



(43) International Publication Date
30 August 2012 (30.08.2012)

(10) International Publication Number
WO 2012/113896 A1

(51) International Patent Classification:

C08F 2/00 (2006.01) *C08F 265/06* (2006.01)
C08F 257/02 (2006.01)

(21) International Application Number:

PCT/EP2012/053124

(22) International Filing Date:

24 February 2012 (24.02.2012)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

11156058.7 25 February 2011 (25.02.2011) EP
11186308.0 24 October 2011 (24.10.2011) EP

(71) Applicants (*for all designated States except US*): **BASF SE** [DE/DE]; 67056 Ludwigshafen (DE). **CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE** [—/FR]; 3, Rue Michel Ange, F-75794 Paris (FR). **ECOLE SUPERIEURE DE CHIMIE-PHYSIQUE-ELECTRONIQUE DE LYON** [—/FR]; 43, Boulevard du 11 Novembre, BP 2077, F-69616 Villeurbanne (FR). **UNIVERSITE CLAUDE BERNARD LYON 1** [—/FR]; 43, Boulevard du 11 Novembre 1918, F-69100 Villeurbanne (FR).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **TERRENOIRE, Alexandre** [FR/DE]; Dornfelderstr. 9, 55576 Sprendlingen (DE). **RECK, Bernd** [DE/DE]; Beim Bergtor 14, 67269 Grünstadt (DE). **ZORN, Matthias** [DE/DE]; Birkenauer Talstr. 89, 69469 Weinheim (DE). **CHARLEUX, Berna-**

dette [FR/FR]; 310 rue Andre Philip, F-69003 Lyon (FR). **CHABROE, Virgine** [FR/FR]; rue Reue Leynaua, F-69001 Lyon (FR). **D'AGOSTO, Franck** [FR/FR]; 2 rue Charlie Chaplin, F-69100 Villeurbanne (FR).

(74) Agent: **REITSTÖTTER, KINZEBACH & PARTNER**; Ludwigsplatz 4, 67059 Ludwigshafen (DE).

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: PROCESS FOR THE PREPARATION OF AN AQUEOUS POLYMER LATEX

(57) Abstract: The present invention relates to a process for the preparation of an aqueous polymer latex, wherein the polymer particles comprise at least a first polymer P1 and at least a second polymer P2 grafted to the first polymer P1.



WO 2012/113896 A1

Process for the preparation of an aqueous polymer latex

Description

- 5 The present invention relates to a process for the preparation of an aqueous polymer latex, wherein the polymer particles comprise at least a first polymer P1 and at least a second polymer P2 grafted to the first polymer P1.

10 Aqueous polymer dispersions find wide application in various technical fields, e.g. as binder systems in paints, in varnishes, in paper coating slips, in leather coating systems, in coating systems for mineral moldings such as fiber cement slabs and concrete roofing shingles, in anticorrosion primers for metals, as binders in nonwovens production, as base materials for adhesives, as additives for hydraulically setting compositions such as plaster or concrete, as additives for clay or loam construction materials, for producing membranes and the like. The solid polymer compositions in particle or powder form that are obtainable from such aqueous dispersions by drying may likewise be employed, and serve, moreover, as additives for a large multiplicity of application fields, such as for modifying plastics, as cement additives, as components of toner formulations, as additives in electrophotographic applications, in bio assays, as colloidal crystals, as pigments, as carrier for drugs or pesticides and the like. Aqueous polymer dispersions of this kind are typically prepared by a free-radical aqueous emulsion polymerisation of ethylenically unsaturated monomers.

25 There is a strong need for polymer dispersions wherein the polymer particles have a modified surface, i.e. where the composition of the surface is different from the core of the polymer particles, in order to tailor the properties of the latex to the desired application.

30 There are numerous approaches to prepare surface modified aqueous polymer dispersions.

The first approach includes the preparation of a polymer latex by emulsion polymerisation of the monomers forming the core of the polymer particles in the presence of a hydrophilic polymer which provides the properties of the surface. However, the grafting of the hydrophilic polymers is rarely satisfactory and this approach is limited to certain types of hydrophilic polymers.

A second approach which may be regarded as an improvement of the first approach includes the polymerisation preparation of a polymer latex by emulsion polymerisation

of the monomers forming the core of the polymer particles in the presence of a macromer, i.e. an oligomer or polymer having an ethylenically unsaturated double bond. However, this approach is limited because to the limited availability of macromers.

5

A third approach includes the grafting of a polymer having a reactive functional group to a polymer latex, where the polymer particles on their surfaces have a plurality of functional groups which are capable of forming covalent bonds with the reactive functional groups of the polymer to be grafted. A modification of this approach includes
10 the preparation of a latex carrying on its surface an anionic or cationic charge and reacting the latex with a polymer of opposite charge.

A forth approach includes sequential emulsion polymerisation of ethylenically unsaturated monomers. In sequential emulsion polymerisation, a first charge of
15 ethylenically unsaturated monomers is emulsion polymerized to form a first polymer latex and then a second or further monomer charges of ethylenically unsaturated monomers are polymerised in the first polymer latex, resulting in polymers having a core-shell structure. Unfortunately, it is difficult to trigger by this process which polymer forms the shell and which the core. Apart from that, sequential emulsion polymerisation
20 is limited to rather hydrophobic polymers.

A recently developed fifth approach includes the polymerisation of ethylenically unsaturated polymers in an aqueous latex, where the polymer particles of the latex include reactive centres which are capable of forming radicals and which thereby
25 initiate the polymerisation of the monomers.

US 7,344,752 describes a process, comprising the steps of forming a monomer solution containing a conjugate acid of a surfactant and an agent for controlled free radical polymerisation, emulsifying the solution in an aqueous solution of a weak base,
30 then initiating a controlled free radical polymerisation in the emulsion to form a first polymer latex and then adding a further monomer and allowing to proceed the polymerisation of the further monomer. However, this method requires to include the polymerisation initiator into the monomers of the first polymerisation step.

35 M. Manuszak Guerrini et al., *Macromol. Rapid Commun.* 21, (2000) 669-674 describe a process for preparing functionalized polymer latexes which comprises preparing an aqueous copolymer latex of styrene with a halogen containing functional monomer such as 2-(2-bromopropionyloxy)ethyl methacrylate by radical emulsion polymerisation and performing polymerisation of 2-hydroxyethyl acrylate or 2-(methacryloyloxy)ethyl

trimethylammonium chloride in this latex in the presence of Cu(I) salts and bidentate nitrogen ligand such as bipyridine. Thereby, only dilute latexes could be obtained.

Apart from that, this process requires the addition of large amounts of Cu(I) salts which are difficult to separate from the latex. A similar process has been described by S. B.

5 Jhaveri et al., J. Polymer Science: Part A: Polymer Chemistry, 45 (2007) 1575-1584.

T. Taniguchi et al., Colloids and surfaces B: Biointerfaces 71 (2009) 194-199 describe a process, where styrene derivative bearing a lactose residue is polymerized in an aqueous polymer latex having α -chloroester groups in the presence of

10 tris[(2-pyridylmethyl)amine]copper(II) dichloride.

Min et al., Macromolecules 42 (2009) 1597-1603 describe a process for preparing surface modified latexes, comprising a sequential emulsion polymerisation of ethylenically unsaturated monomers under so called ATRP (Atom Transfer Radical

15 Polymerisation) conditions. In this process, a microemulsion of a solution of a Cu(II) salt, a bidentate nitrogen ligand and an initiator such as ethyl 2-bromoisobutyrate in the monomers is subjected to polymerisation by heating and after conversion of the monomers a further monomer charge is added and polymerisation is continued.

20 Each of the aforementioned processes requires the use of comparatively high amounts of copper salts. None of the aforementioned processes is suitable for preparing stable polymer latexes of surface modified polymer particles formed from ethylenically unsaturated polymers, where the polymer latexes have a polymer content of more than 10% by weight or even at least 20% by weight or at least 30% by weight.

25

Therefore, it is an object of the present invention to provide a process for the preparation of a surface modified polymer latex based on ethylenically unsaturated polymers, i.e. of a polymer latex, wherein the polymer particles comprise at least a first polymer P1 formed from ethylenically unsaturated monomers M1 and at least a second

30 polymer P2 grafted to the first polymer P1, the second polymer P2 being is formed from ethylenically unsaturated monomers M2 which overcomes the drawbacks of the processes of the prior art. The process should be easy to perform and allow the preparation of stable polymer latexes having a polymer content of more than 10% by weight, preferably at least 20% by weight and in particular at least 30% by weight.

35

It has now been found that the preparation of polymer latexes can be achieved by a sequential polymerisation process which includes steps i. and ii. as defined hereinafter, where the polymerisation of the ethylenically unsaturated monomers in step ii. is achieved by emulsion polymerisation of said ethylenically unsaturated monomers in a

polymer latex of a polymer containing covalently bound halogen atom in the presence of elemental copper and at least one organic compound having at least one nitrogen atom which organic compound is capable of forming a complex with copper ions.

- 5 Therefore, the present invention relates to a process for the preparation of an aqueous polymer latex, wherein the polymer particles comprise at least a first polymer P1 formed from ethylenically unsaturated monomers M1 and at least a second polymer P2 grafted to the first polymer P1, the second polymer P2 being is formed from ethylenically unsaturated monomers M2, which process comprises:
- 10 i. providing an aqueous polymer latex of the first polymer P1 formed from ethylenically unsaturated monomers M1, where the latex contains halogen which is covalently bound to the first polymer P1,
- ii. performing the polymerisation of monomers M2 in the latex of the polymer P1 in the presence of elemental copper and at least one organic compound having at
- 15 least one nitrogen atom which organic compound is capable of forming a complex with copper ions.

The process allows the preparation of stable concentrated aqueous polymer latexes, wherein the concentration of polymer is higher than 10% by weight, in particular at

20 least 20% by weight, especially at least 30% by weight, e.g. from 10 to 70% by weight, in particular from 20 to 70% by weight or from 30 to 65% by weight, based on the total weight of the polymer latex. Moreover, the process does not require the use of copper salts which might be difficult to remove from the latex.

25 The term "elemental copper" as used herein refers to metallic copper in any form but not to chemical compounds containing copper in the oxidation state 0 (hereinafter Cu(0) compound).

The term "halogen" as used herein refers to fluorine, chlorine, bromine or iodine, in

30 particular to chlorine or bromine.

The term "aqueous polymer latex" has to be understood as a dispersion of polymer particles in an aqueous dispersion medium. The aqueous dispersion medium is normally water but it may contain surfactants dissolved therein in order to stabilize the

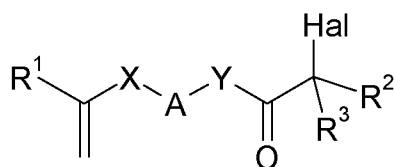
35 polymer particles. The aqueous dispersion medium may also contain organic solvents dissolved therein, e.g. C₁-C₄-alkanols such as methanol, ethanol, propanol, isopropanol or n-butanol or C₂-C₄-polyols.

In a first embodiment of the invention, the polymer P1 of the first polymer latex is a copolymer containing polymerized monomers M1.2 having covalently bound halogen atoms which are preferably selected from chlorine and bromine. Hence, the monomers M1 forming the first polymer P1 comprise at least one monoethylenically monomer M1.1 having no covalent bound halogen atoms and at least a second monomer M1.2 having a covalent bound halogen atom, and optionally one or more further ethylenically unsaturated monomers having 2 or more ethylenically unsaturated double bounds (Monomers M1.3). In general, the amount of monomers M1.1 and M1.2 is at least 95% by weight, in particular at least 99% by weight, based on the total amount of monomers M1. Consequently, the amount of monomers M1.3 will generally not exceed 5% by weight, in particular 1% by weight, based on the total amount of monomers M1. In a particular embodiment of the invention, the monomers M1 do not comprise any monomer M1.3 or not more than 0.1% by weight or not more than 0.01% by weight of monomers M1.3, based on the total amount of monomers M1. In another embodiment of the invention, the monomers M1 include 0.01 to 5% by weight, in particular 0.1 to 1% by weight, based on the total amount of monomers M1, of at least one monomer M1.3. The amount of monomers M1.2 is generally from 0.001 to 10% by weight, in particular from 0.01 to 8% by weight, especially from 0.1 to 5% by weight, based on the total amount of monomers M1.

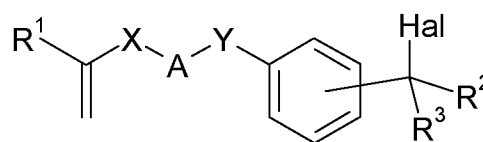
20

Preferred monomers M1.2 carry a halogen atom, in particular a chlorine or bromine atom which is bound at a carbon atom in the α -position of a carbonyl group or of a benzene ring. Suitable monomers M1.2 can be described e.g. by the following formulae M1.2a and M1.2b but are not limited to these.

25



(M1.2a)



(M1.2b)

where

Hal is chlorine or bromine,

R¹ is hydrogen or C₁-C₄-alkyl, in particular hydrogen or methyl,

30 R² is hydrogen or C₁-C₄-alkyl, in particular hydrogen or methyl,

R³ is hydrogen or C₁-C₄-alkyl, in particular methyl,

X indicates a single bond or is O, CH₂O, C(=O)O or C(=O)NR⁴, where the carbon atom of the last 3 radicals is bound to the double bond and R⁴ is hydrogen or C₁-C₄-alkyl,

Y indicates a single bond, or is O or NR⁵, where R⁵ is hydrogen or C₁-C₄-alkyl,

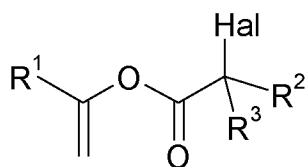
A is C₂-C₁₀-alkylene or a radical A'-[O-A']_n, where A' is C₂-C₄-alkylene, in particular 1,2-ethylene and/or 1,2-propylene, and n is an integer in the range from 1 to 50, or

A-Y indicates a single bond.

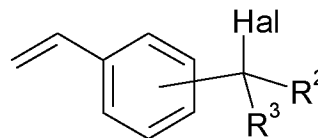
In formula M1.2a, the variable X indicates preferably a single bond or is O, CH₂O or C(=O)O. In a particular embodiment of the monomers of formula M1.2a, A-Y indicates a single bond and X is preferably O or CH₂O. In another particular embodiment, X in formula M1.2a is O, CH₂O or C(=O)O and A is C₂-C₁₀-alkylene, especially 1,2-ethylene or 1,2-propylene, or A is a radical A'-[O-A']_n, where A' is C₂-C₄-alkylene, in particular 1,2-ethylene and/or 1,2-propylene, and n is an integer in the range from 1 to 50, especially in the range from 1 to 20, and Y is O.

In formula M1.2b, the variable X indicates preferably a single bond or is O, CH₂O or C(=O)O. In a particular embodiment of the monomers of formula M1.2b, A-Y indicates a single bond and X is a single bond. In another particular embodiment, X in formula M1.2b is O, CH₂O or C(=O)O and A is C₂-C₁₀-alkylene, especially 1,2-ethylene or 1,2-propylene, or A is a radical A'-[O-A']_n, where A' is C₂-C₄-alkylene, in particular 1,2-ethylene and/or 1,2-propylene, and n is an integer in the range from 1 to 50, especially in the range from 1 to 20, and Y is O.

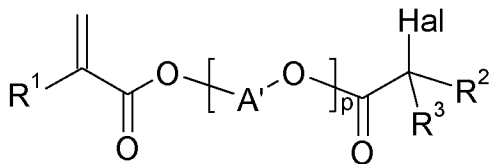
Particular preferred are the following monomer types M1.2a1, M1.2b1, M1.2a2 and M1.2b2:



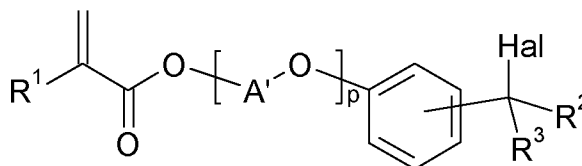
(M1.2a1)



(M1.2b1)



(M1.2a2)



(M1.2b2)

In formulae M1.2a1, M1.2b1, M1.2a2 and M1.2b2 the variables R1, R2, R3, Hal and A' have the definitions given for formulae M1.2a and M1.2b and p is an integer from 1 to 50, in particular from 1 to 20.

- 5 Examples of monomers M1.2 include 4-(α -chloroisopropyl)styrene, 2-(2-bromopropionyloxy)ethyl acrylate, 2-(2-bromopropionyloxy)ethyl methacrylate, 2-(2-chloropropionyloxy)ethyl acrylate, 2-(2-chloropropionyloxy)ethyl methacrylate, 2-bromoisobutyric acid vinyl ester and 2-chloroisobutyric acid vinyl ester.
- 10 It has been found to be advantageous, if the majority of the halogen atoms which are covalently bound to the polymer P1 are located close to the surface of the latex particles, in particular, where at least 50% of the halogen atoms which are covalently bound to the polymer P1 are located close to the surface of the latex particles of the polymer P1. "Close to the surface of the polymer particles" means that the halogen
- 15 atoms are located on the surface or within a distance of at most 10 nm from the surface, i.e. within a shell that forms the surface of the polymer particles and has a thickness of not more than 10 nm. The amount of halogen atoms located close to the surface of the latex particles of the polymer P1 can be easily determined by energy-dispersive X-ray spectroscopy, also termed EDX or EDS.
- 20 The latex of the polymer P1 can be easily obtained by radical emulsion polymerisation of the monomers M1, either in the presence of a chain transfer agent containing halogen atoms or in the presence of at least one monomer M1.2 or in the presence of a combination of both.
- 25 The chain transfer agent should be capable of transferring a halogen atom, in particular a bromine atom. Examples of chain transfer agents include tetrabromomethane, tetrachloromethane, tribromomethane and trichloromethane.
- 30 As pointed out above, the polymer P1 is made from ethylenically unsaturated monomers M1. These monomers may preferably include at least one monomer M1.2 as defined above. Preferably, the monomers M1 comprise at least 80% by weight, e.g. from 80 to 100% by weight, in particular from 90 to 100% by weight, or from 80 to 99.99% by weight, in particular from 90 to 99.9% by weight, based on the total amount
- 35 of monomers M1 and depending on whether the monomer of at least one monoethylenically unsaturated monomer M1.1a having no covalently bound halogen atoms and having a water solubility of at most 60 g/l at 25°C and 1013 mbar, in particular at most 40 g/l at 25°C and 1013 mbar.

Examples of suitable monoethylenically unsaturated monomers M1.1a are:

- monovinylaromatic hydrocarbons;
- esters of monoethylenically unsaturated C₃-C₆ monocarboxylic acids with C₁-C₂₀ alkanols, C₅-C₈ cycloalkanols, phenyl-C₁-C₄ alkanols or phenoxy-C₁-C₄ alkanols, more particularly the aforementioned esters of acrylic acid and also the aforementioned esters of methacrylic acid;
- diesters of monoethylenically unsaturated C₄-C₆ dicarboxylic acids with C₁-C₂₀ alkanols, C₅-C₈ cycloalkanols, phenyl-C₁-C₄ alkanols or phenoxy-C₁-C₄ alkanols, more particularly the aforementioned esters of maleic acid and esters of fumaric acid;
- amides of monoethylenically unsaturated C₃-C₆-monocarboxylic acids with C₄-C₂₀-alkylamines or di-C₂-C₂₀-alkylamines;
- vinyl, allyl, and methallyl esters of saturated aliphatic carboxylic acids, in particular of saturated aliphatic C₂-C₁₈ monocarboxylic acids, especially the vinyl esters.

Examples of esters of monovinylaromatic hydrocarbons include, for example, styrene, vinyltoluenes, tert-butylstyrene, α -methylstyrene, and the like, more particularly styrene.

20

Examples of esters of monoethylenically unsaturated C₃-C₆ monocarboxylic acids with C₁-C₂₀ alkanols, C₅-C₈ cycloalkanols, phenyl-C₁-C₄ alkanols or phenoxy-C₁-C₄ alkanols are, in particular, the esters of acrylic acid such as methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, 2-butyl acrylate, isobutyl acrylate, tert-butyl acrylate, n-hexyl acrylate, 2-ethylhexyl acrylate, 3-propylheptyl acrylate, decyl acrylate, lauryl acrylate, stearyl acrylate, cyclohexyl acrylate, benzyl acrylate, 2-phenylethyl acrylate, 1-phenylethyl acrylate, 2-phenoxyethyl acrylate, and also the esters of methacrylic acid such as methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, 2-butyl methacrylate, isobutyl methacrylate, tert-butyl methacrylate, n-hexyl methacrylate, 2-ethylhexyl methacrylate, decyl methacrylate, lauryl methacrylate, stearyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, 2-phenylethyl methacrylate, 1-phenylethyl methacrylate, and 2-phenoxyethyl methacrylate.

Examples of diesters of monoethylenically unsaturated C₄-C₆ dicarboxylic acids with C₁-C₂₀ alkanols, C₅-C₈ cycloalkanols, phenyl-C₁-C₄ alkanols or phenoxy-C₁-C₄ alkanols are, in particular, the diesters of maleic acid and the diesters of fumaric acid, more particularly di-C₁-C₂₀ alkyl maleinates and di-C₁-C₂₀ alkyl fumarates such as dimethyl

35

maleinate, diethyl maleinate, di-n-butyl maleinate, dimethyl fumarate, diethyl fumarate, and di-n-butyl fumarate.

- Examples of vinyl, allyl, and methallyl esters of saturated aliphatic carboxylic acid
- 5 include in particular the vinyl esters of C₂-C₁₈ monocarboxylic acids such as vinyl acetate, vinyl propionate, vinyl butyrate, vinyl pivalate, vinyl hexanoate, vinyl-2-ethylhexanoate, vinyl laurate, and vinyl stearate, and also the corresponding allyl and methallyl esters.
- 10 Among the monomers M1.1a, the esters of monoethylenically unsaturated C₃-C₆ monocarboxylic acids, more particularly the esters of acrylic acid or of methacrylic acid, with C₁-C₂₀ alkanols, C₅-C₈-cycloalkanols, phenyl-C₁-C₄ alkanols or phenoxy-C₁-C₄ alkanols, diesters of monoethylenically unsaturated C₄-C₆ dicarboxylic acids with C₁-C₂₀ alkanols, C₅-C₈ cycloalkanols, phenyl-C₁-C₄ alkanols or phenoxy-C₁-C₄ alkanols,
- 15 and vinylaromatic hydrocarbons, especially styrene, are preferred.

- Among the monomers M1.1a, the esters of monoethylenically unsaturated C₃-C₆ monocarboxylic acids, more particularly the esters of acrylic acid or of methacrylic acid, with C₁-C₂₀ alkanols, and vinylaromatic hydrocarbons, especially styrene, are
- 20 particularly preferred.

- Among the monomers M1.1a, the esters of acrylic acid with C₂-C₁₀ alkanols (= C₂-C₁₀ alkyl acrylates), the esters of methacrylic acid with C₁-C₁₀ alkanols (= C₁-C₁₀ alkyl methacrylates), and vinylaromatic hydrocarbons, especially styrene, are very
- 25 particularly preferred.

- In one particularly preferred embodiment of the invention, the monomers M1.1a are selected from C₁-C₄ alkyl methacrylates, C₂-C₁₀ alkyl acrylates, styrene, mixtures of C₁-C₄-alkyl methacrylates, mixtures of styrene with C₂-C₁₀ alkyl acrylates, mixtures of
- 30 C₁-C₄ alkyl methacrylates with C₂-C₁₀ alkyl acrylates, and mixtures of C₁-C₄ alkyl methacrylates with styrene and C₂-C₁₀ alkyl acrylates.

- In addition to the monomers M1.1a and optionally M1.2 and/or M1.3, the monomers M1 may comprise up to 10% by weight, in particular not more than 5% by weight, e.g. from
- 35 0.01 to 10% by weight, or from 0.1 to 5% by weight, based on the total weight of monomers M1, of one or more monomers M1.1b having no covalently bound halogen atoms and having a water solubility of at least 60 g/l at 25°C and 1013 mbar, in particular at least 80 g/l at 25°C and 1013 mbar.

Examples of monomers M1.1b are as follows:

- monoethylenically unsaturated C₃-C₈ monocarboxylic acids, such as acrylic acid, methacrylic acid, 2-butenic acid, 3-butenic acid, 2-acryloxyethylacetic acid and 2-methacryloxyethylacetic acid;
- 5 - monoethylenically unsaturated C₄-C₈ monocarboxylic acids, such as maleic acid, itaconic acid and fumaric acid;
- the primary amides of the aforementioned monoethylenically unsaturated C₃-C₈ monocarboxylic acids, more particularly acrylamide and methacrylamide,
- the cyclic amides of the aforementioned monoethylenically unsaturated C₃-C₈ monocarboxylic acids with cyclic amines such as pyrrolidine, piperidine, morpholine or piperazine, more particularly N-acryloylmorpholine or N-methacryloylmorpholine,
- 10 - hydroxyalkyl esters of the aforementioned monoethylenically unsaturated C₃-C₈ monocarboxylic acids, e.g., hydroxyethyl acrylate, hydroxyethyl methacrylate, 2- and 3-hydroxypropyl acrylate, 2- and 3-hydroxypropyl methacrylate,
- 15 - monoesters of the aforementioned monoethylenically unsaturated C₃-C₈ monocarboxylic and C₄-C₈-dicarboxylic acids with C₂-C₄ polyalkylene glycols, more particularly the esters of these carboxylic acids with polyethylene glycol or with alkyl-polyethylene glycols, the (alkyl)polyethylene glycol radical typically having a molecular weight in the range from 100 to 5000, in particular 100 to 3000;
- 20 - N-vinyl amides of aliphatic C₁-C₁₀ carboxylic acids, and N-vinyl lactams, such as N-vinylformamide, N-vinylacetamide, N-vinylpyrrolidone, and N-vinylcaprolactam.
- monoethylenically unsaturated sulfonic acids in which the sulfonic acid group is attached to an aliphatic hydrocarbon radical, and salts thereof, such as vinylsulfonic acid, allylsulfonic acid, methallylsulfonic acid, 2-acrylamido-2-methylpropanesulfonic acid, 2-methacrylamido-2-methylpropanesulfonic acid, 2-acrylamidoethanesulfonic acid, 2-methacrylamidoethanesulfonic acid, 2-acryloyloxyethanesulfonic acid, 2-methacryloyloxyethanesulfonic acid, 30 3-acryloyloxypropanesulfonic acid and 2-methacryloyloxypropanesulfonic acid, and salts thereof,
- vinylaromatic sulfonic acids, i.e., monoethylenically unsaturated sulfonic acids in which the sulfonic acid group is attached to an aromatic hydrocarbon radical, more particularly to a phenyl ring, and salts thereof, such as, for example, styrenesulfonic acids such as 2-, 3- or 4-vinylbenzenesulfonic acid and salts thereof,
- 35 - monoethylenically unsaturated phosphonic acids in which the phosphonic acid group is attached to an aliphatic hydrocarbon radical, and salts thereof, such as vinylphosphonic acid, 2-acrylamido-2-methylpropanephosphonic acid,

- 2-methacrylamido-2-methylpropanephosphonic acid,
 2-acrylamidoethanephosphonic acid, 2-methacrylamidoethanephosphonic acid,,
 2-acryloyloxyethanephosphonic acid, 2-methacryloyloxyethanephosphonic acid,
 3-acryloyloxypropanephosphonic acid and 2-methacryloyloxypropanephosphonic
 5 acid, and salts thereof, and
- monoethylenically unsaturated phosphoric monoesters, more particularly the
 monoesters of phosphoric acid with hydroxy-C₂-C₄ alkyl acrylates and hydroxy-
 C₂-C₄ alkyl methacrylates, such as, for example, 2-acryloyloxyethyl phosphate,
 2-methacryloyloxyethyl phosphate, 3-acryloyloxypropyl phosphate,
 10 3-methacryloyloxypropyl phosphate, 4-acryloyloxybutyl phosphate and
 4-methacryloyloxybutyl phosphate, and salts thereof.

Where the monomers M1.1b are present in their salt form, they have a corresponding
 cation as counterion. Examples of suitable cations are alkali metal cations such as Na⁺
 15 or K⁺, alkaline earth metal ions such as the Ca²⁺ and Mg²⁺ and also ammonium ions
 such as NH₄⁺, tetraalkylammonium cations such as tetramethylammonium,
 tetraethylammonium, and tetrabutylammonium, and also protonated primary,
 secondary and tertiary amines, more particularly those which carry 1, 2 or 3 radicals
 selected from C₁-C₂₀ alkyl groups and hydroxyethyl groups, e.g., the protonated forms
 20 of mono-, di-, and tributylamine, propylamine, diisopropylamine, hexylamine,
 dodecylamine, oleylamine, stearylamine, ethoxylated oleylamine, ethoxylated
 stearylamine, ethanolamine, diethanolamine, triethanolamine or of
 N,N-dimethylethanolamine. Preference is given to the alkali metal salts.

25 Preferred monomers M1.1b are selected from the group of monoethylenically
 unsaturated C₃-C₈ monocarboxylic acids, more particularly acrylic acid and methacrylic
 acid, the amides of the aforementioned monoethylenically unsaturated C₃-C₈
 monocarboxylic acids, more particularly acrylamide and methacrylamide, and the
 hydroxyalkyl esters of the aforementioned monoethylenically unsaturated C₃-C₈
 30 monocarboxylic acids, e.g. hydroxyethyl acrylate, hydroxyethyl methacrylate, 2- and
 3-hydroxypropyl acrylate, 2- and 3-hydroxypropyl methacrylate.

As pointed out above, the monomers M1 may comprise a certain amount of
 ethylenically unsaturated monomers M1.3 having more than 1 ethylenically unsaturated
 35 double bond, e.g., 2, 3 or 4 ethylenically unsaturated double bonds. Examples of
 monomers M1.3 are as follows:

- esters of monohydric, unsaturated alcohols such as allyl alcohol, 1-buten-3-ol, 5-
 hexen-1-ol, 1-octen-3-ol, 9-decen-1-ol, dicyclopentenyl alcohol, 10-undecen-1-ol,
 cinnamyl alcohol, citronellol, crotyl alcohol or cis-9-octadecen-1-ol with one of the

- aforementioned monoethylenically unsaturated C₃-C₈ monocarboxylic acids, more particularly the esters of acrylic acid or of methacrylic acid, especially the allyl esters such as allyl acrylate and allyl methacrylate,
- 5 - di-, tri-, and tetra-esters of the aforementioned monoethylenically unsaturated C₃-C₈ monocarboxylic acids, more particularly the di-, tri-, and tetra-esters of acrylic acid or of methacrylic acid, with aliphatic or cycloaliphatic diols or polyols, more particularly the diesters of acrylic acid or of methacrylic acid with dihydric alcohols, examples being alkanols, such as 1,2-propanediol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 2,3-butanediol, 1,4-butanediol, but-2-ene-1,4-diol, 10 1,2-pentanediol, 1,5-pentanediol, 1,2-hexanediol, 1,6-hexanediol, 1,10-decanediol, 1,2-dodecanediol, 1,12-dodecanediol, neopentyl glycol, 3-methylpentane-1,5-diol, 2,5-dimethyl-1,3-hexanediol, 2,2,4-trimethyl-1,3-pentanediol, 1,2-cyclohexanediol, 1,4-cyclohexanediol, 1,4-bis(hydroxymethyl)-cyclohexane, the mono-neopentylglycol ester of hydroxypivalic acid, 2,2-bis(4-hydroxyphenyl)propane, 2,2-bis[4-(2-hydroxypropyl)phenyl]propane, diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, tripropylene glycol, tetrapropylene glycol, 3-thiapentane-1,5-diol, polyethylene glycols, polypropylene glycols or polytetrahydrofurans having molecular weights of in each case 200 to 10 000, and also the di-, tri-, and tetra-esters of acrylic acid or 20 of methacrylic acid with polyhydric polyols such as trimethylolpropane, glycerol, pentaerythritol, 1,2,5-pentanetriol, 1,2,6-hexanetriol, cyanuric acid, sorbitans, sucrose, glucose or mannose;
- diesters of the aforementioned monohydric, unsaturated alcohols, more particularly of allyl alcohol with dibasic carboxylic acids such as malonic acid, 25 tartaric acid, trimellitic acid, phthalic acid, terephthalic acid, citric acid or succinic acid;
- linear, branched or cyclic, aliphatic or aromatic hydrocarbons which possess at least two ethylenically unsaturated double bonds, which in the case of aliphatic hydrocarbons must not be conjugated, e.g., divinylbenzene, divinyltoluene, 30 1,7-octadiene, 1,9-decadiene, 4-vinyl-1-cyclohexene or trivinylcyclohexane;
- acrylamides, methacrylamides, and N-allylamines of at least difunctional amines. Such amines are, for example, 1,2-diaminoethane, 1,3-diaminopropane, 1,4-diaminobutane, 1,6-diaminohexane, 1,12-dodecanediamine, piperazine, diethylenetriamine or isophoronediamine; and
- 35 - N,N'-divinyl compounds of urea derivatives, at least difunctional amides, cyanurates or urethanes, as for example of urea, ethyleneurea, propyleneurea or tartaramide, e.g., N,N'-divinylethyleneurea or N,N'-divinylpropyleneurea.

Generally, the polymer particles of the polymer P1 of the first polymer latex have an average particle diameter (weight average), determined by dynamic light scattering, in the range from 10 to 1000 nm, in particular from 20 to 800 nm. It has been found to be advantageous, if the polymer particles of the first polymer latex have an average
5 particle diameter (weight average), determined by dynamic light scattering, in the range from 20 to 500 nm, preferably in the range from 30 to 400 nm, and more particularly in the range from 40 to 300 nm.

The particle sizes/particle diameters or particle radii indicated here for the polymer
10 particles are particle diameters as may be determined by means of photon correlation spectroscopy (PCS), also known as quasi-elastic light scattering (QELS) or dynamic light scattering. The average particle diameters constitute the average value of the cumulant analysis (mean of fits). This "mean of fits" is an average, intensity-weighted particle diameter in nm which corresponds to the weight-average particle diameter. The
15 measurement method is described in the ISO 13321 standard. Processes for this purpose are familiar to the skilled worker, moreover, from the relevant technical literature – for example, from H. Wiese in D. Distler, Wässrige Polymerdispersionen, Wiley-VCH 1999, section 4.2.1, p. 40ff and literature cited therein, and also H. Auweter, D. Horn, J. Colloid Interf. Sci. 105 (1985) 399, D. Lilge, D. Horn, Colloid Polym. Sci.
20 269 (1991) 704 or H. Wiese, D. Horn, J. Chem. Phys. 94 (1991) 6429. The particle diameters indicated here relate to the values determined at 20°C and 101.325 hPa on 0.001-1% by weight dispersions. The determination of the average particle diameters may also be performed by means of hydrodynamic chromatography (HDC) using a Particle Size Distribution Analyzer (PSDA, Varian Deutschland GmbH) with a number 2
25 (standard) cartridge at a wavelength of 254 nm (measurement temperature 23°C and measurement time 480 seconds).

The polymer P1 present in the first latex typically has a glass transition temperature in the range from -60 to 150°C. In this context, it has proven advantageous, if the polymer
30 P1 has a glass transition temperature, T_g , of at least -20°C, e.g. from -20°C to 120°C.

By the glass transition temperature T_g here is meant the temperature at the inflection point ("midpoint temperature") determined in accordance with ASTM D 3418-82 by differential scanning calorimetry (DSC) with a scan rate of 10 K/min (cf. Ullmann's
35 Encyclopedia of Industrial Chemistry, 5th edition, volume A 21, VCH Weinheim 1992, p. 169, and also Zosel, Farbe und Lack 82 (1976), pp. 125-134; see also DIN 53765). Alternatively the glass transition temperature T_g may be determined by means of dynamic mechanical analysis (DMA).

In this context, it proves useful to estimate the glass transition temperature T_g of the copolymer P. According to Fox (T.G. Fox, Bull. Am. Phys. Soc. (Ser. II) 1, 123 [1956] and Ullmanns Enzyklopädie der technischen Chemie, Weinheim (1980), pp. 17-18), the glass transition temperature of copolymers with low degrees of crosslinking is given at

5 high molar masses in good approximation by

$$\frac{1}{T_g} = \frac{X^1}{T_g^1} + \frac{X^2}{T_g^2} + \dots + \frac{X^n}{T_g^n}$$

where $X^1, X^2, \dots, X^n$ are the mass fractions of the monomers 1, 2, ..., n and $T_g^1, T_g^2, \dots, T_g^n$ are the glass transition temperatures of the polymers composed in each case only of one of the monomers 1, 2, ..., n, in degrees Kelvin. The latter are known, for example, from Ullmann's Encyclopedia of Industrial Chemistry, VCH, Weinheim, vol. A 21 (1992) p. 169 or from J. Brandrup, E. H. Immergut, Polymer Handbook 3rd ed., J. Wiley, New York 1989.

10

15 For the purpose of stabilizing the polymer particles or the polymer P1, the first latex usually contains at least one surface-active substance (also termed surfactants) which in general is anionic, cationic or nonionic. Such surfactants include anionic, cationic and nonionic emulsifiers and also anionic, cationic and nonionic protective colloids or

20 stabilizers. By emulsifiers are meant, in contradistinction to protective colloids, surface-active substances whose molecular weight (number average) is typically below 2000 g/mol and especially below 1500 g/mol. Protective colloids, in turn, are usually water-soluble polymers having a number-average molecular weight of above 2000 g/mol, in the range from 2000 to 100 000 g/mol, for example, and in the range

25 from 5000 to 50 000 g/mol in particular. It will be appreciated that protective colloids and emulsifiers can be used in a mixture. Preferably, the surfactant do not contain halogen atoms.

The amount of surfactant used in stabilizing the polymer particles is typically in the

30 range from 0.1% to 10%, preferably 0.2% to 5%, by weight, based on 100% by weight of polymer P1, or based on 100% by weight of the constituent monomers M1 of the polymer P1.

In one embodiment of the invention, the latex of the polymer P1 comprises at least one

35 anionic surface-active substance, more particularly at least one anionic emulsifier, and especially at least one anionic emulsifier which has at least one SO_3Z group attached via C atom or an O atom with Z being hydrogen or a suitable counterion, such as an alkali metal, alkaline earth metal or ammonium cation, for example. The surfactants are

in general not polymerizable, i.e., they do not contain ethylenically unsaturated groups which can be polymerized in a free-radical polymerization. Some or all of the emulsifiers, however, may be polymerizable. Such polymerizable emulsifiers comprise ethylenically unsaturated groups and are either nonionic or anionic emulsifiers.

- 5 Polymerizable nonionic emulsifiers are preferably selected from C₂-C₃ alkoxyates of alkenols, more particularly of prop-2-en-1-ol, and monoesters of monoethylenically unsaturated monocarboxylic or dicarboxylic acids with poly-C₂-C₃-alkylene ethers, the degree of alkoxylation being 3 to 100 in each case. Polymerizable anionic emulsifiers are preferably selected from the corresponding sulfuric and phosphoric monoesters of
- 10 the abovementioned nonionic polymerizable emulsifiers.

The nonpolymerizable anionic emulsifiers typically include aliphatic carboxylic acids having in general at least 10 C atoms, e.g., 10 to 20 C atoms, and also their salts, more particularly their ammonium salts and alkali metal salts; aliphatic, araliphatic, and

15 aromatic sulfonic acids having in general at least 6 C atoms, e.g., 6 to 30 C atoms, and also their salts, more particularly their ammonium salts and alkali metal salts; sulfuric monoesters of ethoxylated alkanols and alkylphenols, and also their salts, more particularly their ammonium salts and alkali metal salts; and also alkyl, aralkyl and aryl phosphates, including phosphoric monoesters of alkanols and alkylphenols.

20

Examples of anionic emulsifiers preferred in accordance with the invention are the salts, more particularly the alkali metal salts and ammonium salts, of

- dialkyl esters of sulfosuccinic acid (alkyl radicals: each C₄ to C₁₂) such as dibutyl sulfosuccinate, dihexyl sulfosuccinate, dioctyl sulfosuccinate, di(2-ethylhexyl)

25 sulfosuccinate or didecyl sulfosuccinate,

- alkyl sulfates (alkyl radical: C₈ to C₁₈) such as lauryl sulfate, isotridecyl sulfate or cetyl sulfate, stearyl sulfate;
- of sulfuric monoesters of ethoxylated alkanols (EO degree: 2 to 30, alkyl radical: C₁₀ to C₁₈), such as the sulfates of (poly)ethoxylated lauryl alcohol, of

30 (poly)ethoxylated isotridecanol, of (poly)ethoxylated myristyl alcohol, of (poly)ethoxylated cetyl alcohol, of (poly)ethoxylated stearyl alcohol,

- of sulfuric monoesters of ethoxylated alkylphenols (EO degree: 2 to 30, alkyl radical: C₄ to C₁₈),
- of alkyl sulfonic acids (alkyl radical: C₈ to C₁₈) such as laurylsulfonate and

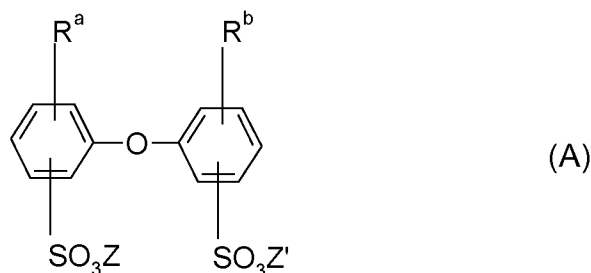
35 isotridecylsulfonate,

- of mono-, di-, and trialkylarylsulfonic acids (alkyl radical: C₄ to C₁₈) such as dibutyl-naphthylsulfonate, cumylsulfonate, octylbenzenesulfonate, nonylbenzenesulfonate, dodecylbenzenesulfonate, and tridecylbenzenesulfonate,
- of sulfuric monoesters of di- or tristyrilphenol ethoxylates (EO degree: 2 to 30);

- of monoesters and diesters of phosphoric acid, including their mixtures with the corresponding triesters, more particularly their esters with C₈-C₂₂ alkanols, (poly)ethoxylated C₈-C₂₂ alkanols, C₄-C₂₂ alkylphenols, (poly)ethoxylated C₄-C₂₂ alkylphenols, or (poly)ethoxylated di- or tristyrylphenols.

5

Examples of suitable anionic emulsifiers are also the compounds, indicated below, of the general formula A



- 10 in which R^a and R^b are hydrogen or C₄-C₁₄ alkyl and are not simultaneously hydrogen, and Z and Z' are suitable cations, examples being alkali metal ions and/or ammonium ions. Preferably, R¹ and R² are hydrogen or linear or branched alkyl radicals having 6 to 18 C atoms, and more particularly having 6, 12 or 16 C atoms, and R^a and R^b are not both simultaneously hydrogen. Z and Z' are preferably sodium, potassium or ammonium ions with sodium being particularly preferred. Particularly advantageous compounds are those in which Z and Z' are sodium, R^a is a branched alkyl radical having 12 C atoms, and R^b is hydrogen or has one of the non-hydrogen definitions indicated for R^a. Use is frequently made of technical mixtures which have a fraction of 50% to 90% by weight of the monoalkylated product, an example being Dowfax® 2A1
- 20 (trademark of the Dow Chemical Company).

- In another embodiment of the invention, the latex of the polymer P1 comprises at least one non-ionic surface-active substance, more particularly at least one non-ionic emulsifier. Suitable non-ionic emulsifiers are, commonly, ethoxylated alkanols having 8 to 36 C atoms, more particularly 10 to 22 C atoms, in the alkyl radical, and ethoxylated mono-, di-, and trialkylphenols having, commonly, 4 to 12 C atoms in the alkyl radicals, the ethoxylated alkanols and alkylphenols commonly having a degree of ethoxylation in the range from 3 to 50.

- 30 In a further embodiment of the invention, the latex of the polymer P1 comprises at least one cationic surface-active substance, more particularly at least one cationic emulsifier. Cationic emulsifiers comprise quaternary ammonium salts, for example trimethyl- and triethyl-C₆-C₃₀-alkylammonium salts such as cocotrimethylammonium salts, trimethylcetyl ammonium salts, dimethyl- and diethyl-di-C₄-C₂₀-alkylammonium salts

such as didecyldimethylammonium salts and dicocodimethylammonium salts, methyl- and ethyl-tri-C₄-C₂₀-alkylammonium salts such as methyltrioctylammonium salts, C₁-C₂₀-alkyl-di-C₁-C₄-alkylbenzylammonium salts such as triethylbenzylammonium salts and cocobenzyltrimethylammonium salts, ethoxylated and quaternized C₆-C₃₀-alkylamines (degree of ethoxylation typically 2 to 49), for example quaternization products of ethoxylated oleylamine with a degree of ethoxylation of 2 to 20, in particular 4 to 8, methyl- and ethyl-di-C₄-C₂₀-alkylpoly(oxyethyl)ammonium salts, for example didecylmethylpoly(oxyethyl)ammonium salts, N-C₆-C₂₀-alkylpyridinium salts, for example N-laurylpyridinium salts, N-methyl- and N-ethyl-N-C₆-C₂₀-alkylmorpholinium salts, and N-methyl- and N-ethyl-N'-C₆-C₂₀-alkylimidazolium salts, in particular the formates, acetates, propionates, hydrogencarbonates, sulfates and methylsulfates.

In a particular embodiment of the invention, the latex of the polymer P1 comprises a combination of at least one anionic surfactant and at least one non-ionic surfactant, more particularly a combination of at least one anionic emulsifier and at least one non-ionic emulsifier.

In a particular embodiment of the invention, the latex of the polymer P1 comprises a combination of at least one cationic surfactant and at least one non-ionic surfactant, more particularly a combination of at least one cationic emulsifier and at least one non-ionic emulsifier.

Other suitable surfactants are found in, for example, Houben-Weyl, Methoden der organischen Chemie, volume 14/1, Makromolekulare Stoffe, Georg Thieme Verlag, Stuttgart, 1961, pp. 192 to 208.

The aqueous latex of the polymer P1 can be principally prepared by any methods for preparing an aqueous latex from ethylenically unsaturated monomers. Preferably, the preparation of the latex of polymer P1 includes the free-radical aqueous emulsion polymerisation of the monomers M1 that constitute the polymer P1.

With this process, a free-radical aqueous emulsion polymerisation of the ethylenically unsaturated monomers M1 is preferably carried out according to a monomer feed process, in which, preferably, at least one particulate seed polymer is introduced in the initial charge in the polymerisation reactor. "Introduce in the initial charge" in this context means that the seed polymer either is added before the beginning of the polymerisation or is formed in the polymerisation reactor before the actual emulsion polymerisation, by means of emulsion polymerisation *in situ*. A monomer feed process means, here and below, that at least 80% and more particularly at least 90% of the

monomers to be polymerized are charged under polymerisation conditions to a polymerisation reactor which already contains a first particulate seed polymer, typically in the form of an aqueous dispersion of the seed polymer.

- 5 The skilled worker understands the term "seed polymer" to refer to a finely divided polymer in the form of an aqueous polymer dispersion. The weight-average particle size of the seed polymers used in the process of the invention (weight average, d_{50}) is typically below 200 nm, frequently in the range from 10 to 150 nm, and more particularly in the range from 20 to 120 nm. The monomer composition of the seed
- 10 polymers is of minor importance. Suitability is possessed both by seed polymers which are constructed predominantly of vinylaromatic monomers, and more particularly of styrene (so-called styrene seed), and by seed polymers which are composed predominantly of C_1 - C_{10} alkylacrylates and/or C_1 - C_{10} alkylmethacrylates such as of a mixture of butyl acrylate and methyl methacrylate for example. Besides these principal
- 15 monomers which account typically for at least 80% and more particularly at least 90% by weight of the seed polymer, the seed polymers may also comprise, in copolymerized form, different monomers, more particularly those having an increased water-solubility, examples being monomers having at least one acid function and/or neutral monomers with increased water-solubility and/or monomers having two or more
- 20 ethylenically unsaturated double bonds (monomers M5). The fraction of such monomers will generally not exceed 20% and more particularly 10% by weight, and is situated, where present, typically in the range from 0.1% to 10% by weight, based on the total amount of the monomers that constitute the seed polymer.
- 25 The free-radical aqueous emulsion polymerisation is performed typically in the presence of surface-active substances as described above. In the process of the preparation of the first polymer latex it is preferred to use exclusively emulsifiers. More particularly it has been found appropriate to use a combination of at least one anionic and at least one nonionic emulsifier as surface-active substance.
- 30 Typically, the surface-active substances are used in amounts of 0.1% to 10% by weight, more particularly in amounts of 0.2% to 5% by weight, based on the weight of the monomers M1 to be polymerized.
- 35 The initiators used for the free-radical emulsion polymerisation are typically substances that form free radicals, including peroxides, hydroperoxides, redox initiators and azo-initiators.

Suitable initiators for the emulsion polymerisation are organic or inorganic peroxide compounds, i.e., compounds having at least one peroxide or hydroperoxide group, examples being ammonium salts and alkali metal salts of peroxodisulfuric acid, e.g., sodium peroxodisulfate, or hydrogen peroxide or organic peroxides, e.g. diacetyl
5 peroxide, di-tert-butyl peroxide, diamyl peroxide, dioctanoyl peroxide, didecanoyl peroxide, dilauroyl peroxide, dibenzoyl peroxide, bis(o-tolyl) peroxide, succinyl peroxide, tert-butyl peracetate, tert-butyl permaleinate, tert-butyl perisobutyrate, tert-butyl perpivalate, tert-butyl peroctoate, tert-butyl perneodecanoate, tert-butyl perbenzoate, tert-butyl peroxide, tert-butyl hydroperoxide, cumene hydroperoxide, tert-
10 butyl peroxy-2-ethylhexanoate, and diisopropyl peroxidicarbamate,.

Also suitable are what are called reduction-oxidation (redox) initiator systems. The redox initiator systems are composed of at least one, usually inorganic reducing agent and one organic or inorganic oxidizing agent. The oxidizing component comprises, for
15 example, the peroxide compounds already stated above. The reducing components comprise, for example, alkali metal salts of sulfurous acid, such as sodium sulfite, sodium hydrogen sulfite, alkali metal salts of disulfurous acid such as sodium disulfite, bisulfite addition compounds with aliphatic aldehydes and ketones, such as acetone bisulfite, or reducing agents such as hydroxymethanesulfinic acid and its salts, or
20 ascorbic acid. The redox initiator systems can be used in combination with soluble metal compounds whose metallic component is able to exist in a plurality of valence states. Typical redox initiator systems are exemplified by ascorbic acid/iron(II) sulfate/sodium peroxodisulfate, tert-butyl hydroperoxide/sodium disulfite, and tert-butyl hydroperoxide/Na hydroxymethanesulfinate. The individual components, the reducing
25 component, for example, may also be mixtures, an example being a mixture of the sodium salt of hydroxymethanesulfinic acid with sodium disulfite.

Particularly suitable are azo-initiators. Azo initiators include compounds having a diazo moiety -N=N- which carries two aliphatic or cycloaliphatic radicals. Examples of these
30 are 2,2'-azobisisobutyronitrile, 2,2'-azobis(2-methylbutyronitrile), 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide], 1,1'-azobis(1-cyclohexanecarbonitrile), 2,2'-azobis(2,4-dimethylvaleronitrile), 4,4'-azobis-(4-cyanopentanoate) and its salts, 2,2'-azobis(N,N'-dimethyleneisobutyroamidine) salts such as the dihydrochloride, and 2,2'-azobis(2-amidinopropane) salts such as the dihydrochloride.

35
Preferably, the initiator is water soluble. Water soluble initiators are e.g. the aforementioned inorganic peroxides and hydroperoxides, the redox initiators and ionic azo initiators, such as 4,4'-azobis-(4-cyanopentanoate) and its salts,

2,2'-azobis(N,N'-dimethyleneisobutyroamidine) salts such as the dihydrochloride, and 2,2'-azobis(2-amidinopropane) salts such as the dihydrochloride.

5 The stated initiators are used mostly in the form of aqueous solutions, the lower concentration being determined by the amount of water that is acceptable in the dispersion, and the upper concentration by the solubility of the respective compound in water. Generally speaking, the concentration is 0.1% to 30%, preferably 0.5% to 20%, more preferably 1.0% to 10%, by weight, based on the solution.

10 The amount of initiators is generally 0.1% to 10% by weight, preferably 0.2% to 5% by weight, based on the monomers to be polymerized. It is also possible for two or more different initiators to be used for the emulsion polymerisation.

15 In the polymerisation of the monomers M1, it is possible to use chain transfer agents which contain halogen atoms. These halogen atoms are transferred to the polymer chain and thus to the polymer P1. Chain transfer agents can be used in amounts of 0.01 to 10% by weight, in particular from 0.1 to 5% by weight, for example, based on the monomers M1 to be polymerized. By this means, the molar mass of the polymer is reduced. If appropriate, it is of advantage to add the regulator in the course of the
20 polymerisation over a relatively long period, parallel, for example, with the addition of the monomers M1. The addition may then be made at a continuous feed rate or with an increasing or decreasing feed rate.

The emulsion polymerisation of the monomers M1 is preferably performed as a feed
25 process, i.e., at least 80%, in particular at least 90% of the monomers M1 to be polymerized are added to the polymerisation reactor in the course of the polymerisation under polymerisation conditions. The addition may be made continuously or in stages. In the course of the polymerisation the monomer composition may be altered once, a number of times or else continuously (gradient procedure).

30 According to a preferred procedure, the polymerisation of the monomers M1 to form the latex P1 is performed in a manner to achieve that a major portion of the halogen atoms bound to the polymer P1 are located close to the surface of the polymer particles of the polymer P1. This can principally be achieved by a sequential emulsion
35 polymerisation which comprises

- i.1) providing an aqueous polymer latex of a first polymer P1' formed essentially from monoethylenically monomers M1.1 having no covalent bound halogen atoms, by emulsion polymerisation of monomers M1.1, and

- i.2) emulsion polymerisation of ethylenically unsaturated monomers M1', comprising the monomers M1.2 having a covalent bound halogen atom or a mixture thereof with monoethylenically monomers M1.1 having no covalent bound halogen atoms or emulsion polymerisation of the remainder of the monomers M1.1 and optionally the monomers M1.2 having a covalent bound halogen atom in the presence of a chain transfer agent having at least one covalent bound halogen atom.

The sequential emulsion polymerisation can be easily performed as a one-pot process, i.e. the polymerisation of the latex of the polymer P1' is performed until a conversion of the monomers forming the polymer P1' is at least 70% or at least 80%, e.g. from 70 to 99% and especially from 80 to 95% of the monomers forming the polymer P1' and then the remainder of the monomers M1 containing the monomers M1.2 and/or the chain transfer agent is introduced into the polymerisation vessel and the emulsion polymerisation is continued. The amount of monomers forming the polymer latex P' will be generally from 50 to 90% of the total amount of monomers M1.

If the emulsion polymerisation of the monomers M1 is performed as a feed process, this can be easily achieved by altering the monomer composition in the feed at a time, when the majority of the monomers M1 to be polymerized, in particular at least 60% and especially at least 70%, e.g. from 60 to 95%, in particular from 70 to 90% by weight, have been introduced into the polymerisation vessel under polymerisation conditions and then the remainder of the monomers M1 containing the monomers M1.2 and/or the chain transfer agent is introduced into the polymerisation vessel and the emulsion polymerisation is continued.

Typically, parallel to the addition of monomer, at least a portion or the entirety of the polymerisation initiator is added. At least 80% of the polymerisation initiator needed for the emulsion polymerisation is typically added, more particularly 85% to 95% of the polymerisation initiator, to the polymerisation reactor in the course of the polymerisation reaction. The polymerisation initiator may be added with a constant rate of addition or with a changing rate of addition, for example, a decreasing or increasing rate.

For the emulsion polymerisation of the monomers M1, polymerisation temperature and polymerisation pressure are of minor importance. The emulsion polymerisation takes place typically at temperatures in the range from 30 to 130°C, preferably in the range from 50 to 100°C. The polymerisation pressure is situated customarily in the region of atmospheric pressure, i.e., at ambient pressure, but may also be slightly above or below, in the range, for example, of 800 to 1500 mbar.

The polymerisation medium for the emulsion polymerisation of the monomers M1 may be composed either just of water or of mixtures of water and water-miscible liquids such as C₁-C₄-alkanols or C₂-C₄ polyols. It is preferred to use just water.

5

The aqueous latex of the polymer P1 obtained in step i. of the inventive process can be used in the following step ii. without further purification. However, it is also possible to perform a physical or chemical desodorisation prior to polymerising the monomers M2 in step ii. of the inventive process. It is also possible to dilute the latex to the desired concentration.

10

In step ii. of the process according to the present invention, the monomers M2 are polymerized in the latex of the polymer P1 provided in step i. of the claimed process. In contrast to the processes described in prior art, the polymerisation can be performed at relatively high concentrations of the polymer latex of the polymer P1. The concentration of the polymer P1 in the latex, wherein the polymerisation of monomers M2 is performed, is preferably in the range from 20 to 70% by weight, in particular from 30 to 65% by weight, based on the total weight of the latex.

15

In step ii. of the process according to the present invention, the monomers M2 are polymerized in the presence of elemental copper and at least one organic compound having at least one nitrogen atom which organic compound is capable of forming a complex with copper ions. Without being bound to theory, it is believed that the polymerisation of the monomers M2 proceeds according to single-electron transfer living radical polymerisation mechanism (SET LRP), where the polymer P1, i.e. the positions to which the halogen atoms are bound, act as an inimer which is activated by copper atoms from the elementary copper which is present in the reaction medium. Presumably, the elemental copper, assisted by the nitrogen containing organic compound, induces a cleavage of the halogen-carbon bond in the polymer P1, thereby generating a radical at the site to which the halogen atom was bound. This radical then initiates the polymerisation of monomers M2. The polymerisation reaction presumably terminates by recombination with the intermediately formed copper halide, thereby leading to a reduction of copper halide and formation of a halogen-carbon bond. Hence, no further conventional polymerisation initiators will generally be used.

25

30

35

By the process according to step ii., an efficient and smooth polymerisation of the monomers M2 is achieved with elemental copper. This is rather surprising since the polymerisation of the monomers M2 involves a reaction between multiple, immiscible

phases, namely the elemental copper on one hand and the water-insoluble polymer P1 on the other hand. The process provides high grafting efficiencies.

5 The form of the elemental copper used in step ii. is of minor importance. The elemental, i.e. metallic, copper may be present in any form, e.g. in the form of copper powder, copper wire, copper granules, copper plates and even in the form of plated parts of the polymerisation reactor which are in contact with the aqueous latex of the polymer P1 such as copper plated stirrer or copper plated walls of the polymerisation reactor. It is advantageous to use the copper in the form of a coarse material, i.e. not in the form of
10 a fine dust or powder, in order to facilitate removal of the elemental copper from the latex formed. Hence, in a particular embodiment of the invention, the elemental copper is present in the form of copper wire or copper plated parts of the polymerisation reactor which are in contact with the aqueous latex of the polymer P1.

15 The purity of the elemental, i.e. metallic, copper may be according to conventional grades of elemental copper. Minor amounts of other metals or oxides do not interfere with the reaction. In general, the copper has a purity of at least 90%.

According to the claimed process, the polymerisation of the monomers M2 is
20 performed in the presence of at least one organic compound having at least one, e.g. 1, 2, 3 or 4 nitrogen atoms and being capable of forming a complex with copper ions. Preferably, this compound is selected from bi- or multidentate compounds having 2, 3 or 4 nitrogen atoms, wherein the nitrogen atoms are arranged in a manner that the compound is capable of forming a chelate with copper ions. It is advantageous, if the
25 nitrogen atoms of these compounds do not carry hydrogen atoms. In particular, the nitrogen atoms are present in the form of secondary imino groups which may or may not be part of an aromatic heterocycle such as a pyridine ring or in the form of tertiary aliphatic or cycloaliphatic amino groups.

30 Suitable examples of compounds that are capable of forming a chelate with copper ions include but are not limited to

- 2,2'-bipyridine,
- 2,2':6'2"-terpyridine,
- N,N-bis-(2-pyridylmethyl)octylamine,
- 35 - bis-[(2-pyridyl)methyl]amine,
- tris-[(2-pyridyl)methyl]amine,
- N,N,N',N'-tetrakis-[(2-pyridyl)methyl]ethylenediamine,
- N,N,N',N'-tetramethylethylenediamine,
- N,N,N',N'',N''-pentamethyldiethylentriamine,

- 1,1,4,7,10,10-hexamethyltriethylenetetramine,
- tris[2-(dimethylamino)ethyl]amine,
- N,N-Dimethyl-N'-[1-pyridin-2-yl-methylidene]-ethane-1,2-diamine,
- 1,4,8,11-tetraaza-1,4,8,11-tetramethylcyclotetradecane and
- 5 - N-propyl-(2-pyridyl)methanimine.

The organic compound having at least one nitrogen atom and being capable of forming a complex with copper ions are normally used in amounts in the range from 0.01 to 1 equivalent (eq.) per halogen atom, in particular from 0.1 to 0.9 eq. per halogen atom
10 present in the latex of the polymer P1.

The polymerisation of the monomers M2 in the presence of elemental copper may be assisted by the addition of copper (II) salts, in particular copper (II) halides. However, such an addition is not necessary. Hence, according to a particular embodiment of the
15 invention, the polymerisation of monomers M2 is performed in the absence of copper salts. According to another particular embodiment of the invention, at least one Cu(II) salt is added to the latex of the polymer P1, wherein the polymerisation of monomers M2 is performed. In this embodiment, the least one Cu(II) salt is added in an amount from 0.01 to 1 eq. in particular in an amount from 0.1 to 0.5 eq. per halogen atom
20 present in the latex of the polymer P1.

For the polymerisation of the monomers M2, polymerisation temperature and polymerisation pressure are of minor importance. The emulsion polymerisation takes place typically at temperatures in the range from 30 to 150°C, preferably in the range
25 from 50 to 120°C. The polymerisation pressure is situated customarily in the region of atmospheric pressure, i.e., at ambient pressure, but may also be slightly above or below, in the range, for example, of 800 to 1500 mbar.

The emulsion polymerisation of the monomers M2 is preferably performed as a feed
30 process, i.e., at least 80%, in particular at least 90% of the monomers M2 to be polymerized are added to the latex of the polymer P1 in the course of the polymerisation under polymerisation conditions. The addition may be made continuously or in stages. In the course of the polymerisation, the monomer composition may be altered once, a number of times or else continuously (gradient
35 procedure).

The polymerisation of the monomers M2 in the latex of the polymer P1 can be performed formed immediately after the preparation of the polymer P1, i.e. in the polymerisation mixture, obtained by emulsion polymerisation of the monomers M1.

However, it is also possible to use the latex of the polymer P1 as a stock latex, as the latex of the polymer P1 is highly stable and can be used after weeks or month in the polymerisation of the monomers M2. Hence, the process of the invention allows for the preparation of large amount of the first polymer latex of the polymer P1 and then to
5 perform in one or more different runs the polymerisation of the monomers M2.

The type of ethylenically unsaturated monomer M2 to be polymerized is of minor importance. For most purposes, however, the majority of monomers M2 will be monoethylenically unsaturated compounds. In general, the monomers M2 comprise at
10 least 95% by weight, in particular at least 99% by weight, based on the total amount of monomers M2, of monoethylenically unsaturated monomers.

It has been found to be advantageous, if the majority of the monomers M2, i.e. at least 50% by weight, in particular at least 90% by weight have a solubility in water of at least
15 0,1 g/l at 25°C and 1 bar.

The process of the present invention is particularly suitable for preparing polymer latexes which are functionalized, i.e. which carry grafted polymer chains carrying functional groups.
20

Therefore, in a preferred embodiment of the invention, the monomers M2 to be polymerized in step ii. of the claimed process comprise at least 20% by weight, in particular at least 50% by weight, at least 70% by weight, based on the total amount of monomers M2, of at least one monoethylenically unsaturated monomer M2.1 having
25 one ore more functional groups, selected from the group consisting of hydroxyl groups (OH), carboxyl groups (COOH), carbamoyl groups (CONH₂), NH-C(O)H, SO₃H, PO₃H₂, poly-C₂-C₄-alkylene ether groups, amino groups, ammonium groups, N-heterocyclic groups, lactone groups, carbonate groups, aldehyde groups, keto groups, urea groups and urethane groups. The remainder are principally monoethylenically unsaturated
30 monomers which do not carry such a functional group. These monomers are hereinafter termed as monomers M2.2.

Examples of monomers M2.1 are selected from the groups consisting of monoethylenically unsaturated C₃-C₆-monocarboxylic acids, the amides thereof, the
35 hydroxyl-C₂-C₄-alkylesters thereof, esters of monoethylenically unsaturated C₃-C₆-monocarboxylic acids with poly-C₂-C₄-alkylene glycols or poly-C₂-C₄-alkylene glycol monoethers, vinyl- and allylethers of poly-C₂-C₄-alkylene glycols or poly-C₂-C₄-alkylene glycol monoethers, monoethylenically unsaturated monomers having a mono- or oligosaccharide moiety, monoethylenically unsaturated sulfonic acids,

monoethylenically unsaturated phosphonic acids, monoethylenically unsaturated monomers having an urea group, monoethylenically unsaturated monomers carrying at least one amino group, monoethylenically unsaturated monomers carrying at least one quaternized ammonium group, N-vinyl lactames, monoethylenically unsaturated ketones and vinyl substituted N-heteroaromatic compounds. Particular preferred examples for monomers M2.1 are the monomers mentioned above as monomers M1.1b.

Particular preferred examples for monomers M2.2 are the monomers mentioned above as monomers M1.1a.

In particularly preferred monomers M2, the ethylenically unsaturated double bond is in the form of an acrylate or methacrylate group or in the form of a N-vinyl group, a vinylether or a vinylester group.

The weight ratio of monomer M2 and polymer P1 will be generally in the range from 1:100 to 10:1, in particular from 1:50 to 5:1, especially from 1:20 to 2:1.

By the process of the present invention a stable polymer latex is obtained, wherein the polymer particles comprise at least a first polymer P1 formed from ethylenically unsaturated monomers M1 and at least a second polymer P2 grafted to the first polymer P1, the second polymer P2 being formed from ethylenically unsaturated monomers M2.

Depending on the relative amounts of polymer P1 and monomers M2 and the concentration of the first polymer latex of the polymer P1 a polymer latex is obtained, wherein the concentration of polymer is higher than 10% by weight, in particular at least 20% by weight, especially at least 30% by weight, e.g. from 10 to 70% by weight, in particular from 20 to 70% by weight or from 30 to 65% by weight, based on the total weight of the polymer latex. The weight ratio of monomer M2 and polymer P1 will also determine the weight ratio of polymer P2 to polymer P1 which is normally in the range from 1:100 to 10:1, in particular from 1:50 to 5:1, especially from 1:20 to 2:1.

Generally, the polymer particles of the latex obtained by the process of the invention have an average particle diameter (weight average), determined by dynamic light scattering, in the range from 20 to 1500 nm, in particular from 50 to 800 nm, depending on the relative amount of monomers M2 and polymer P1 and the particle size of the polymer P1 in the first latex.

The polymer latexes obtained by the process of the invention can be used in any technical fields as described at the outset.

I. General

5

In the examples the following abbreviations are used:

AMPS: 2-Acrylamido-2-methylpropane sulfonic acid;

APEG: Polyethyleneglycol monomethylether methacrylate (M_n 480);

BPEA: 2-(2-bromopropionyloxy)ethyl acrylate;

10

HEA: 2-Hydroxyethylacrylate;

NAM: N-Acryloylmorpholine;

PAM 4000: polyethylenoxide methacrylate (Sipomer PAM 4000 by Rhodia)

PDI: polydispersity index;

PMDETA: Pentamethyl diethylenetriamine;

15

pphm: parts per hundred parts of monomers (corresponds to % by weight, based on the total amount of monomers);

ToF-SIMS: Time of Flight Secondary Ion Mass Spectrometry;

VBC: Vinylbenzylchloride

20

Emulsifier 1: 15 % aqueous solution of sodium dodecylsulfate (Disponil SDS)

2-(2-Bromopropionyloxy) ethyl acrylate) was synthesized by esterification of 2-hydroxyethyl acrylate with 2-bromopropionylbromide according to the procedure described by K. Matyaszevski et al., *Macromolecules*, 1997, 30, 5192-5194)

25

II. Analytics:

The average particle diameter was determined by aid of photon correlation spectroscopy (PCS), also known as quasi-elastic light scattering (QELS) or dynamic light scattering (DLS). The measurement method is described in the ISO13321 standard. In this case, a highly diluted aqueous polymer dispersion ($c \sim 0.005\%$) was analyzed. Measurement configuration: HPPS from Malvern, automated with continuous flow cuvette and Gilson autosampler. Parameters: measurement temperature 22.0°C; measurement time 120 seconds (6 cycles each of 20 s); scatter angle 173°; laser wavelength 633 nm (HeNe); refractive index of medium 1.332 (aqueous); viscosity 0.9546 mPas. The measurement yields an average value of the cumulant analysis (mean of fits). The mean of fits is an average, intensity-weighted particle diameter in nm.

30
35

After grafting The intensity-weight average diameters (D) of the latex particles was measured by dynamic light scattering at a temperature of 25°C using a Zetasizer Nano Series (Nano ZS) from Malvern Instrument using the Zetasizer 6.2 software. Before measurements, the latex samples were diluted in deionized water.

5

Gas chromatography:

Gas chromatography of the polymer dispersion was performed by using a HP6890N gas chromatograph with a 30 m column (DB 5 (5% diphenyl / 95% dimethyl-polysiloxan)) applying a temperature program starting at 120 °C going to 280 °C with a rate of 8°C/min. The injection temperature was 280°C.

10

¹H-NMR:

High-resolution liquid nuclear magnetic resonance (NMR) spectroscopy analyses were carried out on the samples at 22°C using a spectrometer Bruker AC300 operating at 300 MHz and.

15

TOF-SIMS:

Measurements were carried out using a Physical Electronics TRIFT III ToFSIMS instrument operated with a pulsed 22 keV Au⁺ ion gun (ion current of 2 nA) rastered over an area of 300 µm×300 µm. An electron gun was operated in pulsed mode at low electron energy for charge compensation. Ion dose was kept below the static conditions limit. Data were analyzed using the WinCadence software. Mass calibration was performed on hydrocarbon secondary ions. Standard deviations were calculated from measurements performed on three different areas.

20

25

IR-Spectroscopy:

Measurements were performed on a Nicolet iS10 spectrometer with a diamond crystal and DTGS KBr detector. The data were measured with a resolution of 4 cm⁻¹ from 525 cm⁻¹ to 4000 cm⁻¹. A background spectrum was collected and subtracted from the spectrum of the powder sample.

30

Dialysis:

The latices were dialyzed in water for 2 weeks using a Spectra/Por® Dialysis Membrane, MWCO : 12-14,000.

35

Electrolyte Stability:

A drop of the dispersion is added to 5 mL of an aqueous solution of CaCl₂. The solutions hat the following electrolyte concentrations: 0.05 wt%, 0.1 wt%, 0.25 wt%, 0.5 wt%, 0.75 wt%, 1 wt%, 2 wt%, 5 wt%, 10 wt%, 15 wt% or 20 wt%. The stability was

assessed by determining the highest salt concentration of the solution into which the dispersion could be dropped without visible coagulation of the latex.

Freeze Thaw Stability:

- 5 2 mL of the grafted dispersion was frozen for 2 h and thawed. This cycle was repeated for three times. The status of the dispersion was judged by its colloidal stability. Instable latices showed an increase in viscosity and/or visible phase separation.

10 III. Preparation of Functionalized Polymer Latex

Reference Example 1: Dispersion without functionalization (R-1)

- A monomer emulsion was prepared from 335.8 g butylacrylate, 786.4 g
15 methylmethacrylate, 27.8 g butandiol diacrylate, 101.2 g emulsifier 1, 20.3 g sodium hydrogen carbonate solution (6 wt% aqueous solution) and 1061.3 g deionized water. An initiator solution was prepared from 184.6 g of deionized water, 11.5 g 4,4'-azobis (4-cyanovaleric acid) and 45.3 g of a 10 wt.% aqueous solution of NaOH. 381.9 g of deionized water and 10 wt% of the initiator solution (24.1 g) were charged
20 into a 2-liter reactor equipped with a thermocouple, a cooling condenser and a paddle stirrer. The reaction mixture was heated at 70°C for 15 minutes. The monomer emulsion and residual initiator solution were gradually added to the reactor for a total of 180 minutes. After monomer addition was complete, the temperature was held for 60 minutes at 70°C. Afterwards the dispersion was cooled to room temperature. The
25 obtained latex had a solid content of 40 %. The particle diameter was 112 nm with PDI of 0.02.

Reference Example 2: Dispersion containing 0.1 ppm 2-(2-bromopropionyloxy)ethyl acrylate) (R-2)

- 30 A monomer emulsion was prepared from 262 g deionized water, 26.5 g emulsifier 1, 5.6 g of a 6 wt% aqueous sodium hydrogen carbonate solution, 88 g butylacrylate, 190 g methylmethacrylate, and 7.25 g butandiol diacrylate. An initiator solution was prepared from 48.8 g of deionized water, 3 g 4,4'-azobis (4-cyanovaleric acid) and 11.5 g of a 10
35 wt.% aqueous solution of NaOH. 115.9 g of deionized water and 10 wt % (6.3 g) of the initiator solution were charged into a 2-liter reactor equipped with a thermocouple, a cooling condenser and a paddle stirrer containing, and the mixture was heated at 70°C for 15 minutes. Then, the addition of monomer emulsion and the remaining initiator solution was started and the

monomer emulsion was gradually fed to the reactor within 180 minutes while the remaining initiator solution was fed during 215 minutes into the reactor, while keeping the reaction temperature at 70°C. After complete addition of the monomer emulsion, a monomer mixture of 0.3 g 2-(2-bromopropionyloxy) ethyl acrylate), 15.2 g
5 methylmethacrylate and 0.5 g butandioldiacrylat was added during 30 minutes, while keeping the reaction temperature at 70°C. After having completed the monomer addition, the reaction mixture was stirred at 70 °C for further 60 minutes and afterwards cooled to room temperature. The final latex had a solid content of 39 %. The particle diameter was 110 nm with PDI = 0.02. The conversion of 2-(2-bromopropionyloxy)
10 ethyl acrylate), as determined by gas chromatography, was 95 %.

Reference Example 3: Dispersion containing 2.4 pphm 2-(2-bromopropionyloxy) ethyl acrylate) (R-3)

A monomer emulsion was prepared from 261.6 g deionized water, 26.5 g emulsifier 1,
15 5.7 g of a 6 wt% aqueous sodium hydrogen carbonate solution, 87.6 g butylacrylate, 190.1 g methylmethacrylate, and 7.3 g butandioldiacrylat. An initiator solution was prepared from 48.2 g of deionized water, 3 g 4,4'-azobis (4-cyanovaleric acid) and 11.7 g of a 10 wt.% aqueous solution of NaOH.

126.6 g of deionized water and 10 wt % (6.3 g) of the initiator solution were charged into
20 a 2-liter reactor equipped with a thermocouple, a cooling condenser and a paddle stirrer containing, and the mixture was heated at 70°C for 15 minutes. Then, the addition of monomer emulsion and the remaining initiator solution was started and the monomer emulsion was gradually fed to the reactor within 180 minutes while the remaining initiator solution was fed during 215 minutes into the reactor, while keeping
25 the reaction temperature at 70°C. After complete addition of the monomer emulsion, a monomer mixture of 7.5 g 2-(2-bromopropionyloxy) ethyl acrylate), 15.0 g methylmethacrylate and 0.6 g butandioldiacrylat was added during 30 minutes, while keeping the reaction temperature at 70°C. After having completed the monomer addition, the reaction mixture was stirred at 70 °C for further 60 minutes and afterwards
30 cooled to room temperature.

The final latex had a solid content of 39 %. The particle diameter was 110 nm with PDI = 0.02. The conversion of 2-(2-bromopropionyloxy) ethyl acrylate), as determined by gas chromatography was 95 %.

35 Reference Example 4: Dispersion containing 4.6 pphm 2-(2-bromopropionyloxy) ethyl acrylate) (R-4)

A monomer emulsion was prepared from 262.0 g deionized water, 26.5 g emulsifier 1, 5.4 g of a 6 wt% aqueous sodium hydrogen carbonate solution, 87.6 g butylacrylate,

190.1 g methylmethacrylate, and 7.3 g butandioldiacrylat. An initiator solution was prepared from 48.2 g of deionized water, 3 g 4,4'-azobis (4-cyanovaleric acid) and 11.6 g of a 10 wt.% aqueous solution of NaOH.

- 138 g of deionized water deionized water and 10 wt % (6.3 g) of the initiator solutio
5 were charged into a 2-liter reactor equipped with a thermocouple, a cooling condenser and a paddle stirrer containing, and the mixture was heated at 70°C for 15 minutes. Then, the addition of monomer emulsion and the remaining initiator solution was started and the monomer emulsion was gradually fed to the reactor within 180 minutes while the remaining initiator solution was fed during 215 minutes into the reactor, while
10 keeping the reaction temperature at 70°C. After complete addition of the monomer emulsion, a monomer mixture of 14.9 g 2-(2-bromopropionyloxy) ethyl acrylate), 15.0 g methylmethacrylate and 0.7 g butandioldiacrylat was added during 30 minutes. After having completed the monomer addition, the reaction mixture was stirred at 70 °C for further 60 minutes and afterwards cooled to room temperature.
- 15 The final latex had a solid content of 39 %. The particle diameter was 116 nm with PDI = 0.02. The conversion of 2-(2-bromopropionyloxy) ethyl acrylate) determined by gas chromatography was 97 %.

Reference Example 5: Dispersion containing 2.4 pphm vinylbenzylchloride (R-5)

20

- A monomer emulsion was prepared from 261.6 g deionized water, 26.5 g emulsifier 1, 5.7 g of a 6 wt% aqueous sodium hydrogen carbonate solution, 87.6 g butylacrylate, 190.1 g methylmethacrylate, and 7.3 g butandioldiacrylat. An initiator solution was prepared from 48.2 g of deionized water, 3 g 4,4'-azobis (4-cyanovaleric acid) and 11.7
25 g of a 10 wt.% aqueous solution of NaOH.
- 126.6 g of deionized water and 10 wt % (6.3 g) of the initiator solutio were charged into a 2-liter reactor equipped with a thermocouple, a cooling condenser and a paddle stirrer containing, and the mixture was heated at 70°C for 15 minutes. Then, the addition of monomer emulsion and the remaining initiator solution was started and the
30 monomer emulsion was gradually fed to the reactor within 180 minutes while the remaining initiator solution was fed during 215 minutes into the reactor, while keeping the reaction temperature at 70°C. After complete addition of the monomer emulsion, a monomer mixture of 7.5 g vinylbenzylchloride, 15.0 g methylmethacrylate and 0.6 g butandioldiacrylat was added during 30 minutes. After having completed the monomer
35 addition, the reaction mixture was stirred at 70 °C for further 60 minutes and afterwards cooled to room temperature.
- The final latex had a solid content of 39 %. The particle diameter was 115 nm with PDI = 0.02. The conversion of vinylbenzylchloride determined by gas chromatography was 99 %.

For reference examples 2 to 5 it was analytically confirmed by ToF-SIMS measurements that the Br/Cl containing monomer was located in the particle shell.

5 IV. Preparation of Core-Shell Polymer Latex

Comparative Example C1: Core Shell Latex with Hydroxyethylacrylate shell

A monomer emulsion was prepared from 197.7 g deionized water, 28.4 g emulsifier 1,
10 5.9 g of a 6 wt% aqueous sodium hydrogen carbonate solution, 88.2 g butylacrylate,
190.5 g methylmethacrylate, and 7.2g butandioldiacrylat. An initiator solution was
prepared from 48.2 g of deionized water, 3.2 g 4,4'-azobis (4-cyanovaleric acid) and
12.4 g of a 10 wt.% aqueous solution of NaOH.
115.5 g of deionised water and 10.% of an initiator solution (6.7 g), containing 48.2 g of
15 deionized water, 3.2 g 4,4'-Azobis (4-cyanoavelric acid) and 12.4g NaOH (10 wt.% in
water), were charged into a 2-liter reactor equipped with a thermocouple, a cooling
condenser and a paddle stirrer, and heated at 70°C for 15 minutes. The monomer
emulsion was gradually added to the reactor for a total of 180 minutes during 3 hours
and residual initiator solution was fed during 215 minutes. 5 minutes after the monomer
20 emulsion feed was completed, 36.8 g hydroxyethylacrylate were added during 30
minutes. After having completed the monomer addition, the reaction mixture was
stirred at 70 °C for further 60 minutes and afterwards cooled to room temperature.
The final latex had a solid content of 45%. The particle diameter was 115 nm with PDI
= 0.02.

25

General procedure for grafting of hydrophilic monomers on functionalized polymer
latices (Comparative Examples C2 to C4, Examples 5 to 21)

The latex of reference examples 1 to 5 was optionally diluted and sodium p-
30 toluenesulfonate (NMR reference 20 % by weight, based on the hydrophilic monomer)
were mixed and deoxygenated with nitrogen for 30 minutes. A deoxygenated solution
of the respective hydrophilic monomer as given in table 1, PMDETA, 0.1 M aqueous
solution of CuBr₂ or CuCl₂ (and optionally water) was added with stirring. The reaction
mixture was allowed to warm to 25°C and a piece of a copper wire (length stated in
35 table 1) was introduced. The mixture was stirred for the time given in the following table
1. The details are given in the following table 1.

Samples were periodically withdrawn from the reaction mixtures to monitor the
conversion by ¹H NMR. The results are summarized in table 1.

The obtained latices were analyzed gravimetrically with regard to the amount of water soluble polymers dissolved in the serum. The amount polymer in the serum after grafting was gravimetrically determined to < 12 % in each case.

5

In order to show that the polymerization of the hydrophilic monomer occurs on the particle surface the latex was dialyzed in order to remove residual monomers and dissolved polymer. The solid portion of the latex was investigated by IR spectroscopy. In the solid part of the dispersion peaks showing the existence of NAM on the surface could be observed (for Examples Nos. 5, 7, 8 and 9). The peak area increased with increasing amount of hydrophilic monomer added to the solution.

10

The results of freeze-thaw tests and tests of electrolyte stability are summarized in table 2.

15

Table 1:

Example	Latex ¹⁾	Hydrophilic Monomer		Ligand		I ⁵⁾	L ⁶⁾	CuBr	Cu ⁰	time	Conversion ⁷⁾	PD ⁸⁾	SC ⁹⁾
		type	g/g _{pol} ²⁾	type	g/g _{latex} ³⁾	mol eq	mol eq	eq ⁴⁾	[cm]	[h]	[%]	[nm]	[%wt]
C2	R-1	NAM	0,13	PMDETA	0,0066	0	1	0.5	1.5	5	0	n.d.	38
C3	R-4	NAM	0,15	-	-	1	0	0	0	5	0	n.d.	14
C4	R-4	NAM	0,15	-	-	1	0	0	1	5	0	n.d.	14
5	R-4	NAM	0,125	PMDETA	0,0066	1	0.6	0.09	7	6	96	140	38
6	R-4	HEA	0,125	PMDETA	0,003	1	0.5	0.1	3.5	7	97	n.d.	25
7	R-4	NAM	0,25	PMDETA	0,005	1	0.5	0.1	7	8	79	140	40
8	R-4	NAM	0,4	PMDETA	0,0035	1	0.5	0.1	3.5	7	87	n.d.	30
9	R-4	NAM	0,4	PMDETA	0,0036	1	0.5	0.1	7	6	88	260	8
10	R-2	NAM	0.05	PMDETA	0,0001	1	0.6	0.1	3.5	8	30	120	40
11	R-2	PAM 4000	0.05	PMDETA	0,0001	1	0.6	0.1	3.5	8	50	170	35
12	R-2	APEG	0.05	PMDETA	0,0001	1	0.5	0.1	3.5	8	60	120	38
13	R-2	HEA	0.04	PMDETA	0,0001	1	0.5	0.1	3.5	8	50	108	40
14	R-2	HEA	0.05	PMDETA	0,0001	1	0.5	0.1	3.5	8	20	110	42
15	R-5	HEA	0.08	PMDETA	0,0033	1	0.5	0.1	3.5	7	22	n.d.	26
16	R-3	HEA	0.08	PMDETA	0,0019	1	0.5	0.1	3.5	7	100	n.d.	25
17	R-5	NAM	0.05	PMDETA	0,0034	1	0.5	0.1	3.5	7	14	n.d.	25
18	R-3	NAM	0.05	PMDETA	0,0018	1	0.5	0.1	3.5	7	100	n.d.	24
19	R-3	AMPS	0.06	PMDETA	0,0016	1	0.4	0.1	3.5	7	38	n.d.	25

- 1) Latex from Reference Examples 1 to 5
 2) Relative amount of hydrophilic monomer [g] per polymer [g] in Reference latex.
 3) Relative amount of ligand [g] per Reference latex [g].
 5 4) mol Cu(I) per mol of organic halogen in reference latex
 5) eq of inimer (BPEA or VBC)
 6) eq mol of ligand L/ mol initiating monomer (BPEA or VBC)
 7) Conversion of hydrophilic monomer in mol-%
 8) For the latices of examples 5, 7 and 9 to 14 particle diameters (PD) were determined
 10 by dynamic light scattering.
 9) Solid content of the final latex

Table 2:

Example	Freeze Thaw Stability ¹⁾	Electrolyte Stability [wt %] ²⁾
C1	N	n.d.
C2	N	0.1
C3	N	0.1
C4	N	0.1
5	Y	n.d.
6	Y	20
7	Y	10
8	Y	20
9	Y	20
10	Y	20

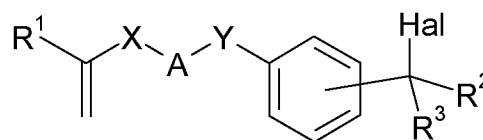
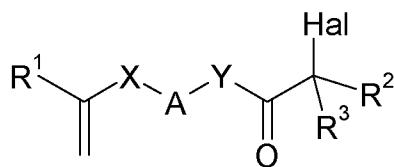
15

1) after 4 cycles

2) %wt concentration of CaCl₂ solution, until which the latex remains stable

We claim:

1. A process for the preparation of an aqueous polymer latex, wherein the polymer particles comprise at least a first polymer P1 formed from ethylenically unsaturated monomers M1 and at least a second polymer P2 grafted to the first polymer P1, the second polymer P2 being is formed from ethylenically unsaturated monomers M2 which process comprises:
 - i. providing an aqueous polymer latex of the first polymer P1 formed from ethylenically unsaturated monomers M1, where the latex contains halogen which is covalently bound to the first polymer P1,
 - ii. performing the polymerisation of monomers M2 in the latex of the polymer P1 in the presence of elemental copper and at least one organic compound having at least one nitrogen atom which organic compound is capable of forming a complex with copper ions.
2. A process for the preparation of an aqueous polymer latex as claimed in claim 1, where in step i. the monomers M1 forming the first polymer P1 comprise at least one monoethylenically monomer M1.1 having no covalent bound halogen atoms and at least a second monomer M1.2 having a covalent bound halogen atom.
3. The process as claimed in claim 2, where the halogen atom of the monomer M1.2 is chlorine or bromine which is bound at a carbon atom in the α -position of a carbonyl group or of a benzene ring.
4. The process as claimed in any of claims 2 or 3, where the monomer M1.2 has one of the following formulae



where

- Hal is chlorine or bromine,
- R¹ is hydrogen or C₁-C₄-alkyl,
- R² is hydrogen or C₁-C₄-alkyl,
- R³ is hydrogen or C₁-C₄-alkyl,
- X indicates a single bond or is O, CH₂O, C(=O)O or C(=O)NR⁴, where the carbon atom of the last 3 radicals is bound to the double bond and R⁴ is hydrogen or C₁-C₄-alkyl,

37

- Y indicates a single bond, or is O or NR⁵, where R⁵ is hydrogen or C₁-C₄-alkyl,
- A is C₂-C₁₀-alkylene or a radical A'-[O-A']_n, where A' is C₂-C₄-alkylene and n is an integer in the range from 1 to 50, or
- 5 A-Y indicates a single bond.
5. The process as claimed in any of claims 2 to 4, where the relative amount monomer M1.2 is from 0,001 to 10% by weight, based on the total amount of monomer M1.
- 10 6. The process as claimed in any of the preceding claims, where the major amount of halogen atoms bound to the polymer P1 is located close to the surface of the latex particles of the polymer P1.
- 15 7. The process as claimed in any of claims 2 to 6, where the latex of the polymer P1 is obtained by sequential emulsion polymerisation which comprises:
- i.1) providing an aqueous polymer latex of a first polymer P1' formed essentially from monoethylenically monomers M1.1 having no covalent bound halogen atoms, by emulsion polymerisation of monomers M1.1, and
- 20 i.2) emulsion polymerisation of ethylenically unsaturated monomers M1', comprising the monomers M1.2 having a covalent bound halogen atom or a mixture thereof with monoethylenically monomers M1.1 having no covalent bound halogen atoms.
- 25 8. The process as claimed in any of the preceding claims, where the latex of the polymer P1 is obtained by emulsion polymerisation of the monomers M1 in the presence of a chain transfer agent containing halogen atoms.
9. The process as claimed in any of the preceding claims, where the polymer particles in the latex of the polymer P1 have an average particle size as determined by light scattering, in the range from 20 to 500 nm.
- 30 10. The process as claimed in any of the preceding claims, where the concentration of the polymer P1 is in the range from 20 to 70% by weight, in particular from 30 to 65% by weight, based on the total weight of the latex, wherein the polymerisation of monomers M2 is performed.
- 35 11. The process as claimed in any of the preceding claims, where the elementary copper is present in the form of copper wire or copper plated parts of the

polymerisation reactor which are in contact with the aqueous latex of the polymer P1.

12. The process as claimed in any of the preceding claims, wherein the
5 polymerisation of monomers M2 is performed in the absence of copper salts.
13. The process as claimed in any of the preceding claims, where at least one Cu(II)
salt is added to the latex of the polymer P1, wherein the polymerisation of
monomers M2 is performed.
10
14. The process as claimed in claim 13, where at least one Cu(II) salt is added in an
amount from 0.01 to 1 eq. per halogen atom present in the latex of the polymer
P1.
15. The process as claimed in any of the preceding claims, where the organic
compound having at least one nitrogen atom and being capable of forming a
complex with copper ions is selected from compounds having 2, 3 or 4 nitrogen
atoms which are capable of forming a chelate with copper ions.
- 20 16. The process as claimed in claim 15, where the nitrogen atoms do not carry
hydrogen atoms.
17. The process as claimed in claims 15 or 16, where the organic compound having
at least one nitrogen atom and being capable of forming a complex with copper
ions is selected from the group consisting of
25
 - 2,2'-bipyridine,
 - 2,2':6'2"-terpyridine,
 - N,N-bis-(2-pyridylmethyl)octylamine,
 - bis-[(2-pyridyl)methyl]amine,
 - 30 - tris-[(2-pyridyl)methyl]amine,
 - N,N,N',N'-tetrakis-[(2-pyridyl)methyl]ethylenediamine,
 - N,N,N',N'-tetramethylethylenediamine,
 - N,N,N',N",N"-pentamethyldiethylentriamine,
 - 1,1,4,7,10,10-hexamethyltriethylentetramine,
 - 35 - N,N-Dimethyl-N'-[1-pyridin-2-yl-methylidene]-ethane-1,2-diamine,
 - tris[2-(dimethylamino)ethyl]amine,
 - 1,4,8,11-tetraaza-1,4,8,11-tetramethylcyclotetradecane and
 - N-propyl-(2-pyridyl)methanimine.

18. The process as claimed in any of the preceding claims, where the organic compound having at least one nitrogen atom and being capable of forming a complex with copper ions is added to the latex of the polymer P1 in an amount from 0.01 to 1 eq. per halogen atom, in particular from 0.1 to 0.9 eq. per halogen atom present in the latex of the polymer P1.
19. The process as claimed in any of the preceding claims, where the monomers M1 comprise at least 80% by weight, based on the total amount of monomers M1, of at least one monoethylenically unsaturated monomer M1.1a having no covalently bound halogen atoms and having a water solubility of at most 60 g/l at 25°C and 1013 mbar.
20. The process as claimed in claim 19, where the monomers M1.1a are selected from monovinylaromatic hydrocarbons, esters of monoethylenically unsaturated C₃-C₆-monocarboxylic acids with C₁-C₂₀-alkanols, C₅-C₈-cycloalkanols, phenyl-C₁-C₄-alkanols or phenoxy-C₁-C₄-alkanols, diesters of monoethylenically unsaturated C₄-C₆-dicarboxylic acids with C₁-C₂₀-alkanols, C₅-C₈-cycloalkanols, phenyl-C₁-C₄-alkanols or phenoxy-C₁-C₄-alkanols, amides of monoethylenically unsaturated C₃-C₆-monocarboxylic acids with C₄-C₂₀-alkylamines or di-C₂-C₂₀-alkylamines, and vinyl esters of saturated aliphatic carboxylic acids.
21. The process as claimed in any of the preceding claims, where the latex of the polymer P1 comprises at least one nonionic and/or anionic surfactant.
22. The process as claimed in any of the preceding claims, where the latex of the polymer P1 comprises at least one anionic surfactant.
23. The process as claimed in any of the claims 1 to 21, where the latex of the polymer P1 comprises at least one cationic surfactant.
24. The process as claimed in any of the preceding claims, where the majority of the monomers M2 to be polymerized in step ii. are feed to the latex or the polymer P1 under polymerisation conditions.
25. The process as claimed in any of the preceding claims, where the monomers M2 comprise at least 95% by weight, based on the total amount of monomers M2, of monoethylenically unsaturated monomers.

26. The process as claimed in any of the preceding claims, where the monomers M2 comprise at least 20% by weight, based on the total amount of monomers M2, of at least one monoethylenically unsaturated monomer M2.1 having one or more functional groups, selected from the group consisting of hydroxyl groups (OH),
5 carboxyl groups (COOH), carbamoyl groups (CONH₂), NH-C(O)H, SO₃H, PO₃H₂, poly-C₂-C₄-alkylene ether groups, amino groups, ammonium groups, N-heterocyclic groups, lactone groups, carbonate groups, aldehyde groups, keto groups, urea groups and urethane groups.
- 10 27. The process as claimed in claim 26, where the monoethylenically unsaturated monomers M2.1 are selected from the groups consisting of monoethylenically unsaturated C₃-C₆-monocarboxylic acids, the amides thereof, the hydroxyl-C₂-C₄-alkylesters thereof, esters of monoethylenically unsaturated C₃-C₆-
15 monocarboxylic acids with poly-C₂-C₄-alkylene glycols or poly-C₂-C₄-alkylene glycol monoethers, vinyl- and allylethers of poly-C₂-C₄-alkylene glycols or poly-C₂-C₄-alkylene glycol monoethers, monoethylenically unsaturated monomers having a mono- or oligosaccharide moiety, monoethylenically unsaturated sulfonic acids, monoethylenically unsaturated phosphonic acids,
20 monoethylenically unsaturated monomers having an urea group, monoethylenically unsaturated monomers carrying at least one amino group, monoethylenically unsaturated monomers carrying at least one quaternized ammonium group, N-vinyl lactames, monoethylenically unsaturated ketones and vinyl substituted N-heteroaromatic compounds.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/053124

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08F2/00 C08F257/02 C08F265/06
ADD.

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

B. FIELDS SEARCHED

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

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	VIKAS MITTAL: "Synthesis of Environmentally Responsive Polymers by Atom Transfer Radical Polymerization: Generation of Reversible Hydrophilic and Hydrophobic Surfaces", POLYMERS, vol. 2, no. 2, 12 May 2010 (2010-05-12), pages 40-56, XP55028959, DOI: 10.3390/polym2020040 paragraph [02.2] ----- -/--	1-27



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"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

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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

5 June 2012

Date of mailing of the international search report

13/06/2012

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Plehiers, Mark

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/053124

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Melissa Manuszak Guerrini ET AL: "Functionalized latexes as substrates for atom transfer radical polymerization", Macromol. Rapid Commun., 10 July 2000 (2000-07-10), pages 669-674, XP55028967, D-69451 Weinheim 2000 Retrieved from the Internet: URL:http://onlinelibrary.wiley.com/store/1 0.1002/1521-3927(20000601)21:10<669::AID-M ARC669>3.0.CO;2-6/asset/669 ftp.pdf?v=1&t= h32yx45o&s=cf2c3cf60ba60de54b9507f4d619bc5 57c697b2e [retrieved on 2012-06-05] cited in the application the whole document -----	1-27
A	ANDREW J. D. MAGENAU ET AL: "ATRP of Methacrylates Utilizing Cu II X 2 /L and Copper Wire", MACROMOLECULES, vol. 43, no. 23, 14 December 2010 (2010-12-14), pages 9682-9689, XP55028972, ISSN: 0024-9297, DOI: 10.1021/ma102051q Experimental Section; page 9683 -----	1-27