substituents are ethinyl, and 1,3-propinyl.

The heterophase medium further comprises one or more polymerizable monomers.

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

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



(IIa)

wherein

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

hydrogen, cyano, fluorine, chlorine, bromine, iodine, 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:

  -CO-, -OCO-, -O(CO)O-, NR^4(CO)-, -NR^4(CO)O-, -O(CO)NR^4-, -(CO)NR^4-, -NR^4(CO)NR^4-, -Si$(R^5)_2$-, -OSi$(R^5)_2$-, -OSi$(R^5)_2$O-, -Si$(R^5)_2$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:

  -O-, -CO-, -OCO-, -O(CO)O-, NR^4(CO)-, -NR^4(CO)O-, -O(CO)NR^4-, -(CO)NR^4-, -NR^4(CO)NR^4-, -Si$(R^5)_2$-, -OSi$(R^5)_2$-, -OSi$(R^5)_2$O-, -Si$(R^5)_2$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:

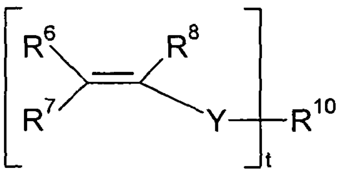
  halogen, cyano, vicinal oxo (forming epoxides), vicinal NR^5 (forming aziridins), C_6-C_{14}-aryl; C_3-C_{14}-heterocyclyl, C_1-C_8-alkylthio, hydroxy, -$SO_2N(R^4)_2$, NR^4SO_2-R^5, -$N(R^4)_2$, -$CO_2N(R^4)_2$, -COR^4, -$OCOR^4$, -O(CO)OR^4, NR^4(CO)R^5, -NR^4(CO)OR^5, O(CO)$N(R^4)_2$, -NR^4(CO)$N(R^4)_2$, -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.

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)

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

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).

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

- 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;

- 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;

- 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 C_1 to C_{20} 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.

Preferred monoolefins are 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 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 and any mixture of the aforementioned monoolefins.

In an embodiment, where an aqueous phase is employed as dispersed phase or continuous phase, preferably as continuous phase, 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.

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.

The weight ratio of photoinitiator to polymerizable monomer in the heterophase medium is typically 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.

In another embodiment 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.

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

In step B), the one or more polymerizable monomers present in the heterophase medium are polymerized by irradiating said heterophase medium with electromagnetic radiation having a wavelength sufficient to induce the generation of radicals whereby the irradiation of the heterophase medium is effected in such a manner that the ratio of the irradiated surface of the heterophase medium and its volume (hereinafter SVR) is at least 200 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 heterophase medium and its volume of at least 200 m^{-1} is for example achieved by irradiation of the surface (S) a of a thin film of heterophase medium (HM) having a uniform layer thickness (L) of 5 mm (see figure 1).

A ratio of the irradiated surface of the heterophase medium and its volume of at least 200 m^{-1} is for example also achieved by irradiation of the surface a of a heterophase medium 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).

In a preferred embodiment the SVR is 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 one embodiment, the irradiation is effected in a transparent tube, tubing or channel having an effective diameter of 10 mm or less, preferably 5 mm or less, for example 0.1 to 5 mm, more 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 step B) irradiation with electromagnetic radiation having a wavelength sufficient to induce the generation of radicals is employed to polymerize the monomers present in the heterophase medium.

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 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 eximer 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.

Even though, at the same level of irradiance, the conditions mentioned above are sufficient to allow the heterophase polymerization to proceed unexpectedly faster than under conditions known so far in the art, it is apparent to those skilled in the art that radical formation depends on the intensity and/or the time of irradiance.

In an 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 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 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 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 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 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 irradiance is effected 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 heterophase medium (200 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.

The irradiation time of the heterophase media may vary depending on the SVR and the intensity of irradiance but typically is for example in the range of from 1s 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 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 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 1s to 30 min, preferably from 5s 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 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

- 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 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.

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

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.

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.-%.

Step B) can be carried out batchwise or continuously, preferably continuously, whereby step B) is more preferably carried out in continuously using a flow-through reactor.

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.

Mechanistic aspects

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 heterophase polymerizations, in particular aqueous emulsion polymerization is rather well understood. The parameters that influence the reaction have been determined, including the relative influences of monomer, surfactant, initiator, temperature and reaction time on the resulting polymer molecular weight, particle size, and other colloid features.

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

A possible explanation of the avalanche-like generation of radicals observed under the conditions set forth above is given below using a photoinitiator of the bisacylphosphine oxide (BAPO) type as an example

$$\mathrm{B\text{-}(P{=}O)\text{-}B} + h\nu \rightarrow \mathrm{R}^{\bullet} + {}^{\bullet}\mathrm{(P{=}O)\text{-}B} \qquad \text{(A)}$$

$$\mathrm{B\text{-}(P{=}O)\text{-}B} + h\nu \rightarrow \mathrm{R}^{\bullet} + {}^{\bullet}\mathrm{(P{=}O)}^{\bullet} + \mathrm{R'}^{\bullet} \qquad \text{(B)}$$

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.

"hν" 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.

$$\mathrm{B}^{\bullet} + n\,\mathrm{M} \rightarrow \mathrm{B\text{-}(M)}_n{}^{\bullet} \qquad \text{(C)}$$

$${}^{\bullet}\mathrm{(P{=}O)\text{-}B} + n\,\mathrm{M} \rightarrow {}^{\bullet}\mathrm{(M)}_n\mathrm{(P{=}O)\text{-}B} \qquad \text{(D)}$$

$${}^{\bullet}\mathrm{(P{=}O)}^{\bullet} + n\,\mathrm{M} \rightarrow {}^{\bullet}\mathrm{(M)}_m\mathrm{(P{=}O)\text{-}\,(M)}_p{}^{\bullet} \qquad \text{(E)} \quad \text{(with } m + p = n\text{)}$$

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.

$$B\text{-}(M)_{n1}^{\bullet} + B\text{-}(M)_{n2}^{\bullet} \rightarrow B\text{-}(M)_{n1}\text{-}(M)_{n2}\text{-}B \quad \text{(F)}$$

$$B\text{-}(M)_{n1}^{\bullet} + {}^{\bullet}(M)_{n2}(P{=}O)\text{-}B \rightarrow B\text{-}(M)_{n1}\text{-}(M)_{n2}(P{=}O)\text{-}B \quad \text{(G)}$$

$$B\text{-}(M)_{n}^{\bullet} + {}^{\bullet}(M)_{m}(P{=}O)\text{-}(M)_{p}^{\bullet} \rightarrow B\text{-}(M)_{n}\text{-}(M)_{m}(P{=}O)\text{-}(M)_{p}^{\bullet} \quad \text{(H)}$$

$${}^{\bullet}(M)_{m1}(P{=}O)\text{-}(M)_{p1}^{\bullet} + {}^{\bullet}(M)_{m1}(P{=}O)\text{-}(M)_{p1}^{\bullet} \rightarrow {}^{\bullet}(M)_{m1}(P{=}O)\text{-}(M)_{p1}\text{-}(M)_{m1}(P{=}O)\text{-}(M)_{p1}^{\bullet} \quad \text{(J)}$$

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:

$${}^{\bullet}(M)_{n}(P{=}O)\text{-}B + h\nu \rightarrow {}^{\bullet}(M)_{n}(P{=}O)^{\bullet} + B^{\bullet} \quad \text{(K)}$$

$$B\text{-}(M)_{n1}\text{-}(M)_{n2}(P{=}O)\text{-}B + h\nu \rightarrow B\text{-}(M)_{n1}\text{-}(M)_{n2}(P{=}O)^{\bullet} + B^{\bullet} \quad \text{(L)}$$

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

$${}^{\bullet}(M)_{m}(P{=}O)\text{-}(M)_{p}^{\bullet} + h\nu \rightarrow {}^{\bullet}(M)_{m}^{\bullet} + {}^{\bullet}(P{=}O)\text{-}(M)_{p}^{\bullet} \quad \text{(M)}$$

$$B\text{-}(M)_{n}\text{-}(M)_{m}(P{=}O)\text{-}(M)_{p}^{\bullet} + h\nu \rightarrow$$
$$B\text{-}(M)_{n}\text{-}(M)_{m}(P{=}O)^{\bullet} + {}^{\bullet}(M)_{p}^{\bullet} \text{ or}$$
$$B\text{-}(M)_{n}\text{-}(M)_{m}^{\bullet} + {}^{\bullet}(P{=}O)^{\bullet}(M)_{p}^{\bullet} \text{ or}$$
$$B\text{-}(M)_{n}\text{-}(M)_{m}^{\bullet} + {}^{\bullet}(P{=}O)^{\bullet} + {}^{\bullet}(M)_{p}^{\bullet} \quad \text{(N)}$$

$${}^{\bullet}(M)_{m1}(P{=}O)\text{-}(M)_{p1}\text{-}(M)_{m1}(P{=}O)\text{-}(M)_{p1}^{\bullet} + h\nu \rightarrow$$
$${}^{\bullet}(M)_{m1}^{\bullet} + {}^{\bullet}(P{=}O)\text{-}(M)_{p1}\text{-}(M)_{m1}(P{=}O)\text{-}(M)_{p1}^{\bullet}$$
$${}^{\bullet}(M)_{m1}(P{=}O)^{\bullet} + {}^{\bullet}(M)_{p1}\text{-}(M)_{m1}(P{=}O)\text{-}(M)_{p1}^{\bullet}$$
$${}^{\bullet}(M)_{m1}(P{=}O)\text{-}(M)_{p1}\text{-}(M)_{m1}^{\bullet} + {}^{\bullet}(P{=}O)\text{-}(M)_{p1}^{\bullet}$$

$$^{\bullet}(M)_{m1}(P{=}O)\text{-}(M)_{p1}\text{-}(M)_{m1}\text{-}(P{=}O)^{\bullet} + {}^{\bullet}(M)_{p1}^{\bullet}$$

etc (P)

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

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.

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.

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)-R^2 group.

Devices suitable to perform the invention

The process can be carried out using every type of device designed to carry out step B) 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 with dimensions to allow irradiation in with the prescribed SVR.

Suitable types of photoreactors include rising or falling film photoreactors and flow-through reactors, in particular microfluidic devices.

Flow- at least one irradiation zone 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 heterophase medium form 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}.

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 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.

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 main drop size ob 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**.

Products and other aspects of the invention

As a result of the polymerization of step B) latices comprising nanoparticles are obtained.

Residual polymerizable monomers, if present at all (see above) are preferably removed from the resulting dispersion by standard stripping or distillation techniques.

In an embodiment, 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.

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.

Depending of the nature of the polymerizable monomers employed, the latices obtained according to the invention comprise a significant fraction of unbranched polymer chains with unexpectedly high molecular weights.

Therefore, one further aspect of the invention relates to latices and polymer nanoparticles obtainable by a process according to the invention.

One further aspect of the invention relates to latices and polymer nanoparticles comprising at least 1 wt.-%, preferably at least 3 wt.-% of polymer chains soluble in tetrahydrofurane at 25°C having a molecular weight of 10'000'000 g/ mol determined by gel permeation chromatography (GPC), in particular as described in the example section.

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°.

The latices comprising polymer nanoparticles obtained typically have an M-PDI of 2 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.

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

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

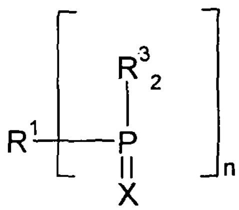
In an embodiment, the aforementioned latices or polymer nanoparticles can be used, for example, in coating, adhesive, ink, and painting materials, precision mold constructions, in the manufacture of electronic articles, for drug delivery systems, diagnostic sensors and contrast agents.

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

Surprisingly, compounds of formula (I) were found to be suitable to carry out the invention which were previously not known to act as photoinitiators.

Therefore one further aspect of the invention relates to the use of compounds of formula (Ia) as photoinitiator, preferably as photoinitiator in a process as described hereinabove.

In formula (Ia)



(Ia)

X, R^1, R^3 and n have the same meaning including their areas of preference as mentioned for formula (I).

A particular compound of formula (Ia) is trisbenzylphosphine oxide.

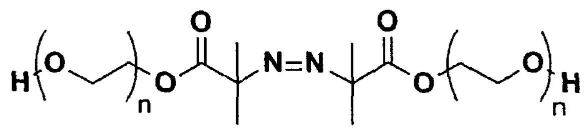
The invention is further illustrated by the examples without being limited thereby.

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 μS 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-initiators

1) 2-(bis(2,4,6-trimethylbenzoyl)phosphoryl)acetic acid sodium salt (BAPO-AA-Na) and
2) the poly(ethylene glycol)-azo-initiator (PEGA200) with an average molecular weight of 568 g/mol and n = 4, 5:



were prepared as described in:

- T. Ott, Dissertation ETH Zürich No. 18055, 2008 for BAPO-AA and BAPO-AA -Na
- Tauer, K., Antonietti, M., Rosengarten, L. & Müller, H. Initiators based on poly(ethylene glycol) for starting heterophase polymerizations: generation of block copolymers and new particle morphologies. Macomol. Chem. Phys. 199, 897-908 (1998) and
- Walz, R., Bömer, B. & Heitz, W. Monomeric and Polymeric Azoinitiators. Macromol. Chem. Phys. 178, 2527-2534 (1977)
  for PEGA 200

2,4,6-Trimethylbenzoyl-diphenylphosphineoxide (MAPO) was obtained from BASF SE, Germany (Lucirin® TPO).

Example i)

2-(bis(2,4,6-trimethylbenzoyl)(hyroxycarbonylmethyl)phosphine sulphide (BAPS-AA) was prepared according to the following procedure:

0.5g bis(mesitoyl)(hydroxycarbonylmethyl)lphosphane (1.20 mmol) which was prepared according to T. Ott, Dissertation ETH Zürich No. 18055, 2008 were dissolved in 10 ml toluene. After addition of 0.5 g elemental sulphur (15.6 mmol) the mixture was stirred for 30 min at room temperature and further 45 min at 80°C. The reaction of the educt was monitored by ^{31}P-NMR.

After disappearance of the educt the solvent was removed in vacuo. After addition of 20 ml hexane insoluble components were filtered off. To fully remove remaining sulphur the hexane solution was stored overnight at -20°C and filtered again. After removal of the solvent the product was obtained as yellowish solid compound

Yield: 55% of theory)
^{31}P-NMR (101,25MHz; C_6D_6): δ= 32.3 (t, $^{2}J_{PH}$=11.4Hz) ppm
UV/VIS (Abs, 1x10^{-4}M, H_3C-CN): λ= 260 (max.); 364 (max.) nm

Further sulphur containing photoinitiators could be prepared accordingly, however with different reaction times and temperatures

Example ii)
(bis(2,4,6-trimethylbenzoyl)(methyl)phosphine sulphide (BAPS-Me) was prepared from (bis(2,4,6-trimethylbenzoyl)(methyl)phosphine according to example i)
Reaction conditions: 30 min at room temperature, 15 min at 70°C

Yield: 90% of theory
^{31}P-NMR (101,25MHz; C_6D_6): δ= 36.7 (q, $^{2}J_{PH}$=12.1Hz) ppm
UV/VIS (Abs, 1x10^{-4}M, H_3C-CN): λ= 257 (max.); 361 (max.) nm

Example iii)
(bis(2,4,6-trimethylbenzoyl)(3-(triethoxysilyl)propyl)-phosphine sulphide was prepared from (bis(2,4,6-trimethylbenzoyl)(3-triethoxysilylpropyl)phosphine according to example i)
Reaction conditions: 30 min at room temperature, 30 min at 70°C

Yield: 92% of theory
^{31}P-NMR (101,25MHz; C_6D_6): δ= 46.2 (q, $^{2}J_{PH}$=8.5 Hz) ppm
UV/VIS (Abs, 1x10^{-4}M, H_3C-CN): λ= 257 (max.); 361 (max.) nm

Example iv)
(bis(2,4,6-trimethylbenzoyl)(3-(diethoxymethylsilyl)propyl)phosphine sulphide was prepared from (bis(2,4,6-trimethylbenzoyl)(3-(diethoxymethylsilyl)propyl)phosphine according to example i)
Reaction conditions: 30 min at room temperature, 30 min at 70°C

Yield: 95% of theory

^{31}P-NMR (101,25MHz; C_6D_6): δ= 45.4 (q, $^2J_{PH}$=12.1 Hz) ppm

UV/VIS (Abs, 1x10^{-4}M, H_3C-CN): λ= 259 (max.); 358 (max.) nm

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 μm and an outlet channel inner diameter of 30 μm. For this micromixer and a 4 mL/min flow rate, the monomer droplet size distribution was quite broad, however, droplets below 1 μm 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 hemicircular 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/m^2 at 578.0 nm, 201 W/m^2 at 546.1 nm 144 W/m^2 at 435.8 nm, 75 W/m^2 at 404.5 nm, 147 W/m^2 at 366.0 nm, 10 W/m^2 at 334.1 nm, 41 W/m^2 at 313.0 nm, 15 W/m^2 at 302.5 nm, 6 W/m^2 at 296.7 nm and 1 W/m^2 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/m^2.

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.

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.
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

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.

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°.

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 µL 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 three 300 x 8 mm columns filled with a MZ-SDplus spherical polystyrene gel (average particle size 5 µm),with pore sizes of 10^3, 10^5, and 10^6 Å, respectively. Average molecular weights, and number of average molecular weight polymers (Mw and, Mn) were calculated based on polystyrene standards (between 500 and $2 \cdot 10^6$ g mol-1 from PSS, Mainz, Germany).

II Photoinitiated heterophase polymerization

Synthesis of latices

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.

Afterwards, the collected products were collected and analysed as described above.

Examples 1 and 2:

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

Ex.	SDS [mg]	PI [mg]	Irradiation time [s]	Flow rate (µl/min)	DLS [nm]	Solids content [%]	Yield [%]
1	300	10	36	4000	61	12	62
2	300	10	72	2000	48	7	36

Examples 3 to 10:

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 (µl/min)	DLS [nm]	Solids content [%]	Yield [%]
3	200	10	36	4000	51	15	79
4	200	10	36	4000	50	14	74
5	300	10	36	4000	45	19	100
6	400	10	36	4000	38	20	100

7	500	10	36	4000	45	19	100
8	500	10	36	4000	37	19	100
9	300	5	36	4000	48	18	95
10	300	15	36	4000	44	19	100

Exemplarily, the molecular mass distribution of the latex obtained in example 7 is given in figure 6. A high weight fraction of polymer chains having a molecular mass of more than 10'000'000 g/mol was obtained.

Similar results can be obtained using the photoinitiators of examples i) to iv)

Examples 11 to 13:

Monomer: styrene

Photoinitiator: Trisbenzylphosphineoxide (TBPO)

Ex.	SDS [mg]	PI [mg]	Irradiation time [s]	Flow rate (µl/min)	DLS [nm]	Solids content [%]	Yield [%]
11	300	5	72	2000	150	3	16
12	300	5	72	2000	75	5	26
13	300	5	72	2000	54	5	26

Examples 14 to 19:

Monomer: methyl methacrylate (MMA)

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 (µl/min)	DLS [nm]	Solids content [%]	Yield [%]
14	200	10	36	4000	50	13	68
15	200	10	72	2000	51	15	79
16	200	10	144	1000	40	17	90
17	300	10	144	1000	45	19	100
18	400	10	144	1000	38	20	100
19	500	10	144	1000	39	20	100

Examples 20 to 26:

Monomer: butyl methacrylate (BMA)

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 (µl/min)	DLS [nm]	Solids content [%]	Yield [%]
21	400	10	72	2000	31	13	72
22	500	10	72	2000	34	20	100
23	200	10	72	2000	43	16	84
24	300	10	72	2000	34	17	89
25	400	10	72	2000	32	17	89
26	100	10	72	2000	52	8	42

Example 27 (for comparison):

Monomer: styrene

Photoinitiator: none

Ex.	SDS [mg]	PI [mg]	Irradiation time [s]	Flow rate (µl/min)	DLS [nm]	Solids content [%]	Yield [%]
27	400	0	72	2000	-	0	0

Examples 28 and 29 (for comparison):

In order to compare the particle sizes and molecular weights of latices prepared according to the invention with conventional polymers prepared by thermally initiated emulsion polymerisations comparison examples 28 and 29 were carried out as follows:

- Batch emulsion polymerization in a glass reactor (40 g water, 10 g styrene, 0.32 g potassium peroxodisulfate (example 28) or 0.673 g PEGA200 (example 29) and various amounts of SDS)
- emulsification was effected by stirring
- Temperature: 80 °C

The results are given in figures 7 and 8 and compared to the latices obtained according to examples 5 and 7 to 10.

In figure 7, a correlation of particle size (as measured by DLS) and surfactant (SDS) concentration is shown.

The black squares show the particle sizes of examples 5 and 7 to 10, the white squares the particle sizes of comparison example 28 and the gray squares the particle sizes of comparison example 29.

As a result, no substantial difference is observed for particle sizes as compared to conventional emulsion polymerisation.

In figure 8, a correlation of the number average molecular weights (as measured by GPC) and surfactant (SDS) concentration is shown.

The black squares show the molecular weights of examples 5 and 7 to 10, the white squares the molecular weights of comparison example 28 and the gray squares the molecular weights of comparison example 29.

As a result, much higher molecular weights are observed for latices prepared according to the invention.

Claims:

1. A process for the preparation of polymer latices by photo-initiated heterophase polymerization comprising 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

   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

   whereby

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

   whereby

   - the irradiation of the heterophase medium is effected in such a manner that the ratio of the irradiated surface of the heterophase medium and its volume is at least 200 m^{-1}.

2. The process according to claim 1, wherein the heterophase medium 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.-%.

3. The process according to claim 1 or 2, wherein the heterophase medium is an emulsion.

4. The process according to anyone of claims 1 to 3, wherein the heterophase medium is an emulsion comprising an aqueous continuous phase and an organic dispersed phase.

5. The process according to claim 4, wherein the aqueous phase comprises either 0 wt.-%, or from more than 0 to 20 wt-% of water-miscible organic solvents.

6. The process according to claim 4 or 5, wherein the aqueous phase comprises salts.

7. The process according to anyone of claims 4 to 6, 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.

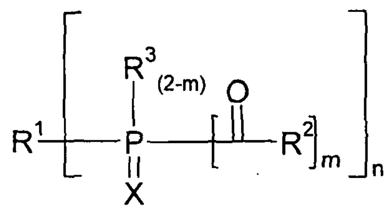
8. The process according to anyone of claims 1 to 7, wherein step A) is carried out continuously.

9. The process according to anyone of claims 1 to 8, wherein the heterophase medium comprises non-ionic, cationic, anionic or amphoteric surfactants.

10. The process according to anyone of claims 1 to 9, 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.

11. The process according to anyone of claims 1 to 10, wherein the weight ratio of the continuous phase and the dispersed phase is between 1:2 and 500:1, preferably, between 1.5:1 and 20:1.

12. The process according to anyone of claims 1 to 11, wherein the photoinitiators are selected from compounds of formula (I):



(I)

wherein

n is 1 or 2 or a higher integer,

m is 0, 1 or 2,

X is sulphur or oxygen

R^1, if n = 1 is C_6-C_{14}-aryl or C_3-C_{14}- heterocyclyl or

is C_1-C_{18}-alkoxy, -$N(R^4)_2$, C_1-C_{18}-alkyl, C_2-C_{18}-alkenyl or C_2-C_{18}-alkinyl

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

-O-, -S-, -SO_2-, -SO-, -SO_2NR^4-, NR^4SO_2-, -NR^4-, -$N^+(R^4)_2An^-$-, -CO-, -O(CO)-, (CO)O-, -O(CO)O-, -$NR^4(CO)NR^4$-, $NR^4(CO)$-, -$(CO)NR^4$-, -$NR^4(CO)O$-, -$O(CO)NR^4$-, -$Si(R^5)_2$-, -$OSi(R^5)_2$-, -$OSi(R^5)_2O$-, -$Si(R^5)_2O$-,

and which is either not, once, twice or more than twice interrupted by bivalent residues selected from the group consisting of C_3-C_{14}-heterocyclo-diyl, C_3-C_{14}- heterocyclo-diylium$^+An^-$ 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:

halogen, cyano, azido, vicinal oxo (forming epoxides), vicinal NR^5 (forming aziridins), C_6-C_{14}-aryl, C_1-C_8-alkoxy, C_1-C_8-alkylthio, hydroxy, -SO_3M, -COOM, PO_3M_2, -$PO(N(R^5)_2)_2$, $PO(OR^5)_2$, -$SO_2N(R^4)_2$, -$N(R^4)_2$, -$N^+(R^4)_3An^-$, C_3-C_{14}-heterocyclylium$^+An^-$, -$CO_2N(R^4)_2$, -COR^4, -$OCOR^4$, -$NR^4(CO)R^5$, -$(CO)OR^4$, -$NR^4(CO)N(R^4)_2$, $NR^4SO_2R^4$, -$Si(OR^5)_y(R^5)_{(3-y)}$, -$OSi(OR^5)_y(R^5)_{(3-y)}$ with y = 1, 2 or 3,

R^1, if n = 2 is C_6-C_{15}-aryldiyl or C_3-C_{14}- heterocyclo-diyl

is C_1-C_{18}-alkanediyl, C_2-C_{18}-alkenediyl or C_2-C_{18}-alkinediyl,

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

-O-, -S-, -SO_2-, -SO-, -SO_2NR^4-, NR^4SO_2-, -NR^4-, -$N^+(R^4)_2An^-$-, -CO-, -O(CO)-, (CO)O-, -O(CO)O-, -$NR^4(CO)NR^4$-, $NR^4(CO)$-, -$(CO)NR^4$-, -$NR^4(CO)O$-, -$O(CO)NR^4$-, -$Si(R^5)_2$-, -$OSi(R^5)_2$-, -$OSi(R^5)_2O$-, -$Si(R^5)_2O$-, and which is either not, once, twice or more than twice interrupted by bivalent residues selected from the group consisting of C_3-C_{14}-heterocyclo-diyl, C_3-C_{14}- heterocyclo-diylium$^+$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:

halogen, cyano, azido, vicinal oxo (forming epoxides), vicinal NR^5 (forming aziridins), C_6-C_{14}-aryl, C_1-C_8-alkoxy, C_1-C_8-alkylthio, hydroxy, -SO_3M, -COOM, PO_3M_2, -$PO(N(R^5)_2)_2$, $PO(OR^5)_2$, -$SO_2N(R^4)_2$, -$N(R^4)_2$, -$N^+(R^4)_3An^-$, C_3-C_{14}-heterocyclylium$^+$An$^-$, -$CO_2N(R^4)_2$, -COR^4, -$OCOR^4$, -$NR^4(CO)R^5$, -$(CO)OR^4$, -$NR^4(CO)N(R^4)_2$, $NR^4SO_2R^4$, -$Si(OR^5)_y(R^5)_{(3-y)}$, -$OSi(OR^5)_y(R^5)_{(3-y)}$ with y = 1, 2 or 3,

or is bivalent bis(C_6-C_{15})-aryl, which is either not or once interrupted by groups selected from the group consisting of:

-O-, -S-, -SO_2-, -SO-, C_4-C_{18}-alkanediyl, C_2-C_{18}-alkenediyl,

R^1, 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,

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-,

and which is either not, once, twice or more than twice interrupted by bivalent residues selected from the group consisting of heterocyclo-diyl, heterocyclo-diylium$^+$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:

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-, -$OCOR^5$, -$O(CO)OR^5$, $NR^4(CO)R^4$, -$NR^4(CO)OR^4$, $O(CO)N(R^4)_2$, -$NR^4(CO)N(R^4)_2$,

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

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,

M is hydrogen, or 1/q equivalent of an q-valent metal ion or is a C_3-C_{14}-heterocyclylium 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.

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

X is oxygen

n is 1,

m is 1 or 2,

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:

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}-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 C_3-C_{14}-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 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.

14. The process according to anyone of claims 1 to 13, wherein one or more photoinitiators of formula (I) are used, wherein in formula (I):

X is oxygen

n is 1,

m is 1 or 2,

R^1 and R^3 are different or identical and are 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-, -NR^4-, preferably in case of -O- to form polyethyleneglycolether groups $[-CH_2CH_2-O]_x$-H, $[-CH_2CH_2-O]_{(x-1)}$-CH_3 or $[-CH_2CH_2-O]_{(x-1)}$-CH_2CH_3 with x being an integer from 1 to 8

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, -SO_3M, -COOM, -$CON(R^4)_2$, -$N(R^4)_2$, -$N^+(R^4)_3An^-$, heterocyclylium$^+An^-$, preferably –COOM, more preferably once by COOM and

R^2 is C_6-C_{14}-aryl, preferably 2,4,6-trimethylphenyl (mesityl) or 2,6-dimethoxyphenyl, whereby in case of m = 2 the substituents R^2 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

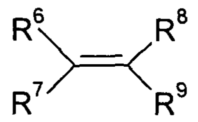
R^4 is independently selected from the group consisting of hydrogen, C_1-C_8-alkyl, C_6-C_{14}-aryl and C_3-C_{14}-heterocyclyl or $N(R^4)_2$ as a whole is a N-containing C_3-C_{14}-heterocycle, or $N^+(R^4)_2An^-$ and $N^+(R^4)_3An^-$ as a whole are or contain a N-containing C_3-C_{14}-heterocyclyl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

M is hydrogen, or 1/q equivalent of an q-valent metal ion or is a C_3-C_{14}-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 C_3-C_{14}-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

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 ae selected from the group consisting of 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 and 2,4,6-trimethylbenzoyl-diphenylphosphineoxide.

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, cyano, fluorine, chlorine, bromine, iodine, 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:

  -CO-, -OCO-, -O(CO)O-, NR^4(CO)-, -NR^4(CO)O-, -O(CO)NR^4-, -(CO)NR^4-, -NR^4(CO)NR^4-, -Si$(R^5)_2$-, -OSi$(R^5)_2$-, -OSi$(R^5)_2$O-, -Si$(R^5)_2$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:

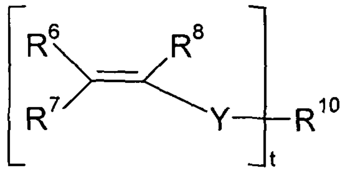
  -O-, -CO-, -OCO-, -O(CO)O-, NR^4(CO)-, -NR^4(CO)O-, -O(CO)NR^4-, -(CO)NR^4-, -NR^4(CO)NR^4-, -Si$(R^5)_2$-, -OSi$(R^5)_2$-, -OSi$(R^5)_2$O-, -Si$(R^5)_2$O-

- 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, $-SO_2N(R^4)_2$, $NR^4SO_2-R^5$, $-N(R^4)_2$, $-CO_2N(R^4)_2$, $-COR^4$, $-OCOR^4$, $-O(CO)OR^4$, $NR^4(CO)R^5$, $-NR^4(CO)OR^5$, $O(CO)N(R^4)_2$, $-NR^4(CO)N(R^4)_2$, $-OSi(OR^5)_{y-3}(R^5)_y$, $-Si(OR^5)_{y-3}(R^5)_y$ 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



(IIb)

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

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

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:

- 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 C_1-C_8-alkyl esters of the aforementioned acids and where applicable C_1-C_8-alkyl diesters;
- ethyl vinyl ether and isobutyl vinyl ether;
- vinyl acetate;
- vinylpyridine, styrene and styrene substituted by C_1-C_8-alkyl- or halogen or sulfonic acid salts at the aromatic ring
- trimethoxyvinylsilane, triethoxyvinylsilane.
- 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;
- butadiene, isoprene, chloroprene, 2,4-dimethylbutadiene, cyclopentadiene, methylcyclopentadiene, cyclohexadiene, divinyl-benzene, 1-vinyl-cyclohexadiene, norbornadiene, 2-isopropenylnorbornene, 2-vinyl-norbornene, diisopropenylbenzene, divinyltoluene, divinylxylene and C_1 to C_{20} 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.

18. The process according to anyone of claims 1 to 17, wherein the dispersed phase or continuous phase is an aqueous phase and 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.

19. The process according to anyone of claims 1 to 18, wherein 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.

20. The process according to anyone of claims 1 to 19, wherein the weight ratio of photoinitiator to polymerizable monomer in the heterophase medium is between 1:5 and 1:100'000, preferably between 1: 10 and 1:10'000 and more preferably 1:50 to 1:2'000.

21. The process according to anyone of claims 1 to 20, wherein 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.

22. The process according to anyone of claims 1 to 21, wherein in step A) the photoinitiator is added partially or completely.

23. The process according to anyone of claims 1 to 22, wherein in step B), the irradiation of the heterophase medium is effected in such a manner that the ratio of the irradiated surface of 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}.

24. The process according to anyone of claims 1 to 23, wherein in step B), 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.

25. The process according to anyone of claims 1 to 24, wherein irradiation is effected at average intensities of at least 50 W per square meter of irradiated surface of 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.

26. The process according to anyone of claims 1 to 25, 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.

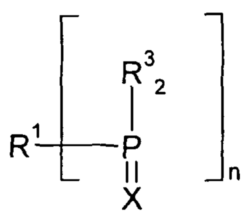
27. The process according to anyone of claims 1 to 26, wherein step B) is carried out continuously, preferably in a flow-through reactor.

28. The process according to anyone of claims 1 to 27, wherein step B) is carried out in a transparent tube, tubing or channel having an effective diameter of 5 mm or less, preferably 2 mm or less, and more preferably 1 mm or less.

29. The latices and polymer particles obtainable by a process according to anyone of claims 1 to 28.

30. Latices and polymer nanoparticles comprising at least 1 wt.-%, preferably at least 3 wt.-% of polymer chains soluble in tetrahydrofurane at 25°C having a molecular weight of 10´000´000 g/ mol determined by gel permeation chromatography (GPC).

31. Use of compounds of formula (Ia) as photoinitiator:



(Ia)

wherein X, R^1, R^3 and n have the same meaning as given in claims 12, 13 or 14.

Fig 1/8

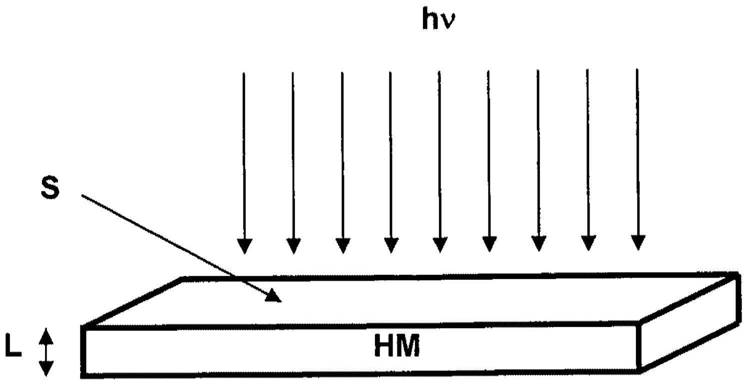


Fig 2/8

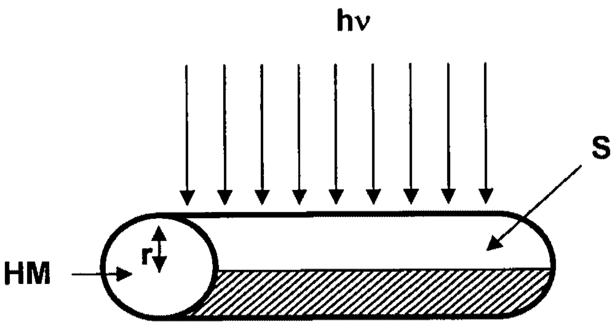


Fig 3/8

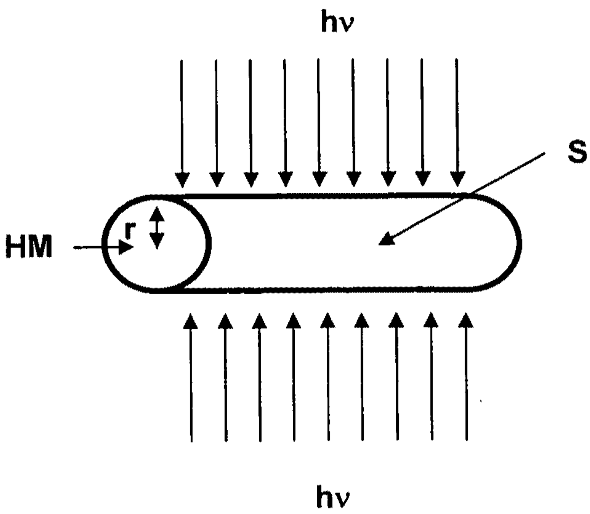


Fig 4/8

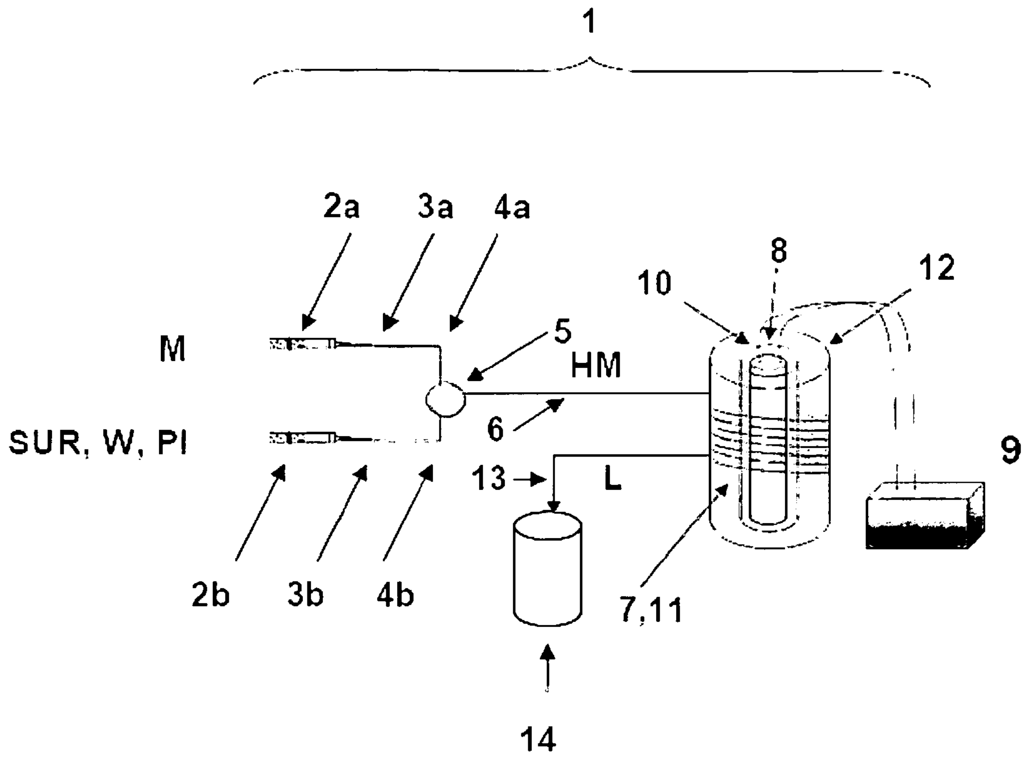

1
2a
3a
4a
8
10
12
M
5
HM
SUR, W, PI
6
9
13
L
2b
3b
4b
7,11
14

Fig 5/8

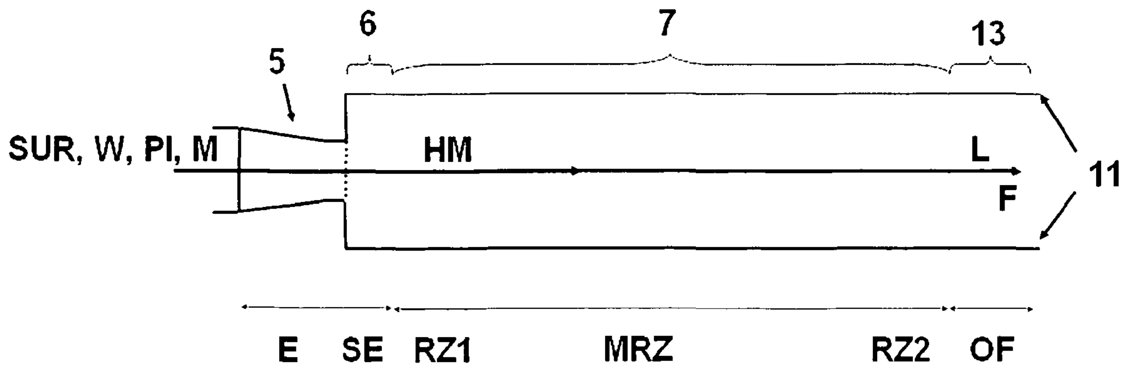

6
7
13
5
SUR, W, PI, M
HM
L
F
11
E
SE
RZ1
MRZ
RZ2
OF

Fig 6/8

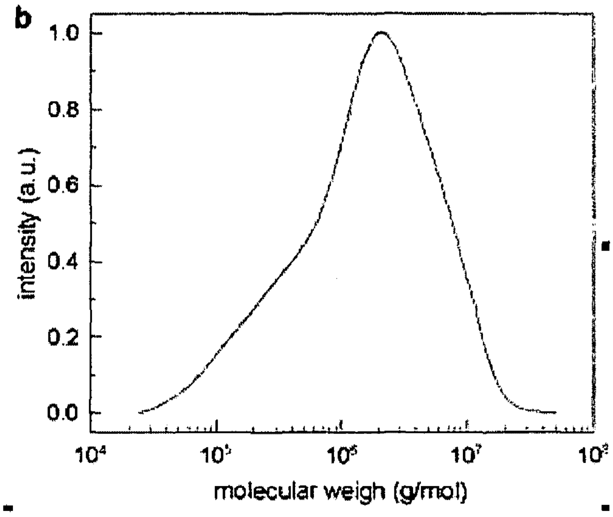

b
1.0
0.8
0.6
0.4
0.2
0.0
intensity (a.u.)
10⁴
10⁵
10⁶
10⁷
10⁸
molecular weigh (g/mol)

Fig 7/8

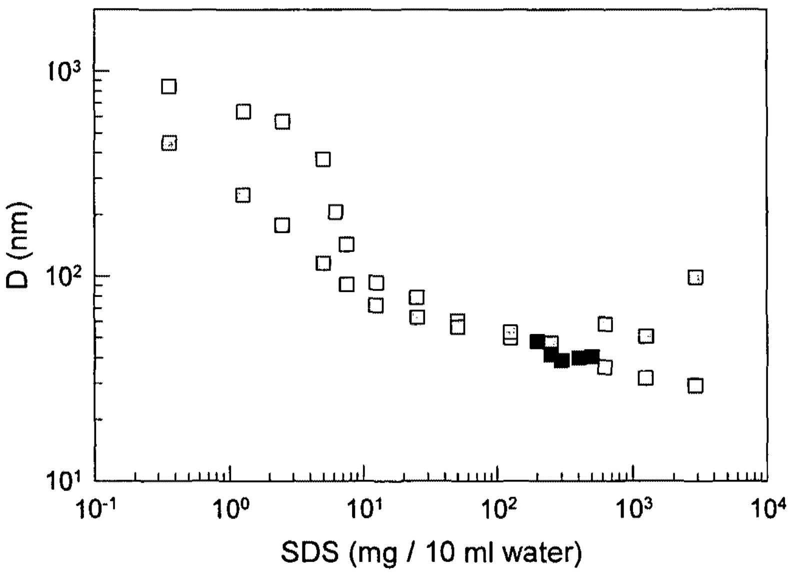
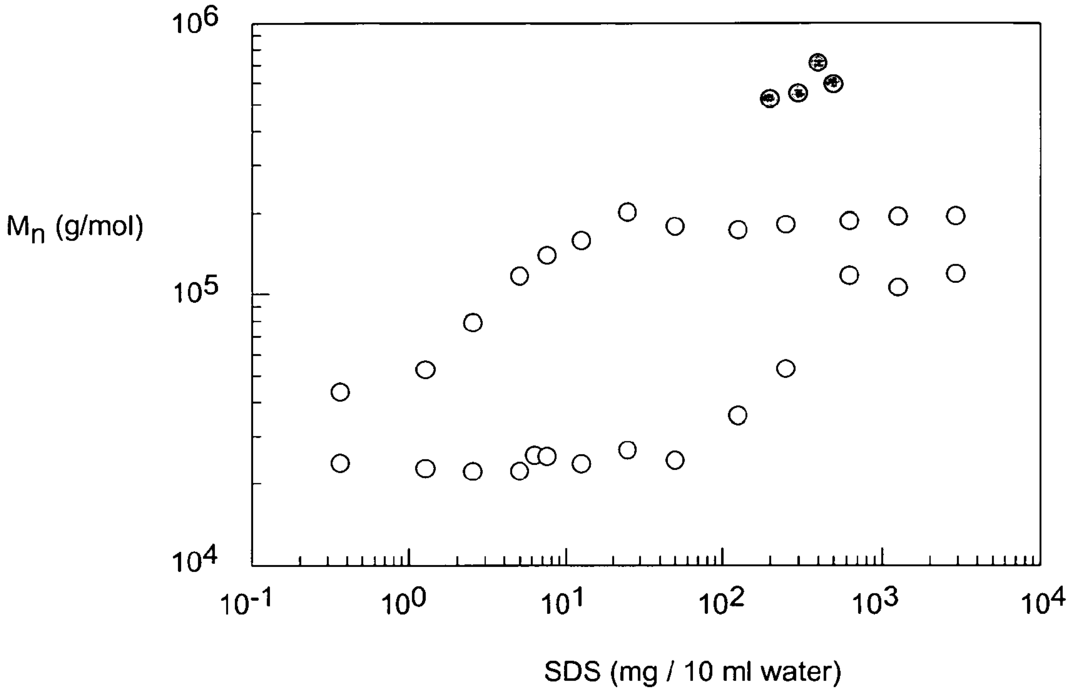

10³
10²
10¹
D (nm)
10⁻¹
10⁰
10¹
10²
10³
10⁴
SDS (mg / 10 ml water)

Fig 8/8



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/005206

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F2/24 C08F2/48 C08F12/08 C08F20/12 C08F20/18
B82Y40/00 C08F8/40
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B82Y C08F C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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 35 - page 2, line 10 page 11, line 30 - page 16, line 10 page 20, line 24 - line 33 page 23, line 4 - line 19; claims 1-15	29,31

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 January 2012	27/01/2012

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Gold, Josef

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	A. CHEMTOB, B. KUNSTLER, C. CROUTXÉ-BARGHORN, S. FOUCHARD: "Photoinduced miniemulsion polymerization", COLLOID POLYM. SCI., vol. 288, 17 February 2010 (2010-02-17), pages 579-587, XP002628533, DOI: 10.1007/s00396-010-2190-1 *example, table 2* -----	1-31
X,P	WO 2010/121387 A1 (ETH ZUERICH [CH]; GRUETZMACHER HANSJOERG [CH]; OTT TIMO [CA]) 28 October 2010 (2010-10-28) claims 1-15; examples 2-23 -----	29,31
X	WO 2008/003601 A1 (CIBA SC HOLDING AG [CH]; SCHELLENBERG CARSTEN [DE]; AUSCHRA CLEMENS [D) 10 January 2008 (2008-01-10) page 5, line 14 - line 15; examples 8,9,A5 page 16, line 16 - page 17, line 9 page 1 -----	1-31
X	US 2008/145660 A1 (WANG XIAORONG [US] ET AL) 19 June 2008 (2008-06-19) paragraph [0049] - paragraph [0050]; claim 15 -----	29,30

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2011/005206

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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