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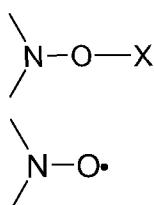
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(54) Title: COLOR FILTER COMPOSITION

(57) **Abstract:** The invention relates to a color filter composition comprising a) a photoresist binder, b) a transparent pigment, c) optionally a solvent and/or optionally a photoinitiator or a photolatent catalyst, d) a dispersant which is a polymer or copolymer obtainable by a process comprising the steps of a1) polymerizing in a first step one or more ethylenically unsaturated monomers in the presence of at least one nitroxylether having the structural element wherein X represents a group having at least one carbon atom and is such that the free radical X derived from X is capable of initiating polymerization; or a2) polymerizing in a first step one or more ethylenically unsaturated monomers in the presence of at least one stable free nitroxyl radical and a free radical initiator; wherein at least one monomer used in the steps a1) or a2) is a C₁-C₆ alkyl or hydroxy C₁-C₆ alkyl ester of acrylic or methacrylic acid; and a second step b) comprising the modification of the polymer or copolymer prepared under a1) or a2) by a transesterification reaction, an amidation, hydrolysis or anhydride modification or a combination thereof, and optionally in addition by quaternization.

Color filter composition

The present invention relates to a color filter composition and to a method for producing a color filter.

5 Typical methods for producing color filters are, for example, dyeing method, printing method, pigment dispersion method and electrodeposition method. Among them, particularly, the pigment dispersion method is widely used owing to the high precision in the position of color filter pixels, film thickness and the like, excellent durability such as light resistance and thermal resistance, and less defects of pinhole and the like. In the pigment dispersion

10 method a pigment-dispersed photosensitive resin layer is formed on a substrate and patterned into a single-color pattern. This process is repeated three times to obtain R, G, and B color filter layers.

The Japanese Patent Publication **JP2002031713 (Mitsubishi)** discloses an alkaline

15 developable composition for the manufacturing of a color filter. The composition for the color filter contains a binder resin and/or a compound having a polymerizable group, provided with an acidic group (1), a pigment (2) and a dispersing agent (3). The dispersing agent is an A-B block copolymer consisting of an A block with a quaternary ammonium base in a side chain.

20 The Japanese Patent Publication **JP2004339330 (Dainippon Printing)** discloses a method for producing a color filter by using a thermosetting ink.

The pigment dispersion for the thermosetting ink and the thermosetting ink comprise each at least a pigment, a pigment dispersant composed of a copolymer, which contains a molecular structure in which at least a constituent unit containing a specific quaternary ammonium base

25 and a constituent unit containing a specific ester structure are coupled.

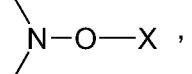
There is still a need to find further suitable dispersants having improved dispersing properties.

30 It has now been found that copolymers prepared by a controlled radical polymerization process as disclosed in the International Publication WO2006074969 (Application No. PCT/EP2006/050000 show improved dispersing properties when used as color filter compositions.

Thus, the invention relates to a color filter composition comprising

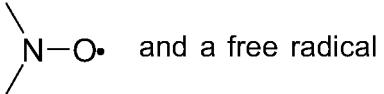
- a) a photoresist binder,
- b) a transparent pigment,
- c) optionally a solvent and/or optionally a photoinitiator or a photolatent catalyst,
- 5 d) a dispersant which is a polymer or copolymer obtainable by a process comprising the steps of

a1) polymerizing in a first step one or more ethylenically unsaturated monomers in the

presence of at least one nitroxylether having the structural element 

wherein **X** represents a group having at least one carbon atom and is such that the free radical $X\bullet$ derived from X is capable of initiating polymerization; or

a2) polymerizing in a first step one or more ethylenically unsaturated monomers in the

presence of at least one stable free nitroxyl radical 

initiator; wherein at least one monomer used in the steps a1) or a2) is a C_1 - C_6 alkyl or hydroxy C_1 - C_6 alkyl ester of acrylic or methacrylic acid; and

b) in a second step modification of the polymer or copolymer prepared under a1) or a2) by a transesterification reaction, an amidation, hydrolysis or anhydride modification or a combination thereof; and optionally in addition by quaternization.

20

Definitions

The term **photoresist binder** refers to a photosensitive resin which is preferably an acid-curable resin or a photo curable resin such as acrylate, photo curable acrylate oligomer, polyester, alkyd, melamine, urea, epoxy and phenolic resins or mixtures thereof. Acid-

25 curable resins of that kind are generally known and are described, for example, in "Ullmann's Encyclopdie der technischen Chemie", Edition 4, Vol. 15 (1978), pp. 613-628.

Preferred are (meth)acrylate/(meth)acrylic acid copolymers.

Preferable examples of copolymers are copolymers of methyl (meth)acrylate and (meth)acrylic acid, copolymers of benzyl (meth)acrylate and (meth)acrylic acid, copolymers of

30 methyl (meth)acrylate/, ethyl (meth)acrylate and (meth)acrylic acid, copolymers of benzyl

(meth)acrylate, (meth)acrylic acid and styrene, copolymers of benzyl (meth)acrylate, (meth)acrylic acid and 2-hydroxyethyl (meth)acrylate, copolymers of methyl (meth)acrylate/, butyl (meth)acrylate, (meth)acrylic acid and styrene, copolymers of methyl (meth)acrylate, benzyl (meth)acrylate, (meth)acrylic acid and hydroxyphenyl (meth)acrylate, copolymers of 5 methyl (meth)acrylate, (meth)acrylic acid and polymethyl (meth)acrylate macromonomer, copolymers of benzyl (meth)acrylate, (meth)acrylic acid and polymethyl (meth)acrylate macromonomer, copolymers of tetrahydrofurfuryl (meth)acrylate, styrene and (meth)acrylic acid, copolymers of methyl (meth)acrylate, (meth)acrylic acid and polystyrene macro-10 monomer, copolymers of benzyl (meth)acrylate, (meth)acrylic acid and polystyrene macro- monomer, copolymers of benzyl (meth)acrylate, (meth)acrylic acid, 2-hydroxyethyl (meth)- acrylate and polystyrene macromonomer, copolymers of benzyl (meth)acrylate, (meth)acrylic acid, 2-hydroxypropyl (meth)acrylate and polystyrene macro monomer, copolymers of benzyl 15 (meth)acrylate, (meth)acrylic acid, 2-hydroxy-3-phenoxypropyl (meth)acrylate and polymethyl (meth)acrylate macromonomer, copolymers of methyl (meth)acrylate, (meth)acrylic acid, 2- hydroxyethyl (meth)acrylate and polystyrene macromonomer, copolymers of benzyl (meth)- acrylate, (meth)acrylic acid, 2-hydroxyethyl (meth)acrylate and polymethyl (meth)acrylate macromonomer, copolymers of N- phenylmaleimide, benzyl (meth)acrylate, (meth)acrylic acid and styrene, copolymers of benzyl (meth)acrylate, (meth)acrylic acid, N-phenyl- 20 maleimide, mono-[2- (meth)acryloyloxyethyl] succinate and styrene, copolymers of allyl (meth)acrylate, (meth)acrylic acid, N-phenylmaleimide, mono-[2-(meth)acryloyloxyethyl] succinate and styrene, copolymers of benzyl (meth)acrylate, (meth)acrylic acid, N-phenyl- maleimide, glycerol mono(meth)acrylate and styrene, copolymers of benzyl (meth)acrylate, [omega]- carboxypolycaprolactone mono(meth)acrylate, (meth)acrylic acid, N-phenyl- 25 maleimide, glycerol mono(meth)acrylate and styrene, and copolymers of benzyl (meth)- acrylate, (meth)acrylic acid, N-cyclohexylmaleimide and styrene.

A photo curable acrylate oligomer is preferably present in addition to the photo curable resin. Photo curable acrylate oligomers usable herein include dipentaerythritol hexaacryl (DPHA), dipentaerythritol pentaacrylate (DPPA), pentaerythritol triacrylate (PETTA), trimethylol- 30 propane triacrylate (TMPTA), and trimethylolpropane triacrylate (TMPTA) and the like.

The term **transparent pigment** refers to a pigment which gives a transparently colored ink when dispersed.

The pigment may be inorganic or preferably organic, for example carbon black or pigments of the 1-aminoanthraquinone, anthanthrone, anthrapyrimidine, azo, azomethine, quinacridone, quinacridonequinone, quinophthalone, dioxazine, diketopyrrolopyrrole, flavanthrone, indanthrone, isoindoline, isoindolinone, isoviolanthrone, perinone, perylene, phthalocyanine, 5 pyranthrone or thioindigo series, including those, where applicable, in the form of metal complexes or lakes, in particular unsubstituted or partially halogenated phthalocyanines such as copper, zinc or nickel phthalocyanines, 1,4-diketo-3,6-diaryl-pyrrolo[3,4-c]pyrroles, dioxazines, isoindolinones, indanthrones, perylenes and quinacridones. Azo pigments may be, for example, mono- or dis-azo pigments from any known sub-class, obtainable, for 10 example, by coupling, condensation or lake formation.

Notably useful are the pigments described in the Colour Index, including Pigment Yellow 1, 3, 12, 13, 14, 15, 17, 24, 34, 42, 53, 62, 73, 74, 83, 93, 95, 108, 109, 110, 111, 119, 120, 123, 128, 129, 139, 147, 150, 151, 154, 164, 168, 173, 174, 175, 180, 181, 184, 185, 188, 15 191, 191:1, 191:2, 193, 194 and 199; Pigment Orange 5, 13, 16, 22, 31, 34, 40, 43, 48, 49, 51, 61, 64, 71, 73 and 81; Pigment Red 2, 4, 5, 23, 48, 48:1, 48:2, 48:3, 48:4, 52:2, 53:1, 57, 57:1, 88, 89, 101, 104, 112, 122, 144, 146, 149, 166, 168, 170, 177, 178, 179, 181, 184, 185, 190, 192, 194, 202, 204, 206, 207, 209, 214, 216, 220, 221, 222, 224, 226, 242, 248, 254, 255, 262, 264, 270 and 272; Pigment Brown 23, 24, 25, 33, 41, 42, 43 and 44; Pigment 20 Violet 19, 23, 29, 31, 37 and 42; Pigment Blue 15, 15:1, 15:2, 15:3, 15:4, 15:6, 16, 25, 26, 28, 29, 60, 64 and 66; Pigment Green 7, 17, 36, 37 and 50; Pigment Black 7, 12, 27, 30, 31, 32 and 37; Vat Red 74; 3,6-di(3',4'-dichloro-phenyl)-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione, 3,6-di(4'-cyano-phenyl)-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione and 3-phenyl-6-(4'-tert-butyl-phenyl)-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione; and mixtures and solid 25 solutions thereof.

Solvent

Normally the compositions according to the invention are dissolved in a suitable solvent before application to the substrate. Examples of such solvents include ethylene dichloride, 30 cyclohexanone, cyclopentanone, 2-heptanone, gamma-butyrolactone, methyl ethyl ketone, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, 2-methoxyethyl acetate, 2-ethoxyethyl acetate, 2-ethoxyethanol, diethyl glycol dimethyl ether, ethylene glycol monoethyl ether acetate, propylene glycol monomethyl ether, propylene glycol monomethyl ether acetate, toluene, ethyl acetate, methyl lactate, ethyl lactate, methylmethoxy propionate,

ethylethoxy propionate, methyl pyruvate, ethyl pyruvate, propyl pyruvate, N,N-dimethyl-formamide, dimethyl sulfoxide, N-methylpyrrolidone and tetrahydrofuran. Such solvents can be used individually or in combinations. Preferred examples thereof are esters, such as 2-methoxyethyl acetate, ethylene glycol monoethyl ether acetate, propylene glycol mono-

5 methyl ether acetate, methylmethoxy propionate, ethylethoxy propionate and ethyl lactate.

Photoinitiator:

Any photoinitiator or photolatent catalyst may be used when desired. The photoinitiator or photolatent catalyst is not limited. Preferred are photoinitiators selected from

- 10 1. Alpha-hydroxyketones (AHK), alpha-alkoxyketones(benzildimethylketals DBK) and alpha-aminoketones (AAK),
2. Benzophenones,
3. Mono- and bisacylphosphine oxides (BAPO),
4. Phenyl-glyoxylates,
- 15 5. Isopropylthioxanthone (ITX),
6. Oxime-esters,
7. Aminobenzoates
8. Latent acids and bases

and blends thereof.

20

Dispersant

Preferably the first polymerization step is carried out according to the polymerization reactions a1)

25

Preferably the second step b) is a transesterification reaction or amidation reaction. Particularly preferred is a transesterification reaction.

30

The transesterification preferably comprises the removal of the C₁-C₆ alcohol by-product by distillation.

In another embodiment the second step b) is a transesterification reaction followed by a quaternization.

In a specific embodiment step a1 or a2 of the above described process is carried out twice and a block copolymer is obtained wherein in the first or second radical polymerization step the monomer or monomer mixture contains 50 to 100% by weight, based on total monomers, of a C₁-C₆ alkyl or hydroxy C₁-C₆ alkyl ester of acrylic or methacrylic acid and in the second or 5 first radical polymerization step respectively, the ethylenically unsaturated monomer contains no primary or secondary ester bond.

When a block copolymer is prepared it is preferred that in the first polymerization step the monomer or monomer mixture contains from 50 to 100% by weight based on total monomers 10 of a C₁-C₆ alkyl or hydroxy C₁-C₆ alkyl ester of acrylic or methacrylic acid and in the second polymerization step the ethylenically unsaturated monomer is 4-vinyl-pyridine or pyridinium-ion, 2-vinyl-pyridine or pyridinium-ion, vinyl-imidazole or imidazolinium-ion, dimethylacrylamide, 3-dimethylaminopropylmethacrylamide, styrene, α -methyl styrene, p-methyl styrene or p-tert-butyl-styrene.

15

In a specific embodiment of the invention the block copolymer is a gradient block copolymer.

As mentioned above it is mandatory that the polymer or copolymer is prepared by controlled free radical polymerization (CFRP). Solomon et al. in US 4,581,429 have firstly described 20 such processes using stable free nitroxyl radicals as controlling agents. These are the steps defined under a1) and a2) above.

U.S. 4,581,429 discloses a free radical polymerization process by controlled or "living" growth of polymer chains, which produces defined oligomeric homopolymers and copolymers, 25 including block and graft copolymers. Disclosed is the use of initiators of the partial formula R'R"NO-X. In the polymerization process the free radical species R'R"NO• and •X are generated. •X is a free radical group, e.g. a tert.-butyl or cyanoisopropyl radical, capable of polymerizing monomer units containing ethylene groups.

30 A variation of the above process is disclosed in US 5 322 912 (Xerox) wherein the combined use of a free radical initiator and a stable free radical agent of the basic structure R'R"NO• for the synthesis of homopolymers and block copolymers is described.

These processes are useful for the preparation of homo-, random-, block-, tapered-, graft- or comb (co)polymers, which have a narrow molecular weight distribution and hence a low polydispersity index.

For example the structural element $\text{N}-\text{O}-\text{X}$ or $\text{N}-\text{O}\cdot$ may be part of a cyclic ring system or substituted to form a acyclic structure.

Suitable nitroxylethers and nitroxyl radicals are principally known from US-A-4 581 429 or EP-A-621 878.

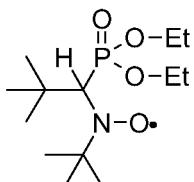
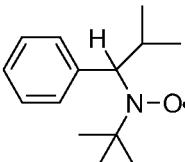
Particularly useful are the open chain compounds described in WO 98/13392 (Akzo), WO 10 99/03894 (Ciba) and WO 00/07981 (Ciba), the piperidine derivatives described in WO 99/67298 (Ciba) and GB 2335190 (Ciba) or the heterocyclic compounds described in GB 2342649 (Ciba) and WO 96/24620 (Atochem).

Further suitable nitroxylethers and nitroxyl radicals are described in WO 02/4805 (Ciba) and 15 in WO 02/100831 (Ciba).

Nitroxylethers and nitroxyl radicals with more than one nitroxyl group in the molecule are for example described in US 6,573,347 (Ciba), WO 01/02345 (Ciba) and WO 03/004471 (Ciba). These compounds are ideally suitable when branched, star or comb (co)polymers are 20 prepared.

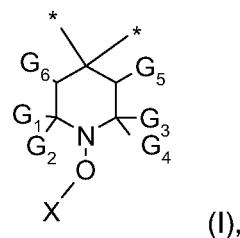
In the context of the present invention the terms alkoxyamine and nitroxylether are used as equivalents.

25 Stable free radicals having a structural element $\text{N}-\text{O}\cdot$ are for example disclosed in EP-A-621 878 (Xerox).

Examples, such as  or  are given in WO96/24620 (Atochem).

Preferably the structural element $\text{N}-\text{O}-\text{X}$ or $\text{N}-\text{O}\bullet$ is part of a 5 or 6-membered heterocyclic ring, which optionally has an additional nitrogen or oxygen atom in the ring system. Substituted piperidine, morpholine and piperazine derivatives are particularly useful.

5 In one preferred embodiment, the structural element $\text{N}-\text{O}-\text{X}$ is a structural element of formula (I),



wherein

G₁, G₂, G₃, G₄ are independently C₁-C₆alkyl or G₁ and G₂ or G₃ and G₄, or G₁ and G₂ and G₃

10 and G₄ together form a C₅-C₁₂cycloalkyl group;

G₅, G₆ independently are H, C₁-C₁₈alkyl, phenyl, naphthyl or a group -COOC₁-C₁₈alkyl;

X is selected from the group consisting of -CH₂-phenyl, CH₃CH-phenyl, (CH₃)₂C-phenyl,

(C₅-C₆cycloalkyl)₂CCN, (CH₃)₂CCN, , , -CH₂CH=CH₂, CH₃CH-

CH=CH₂, (C₁-C₄alkyl)CR₂₀-C(O)-phenyl, (C₁-C₄)alkyl-CR₂₀-C(O)-(C₁-C₄)alkoxy, (C₁-C₄)alkyl-

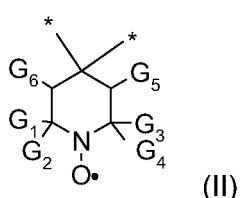
15 CR₂₀-C(O)-(C₁-C₄)alkyl, (C₁-C₄)alkyl-CR₂₀-C(O)-N-di(C₁-C₄)alkyl, (C₁-C₄)alkyl-CR₂₀-C(O)-

NH(C₁-C₄)alkyl, (C₁-C₄)alkyl-CR₂₀-C(O)-NH₂, wherein R₂₀ is hydrogen or (C₁-C₄)alkyl and

* denotes a valence.

In another preferred embodiment the structural element $\text{N}-\text{O}\bullet$ is a structural element of

20 formula (II),



wherein

- 9 -

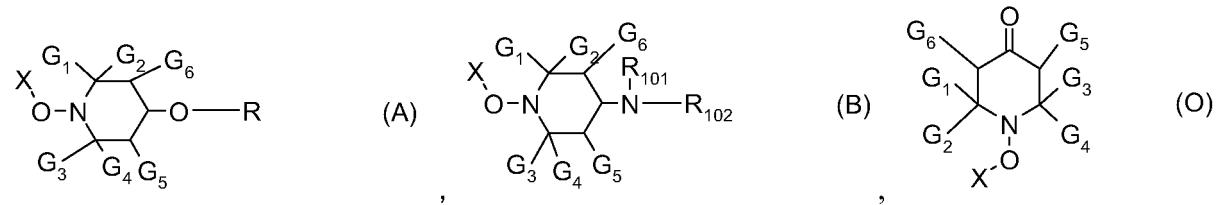
G₁, G₂, G₃, G₄ are independently C₁-C₆alkyl or G₁ and G₂ or G₃ and G₄, or G₁ and G₂ and G₃ and G₄ together form a C₅-C₁₂cycloalkyl group;

G₅, G₆ independently are H, C₁-C₁₈alkyl, phenyl, naphthyl or a group -COOC₁-C₁₈alkyl;

* denotes a valence.

5

In particular the structural element of formula (I) is of formula A, B or O,



wherein

10 **R** is hydrogen, C₁-C₁₈alkyl which is uninterrupted or interrupted by one or more oxygen atoms, cyanoethyl, benzoyl, glycidyl, a monovalent radical of an aliphatic carboxylic acid having 2 to 18 carbon atoms, of a cycloaliphatic carboxylic acid having 7 to 15 carbon atoms, or an α,β -unsaturated carboxylic acid having 3 to 5 carbon atoms or of an aromatic carboxylic acid having 7 to 15 carbon atoms;

15 **R**₁₀₁ is C₁-C₁₂alkyl, C₅-C₇cycloalkyl, C₇-C₈aralkyl, C₂-C₁₈alkanoyl, C₃-C₅alkenoyl or benzoyl; **R**₁₀₂ is C₁-C₁₈alkyl, C₅-C₇cycloalkyl, C₂-C₈alkenyl unsubstituted or substituted by a cyano, carbonyl or carbamide group, or is glycidyl, a group of the formula -CH₂CH(OH)-Z or of the formula -CO-Z or -CONH-Z wherein **Z** is hydrogen, methyl or phenyl;

16 **G**₆ is hydrogen and

20 **G**₅ is hydrogen or C₁-C₄alkyl,
G₁ and **G**₃ are methyl and **G**₂ and **G**₄ are ethyl or propyl or **G**₁ and **G**₂ are methyl and **G**₃ and **G**₄ are ethyl or propyl; and

25 **X** is selected from the group consisting of -CH₂-phenyl, CH₃CH-phenyl, (CH₃)₂C-phenyl, (C₅-C₆cycloalkyl)₂CCN, (CH₃)₂CCN,  ,  , -CH₂CH=CH₂, CH₃CH-

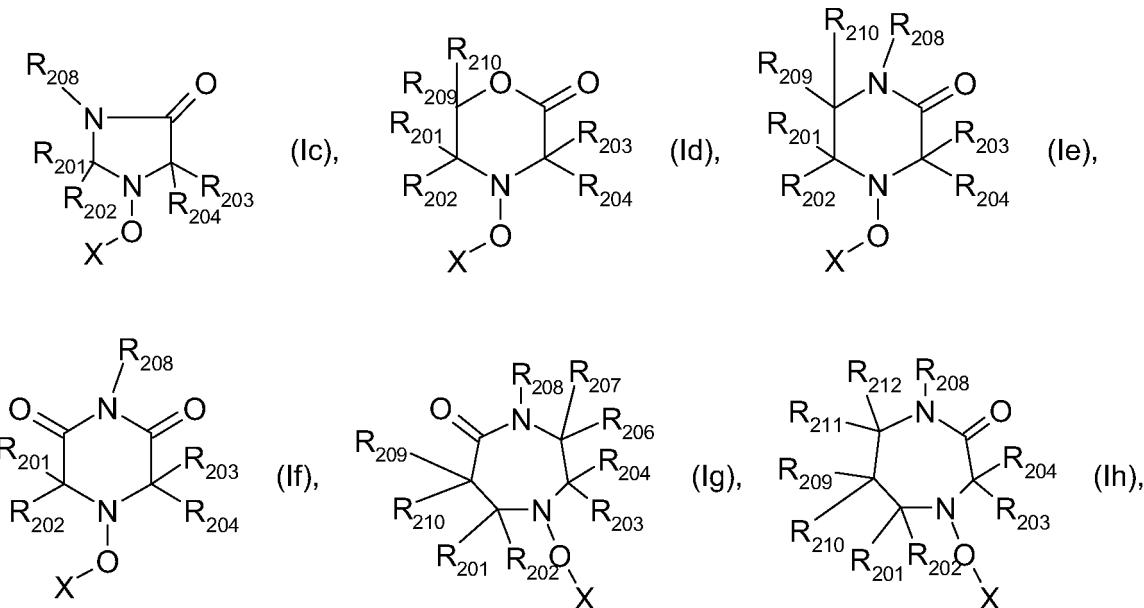
26 CH=CH₂, (C₁-C₄alkyl)CR₂₀-C(O)-phenyl, (C₁-C₄)alkyl-CR₂₀-C(O)-(C₁-C₄)alkoxy, (C₁-C₄)alkyl-CR₂₀-C(O)-(C₁-C₄)alkyl, (C₁-C₄)alkyl-CR₂₀-C(O)-N-di(C₁-C₄)alkyl, (C₁-C₄)alkyl-CR₂₀-C(O)-NH(C₁-C₄)alkyl, (C₁-C₄)alkyl-CR₂₀-C(O)-NH₂, wherein **R**₂₀ is hydrogen or (C₁-C₄)alkyl.

The above compounds and their preparation are described in GB2335190 and GB2361235.

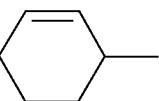
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- 10 -

Another preferred group of nitroxylethers are those of formula (Ic), (Id), (Ie), (If), (Ig) or (Ih)



wherein

- 5 **R₂₀₁, R₂₀₂, R₂₀₃ and R₂₀₄** independently of each other are C₁-C₁₈alkyl, C₃-C₁₈alkenyl, C₃-C₁₈alkinyl, C₁-C₁₈alkyl, C₃-C₁₈alkenyl, C₃-C₁₈alkinyl which are substituted by OH, halogen or a group -O-C(O)-R₂₀₅, C₂-C₁₈alkyl which is interrupted by at least one O atom and/or NR₂₀₅ group, C₃-C₁₂cycloalkyl or C₆-C₁₀aryl or R₂₀₁ and R₂₀₂ and/or R₂₀₃ and R₂₀₄ together with the linking carbon atom form a C₃-C₁₂cycloalkyl radical;
- 10 **R₂₀₅, R₂₀₆ and R₂₀₇** independently are hydrogen, C₁-C₁₈alkyl or C₆-C₁₀aryl; **R₂₀₈** is hydrogen, OH, C₁-C₁₈alkyl, C₃-C₁₈alkenyl, C₃-C₁₈alkinyl, C₁-C₁₈alkyl, C₃-C₁₈alkenyl, C₃-C₁₈alkinyl which are substituted by one or more OH, halogen or a group -O-C(O)-R₂₀₅, C₂-C₁₈alkyl which is interrupted by at least one O atom and/or NR₂₀₅ group, C₃-C₁₂cycloalkyl or C₆-C₁₀aryl, C₇-C₉phenylalkyl, C₅-C₁₀heteroaryl, -C(O)-C₁-C₁₈alkyl, -O-C₁-C₁₈alkyl or -COOC₁-C₁₈alkyl;
- 15 **R₂₀₉, R₂₁₀, R₂₁₁ and R₂₁₂** are independently hydrogen, phenyl or C₁-C₁₈alkyl; and X is selected from the group consisting of -CH₂-phenyl, CH₃CH-phenyl, (CH₃)₂C-phenyl, (C₅-C₆cycloalkyl)₂CCN, (CH₃)₂CCN,  ,  , -CH₂CH=CH₂, CH₃CH-
- 20 CH=CH₂ (C₁-C₄alkyl)CR₂₀-C(O)-phenyl, (C₁-C₄)alkyl-CR₂₀-C(O)-(C₁-C₄)alkoxy, (C₁-C₄)alkyl-CR₂₀-C(O)-(C₁-C₄)alkyl, (C₁-C₄)alkyl-CR₂₀-C(O)-NH(C₁-C₄)alkyl, (C₁-C₄)alkyl-CR₂₀-C(O)-NH₂, wherein **R₂₀** is hydrogen or (C₁-C₄)alkyl.

- 11 -

More preferably in formula (Ic), (Id), (Ie), (If), (Ig) and (Ih) at least two of R_{201} , R_{202} , R_{203} and R_{204} are ethyl, propyl or butyl and the remaining are methyl; or

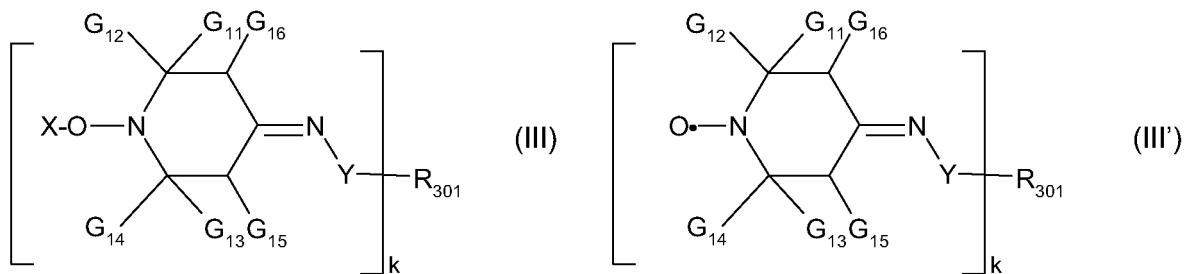
R_{201} and R_{202} or R_{203} and R_{204} together with the linking carbon atom form a C_5 - C_6 cycloalkyl radical and one of the remaining substituents is ethyl, propyl or butyl.

5

Most preferably X is CH_3CH -phenyl.

The above compounds and their preparation are described in GB 2342649.

10 Further suitable compounds are the 4-imino compounds of formula (III) or (III')



wherein

G₁₁, G₁₂, G₁₃ and G₁₄ are independently C_1 - C_4 alkyl or G₁₁ and G₁₂ together and G₁₃ and G₁₄ together, or G₁₁ and G₁₂ together or G₁₃ and G₁₄ together are pentamethylene;

15 **G₁₅ and G₁₆** are each independently of the other hydrogen or C_1 - C_4 alkyl;

X is as defined above;

k is 1, 2, 3, or 4

Y is O or NR₃₀₂ or when k is 1 and R₃₀₁ represents alkyl or aryl Y is additionally a direct bond;

R₃₀₂ is H, C_1 - C_{18} alkyl or phenyl;

20

if k is 1

R₃₀₁ is H, straight or branched C_1 - C_{18} alkyl, C_3 - C_{18} alkenyl or C_3 - C_{18} alkinyl, which may be unsubstituted or substituted, by one or more OH, C_1 - C_8 alkoxy, carboxy, C_1 - C_8 alkoxycarbonyl; C_5 - C_{12} cycloalkyl or C_5 - C_{12} cycloalkenyl;

25 phenyl, C_7 - C_9 phenylalkyl or naphthyl which may be unsubstituted or substituted by one or more C_1 - C_8 alkyl, halogen, OH, C_1 - C_8 alkoxy, carboxy, C_1 - C_8 alkoxycarbonyl;

-C(O)- C_1 - C_{36} alkyl, or an acyl moiety of a α,β -unsaturated carboxylic acid having 3 to 5 carbon atoms or of an aromatic carboxylic acid having 7 to 15 carbon atoms;

- 12 -

-SO₃⁻Q⁺, -PO(O⁻Q⁺)₂, -P(O)(OC₁-C₈alkyl)₂, -P(O)(OH₂)₂, -SO₂-OH, -SO₂-C₁-C₈alkyl, -CO-NH-C₁-C₈alkyl, -CONH₂, COO-C₁-C₈alkyl₂, COOH or Si(Me)₃, wherein Q⁺ is H⁺, ammonium or an alkali metal cation;

5 **if k is 2**

R₃₀₁ is C₁-C₁₈alkylene, C₃-C₁₈alkenylene or C₃-C₁₈alkinylene, which may be unsubstituted or substituted, by one or more OH, C₁-C₈alkoxy, carboxy, C₁-C₈alkoxycarbonyl; or xylylene; or R₃₀₁ is a bisacyl radical of an aliphatic dicarboxylic acid having 2 to 36 carbon atoms, or a cycloaliphatic or aromatic dicarboxylic acid having 8-14 carbon atoms;

10

if k is 3,

R₃₀₁ is a trivalent radical of an aliphatic, cycloaliphatic or aromatic tricarboxylic acid;

and

15 **if k is 4**, R₃₀₁ is a tetravalent radical of an aliphatic, cycloaliphatic or aromatic tetracarboxylic acid.

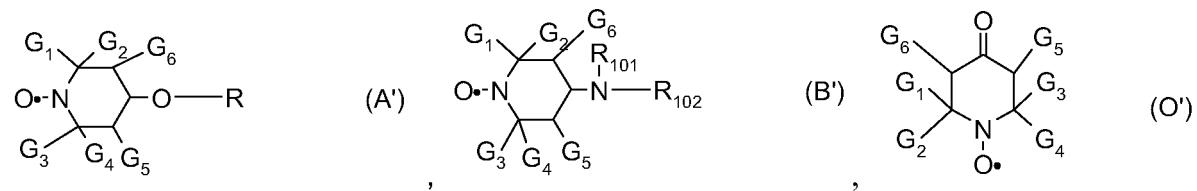
Preferably G₁₆ is hydrogen and G₁₅ is hydrogen or C₁-C₄alkyl, in particular methyl, and G₁₁ and G₁₃ are methyl and G₁₂ and G₁₄ are ethyl or propyl or G₁₁ and G₁₂ are methyl and G₁₃ and G₁₄ are ethyl or propyl.

20

The 4 imino compounds of formula III can be prepared for example according to E.G. Rozantsev, A.V. Chudinov, V.D. Sholle.: Izv. Akad. Nauk. SSSR, Ser. Khim. (9), 2114 (1980), starting from the corresponding 4-oxonitroxide in a condensation reaction with hydroxylamine and subsequent reaction of the OH group. The compounds are described WO 02/100831

25 (Ciba)

In particular the structural element of formula (II) is of formula A', B' or O',



wherein

30 **R** is hydrogen, C₁-C₁₈alkyl which is uninterrupted or interrupted by one or more oxygen atoms, cyanoethyl, benzoyl, glycidyl, a monovalent radical of an aliphatic carboxylic

acid having 2 to 18 carbon atoms, of a cycloaliphatic carboxylic acid having 7 to 15 carbon atoms, or an α,β -unsaturated carboxylic acid having 3 to 5 carbon atoms or of an aromatic carboxylic acid having 7 to 15 carbon atoms;

R₁₀₁ is C₁-C₁₂alkyl, C₅-C₇cycloalkyl, C₇-C₈aralkyl, C₂-C₁₈alkanoyl, C₃-C₅alkenoyl or benzoyl;

5 **R₁₀₂** is C₁-C₁₈alkyl, C₅-C₇cycloalkyl, C₂-C₈alkenyl unsubstituted or substituted by a cyano, carbonyl or carbamide group, or is glycidyl, a group of the formula -CH₂CH(OH)-Z or of the formula -CO-Z or -CONH-Z wherein **Z** is hydrogen, methyl or phenyl;

G₆ is hydrogen and

G₅ is hydrogen or C₁-C₄alkyl,

10 **G₁ and G₃** are methyl and **G₂ and G₄** are ethyl or propyl or G₁ and G₂ are methyl and G₃ and G₄ are ethyl or propyl.

The alkyl radicals in the various substituents may be linear or branched. Examples of alkyl containing 1 to 18 carbon atoms are methyl, ethyl, propyl, isopropyl, butyl, 2-butyl, isobutyl, t-butyl, pentyl, 2-pentyl, hexyl, heptyl, octyl, 2-ethylhexyl, t-octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, hexadecyl and octadecyl.

Alkenyl with 3 to 18 carbon atoms is a linear or branched radical as for example propenyl, 20 2-butenyl, 3-butenyl, isobut enyl, n-2,4-pentadienyl, 3-methyl-2-butenyl, n-2-octenyl, n-2-dodecenyl, iso-dodecenyl, oleyl, n-2-octadecenyl or n-4-octadecenyl. Preferred is alkenyl with 3 to 12, particularly preferred with 3 to 6 carbon atoms.

Alkinyl with 3 to 18 is a linear or branched radical as for example propinyl 25 (—CH₂-C≡CH), 2-butinyl, 3-butinyl, n-2-octinyl, or n-2-octadecinyl. Preferred is alkinyl with 3 to 12, particularly preferred with 3 to 6 carbon atoms.

Examples for hydroxy substituted alkyl are hydroxy propyl, hydroxy butyl or hydroxy hexyl.

30 Examples for halogen substituted alkyl are dichloropropyl, monobromobutyl or trichlorohexyl.

C₂-C₁₈alkyl interrupted by at least one O atom is for example -CH₂-CH₂-O-CH₂-CH₃, -CH₂-CH₂-O-CH₃- or -CH₂-CH₂-O-CH₂-CH₂-O-CH₂-CH₃-.

It is preferably derived from polyethylene glycol. A general description is $-((\text{CH}_2)_a\text{O})_b\text{-H/CH}_3$, wherein a is a number from 1 to 6 and b is a number from 2 to 10.

$\text{C}_2\text{-C}_{18}\text{alkyl}$ interrupted by at least one NR_{205} group may be generally described as

5 $-((\text{CH}_2)_a\text{-NR}_{205})_b\text{-H/CH}_3$, wherein a, b and R_{205} are as defined above.

$\text{C}_3\text{-C}_{12}\text{cycloalkyl}$ is typically, cyclopropyl, cyclopentyl, methylcyclopentyl, dimethylcyclopentyl, cyclohexyl, methylcyclohexyl or trimethylcyclohexyl.

10 $\text{C}_6\text{-C}_{10}$ aryl is e.g. phenyl or naphthyl, but also comprised are $\text{C}_1\text{-C}_4\text{alkyl}$ substituted phenyl, $\text{C}_1\text{-C}_4\text{alkoxy}$ substituted phenyl, hydroxy, halogen or nitro substituted phenyl. Examples for alkyl substituted phenyl are ethylbenzene, toluene, xylene and its isomers, mesitylene or isopropylbenzene. Halogen substituted phenyl is e.g. dichlorobenzene or bromotoluene.

15 Alkoxy substituents are typically methoxy, ethoxy, propoxy or butoxy and their corresponding isomers.

$\text{C}_7\text{-C}_9\text{phenylalkyl}$ is benzyl, phenylethyl or phenylpropyl.

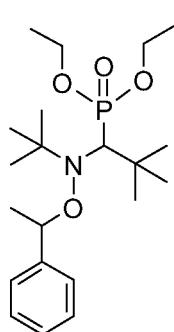
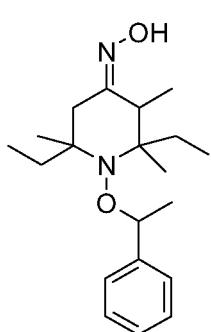
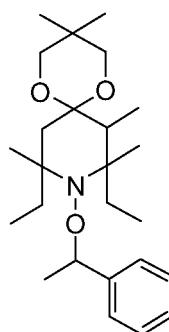
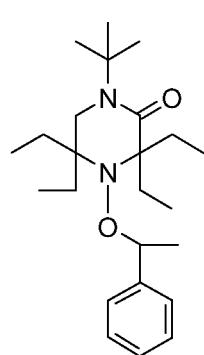
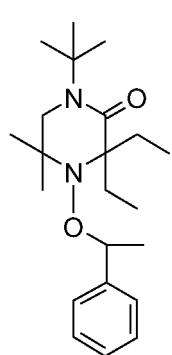
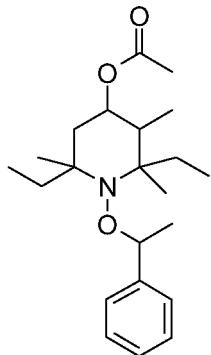
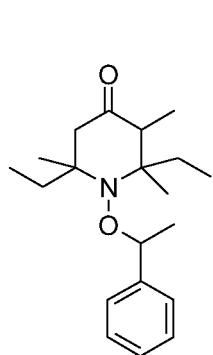
20 $\text{C}_5\text{-C}_{10}\text{heteroaryl}$ is for example pyrrol, pyrazol, imidazol, 2, 4, dimethylpyrrol, 1-methylpyrrol, thiophene, furane, furfural, indol, cumarone, oxazol, thiazol, isoxazol, isothiazol, triazol, pyridine, α -picoline, pyridazine, pyrazine or pyrimidine.

25 If R is a monovalent radical of a carboxylic acid, it is, for example, an acetyl, propionyl, butyryl, valeroyl, caproyl, stearoyl, lauroyl, acryloyl, methacryloyl, benzoyl, cinnamoyl or β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionyl radical.

$\text{C}_1\text{-C}_{18}\text{alkanoyl}$ is for example, formyl, propionyl, butyryl, octanoyl, dodecanoyl but preferably acetyl and $\text{C}_3\text{-C}_5\text{alkenoyl}$ is in particular acryloyl.

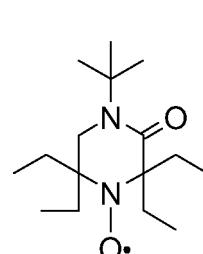
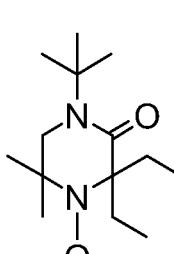
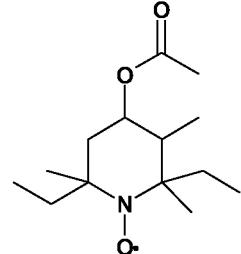
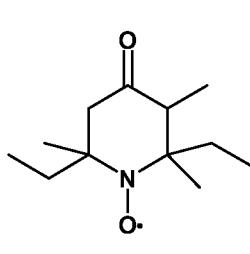
30 In particular polymerization process a1) is very suitable. When process a1) is used the nitroxylether according to the structures outlined above splits between the O-X bond. The regulating fragment in formula (I) corresponds to the O-N fragment and the initiating fragment (In) corresponds to the C centered radical of the group X.

Particularly suitable nitroxylethers and nitroxyl radicals are those of formulae



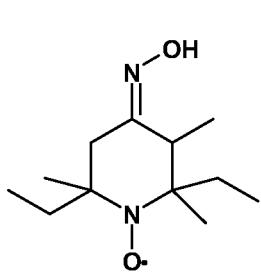
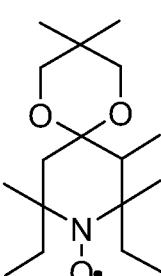
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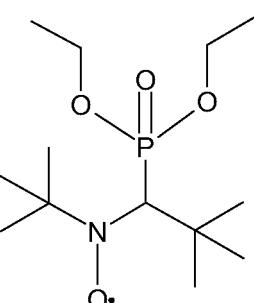


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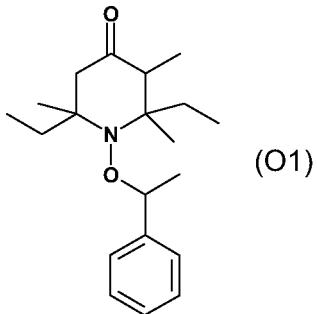


or



.

In a very specific embodiment of the invention, the polymer or copolymer is prepared with a compound of formula (O1)



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

When monomer mixtures are used mol% is calculated on the average molecular weight of
10 the mixture.

When the process according to route **a2)** is chosen, the free radical initiator is preferably an azo compound, a peroxide, perester or a hydroperoxide.

15 Specific preferred radical sources are 2,2'-azobisisobutyronitrile, 2,2'-azobis(2-methylbutyronitrile), 2,2'-azobis(2,4-dimethylvaleronitrile), 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile), 1,1'-azobis(1-cyclohexanecarbonitrile), 2,2'-azobis(isobutyramide) dihydrate, 2-phenylazo-2,4-dimethyl-4-methoxyvaleronitrile, dimethyl-2,2'-azobisisobutyrate, 2-(carbamoylazo)isobutyronitrile, 2,2'-azobis(2,4,4-trimethylpentane), 2,2'-azobis(2-methylpropane),
20 2,2'-azobis(N,N'-dimethyleneisobutyramidine), free base or hydrochloride, 2,2'-azobis(2-amidinopropane), free base or hydrochloride, 2,2'-azobis{2-methyl-N-[1,1-bis(hydroxymethyl)ethyl]propionamide} or 2,2'-azobis{2-methyl-N-[1,1-bis(hydroxymethyl)-2-hydroxyethyl]propionamide; acetyl cyclohexane sulphonyl peroxide, diisopropyl peroxy dicarbonate, t-amyl perneodecanoate, t-butyl perneodecanoate, t-butyl perpivalate, t-amylperpivalate,
25 bis(2,4-dichlorobenzoyl)peroxide, diisononanoyl peroxide, didecanoyl peroxide, dioctanoyl peroxide, dilauroyl peroxide, bis (2-methylbenzoyl) peroxide, disuccinic acid peroxide, diacetyl peroxide, dibenzoyl peroxide, t-butyl per 2-ethylhexanoate, bis-(4-chlorobenzoyl)-peroxide, t-butyl perisobutyrate, t-butyl permaleinate, 1,1-bis(t-butylperoxy)3,5,5-trimethyl-

cyclohexane, 1,1-bis(t-butylperoxy)cyclohexane, t-butyl peroxy isopropyl carbonate, t-butyl perisononaoate, 2,5-dimethylhexane 2,5-dibenzoate, t-butyl peracetate, t-amyl perbenzoate, t-butyl perbenzoate, 2,2-bis (t-butylperoxy) butane, 2,2 bis (t-butylperoxy) propane, dicumyl peroxide, 2,5-dimethylhexane-2,5-di-t-butylperoxide, 3-t-butylperoxy 3-phenylphthalide, di-t-

5 amyl peroxide, α , α' -bis(t-butylperoxy isopropyl) benzene, 3,5-bis (t-butylperoxy)3,5-dimethyl 1,2-dioxolane, di-t-butyl peroxide, 2,5-dimethylhexyne-2,5-di-t-butylperoxide, 3,3,6,6,9,9-hexamethyl 1,2,4,5-tetraoxa cyclononane, p-menthane hydroperoxide, pinane hydroperoxide, diisopropylbenzene mono- α -hydroperoxide, cumene hydroperoxide or t-butyl hydroperoxide.

10

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

15 The molar ratio of the radical source to the nitroxyl radical may be from 1:10 to 10:1, preferably from 1:5 to 5:1 and more preferably from 1:2 to 2:1.

20 The polymer or copolymer can also be prepared in a controlled way by atom transfer radical polymerization (ATRP). This type of polymerization is, for example, described in WO 96/30421.

25 Reversible addition fragmentation chain transfer polymerization (RAFT) is also a well known controlled free radical polymerization technique and for example described in WO 98/01478, WO98/58974, WO 99/31144, WO 99/05099, WO 02/094887, WO 02/26836, WO 01/42312, WO 00/75207, and WO 99/35177.

30 The polymer or copolymer prepared according to steps a1) or a2) has preferably a polydispersity index of 1.0 to 2.2, more preferably from 1.1 to 1.9 and most preferably from 1.1 to 1.5.

30

As already mentioned above the second reaction step b), i. e. the polymer analogous reaction, is a transesterification reaction, an amidation, hydrolysis or anhydride modification or a combination thereof., and optionally in addition by quaternization.

Hydrolysis means the cleavage of an ester bond under alkaline or acidic conditions and can be carried out when the polymer or copolymer contains ester functionalities. The degree of hydrolysis may vary in a wide range and depends on reaction time and conditions. For example 5 to 100%, preferably 10% to 70% of the ester functionalities may be hydrolyzed, to 5 form the free acid group, from which also a salt can be prepared. The metal ion is preferably an alkali metal ion, such as Li^+ , Na^+ or K^+ or an ammonium cation, such as NH_4^+ or NR_{404}^+ , wherein R_{404} is hydrogen or $\text{C}_1\text{-C}_{18}\text{alkyl}$.

Anhydride modification can be carried out when the polymer or copolymer contains 10 hydroxyl functionalities. The hydroxyl functionalities come for example from hydroxyl functional monomers, such as hydroxyethyl acrylate or methacrylate. Virtually all aliphatic or aromatic anhydrides can be used in the modification process. Examples for anhydrides are maleic acid anhydride, pyromelic acid anhydride, cyclohexyldiacid anhydride, succinic acid anhydride, camphoric acid anhydride.

15

Transesterification means to replace the alcohol radical in an ester group of the polymer or copolymer by another alcohol radical. Preferably the alcohol radical to be replaced is methanol, ethanol, propanol or butanol. Typically the transesterification reaction is carried out at elevated temperatures, typically 70 – 200°C, by reacting the CFRP polymer with the 20 corresponding alcohol using well-known catalysts, such as tetra-isopropyltitanate, tetra-butyltitanate, alkali- or earth alkali alcoholates like NaOMe or LiOMe . Typically the low boiling product alcohol is removed from the transterification reaction mixture by distillation. If needed, catalyst residues may be removed by adsorption or extraction or otherwise processed or inactivated by known methods, like hydrolysis with water or acids.

25

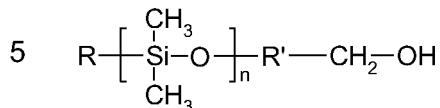
The choice of the replacing alcohol is important. The replacing alcohol controls the properties of the resulting copolymer.

Using a polar replacing alcohol such as alcohols having e.g. the following formula 30 $\text{R}-[\text{O}-\text{CH}_2-\text{CH}_2]_n-\text{OH}$, e.g. methoxypoly4ethylene glycol (MPEG-OH), it is possible to obtain a water soluble resulting polymer. Of course the solubility depends on the amount of transesterified monomer units. At least 40 % of the units should be transesterified to obtain the desired effect.

- 19 -

If solubility in organic solvents is required non polar alcohols like higher molecular weight branched aliphatic alcohols can be beneficial.

If polymers with low surface tension are desired, alcohols containing siloxane groups are preferred, e.g. with the following formula



or partly or fully fluorinated primary alcohols can be used instead or in addition.

If a solid copolymer is required, solid alcohols or polar alcohols which are able to raise the glass transition temperature (Tg) or impart side chain crystallinity should be used. An 10 example is behenyl alcohol.

The replacing alcohol radical is typically an aliphatic C₆-C₃₆alcohol or a precursor of an alcohol, having at least one -OH group. The alcohol may also be interrupted by 1 to 20 O or 15 N atoms or substituted by halogen, perfluoralkyl, NH₂, NH(C₁-C₁₈alkyl), N(C₁-C₁₈alkyl)₂, COO(C₁-C₁₈alkyl), CON(C₁-C₁₈alkyl)₂, CONH(C₁-C₁₈alkyl), CONH₂, COOH, COO⁻, O(C₁-C₁₈alkyl) or with a Si, P or S containing group, for example alkylhydroxysilicones. The alcohol may also contain heterocyclic ring structures, such as 1-(2-hydroxyethyl)-2-pyrrolidinone, 1-(2-hydroxyethyl)-2-imidazolidinone, 2-(2-hydroxyethyl)pyridine, N-2-hydroxyethyl)phtalimide, 4-(2-hydroxyethyl)morpholine, 1-(2-hydroxyethyl)piperazine, N-hydroxymethylphthalimide, 3-20 hydroxymethylpyridine or (4-pyridyl)-1-propanol.

The alcohols, which are interrupted by O or N atoms are not limited to 36 C atoms. These can be oligomeric or polymeric alcohols also. Examples of alcohols interrupted by O atoms are methoxypolyethyleneglycols or all kinds of adducts of ethyleneoxide and/or propylene-25 oxide (EO/PO). Such EO/PO-adducts can be random or block type structures.

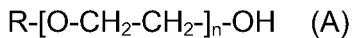
Preferably the alcohol is an unsubstituted linear or branched C₈-C₃₆alkyl mono alcohol or a mono alcohol derived from ethylenoxide, propylenoxide or mixtures thereof with up to 100 C atoms. Especially preferred is MPEG-OH.

30

It is also possible to use fatty acid alcohol ethoxylates, alkylphenolethoxylates, alkoxylates of all kinds of monofunctional alcohols or phenols or secondary amines.

- 20 -

Preferably the alkoxylate is an ethoxylate of a primary alcohol or alkylphenol of structure (A):

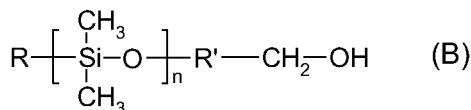


wherein R is saturated or unsaturated, linear or branched chain alkyl with 1 –22 carbon atoms, or alkylaryl or dialkylaryl with up to 24 carbon atoms and n is 1 to 50.

5

Referring to an other embodiment the alcohol is an unsubstituted linear or branched C₈-C₃₆alkyl mono alcohol or mixtures thereof. An example is a mixture of iso C₁₂-C₁₅ alcohol. Non-polar polymers or copolymers are obtained.

10 In another embodiment, the macroalcohol is a primary OH-functional silicone oligomer. Preferred are polydimethylsilicone oligomers of structure (B):



wherein

R is C₁-C₁₈alkyl, phenyl or C₇-C₁₅aralkyl; n is 1 to 50 and R' is a linking group with 1 to 20

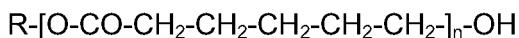
15 carbon atoms.

Typical linking groups are C₁-C₁₈alkylene, phenylene or C₁-C₁₈alkylene interrupted by 1 to 6 oxygen atoms.

20 In another embodiment the alcohol is a partly or fully fluorinated primary alcohols. Examples of commercial fluorinated alcohol mixtures are: Zonyl BA®, Zonyl BA-L®, Zonyl BA-LD®, Zonyl BA-N® from Du Pont.

Aryl is phenyl or naphthyl, preferably phenyl.

25 Precursors of alcohols are for example macroalcohols, such as poly- ϵ -caprolactone oligomers or ϵ -caprolactone adducts and similar lactone adducts (e.g. based on valerolactone) or mixed adducts of ϵ -caprolactone and valerolactone. Typical lactone adducts are adducts of ϵ -caprolactone to long chain fatty alcohols of structure:



30 wherein R is saturated or unsaturated, linear or branched chain alkyl with 8 –22 carbon atoms or alkylaryl or dialkylaryl with up to 24 carbon atoms and n is 1 to 50.

It is also possible to use macroalcohols based on polyolefins, which have typically molecular weights up to 5000, preferably up to 2000.

Yet another embodiment are unsaturated alcohols containing carbon-carbon double bonds or 5 carbon triple bonds. An example is oleyl alcohol. Regarding triple bond preferred are primary alkinols like propargyl alcohol and higher homologues like alkylsubstituted propargylalcohol.

Preferably the alcohol is a monoalcohol and is a primary or secondary alcohol. Most preferred are primary alcohols or alcohol mixtures like Lial 125.

10

Preferably the alcohol or alcohol mixture is non-volatile and has a boiling point or range of at least 100°C, more preferably of at least 200°C.

15

The **quaternization** means the formation of ammonium salts of the amino group present in amino monomers selected from the group consisting of amino substituted styrene, (C₁-C₄alkyl)₁₋₂amino substituted styrene, N-mono-(C₁-C₄alkyl)₁₋₂aminoC₂-C₄alkyl(meth)-acrylamide and N,N-di-(C₁-C₄alkyl)₁₋₂amino-C₂-C₄alkyl(meth)acrylamide, vinylpyridine or C₁-C₄alkyl substituted vinylpyridine, vinylimidazole and C₁-C₄alkyl substituted vinylimidazole.

20

Representative N-mono-(C₁-C₄alkyl)₁₋₂amino-C₂-C₄alkyl(meth)acrylamide and N,N-di-(C₁-C₄alkyl)₁₋₂amino-C₂-C₄alkyl(meth)acrylamide are 2-N-tert-butylamino- or 2-N,N-dimethyl-aminoethylacrylamide or 2-N-tert-butylamino- or 2-N,N-dimethylaminopropylmethacrylamide.

25

Quaternization is effected with active alkyl halides or alkyl esters of organic sulphonic acids. In this case examples of preferred salt forming components are benzylchloride, 2-chlorobenzylchloride, 4-chlorobenzylchloride, 2,4-dichlorobenzylchloride, p-toluene sulphonic acid methyl ester, p-toluene sulphonic acid ethyl ester, especially preferred 4-chlorobenzylchloride.

30

Under the term **amidation** there is understood the modification of the ester function of a polyacrylate with an amine under the formation of an amide bond. Preferably the amine is a monofunctional primary or secondary amine, most preferably a primary aliphatic or aromatic amine. The reaction of the amine with the ester function of the CFRP polymer is typically conducted at elevated temperatures of 70 –200°C, optionally in presence of catalysts. In a

preferred process, the resulting alcohol is removed during the amidation reaction by distillation.

Preferably the amine has a high boiling point or boiling range of above 100°C.

5

Typical amines are primary aliphatic or aromatic amines with up to 36 carbon atoms, linear, branched or cyclic. The amine may contain heteroatoms O or N.

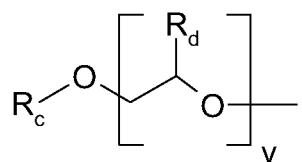
10 In a preferred embodiment there are oligomers and macroamines with a single primary amine and molecular weights of up to 5000. Typical examples are primary amine end-functional alkoxylates. Especially preferred are also primary amines containing other polar groups like ether, ester and amide groups.

15 In principal the monomer in step a1 or a2 can be selected from isoprene, 1,3-butadiene, α -C₅-C₁₈alkene, 4-vinyl-pyridine or pyridinium-ion, 2-vinyl-pyridine or pyridinium-ion, vinyl-imidazole or imidazolinium-ion, dimethylacrylamide, 3-dimethylaminopropylmethacrylamide, styrene, α -methyl styrene, p-methyl styrene, p-tert-butyl-styrene or a compound of formula CH₂=C(R_a)-(C=Z)-R_b, wherein R_a is hydrogen or C₁-C₄alkyl, R_b is NH₂, O⁻(Me⁺), unsubstituted C₁-C₁₈alkoxy, C₂-C₁₀₀alkoxy interrupted by at least one N and/or O atom, or hydroxy-20 substituted C₁-C₁₈alkoxy, unsubstituted C₁-C₁₈alkylamino, di(C₁-C₁₈alkyl)amino, hydroxy-substituted C₁-C₁₈alkylamino or hydroxy-substituted di(C₁-C₁₈alkyl)amino, -O-CH₂-CH₂-N(CH₃)₂ or -O-CH₂-CH₂-N⁺H(CH₃)₂ An⁻;
An⁻ is a anion of a monovalent organic or inorganic acid;
Me is a monovalent metal atom or the ammonium ion.

25 Z is oxygen or sulfur

Preferred are 3-dimethylaminopropylmethacrylamide, 2-vinyl-pyridine, 4-vinyl-pyridine, hydroxyethylacrylate, hydroxyproylacrylate, n-butylacrylate, styrene.

30 Examples for R_b as C₂-C₁₀₀alkoxy interrupted by at least one O atom are of formula

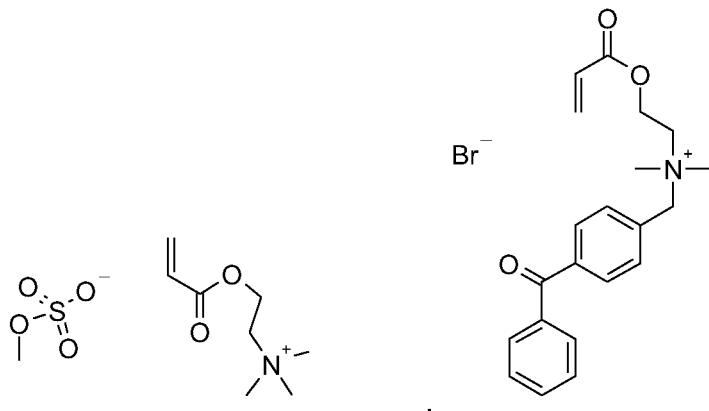


, wherein R_c is C_{1-25} alkyl, phenyl or phenyl substituted by C_{1-18} alkyl,

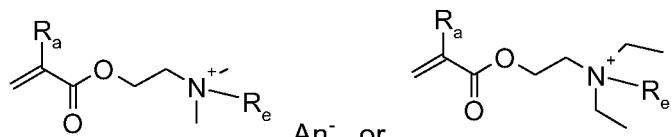
C_{18} alkyl, R_d is hydrogen or methyl and v is a number from 1 to 50. These monomers are for example derived from non ionic surfactants by acrylation of the corresponding alkoxylated alcohols or phenols. The repeating units may be derived from ethylene oxide, propylene oxide or mixtures of both.

5

Further examples of suitable acrylate or methacrylate monomers are given below.

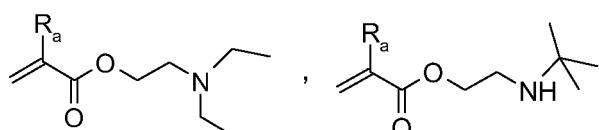


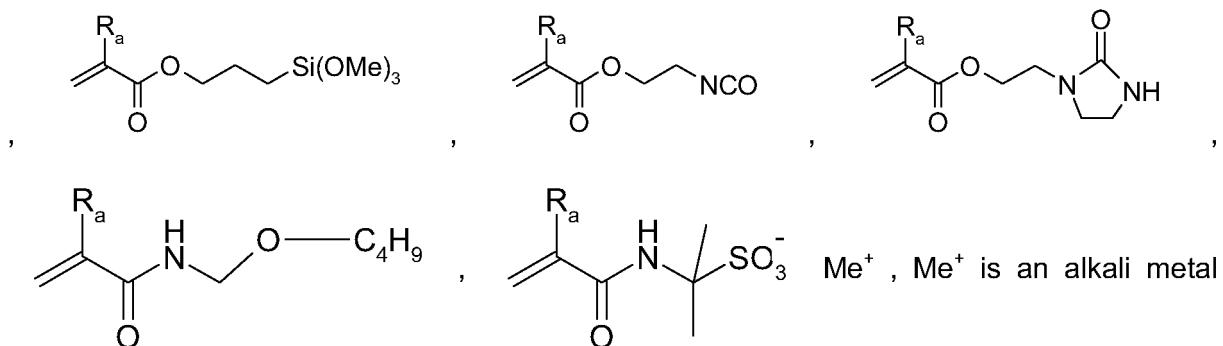
10



An^- or An^- , wherein An^- and R_a have the meaning as defined above and R_e is methyl, benzyl or benzoylbenzyl. An^- is preferably Cl^- , Br^- or $^3O_3S-O-CH_3$.

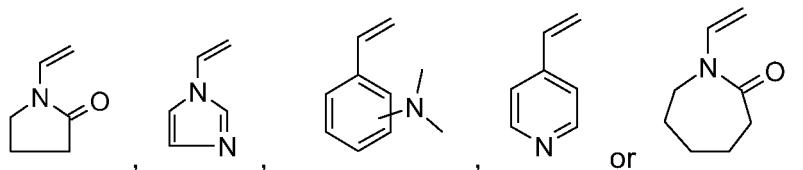
15 Further acrylate monomers are





cation or the ammonium cation. Useful are also silicone functional (meth)acrylates.

5 Examples for suitable monomers other than acrylates are



Preferably R_a is hydrogen or methyl, R_b is NH_2 , glycidyl, unsubstituted or with hydroxy substituted $\text{C}_1\text{-C}_4$ alkoxy, unsubstituted $\text{C}_1\text{-C}_4$ alkylamino, di($\text{C}_1\text{-C}_4$ alkyl)amino, hydroxy-substituted $\text{C}_1\text{-C}_4$ alkylamino or hydroxy-substituted di($\text{C}_1\text{-C}_4$ alkyl)amino; and Z is oxygen.

For example the ethylenically unsaturated monomer is selected from the group consisting of ethylene, propylene, n-butylene, i-butylene, styrene, substituted styrene, conjugated dienes, acrolein, vinyl acetate, vinylpyrrolidone, vinylimidazole, maleic anhydride, (alkyl)acrylic acid-anhydrides, (alkyl)acrylic acid salts, (alkyl)acrylic esters, (alkyl)acrylonitriles, (alkyl)acrylamides, vinyl halides or vinylidene halides.

For instance the ethylenically unsaturated monomer is styrene, substituted styrene, methylacrylate, ethylacrylate, butylacrylate, isobutylacrylate, tert. butylacrylate, hydroxyethylacrylate, hydroxypropylacrylate, dimethylaminoethylacrylate, methyl(meth)acrylate, ethyl(meth)acrylate, butyl(meth)acrylate, hydroxyethyl(meth)acrylate, hydroxypropyl(meth)acrylate, dimethylaminoethyl(meth)acrylate, acrylonitrile, methacrylonitrile, acrylamide, methacrylamide or dimethylaminopropyl-methacrylamide.

Very suitable monomers are for example styrene, C₁-C₈alkylesters of acrylic or methacrylic acid, such as n-butylacrylate or methacrylate, acrylonitrile or methacrylonitrile, in particular styrene, acrylonitrile and n-butylacrylate.

5 It is also possible to use mixtures of the afore mentioned monomers, in particular styrene/acrylonitrile, styrene/butylacrylate, styrene/methylmethacrylate and styrene/butylmethacrylate

Preference is given to a polymerizable composition wherein the ethylenically unsaturated monomer is a compound of formula CH₂=C(R_a)-(C=Z)-R_b, wherein Z is O or S;

10 R_a is hydrogen or C₁-C₄alkyl;
R_b is NH₂, O⁻(Me⁺), glycidyl, unsubstituted C₁-C₁₈alkoxy, C₂-C₁₀₀alkoxy interrupted by at least one N and/or O atom, or hydroxy-substituted C₁-C₁₈alkoxy, unsubstituted C₁-C₁₈alkylamino, di(C₁-C₁₈alkyl)amino, hydroxy-substituted C₁-C₁₈alkylamino or hydroxy-substituted di(C₁-C₁₈alkyl)amino, -O-CH₂-CH₂-N(CH₃)₂ or -O-CH₂-CH₂-N⁺H(CH₃)₂ An⁻;

15 An⁻ is a anion of a monovalent organic or inorganic acid;
Me is a monovalent metal atom or the ammonium ion.

20 All possible polymer chain structures are comprised: e.g. linear or branched. If the monomers are selected from chemically different monomers, all possible monomer sequence structures are comprised, e.g. random-, blocklike, multiblock-, tapered- or gradient arrangement of the different monomers.

Under gradient polymers or gradient arrangement there are understood block copolymers, which are prepared in such a way, that the intersection between the two blocks is not a sharp 25 boundary, but represents a continuous transition from one type of monomer to another type of monomer, i.e. both monomers extending to both blocks. This type of polymers can be obtained when the polymerization process is carried out for example in one step using monomers of different copolymerization parameters or by a multistep procedure, in which the monomer composition is stepwise changed by addition of appropriate amounts of another 30 type of monomer. Another preferred procedure for the synthesis of gradient polymers is by using continuous feed processes, in which for example the controlled polymerization is started with a first monomer and before complete conversion, a second monomer is continuously fed to the reaction mixture, thus realizing a continuous transition along the polymer chains.

When step a1 or a2 of the process is carried out twice and a block copolymer is obtained for example the monomer or monomer mixture of the first radical polymerization contains from 50 to 100% by weight based on total monomers of a C₁-C₄ alkyl or hydroxyalkyl ester of 5 acrylic or methacrylic acid and the second radical polymerization contains a monomer or monomer mixture possessing no primary or secondary ester bond.

Suitable monomers for the second radical polymerization do not react in the postmodification reaction, such as vinyl aromatic monomers or vinyl-aza-heterocycles.

10

Examples are 4-vinyl-pyridine(pyridinium-ion), 2-vinyl-pyridine(pyridinium-ion), vinyl-imidazole(imidazolinium-ion), dimethylacrylamide, acrylnitrile, 3-dimethylaminopropyl-methacryl-amide, styrene or substituted styrenes .

15 Naturally the sequence of the first and second radical polymerization can also be reversed.

When a block copolymer is prepared it is preferred that in the first polymerization the monomer or monomer mixture contains from 50 to 100% by weight based on total monomers of a C₁-C₆ alkyl or hydroxyalkyl ester of acrylic or methacrylic acid and in the second 20 polymerization the ethylenically unsaturated monomer is 4-vinyl-pyridine or pyridinium-ion, 2-vinyl-pyridine or pyridinium-ion, vinyl-imidazole or imidazolinium-ion, dimethylacrylamide, 3-dimethylaminopropylmethacrylamide, styrene, α -methyl styrene, p-methyl styrene or p-tert-butyl-styrene.

25 In another specific embodiment of the invention, the monomers of the controlled polymer prepared according to a first step a1) or a2) contain aminic or acid groups, is than modified in a second step by a transesterification reaction, an amidation, hydrolysis or anhydride modification and thereafter the aminic or acid groups of the modified controlled polymer are converted to salt structures by reaction with a salt forming component. Typical salt forming 30 components for amino groups are for example organic or inorganic acids or alkylhalogenides, especially such salt forming components, which are based on organic cyclic acids or cyclic alkylhalogenides. Typical examples of such salt forming components are described in EP 1275689 (Ciba) and WO 03/046029 (Ciba)

Typical salt forming components for acid groups on the modified controlled polymer are inorganic bases, such as NaOH, KOH, NH4OH or volatile aminoalcohols, such as 2-dimethylaminoethanol or 2-amino-2-methylpropanol (AMP), which are frequently used in coatings.

5

It is also possible to choose the monomers in the polymerization steps and the post modification reaction in such a way, that a lower critical solution temperature (LCST) in water or water rich solvent mixtures is obtained for the final polymer or copolymer.

10 This means, that the polymer or copolymer shows a good solubility at low temperatures and a decreasing solubility at high temperatures. This effect is for example described by Hammouda, B.; Ho, D.; Kline, S in Macromolecules (2002), 35(22), 8578-8585).

15 The invention further relates to a method for producing a color filter, which comprises coating the color filter composition described above on a substrate, followed by exposure and development.

20 A "substrate" means any carrier material adapted to be coated with photoresist layers for the purpose of exposure. For this purpose frequently glass plates are used, which may be colored black or coated. Furthermore, plastic foils or metal foils that are already provided with a grating image, preferably in the form of an embossing, are suitable as substrates.

25 Examples of the coating of the photosensitive film include slit coating using a coating device having slit type nozzles, slit-and-spin coating that first coats using a nozzle and then coats using a spin coater, die coating, and curtain flow coating. Of these coating methods, the slit-and-spin coating is preferred. After the coating, the photosensitive resin composition may be prebaked to remove volatile ingredients such as solvents, thereby forming the photosensitive resin film containing substantially no volatile ingredient. The photosensitive resin film may 30 have a thickness of about 1 to 10 μm .

Next, the photosensitive film is subjected to a first exposure through a mask. The mask has a pattern suitable for the function of the hardened resin pattern.

The photoresist resin film is then developed by puddle development, immersion development, or spray development. The development may be performed by using an alkaline aqueous solution. The alkaline aqueous solution contains an inorganic alkaline compound or an organic alkaline compound.

5

The invention further relates to the use of a dispersant as disclosed above in a color filter composition.

10

Examples

The following examples illustrate the invention.

Materials use and their abbreviations:

Monomers: butylacrylate (BA), hydroxyethylacrylate (HEA), hydroxypropylacrylate (HPA),
15 4-vinyl-pyridine (4-VP), styrene (S), dimethylaminopropyl methacrylate (DMAPMA)

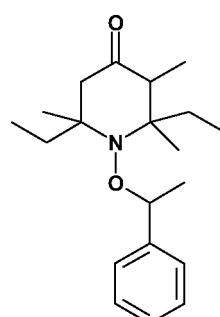
Modification agents: cyclohexylacid anhydride (CHAA), succinic acid anhydride (SAA), methoxy-poly-ethyleneglycole (MPEG 550-OH), Lial 125 is a mixture of iso-C₁₂-C₁₅ alcohols, available from Condea

20

Solvents: methoxypropylacetate (MPA), Xylene, methoxypropanol (MP), polystyrene (PS), tetrahydrofurane (THF), polyethyleneoxide (POE/PEG), methoxytriglycol (MTG).

ATRP process: initiator is 2-bromoethylpropionate (MBP), the catalyst is CuBr/CuBr₂, the
25 ligand is N,N,N',N",N"-pentamethyldiethyltriamine (PMDETA).

NOR Initiator/regulator is compound O1



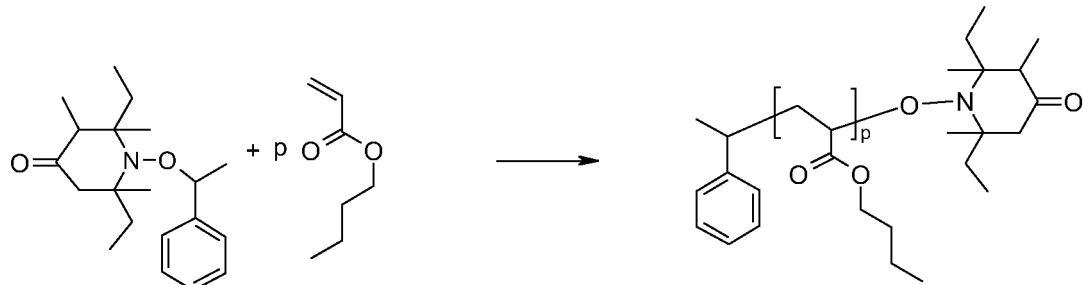
(O1), which is prepared

according to GB 2335190.

All other materials are commercially available and were used as received.

A) Preparation of Polymers and Copolymers

Example A1: Synthesis of a linear polymer poly(BA)

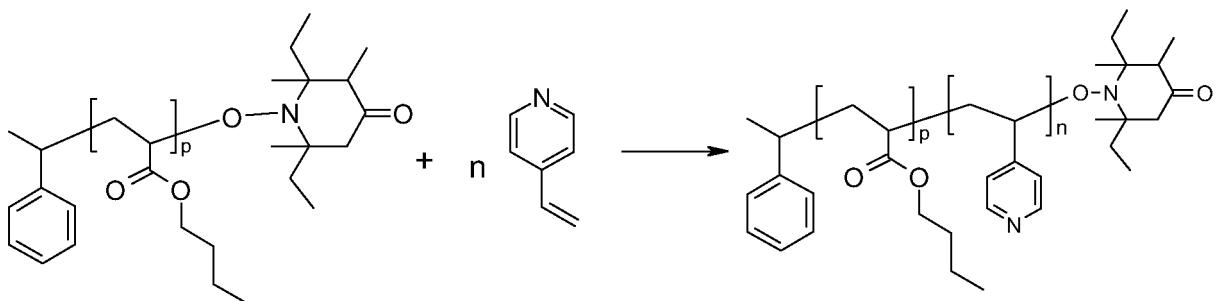


5

In a 3-necked 1000ml round bottom flask with magnetic stirring bar, cooler, thermometer, dropping funnel 150.10 g n-butylacrylate (n-BA, 128.17g/mol), 8.55g compound O1 (317.48g/mol) and 122.13g of MPA were added, three times degassed with N₂/vacuum and polymerized at 135°C under N₂ until a conversion of around 8 mol% is reached. 338.89 g of 10 n-BA is slowly added to the reaction with the dropping funnel and polymerized at 135°C under N₂ until a conversion of around 48 mol%. Residual monomers and solvents were distilled off at 80°C and 12 mbar.

Yield 47%, GPC (THF, PS-Standard, Mn=7800 g/mol, PD=1.27), liquid.
15 According to analysis via ¹H-NMR, the degree of polymerization is 75.

Example A2: Synthesis of a linear block copolymer poly(n-BA-b-4VP)



20 In a 3-necked 500ml round bottom flask with magnetic stirring bar, cooler, thermometer 214.18 g poly(n-BA) of example A1, 70.90g 4-vinylpyridine (4-VP, 105.14 g/mol) and 79.70g of MPA are added, three times degassed with N₂/vacuum and polymerized at 125°C under N₂ for 8h. Residual monomers and solvents are distilled off at 80°C and 12 mbar.

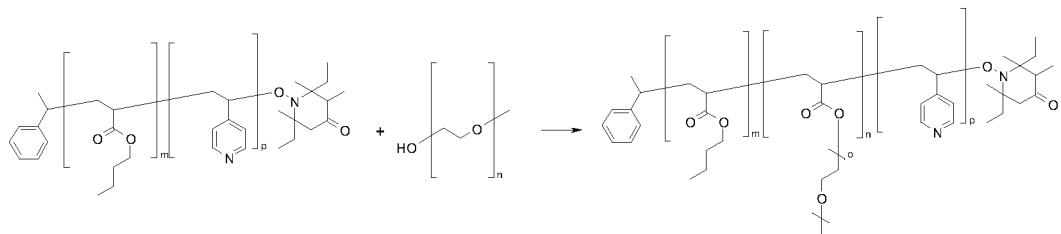
- 30 -

Yield 85%, GPC (THF, PS-Standard, Mn=8600 g/mol, PD=1.24), liquid.

According to analysis via $^1\text{H-NMR}$, the degree of polymerization is: P(BA-b-4VP) = 75-b-14.

5

Example A3: Poly(n-BA-MPEGA-b-4-VP)



Transesterification using MPEG-OH

In a 500 mL flask equipped with a magnetic stirring bar, distillation column with dry ice 10 acetone cooling 92.8 g of Poly(n-BA-b-4-VP) according to example A2 in 107.2 g of Xylene and 114.7 g of MPEG-OH (Mn=550 g/mol) are added and dried by azeotropic distillation of the xylene. Three portions of 0.36 g of tera(isopropyl)orthotitanate are added during 3 h at 190-205 °C. The formed n-Butanol is distilled off at low pressure.

15 187.7 g of Poly(n-BA-MPEGA-b-4-VP) are obtained. Mn=17500 g/mol, PDI=1.6, OH-value=0.05 meq/g. Analysis via GPC as well as $^1\text{H-NMR}$ indicate almost quantitative conversion of the MPEG-OH.

The resulting polymer is well soluble in water and shows an LCST-type solution behaviour 20 (LCST = lower critical solution temperature), i.e. the solubility of the polymer decreases with increasing temperature). A 35 wt% solution of the endproduct polymer in water is a clear solution at room temperature, but becomes turbid at elevated temperatures above 70°C. The resulting polymer also formed clear 10 wt% solutions in following organic solvents: butyl acetate, methoxypropylacetate, methoxipropanol, butylglycol and xylene.

25

Example A4: Synthesis of a linear polymer poly(BA)

In a 6 liter reactor equipped with stirrer, cooler, thermometer, and monomer feed pumps 1519 g n-Butylacrylate, 209 g compound O1 were added, three times degassed with 30 N_2 /vacuum and heated to 115°C under N_2 , where a continuous feed of n-butylacrylate was

- 31 -

started over 4 hours and at the same time the reaction mass slowly heated to 135°C. After the end of the monomer feed, the reaction mass was further reacted for 5 h until a solids content of 55% was reached. Afterwards, the non reacted monomer was removed by vacuum distillation.

5

2812g of Poly(n-BA) are obtained as liquid polymer, Mn = 4554, PDI=1.18

According to analysis via $^1\text{H-NMR}$, the degree of polymerization is: P(nBA) = 35.

10 Example A5: Synthesis of a linear block copolymer poly(n-BA-b-4VP)

In the same reactor as in Ex. A4, 2674 g of polymer **A4** were loaded together with 1133 g 4-vinylpyridine and heated under N_2 to 135°C and reacted for 3.5 h until a solids content of 91% was reached. This polymer was used for subsequent transesterifications without further removal of non-reacted 4-vinylpyridine.

15

3732 g of Polymer P(nBA-b-4VP) were isolated from the reactor, Mn =4779, PDI = 1.19

According to analysis via $^1\text{H-NMR}$, the degree of polymerization is: P(nBA-b-4VP) = 35-b-14.

20 Example A6: Synthesis of block copolymer Poly(n-BA-MPEGA-b-4-VP)

Transesterification using MPEG-OH

In the same reactor as in example A4, 3730 g of the polymer **A5** were loaded together with 3503 g of MPEG-OH (M= 550 g/mol) and subjected to vacuum degassing at 130°C for one hour to remove non-reacted 4-vinylpyridine. 12.0 g of LiOMe-solution (10 wt% lithium methanolate in methanol were added slowly and the transesterification started by distilling off n-Butanol at 130°C and reduced pressure. Additional 5 portions of catalyst were added after every hour: 2 x 12.0 g and additional 3 x 14.5 g of LiOMe-solution. After 6 h the reaction was completed by collecting the calculated amount of n-butanol.

25

30 6322 g of viscous polymer were obtained; Mn = 8829, PDI = 1.36

Anaylsis via GPC as well as $^1\text{H-NMR}$ indicate almost quantitative conversion of the MPEG-OH.

According to analysis via $^1\text{H-NMR}$, the degree of polymerization is: $P[(\text{nBA-MPEGA})-\text{b-4VP}] = (23-12)-\text{b-14}$.

OH-number titration: 0.20 meq/g

Amine number titration: 69 mg KOH/g

5 The 50 wt% solids solution in water displays an LCST of 67°C.

Aside from water, the polymer **A6** gives clear solutions 10 wt% in following organic solvents: butyl acetate, methoxypropylacetate, methoxypropanol, butylglycol and xylene.

For testing as pigment dispersant part of the polymer **A6** was dissolved in water to give a clear 50 wt% solids solution, other parts of the polymer were dissolved in various other 10 organic solvents.

Example A7: Synthesis of a random copolymer Poly(n-BA-MPEGA)

In the same reactor as in example A4 were loaded 500g of a poly(n-BA) ($M_n = 8304$, PDI = 1.21), which was made analog polymer **A4** and 500g of **MPEG-OH** ($M = 550$ g/mol). The

15 mixture was heated to 128°C, than 21 g of LiOMe catalysts solution (10 wt% in methanol) were added slowly and n-butanol was slowly distilled off under reduced pressure. Catalyst addition was repeated 5 times each after one hour with 21 g catalyst solution. The transesterification was conducted in total for 6 h until the calculated amount of n-butanol had been distilled off.

20

918 g of polymer were obtained; $M_n = 13305$, PDI = 1.31

Anaylsis via GPC as well as $^1\text{H-NMR}$ indicate almost quantitative conversion of the MPEG-OH.

According to analysis via $^1\text{H-NMR}$, the degree of polymerization is: $P(\text{nBA-MPEGA}) = (58-$

25 19).

The 50 wt% solids solution in water displays an LCST of 70°C.

For testing as pigment dispersant part of the polymer **A7** was dissolved in water to give a clear 50 wt% solids solution.

Example A8: Synthesis of a random copolymer Poly(n-BA-MPEGA) comprising different
MPEG-OH: MPEG350, MPEG500, MPEG2000

In a 250 mL flask equipped with a magnetic stirring bar and distillation column are loaded 65 g of a P(nBA) (Mn = 8386, PD = 1.21; made analog to example A4), 7.5 g of **MPEG-OH** (M = 350), 7.5 g MPEG-OH (M = 500) and 20 g MPEG-OH (M = 2000). The mixture was heated to 125°C and 2 g of LiOMe catalyst solution (10 wt% in MeOH) were slowly added. The transesterification was started by slowly distilling off n-butanol under reduced pressure and increasing the temperature to 130°C. Two additional portions each of 2 g catalyst solution were added after 1 h and 2 h later. After 4 h total reaction time the transesterification was terminated after the calculated amount of n-butanol had been distilled off.

84 g of polymer were obtained; Mn = 10490, PDI = 1.61

Analysis via GPC as well as ¹H-NMR indicate almost quantitative conversion of the MPEG-OH-mixture.

According to analysis via ¹H-NMR, the degree of polymerization is: P(nBA-MPEGA-mix) = (69-7).

Example A9: Synthesis of a random copolymer Poly(n-BA-MPEGA) comprising different
MPEG-OH: MPEG350, MPEG500, MPEG5000

In a 250 mL flask equipped with a magnetic stirring bar and distillation column are loaded 65 g of a P(nBA) (Mn = 8386, PD = 1.21; made analog to example A4), 7.5 g of **MPEG-OH** (M = 350), 7.5 g MPEG-OH (M = 500) and 20 g MPEG-OH (M = 5000). The mixture was heated to 125°C and 2 g of LiOMe catalyst solution (10 wt% in MeOH) were slowly added. The transesterification was started by slowly distilling off n-butanol under reduced pressure and increasing the temperature to 130°C. Two additional portions each of 2 g catalyst solution were added after 1 h and 2 h later. After 4 h total reaction time the transesterification was terminated after the calculated amount of n-butanol had been distilled off.

83 g of polymer were obtained; Mn = 9563, PDI = 1.75

Analysis via GPC as well as ¹H-NMR indicate almost quantitative conversion of the MPEG-OH-mixture.

According to analysis via ¹H-NMR, the degree of polymerization is: P(nBA-MPEGA-mix) = (71-6).

Example A10: Synthesis of a random copolymer Poly(n-BA-MPEGA-OleA) comprising unsaturated groups

In a 250 mL flask equipped with a magnetic stirring bar and distillation column are loaded 38 g of a P(nBA) (Mn = 8386, PD = 1.21; made analog to example A4), 35 g MPEG-OH (M = 500) and 27 g **oleyl alcohol** (techn. grade). The mixture was heated to 125°C and 2 g of LiOMe catalyst solution (10 wt% in MeOH) were slowly added. The transesterification was started by slowly distilling off n-butanol under reduced pressure and increasing the temperature to 135°C. Two additional portions each of 2 g catalyst solution were added after 1 h and 2 h later. After 4 h total reaction time the transesterification was terminated after the calculated amount of n-butanol had been distilled off. 78 g of liquid polymer were obtained; Mn = 13374, PDI = 1.87

Analysis via GPC as well as $^1\text{H-NMR}$ indicate almost quantitative conversion of the MPEG-OH and the unsaturated oleyl alcohol.

According to analysis via $^1\text{H-NMR}$, the degree of polymerization is: P(nBA-MPEGA-OleA) = 15 (32-18-26).

Example A11: Synthesis of a non-polar block copolymer Poly[(n-BA-iC12-15A)-b-4VP]

In a 250 ml flask equipped with a magnetic stirring bar and distillation column are loaded 20 83.3 g of a 60wt% MPA-solution of a diblock copolymer P(nBA-b-4VP) (synthesized analog polymer A5; degree of polymerization = 76-b-14, Mn = 8834, PD = 1.27) and 54.1 g of a branched **iso-C12-15-alcohol** mixture (Lial 125, Condea). After heating the mixture to 125°C, the MPA was distilled under reduced pressure before adding 0.28 g catalyst solution (Ti(AcAc)₂(iOPr)₂ Titan-bis-acetylacetato-bis-isopropylate, 75 wt% in isopropanol). The 25 transesterification was started by slowly distilling off n-Butanol under reduced pressure and increasing the temperature to 145°C. Two additional portions each of 0.28 g catalyst solution were added after 1 h and 2 h later. After 4 h total reaction time the transesterification was terminated after no further n-butanol formation was observed.

30 76 g of liquid block copolymer were obtained; Mn = 12216, PDI = 1.27

Analysis via GPC as well as $^1\text{H-NMR}$ indicated almost quantitative conversion of the MPEG-OH and the branched iC12-C15-alcohol.

According to combined analysis of $^1\text{H-NMR}$ and GPC, the degree of polymerization is: P[(nBA-iC12-15A)-b-4VP] = (16-60)-b-14.

- 35 -

Example A12: Synthesis of a block copolymer Poly(n-BA-b-S)

In a 500 ml flask equipped with a magnetic stirring bar and distillation column are loaded 210 g of a P(nBA) (synthesized analog polymer A4; degree of polymerization = 76, Mn = 8547, PDI = 1.19) and 90 g of **styrene** and were heated under N2 to 125°C. After 5 h the reaction 5 was terminated and the non-reacted styrene was distilled off at reduced pressure.

175 g of block copolymer were obtained; Mn = 11828, PDI = 1.21

According to analysis of ¹H-NMR the degree of polymerization is: P(nBA-b-S) = (75-b-40).

The resultant very high viscous block copolymer was diluted with MPA to a clear 60 wt% 10 solution.

Example A13: Synthesis of a non-polar block copolymer Poly[(n-BA-iC12-15A)-b-S]

In a 250 ml flask equipped with a magnetic stirring bar and distillation column are loaded 50 15 g of a 60wt% MPA-solution of the diblock copolymer **A12** P(nBA-b-S) = 75-b-40) and 26.3 g of a branched **iso-C12-15-alcohol** mixture (Lial 125, Condea). After heating the mixture to 125°C, the MPA was distilled off under reduced pressure before adding 0.15 g catalyst solution (Ti(AcAc)₂(iOPr)₂ Titan-bis-acetylacetone-bis-isopropylate, 75 wt% in isopropanol). The transesterification was started by slowly distilling off n-Butanol under reduced pressure 20 and increasing the temperature to 145°C. Two additional portions each of 0.15 g catalyst solution were added after 2 h and 4 h later. After 6 h total reaction time the reaction was terminated after no further n-butanol formation was observed.

49 g of liquid block copolymer were obtained; Mn = 15072, PDI = 1.21

25 Analysis via GPC as well as ¹H-NMR indicated good conversion of the branched iC12-C15-alcohol.

According to combined analysis of ¹H-NMR and GPC, the degree of polymerization is: P[(nBA-iC12-15A)-b-S = (15-60)-b-40.

30

Example A14: Synthesis of a block copolymer Poly(n-BA-b-DMAPMA)

In a 500 ml flask equipped with a magnetic stirring bar and distillation column are loaded 150 g of a P(nBA) (synthesized analog polymer A4; degree of polymerization = 76, Mn = 8547, PDI = 1.19) and 150 g of dimethylaminopropyl methacrylamide (**DMAPMA**) and were heated

- 36 -

under N₂ to 145°C. After 4.5h the reaction was terminated and non-reacted monomer DMAPMA was distilled off at high vacuum.

179 g of block copolymer were isolated; Mn = 6874, PDI = 1.41 (the apparent molecular

5 weight via GPC appeared lower than the starting precursor)

According to analysis of ¹H-NMR the degree of polymerization is: P(nBA-b-DMAPMA) = (75-b-23).

The resultant high viscous block copolymer was diluted with MPA to a clear 60 wt% solution.

10 Example A15: Synthesis of block copolymer Poly(n-BA-MPEGA-b-DMAPMA)

Transesterification using MPEG-OH

50 g of the polymer Poly(n-BA-b-DMAPMA) (synthesized according to polymer A14) are loaded together with 50 g of **MPEG-OH** (M= 550 g/mol) and subjected to vacuum degassing

15 at 130°C for one hour to remove non-reacted DMAPMA. 2 g of LiOMe-solution (10 wt% lithium methanolate in methanol are added slowly and the transesterification started by distilling off n-Butanol at 130°C and reduced pressure. Catalyst addition is repeated 2 times each after one hour with 2 g catalyst solution. The transesterification is conducted in total for 3 h until the calculated amount of n-butanol had been distilled off.

20

100 g of polymer are obtained; Mn = 112449, PDI = 1.79

Anaylsis via GPC as well as ¹H_NMR indicate almost quantitative conversion of the MPEG-OH.

According to combined analysis of ¹H-NMR and GPC, the degree of polymerization is:

25 P[(nBA-MPEG)-b-DMAPMA] = (51-14)-b-14.

Example A16: Synthesis of a random copolymer Poly(n-BA-MPEGA-b-DMAPMA) comprising different MPEG-OH: MTG, MPEG500

30 In a 200 ml flask equipped with a magnetic stirring bar and distillation column are loaded 35 g of a Poly(n-BA-b-DMAPMA) (synthesized according to polymer A14), 15 g of **MTG** (M = 164.2), 50 g **MPEG-OH** (M = 500). The mixture is heated to 80°C and 2 g of LiOMe catalyst solution (10 wt% in MeOH) are slowly added. The transesterification is started by slowly distilling off n-butanol under reduced pressure and increasing the temperature to 120°C. Two

additional portions each of 2 g catalyst solution are added after 1 h and 2 h later. After 3 h total reaction time the transesterification is terminated after the calculated amount of n-butanol had been distilled off.

5 100 g of polymer are obtained; Mn = 11265, PDI = 1.69

Analysis via GPC as well as $^1\text{H-NMR}$ indicate almost quantitative conversion of the MPEG-OH-mixture.

According to analysis via $^1\text{H-NMR}$, the degree of polymerization is: P[(nBA-MPEG500A-MTGA)-b-DMAPMA] = (37-20-19)-b-14.

10

Example A17: Synthesis of a random copolymer Poly(n-BA-MPEGA-b-DMAPMA) comprising different MPEG-OH: MTG, MPEG500

In a 200 ml flask equipped with a magnetic stirring bar and distillation column are loaded 40

15 g of a Poly(n-BA-b-DMAPMA) (synthesized according to polymer A14), 20 g of **MTG** (M = 164.2), 40 g **MPEG-OH** (M = 500). The mixture is heated to 80°C and 2 g of LiOMe catalyst solution (10 wt% in MeOH) are slowly added. The transesterification is started by slowly distilling off n-butanol under reduced pressure and increasing the temperature to 120°C. Two additional portions each of 2 g catalyst solution are added after 1 h and 2 h later. After 3 h 20 total reaction time the transesterification is terminated after the calculated amount of n-butanol had been distilled off.

103 g of polymer are obtained; Mn =, PDI =

Analysis via GPC as well as $^1\text{H-NMR}$ indicate almost quantitative conversion of the MPEG-25 OH-mixture.

According to analysis via $^1\text{H-NMR}$, the degree of polymerization is: P[(nBA-MPEG500A-MTGA)-b-DMAPMA] = (40-14-22)-b-14.

30 Example A18: Synthesis of a random copolymer Poly(n-BA-MPEGA-b-DMAPMA) comprising different MPEG-OH: MTG, MPEG500

In a 200 ml flask equipped with a magnetic stirring bar and distillation column are loaded 40 g of a Poly(n-BA-b-DMAPMA) (synthesized according polymer A14), 30 g of **MTG** (M = 164.2), 30 g **MPEG-OH** (M = 500). The mixture is heated to 80°C and 2 g of LiOMe catalyst

solution (10 wt% in MeOH) are slowly added. The transesterification is started by slowly distilling off n-butanol under reduced pressure and increasing the temperature to 120°C. Two additional portions each of 2 g catalyst solution are added after 1 h and 2 h later. After 3 h total reaction time the transesterification is terminated after the calculated amount of n-
5 butanol had been distilled off.

100 g of polymer are obtained; Mn =, PDI =

Analysis via GPC as well as $^1\text{H-NMR}$ indicate almost quantitative conversion of the MPEG-OH-mixture.

10 According to analysis via $^1\text{H-NMR}$, the degree of polymerization is: P[(nBA-MPEG500A-MTGA)-b-DMAPMA] = (33-11-33)-b-14.

Example A19: Synthesis of block copolymer Poly(n-BA-MPEGA-b-DMAPMA)

15 Transesterification using MPEG-OH

In the reactor , 121.5 g of Poly(n-BA-b-DMAPMA) (synthesized according to polymer A14) are loaded together with 49.8 g of **MPEG-OH** (M= 550 g/mol) and subjected to vacuum degassing at 130°C for one hour to remove non-reacted DMAPMA. 0.33 g of LiOMe-solution (10 wt% lithium methanolate in methanol are added slowly and the transesterification started
20 by distilling off n-Butanol at 130°C and reduced pressure. Catalyst addition is repeated 3 times each after one hour with 0.33 g catalyst solution. The transesterification is conducted in total for 6 h until the calculated amount of n-butanol had been distilled off.

166 g of polymer are obtained; Mn = 6972, PDI = 2.12

25 Anaylsis via GPC as well as $^1\text{H-NMR}$ indicate almost quantitative conversion of the MPEG-OH.

According to combined analysis of $^1\text{H-NMR}$ and GPC, the degree of polymerization is: P[(nBA-MPEGA)-b-DMAPMA] = (62-15)-b-16.

Example A20: Synthesis of block copolymer Poly(n-BA-MPEGA-b-DMAPMA)Transesterification using MPEG-OH

In the reactor , 109.2 g of Poly(n-BA-b-DMAPMA) (synthesized according to polymer A14) are loaded together with 44.7 g of **MPEG-OH** (M= 550 g/mol) and subjected to vacuum
5 degassing at 130°C for one hour to remove non-reacted DMAPMA. 1.19 g of catalyst solution (Ti(AcAc)2(iOPr)2 Titan-bis-acetylacetone-bis-isopropylate, 75 wt% in isopropanol) are added slowly and the transesterification started by distilling off n-Butanol at 165°C and reduced pressure. Catalyst addition is repeated 2.5 times each after one hour with 1.19 g catalyst solution. The transesterification is conducted in total for 3.5 h until the calculated
10 amount of n-butanol had been distilled off.

149 g of polymer are obtained; Mn = 8498, PDI = 2.40.

Anaylsis via GPC as well as $^1\text{H-NMR}$ indicate almost quantitative conversion of the MPEG-OH.

15 According to combined analysis of $^1\text{H-NMR}$ and GPC, the degree of polymerization is:
 $P[(\text{nBA-MPEGA})\text{-b-DMAPMA}] = (65\text{-}12)\text{-b-}16$.

Example A21: Synthesis of block copolymer Poly(n-BA-MPEGA-b-DMAPMA)Transesterification using MPEG-OH

In the reactor , 102.3 g of Poly(n-BA-b-DMAPMA) (synthesized according to polymer A14) are loaded together with 65.2 g of **MPEG-OH** (M= 550 g/mol) and subjected to vacuum
20 degassing at 160°C for one hour to remove non-reacted DMAPMA. 0.43 g of catalyst solution (Ti(AcAc)2(iOPr)2 Titan-bis-acetylacetone-bis-isopropylate, 75 wt% in isopropanol) are added slowly and the transesterification started by distilling off n-Butanol at 165°C and reduced pressure. Catalyst addition is repeated 4 times each after one hour with 0.43 g catalyst solution. The transesterification is conducted in total for 5 h until the calculated
25 amount of n-butanol had been distilled off.

30 163 g of polymer are obtained; Mn = 8364, PDI = 1.62

Anaylsis via GPC as well as $^1\text{H-NMR}$ indicate almost quantitative conversion of the MPEG-OH.

According to combined analysis of $^1\text{H-NMR}$ and GPC, the degree of polymerization is:
 $P[(\text{nBA-MPEGA})\text{-b-DMAPMA}] = (60\text{-}17)\text{-b-}16$.

- 40 -

Example A22: Synthesis of block copolymer Poly(n-BA-MPEGA-b-DMAPMA)

Transesterification using MPEG-OH

In the reactor, 102.6 g of Poly(n-BA-b-DMAPMA) (synthesized according to polymer A14) are loaded together with 98.1 g of **MPEG-OH** (M= 550 g/mol) and subjected to vacuum
5 degassing at 160°C for one hour to remove non-reacted DMAPMA. 0.52 g of catalyst solution (Ti(AcAc)2(iOPr)2 Titan-bis-acetylacetato-bis-isopropylate, 75 wt% in isopropanol) are added slowly and the transesterification started by distilling off n-Butanol at 165°C and reduced pressure. Catalyst addition is repeated 4 times each after one hour with 0.52g catalyst solution. The transesterification is conducted in total for 5 h until the calculated
10 amount of n-butanol had been distilled off.

196 g of polymer are obtained; Mn = 9060, PDI = 1.66

Anaylsis via GPC as well as $^1\text{H-NMR}$ indicate almost quantitative conversion of the MPEG-OH.

15 According to combined analysis of $^1\text{H-NMR}$ and GPC, the degree of polymerization is:
 $P[(\text{nBA-MPEG})\text{-b-DMAPMA}] = (51\text{-}26)\text{-b-}16$.

Example A23: Synthesis of block copolymer Poly(n-BA-MPEGA-b-DMAPMA)

Transesterification using MPEG-OH

In the reactor, 71.2 g of Poly(n-BA-b-DMAPMA) (synthesized according to polymer A14) are loaded together with 102.1 g of **MPEG-OH** (M= 550 g/mol) and subjected to vacuum
25 degassing at 160°C for one hour to remove non-reacted DMAPMA. 0.6 g of catalyst solution (Ti(AcAc)2(iOPr)2 Titan-bis-acetylacetato-bis-isopropylate, 75 wt% in isopropanol) are added slowly and the transesterification started by distilling off n-Butanol at 165°C and reduced pressure. Catalyst addition is repeated 4 times each after one hour with 0.6 g catalyst solution. The transesterification is conducted in total for 5 h until the calculated amount of n-butanol had been distilled off.

30 170.2 g of polymer are obtained; Mn = 10053, PDI = 1.71

Anaylsis via GPC as well as $^1\text{H-NMR}$ indicate almost quantitative conversion of the MPEG-OH.

According to combined analysis of $^1\text{H-NMR}$ and GPC, the degree of polymerization is:
 $P[(\text{nBA-MPEG})\text{-b-DMAPMA}] = (39\text{-}38)\text{-b-}16$.

Example A24: Synthesis of block copolymer Poly(n-BA-MPEGA-b-DMAPMA)Transesterification using MPEG-OH

In the reactor, 54 g of Poly(n-BA-b-DMAPMA) (synthesized according to polymer A14) are loaded together with 120.5 g of **MPEG-OH** (M= 550 g/mol) and subjected to vacuum
5 degassing at 160°C for one hour to remove non-reacted DMAPMA. 2.75 g of catalyst solution (Ti(AcAc)2(iOPr)2 Titan-bis-acetylacetato-bis-isopropylate, 75 wt% in isopropanol) are added slowly and the transesterification started by distilling off n-Butanol at 165°C and reduced pressure. Catalyst addition is repeated 2 times each after 1 hour with 1.38 and 2.75 g catalyst solution. The transesterification is conducted in total for 6 h until the calculated
10 amount of n-butanol had been distilled off.

172 g of polymer are obtained; Mn = 11051, PDI = 1.72

Anaylsis via GPC as well as ¹H_NMR indicate almost quantitative conversion of the MPEG-OH.

15 According to combined analysis of ¹H-NMR and GPC, the degree of polymerization is:
P[(nBA-MPEG)-b-DMAPMA] = (23-54)-b-16.

Example A25: Synthesis of a block copolymer Poly (n-BA-MPEGA-iC12-15A)-b-DMAPMA)20 Transesterification using MPEG-OH and Lial 125

In a 250 ml flask equipped with a magnetic stirring bar and distillation column are loaded 75 g of a Poly(n-BA-b-DMAPMA) (synthesized according to polymer A14), 36.2 g **MPEG-OH** (M = 500) and 12.1 g **Lial 125** (techn. grade). The mixture is heated to 130°C and 2.4 g of LiOMe catalyst solution (10 wt% in MeOH) are slowly added. The transesterification is started by slowly distilling off n-butanol under reduced pressure and increasing the temperature to 125°C. Two additional portions each of 2.4 g catalyst solution are added after 1 h and 1 h later. After 3 h total reaction time the transesterification is terminated after the calculated amount of n-butanol had been distilled off.

30 120.5 g of liquid polymer are obtained; Mn = 8637, PDI = 1.92

Analysis via GPC as well as ¹H-NMR indicate almost quantitative conversion of the MPEG-OH and Lial 125.

According to analysis via ¹H-NMR, the degree of polymerization is: P(n-BA-MPEGA-iC12-15A)-b-DMAPMA = (53-13-10)-14.

Example A26: Synthesis of a block copolymer Poly (n-BA-MPEGA-iC12-15A)-b-DMAPMA)Transesterification using MPEG-OH and Lial 125

In a 250 ml flask equipped with a magnetic stirring bar and distillation column are loaded 70.1 g of a Poly(n-BA-b-DMAPMA) (synthesized according to polymer A14), 22.5 g **MPEG-**

5 **OH** (M = 500) and 22.5 g **Lial 125** (techn. grade). The mixture is heated to 130°C and 2.25 g of LiOMe catalyst solution (10 wt% in MeOH) are slowly added. The transesterification is started by slowly distilling off n-butanol under reduced pressure and increasing the temperature to 125°C. Two additional portions each of 2.25 g catalyst solution are added after 1 h and 1 h later. After 4 h total reaction time the transesterification is terminated after

10 the calculated amount of n-butanol had been distilled off.

112.6 g of liquid polymer are obtained; Mn = 8382, PDI = 1.92

Analysis via GPC as well as $^1\text{H-NMR}$ indicate almost quantitative conversion of the MPEG-OH and Lial 125.

15 According to analysis via $^1\text{H-NMR}$, the degree of polymerization is: P(n-BA-MPEGA-iC12-15A)-b-DMAPMA = (47-10-19)-14.

Example A27: Synthesis of a block copolymer Poly (n-BA-MPEGA-iC12-15A)-b-DMAPMA)Transesterification using MPEG-OH and Lial 125

In a 250 ml flask equipped with a magnetic stirring bar and distillation column are loaded 72 g of a Poly(n-BA-b-DMAPMA) (synthesized according to polymer A14), 11.6 g **MPEG-OH**

25 (M = 500) and 34.7 g **Lial 125** (techn. grade). The mixture is heated to 130°C and 2.31 g of LiOMe catalyst solution (10 wt% in MeOH) are slowly added. The transesterification is started by slowly distilling off n-butanol under reduced pressure and increasing the temperature to 125°C. Two additional portions each of 2.31 g catalyst solution are added after 1 h and 1 h later. After 4 h total reaction time the transesterification is terminated after

the calculated amount of n-butanol had been distilled off.

30 115 g of liquid polymer are obtained; Mn = 9488, PDI = 1.77

Analysis via GPC as well as $^1\text{H-NMR}$ indicate almost quantitative conversion of the MPEG-OH and Lial 125.

According to analysis via $^1\text{H-NMR}$, the degree of polymerization is: P(n-BA-MPEGA-iC12-15A)-b-DMAPMA = (54-2-20)-14.

Example A28: Synthesis of a block copolymer Poly (n-BA-iC12-15A)-b-DMAPMA)Transesterification using Lial 125

In a 250 ml flask equipped with a magnetic stirring bar and distillation column are loaded 89.8 g of a Poly(n-BA-b-DMAPMA) (synthesized according to polymer A14), 57.7 g **Lial 125** (techn. grade). The mixture is heated to 130°C and 2.9 g of LiOMe catalyst solution (10 wt% in MeOH) are slowly added. The transesterification is started by slowly distilling off n-butanol under reduced pressure and increasing the temperature to 125°C. Two additional portions each of 2.9 g catalyst solution are added after 1 h and 1 h later. After 3 h total reaction time the transesterification is terminated after the calculated amount of n-butanol had been distilled off.

144 g of liquid polymer are obtained; Mn = 10215, PDI = 1.70

Analysis via GPC as well as $^1\text{H-NMR}$ indicate almost quantitative conversion of the Lial 125.

According to analysis via $^1\text{H-NMR}$, the degree of polymerization is: P(n-BA-iC12-15A)-b-DMAPMA = (52-24)-14.

Example A29: Synthesis of a block copolymer Poly (n-BA-MPEGA-iC12-15A)-b-DMAPMA)Transesterification using MPEG-OH and Lial 125

In a 250 ml flask equipped with a magnetic stirring bar and distillation column are loaded 535.5 g of a Poly(n-BA-b-DMAPMA) (synthesized according to polymer A14), 84.8 g **MPEG-OH** ($M = 500$) and 254.4 g **Lial 125** (techn. grade). The mixture is heated to 140°C and 5.5 g of LiOMe catalyst solution (10 wt% in MeOH) are slowly added. The transesterification is started by slowly distilling off n-butanol under reduced pressure and increasing the temperature to 140°C. Two additional portions each of 5.5 g catalyst solution are added after 1 h and 1 h later. After 3 h total reaction time the transesterification is terminated after the calculated amount of n-butanol had been distilled off.

751 g of liquid polymer are obtained; Mn = 9488, PDI = 1.77

Analysis via GPC as well as $^1\text{H-NMR}$ indicate almost quantitative conversion of the MPEG-OH and Lial 125.

According to analysis via $^1\text{H-NMR}$, the degree of polymerization is: P(n-BA-MPEGA-iC12-15A)-b-DMAPMA = (52-4-23)-21.

Example A30: Synthesis of a block copolymer Poly (n-BA-MPEGA-iC12-15A)-b-DMAPMA)Transesterification using MPEG-OH and Lial 125

In a 250 ml flask equipped with a magnetic stirring bar and distillation column are loaded 577.5 g of a Poly(n-BA-b-DMAPMA) (synthesized according to polymer A14), 91.4 g **MPEG-5 OH (M = 500)** and 274.3 g **Lial 125** (techn. grade). The mixture is heated to 140°C and 7.4 g of catalyst solution (Ti(AcAc)2(iOPr)2 Titan-bis-acetylacetato-bis-isopropylate, 75 wt% in isopropanol) are added slowly and the transesterification started by distilling off n-Butanol at 150°C and reduced pressure. Two additional portions each of 7.4 g catalyst solution are added after 1 h and 1 h later. After 3 h total reaction time the transesterification is terminated 10 after the calculated amount of n-butanol had been distilled off.

826g of liquid polymer are obtained; Mn = 9488, PDI = 1.77

Analysis via GPC as well as $^1\text{H-NMR}$ indicate almost quantitative conversion of the MPEG-OH and Lial 125.

15 According to analysis via $^1\text{H-NMR}$, the degree of polymerization is: P(n-BA-MPEGA-iC12-15A)-b-DMAPMA = (52-4-23)-21.

Example A31: Synthesis of a block copolymer Poly (n-BA-MPEGA-iC12-15A)-b-DMAPMA)Transesterification using MPEG-OH and Lial 125

In a 250 ml flask equipped with a magnetic stirring bar and distillation column are loaded 151.4 g of a Poly(n-BA-b-DMAPMA) (synthesized according to polymer A14), 101.0 g **MPEG-OH (M = 500)**. The mixture is heated to 130°C and 2.04 g of catalyst solution (Ti(AcAc)2(iOPr)2 Titan-bis-acetylacetato-bis-isopropylate, 75 wt% in isopropanol) are 25 added slowly and the transesterification started by distilling off n-Butanol at 155°C and reduced pressure. Two additional portions each of 2.04 g catalyst solution are added after 1 h and 1 h later. After 3 h total reaction time the transesterification is terminated after the calculated amount of n-butanol had been distilled off.

30 238.1g of liquid polymer are obtained; Mn = 7417, PDI = 1.51

Analysis via GPC as well as $^1\text{H-NMR}$ indicate almost quantitative conversion of the MPEG-OH.

According to analysis via $^1\text{H-NMR}$, the degree of polymerization is: P(n-BA-MPEGA-iC12-15A)-b-DMAPMA = (62-15)-17.

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Example A32: Synthesis of a block copolymer Poly (n-BA-MPEGA-iC12-15A)-b-DMAPMA)

Transesterification using MPEG-OH and Lial 125

In a 250 ml flask equipped with a magnetic stirring bar and distillation column are loaded 150 g of a Poly(n-BA-b-DMAPMA) (synthesized according to polymer A14), 75 g **MPEG-OH** (M = 500) and 25 g **Lial 125** (techn. grade). The mixture is heated to 150°C and 2.02 g of catalyst solution (Ti(AcAc)2(iOPr)2 Titan-bis-acetylacetone-bis-isopropylate, 75 wt% in isopropanol) are added slowly and the transesterification started by distilling off n-Butanol at 155°C and reduced pressure. Two additional portions each of 2.02 g catalyst solution are added after 1 h and 1 h later. After 3 h total reaction time the transesterification is terminated 10 after the calculated amount of n-butanol had been distilled off.

235.8g of liquid polymer are obtained; Mn = 7585, PDI = 1.53

Analysis via GPC as well as $^1\text{H-NMR}$ indicate almost quantitative conversion of the MPEG-OH and Lial 125.

15 According to analysis via $^1\text{H-NMR}$, the degree of polymerization is: P(n-BA-MPEGA-iC12-15A)-b-DMAPMA = (54-13-9)-17.

Example A33: Synthesis of a block copolymer Poly (n-BA-MPEGA-iC12-15A)-b-DMAPMA)

Transesterification using MPEG-OH and Lial 125

In a 250 ml flask equipped with a magnetic stirring bar and distillation column are loaded 150 g of a Poly(n-BA-b-DMAPMA) (synthesized according to polymer A14), 50 g **MPEG-OH** (M = 500) and 50 g **Lial 125** (techn. grade). The mixture is heated to 150°C and 2.02 g of catalyst solution (Ti(AcAc)2(iOPr)2 Titan-bis-acetylacetone-bis-isopropylate, 75 wt% in isopropanol) are added slowly and the transesterification started by distilling off n-Butanol at 155°C and reduced pressure. Two additional portions each of 2.02g catalyst solution are added after 1 h and 1 h later. After 3 h total reaction time the transesterification is terminated 25 after the calculated amount of n-butanol had been distilled off.

30 235.8g of liquid polymer are obtained; Mn = 7574, PDI = 1.48

Analysis via GPC as well as $^1\text{H-NMR}$ indicate almost quantitative conversion of the MPEG-OH and Lial 125.

According to analysis via $^1\text{H-NMR}$, the degree of polymerization is: P(n-BA-MPEGA-iC12-15A)-b-DMAPMA = (51-8-17)-17.

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Example A34: Synthesis of a block copolymer Poly (n-BA-MPEGA-iC12-15A)-b-DMAPMA)

Transesterification using MPEG-OH and Lial 125

In a 250 ml flask equipped with a magnetic stirring bar and distillation column are loaded 153.7 g of a Poly(n-BA-b-DMAPMA) (synthesized according to polymer A14), 25.6 g **MPEG-**

5 **OH (M = 500)** and 76.8 g **Lial 125** (techn. grade). The mixture is heated to 150°C and 2.07 g of catalyst solution ($Ti(AcAc)_2(iOPr)_2$ Titan-bis-acetylacetato-bis-isopropylate, 75 wt% in isopropanol) are added slowly and the transesterification started by distilling off n-Butanol at 155°C and reduced pressure. Two additional portions each of 2.07g catalyst solution are added after 1 h and 1 h later. After 3 h total reaction time the transesterification is terminated

10 after the calculated amount of n-butanol had been distilled off.

241.6g of liquid polymer are obtained; $M_n = 7260$, PDI = 1.54

Analysis via GPC as well as 1H -NMR indicate almost quantitative conversion of the MPEG-OH and Lial 125.

15 According to analysis via 1H -NMR, the degree of polymerization is: P(n-BA-MPEGA-iC12-15A)-b-DMAPMA = (48-3-25)-17.

Example A35: Synthesis of a block copolymer Poly (n-BA-MPEGA-iC12-15A)-b-DMAPMA)

20 Transesterification using MPEG-OH and Lial 125

In a 250 ml flask equipped with a magnetic stirring bar and distillation column are loaded 152.7 g of a Poly(n-BA-b-DMAPMA) (synthesized according to polymer A14), 101.8 g **Lial**

125 (techn. grade). The mixture is heated to 130°C and 2.06 g of catalyst solution ($Ti(AcAc)_2(iOPr)_2$ Titan-bis-acetylacetato-bis-isopropylate, 75 wt% in isopropanol) are

25 added slowly and the transesterification started by distilling off n-Butanol at 150°C and reduced pressure. Two additional portions each of 2.06g catalyst solution are added after 1 h and 1 h later. After 3 h total reaction time the transesterification is terminated after the calculated amount of n-butanol had been distilled off.

30 240.1g of liquid polymer are obtained; $M_n = 6766$, PDI = 1.58

Analysis via GPC as well as 1H -NMR indicate almost quantitative conversion of Lial 125.

According to analysis via 1H -NMR, the degree of polymerization is: P(n-BA-iC12-15A)-b-DMAPMA = (46-30)-17.

Example A36: Synthesis of a block copolymer Poly (n-BA-MPEGA-iC12-15A)-b-DMAPMA)
Transesterification using MPEG-OH and Lial 125

In a 250 mL flask equipped with a magnetic stirring bar and distillation column are loaded
5 152.7 g of a Poly(n-BA-b-DMAPMA) (synthesized analog polymer A14), 101.8 g **Lial 125** (techn. grade). The mixture is heated to 130°C and 2.06 g of catalyst solution (Ti(AcAc)2(iOPr)2 Titan-bis-acetylacetone-bis-isopropylate, 75 wt% in isopropanol) are added slowly and the transesterification started by distilling off n-Butanol at 150°C and reduced pressure. Two additional portions each of 2.06g catalyst solution are added after 1 h
10 and 1 h later. After 3 h total reaction time the transesterification is terminated after the calculated amount of n-butanol had been distilled off.

240.1g of liquid polymer are obtained; Mn = 6766, PDI = 1.58

Analysis via GPC as well as ¹H-NMR indicate almost quantitative conversion of Lial 125.

15 According to analysis via ¹H-NMR, the degree of polymerization is: P(n-BA-iC12-15A)-b-DMAPMA = (46-30)-17.

Synthesis of a block copolymer Poly (n-BA-MPEGA-iC12-15A)-b-(DMAPMA-CIBnDMAPMA)
quaternization

20 In a 100 ml flask equipped with a magnetic stirring bar and distillation column are loaded 15 g of a Poly (n-BA-MPEGA-iC12-15A)-b-DMAPMA), 0.9 g o-Chlorobenzylchloride and 15g of 1-methoxy-2-propanol. The mixture is heated to 95°C for 4 h.

After the reaction, 30.9g of liquid polymer are obtained; Mn =, PDI =

¹H-NMR indicates quantitative conversion for quaternization.

25 (n-BA-MPEGA-iC12-15A)-b-(DMAPMA-CIBnDMAPMA)= (52-4-23)-(15-6).

Preparation of Poly(benzylmethacrylate-co-methacrylic acid) – binder:

30 24 g of benzyl-methacrylate, 6 g of methacrylic acid and 0.525 g of azobisisobutyronitrile (AIBN) are dissolved in 90 ml of propylene glycol 1-monomethyl ether 2-acetate (PGMEA). The resulting reaction mixture is placed in a preheated oil bath at 80°C. After stirring for 5 hours at 80°C under nitrogen, the resulting viscous solution is cooled to room temperature and used without further purification. The solid content is about 25%.

Preparation of dispersion films for color filter:

The following substances are placed into a 37 ml screw bottle:

for PG36/PY150 system

2.0 g	pigment
13.4 g	propylene glycol 1-monomethyl ether 2-acetate
0.6 g	dispersant (solid)
4.0 g	binder (25wt% in PGMEA as mentioned above)
50.0 g	zircon beads

5 for PB15:6 system

1.0 g	pigment
9.8 g	propylene glycol 1-monomethyl ether 2-acetate
0.36 g	dispersant (solid)
4.0 g	binder (25wt% in PGMEA as mentioned above)
0.04 g	Solsperse 5000 (Avecia Limited)
50.0 g	zircon beads

for PR254 system

1.0 g	pigment
8.6 g	propylene glycol 1-monomethyl ether 2-acetate
0.2 g	dispersant (solid)
3.2 g	binder (25wt% in PGMEA as mentioned above)
50.0 g	zircon beads

Standard CF grade pigments used for the examples:

10 C.I. Pigment Green 36 : Lionol Green 6YK, TOYO INK MFG Co. Ltd.
 C.I. Pigment Yellow 150 : Yellow E4GN-GT, Bayer AG
 C.I. Pigment Blue 15:6 : Lionol Blue E, TOYO INK MFG Co. Ltd.
 C.I. Pigment Red 254 : IRGAPHOR RED BT-CF, Ciba Specialty Chemicals

15 Standard high molecular weight dispersants used for the examples:

Ciba EFKA 4300, 4330, 4047 : Ciba Specialty Chemicals
 Disperbyk 2000, 2001 : Altana - BYK Chemie
 Ajisper PB821 : Ajinomoto Fine Techno

The bottle is sealed with an inner cup and then applied to a paint conditioner for 3 hours to give the final dispersion. The dispersion thus obtained is cast onto a glass substrate by means of a spin coating, wherein a layer thickness is adjusted to give a film having a desired 5 color points (by standard C light, observation 2 degree) by controlling rotation speed, then dried at 60 °C for 1 hour.

Optical properties of the dispersion films thus obtained are measured by use of a spectrophotometer (UV-2500PC, Shimadzu) and contrast measurement equipment (Model 10 CT-1, Tsubosaka Electric Co., Ltd). The color points (C.I.E. 1931 x, y chromaticity diagram) are calculated using standard C light.

Viscosity measurements are performed by using a Brookfield Rheometer (Model DV-III) with a cone/plate set-up at 25 °C.

15

For the particle size measurement dynamic light scattering (DLS) is used (Mircotrac UPA, Microtrac Inc., Nikkiso). For the measurement samples are diluted with PGMEA by factor of 100.

20

Developability of the dispersion films are tested by dipping to alkaline developer (Semi Clean DL-A4, Yokohama Oil & Fats Industry Co., LTD / water = 1 / 9). Classify developability to 3 types. Dissolve, Dissolve then Peel, Peel. Dissolve type is suitable for color filter application.

25

Table 1: Performance data for a pigment system PG36(50%)/PY150(50%)

sample details		initial viscosity		1week viscosity		color property (y=0.60)		
		[mPa s]		[mPa s]		x	Y	contrast
dispersant	solids [%]	11.5 rpm	115 rpm	11.5 rpm	115 rpm			
A27	50	17	12	25	19	0.304	58.6	4063
A14	50	41	23	51	29	0.305	58.5	3997

Table 2 : Developerbility for a pigment system PG36(50%)/PY150(50%)

sample details dispersant	solids [%]	developerbility
A27	50	Dissolve only
A14	50	Dissolve then Peel

In these examples, A27 related to this invention is compared to A14.

5 A27 gives lower initial viscosity, lower 1 week viscosity and higher contrast than A14.

In addition, A27 has the most suitable developerbility for color filter application.

Table 3: Performance data for a pigment system PB15:6

10

sample details dispersant	solids [%]	initial viscosity [mPa s]		1 week viscosity [mPa s]		color property (y=0.13)		
		11.5 rpm	115 rpm	11.5 rpm	115 rpm	x	y	contrast
A36	50	17	10	2	8	0.135	17.0	4360
A14	50	22	15	18	14	0.135	17.0	4270
A14a	50	60	10	7	10	0.135	17.0	4300

A14a: the polymer of Example A14 (Poly(n-BA-b-DMAPMA)) is 30% quaternized with 4-chlorobenzylchloride.

Table 4 : Developerbility for a pigment system PB15:6

sample details		developerbility
dispersant	solids [%]	
A36	50	Dissolve only
A14a	50	Dissolve then Peel

In these examples, A36 related to this invention is compared to A14 (Poly(n-BA-b-DMAPMA)) and to A14a which is the polymer of Example A14 (Poly(n-BA-b-DMAPMA)) 30% quaternized with 4-chlorobenzylchloride.

5 A36 gives lower initial viscosity, lower 1 week viscosity and higher contrast than A14, A14a
In addition, A36 has the most suitable developerbility for color filter application.

10 Table 5: Performance data for a pigment system PG36(50%)/PY150(50%)

sample details	solids [%]	initial viscosity [mPa s]		1week viscosity [mPa s]		color property (y=0.60)		
		11.5 rpm	115 rpm	11.5 rpm	115 rpm	x	y	contrast
A27	50	17	12	25	19	0.304	58.6	4063
Ajisper PB821	100	15	14	152	54	0.306	58.3	3570
Disperbyk 2000	40	45	26	191	53	0.305	58.1	3783
Disperbyk 2001	46	36	23	301	62	0.308	58.5	3822

Table 6: Developerbility for a pigment system PG36(50%)/PY150(50%)

sample details		developerbility
dispersant	solids [%]	
A27	50	Dissolve only
Ajisper PB821	100	Peel only
Disperbyk 2000	40	no data
Disperbyk 2001	46	Peel only

In these examples, A27 related to this invention is compared to different commercial available dispersants which are used for color filter application.

5 A27 gives lower initial viscosity, lower 1 week viscosity and higher contrast than commercial available dispersants.

In addition, A27 has the most suitable developerbility for color filter application.

Table 7: Performance data for a pigment system PR 254

sample details		initial viscosity [mPa·s]		particle size [µm]	
dispersant	solids [%]	11.5 rpm	115 rpm	D50	D90
Ciba EFKA-4047	35	139	36	0.25	0.34
Ciba EFKA-4300	65	126	36	0.24	0.46
Ciba EFKA-4330	65	100	34	0.24	0.35
Example A2	60	134	55	0.15	0.25
Comparative					
Example A3	60	104	44	0.15	0.24

In this example A3 related to this invention is compared to different commercial available dispersants. Example A3 gives smaller particle size, which is an indication for an improved dispersion containing primary particles only. A complete de-agglomeration is achieved.

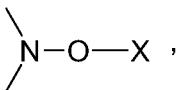
Claims

1. A color filter composition comprising

- a) a photoresist binder,
- b) a transparent pigment,

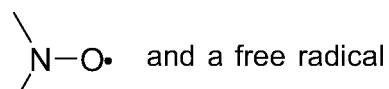
5 c) optionally a solvent and/or optionally a photoinitiator or a photolatent catalyst,
d) a dispersant which is a polymer or copolymer obtainable by a process comprising the
steps of

a1) polymerizing in a first step one or more ethylenically unsaturated monomers in the

presence of at least one nitroxylether having the structural element  ,

10 wherein **X** represents a group having at least one carbon atom and is such that the
free radical **X•** derived from **X** is capable of initiating polymerization; or

a2) polymerizing in a first step one or more ethylenically unsaturated monomers in the

presence of at least one stable free nitroxyl radical  and a free radical

15 initiator; wherein at least one monomer used in the steps a1) or a2) is a C₁-C₆ alkyl
or hydroxy C₁-C₆ alkyl ester of acrylic or methacrylic acid; and a second step

b) comprising the modification of the polymer or copolymer prepared under a1) or a2)
by a transesterification reaction, an amidation, hydrolysis or anhydride modification
or a combination thereof.

20

2. A color filter composition according to claim 1, wherein the dispersant is a polymer or
copolymer obtainable by a process comprising the steps of a1) or a2) as defined in claim 1
and a second step

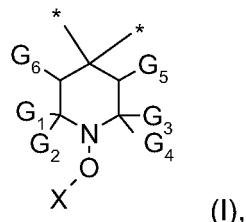
25 b) comprising the modification of the polymer or copolymer prepared under a1) or a2)
by a transesterification reaction, an amidation, hydrolysis or anhydride modification
or a combination thereof and in addition by quaternization.

3. A color filter composition according to claim 1 wherein the first polymerization step is carried out according to a1).

5 4. A color filter composition according to claim 1 wherein the second step b) is a transesterification reaction.

5. A color filter composition according to claim 1 wherein the structural element $\begin{array}{c} \diagup \\ \diagdown \end{array} \text{N-O-X}$ is

10 a structural element of formula (I)



wherein

G₁, G₂, G₃, G₄ are independently C₁-C₆alkyl or G₁ and G₂ or G₃ and G₄, or G₁ and G₂ and G₃ and G₄ together form a C₅-C₁₂cycloalkyl group;

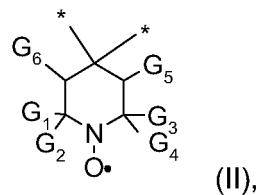
15 **G₅, G₆** independently are H, C₁-C₁₈alkyl, phenyl, naphthyl or a group COOC₁-C₁₈alkyl; X is selected from the group consisting of -CH₂-phenyl, CH₃CH-phenyl, (CH₃)₂C-phenyl, (C₅-C₆cycloalkyl)₂CCN, (CH₃)₂CCN, , , -CH₂CH=CH₂, CH₃CH-

CH=CH₂ (C₁-C₄alkyl)CR₂₀-C(O)-phenyl, (C₁-C₄)alkyl-CR₂₀-C(O)-(C₁-C₄)alkoxy, (C₁-C₄)alkyl-CR₂₀-C(O)-(C₁-C₄)alkyl, (C₁-C₄)alkyl-CR₂₀-C(O)-N-di(C₁-C₄)alkyl, (C₁-C₄)alkyl-CR₂₀-C(O)-

20 NH(C₁-C₄)alkyl, (C₁-C₄)alkyl-CR₂₀-C(O)-NH₂, wherein R₂₀ is hydrogen or (C₁-C₄)alkyl and * denotes a valence.

6. A color filter composition according to claim 1 wherein the structural element $\begin{array}{c} \diagup \\ \diagdown \end{array} \text{N-O•}$ is a

25 structural element of formula (II)

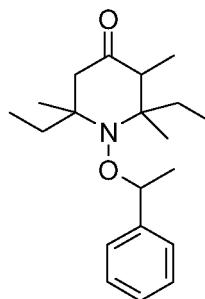


wherein

G₁, G₂, G₃, G₄ are independently C₁-C₆alkyl or G₁ and G₂ or G₃ and G₄, or G₁ and G₂ and G₃ and G₄ together form a C₅-C₁₂cycloalkyl group;

5 **G₅, G₆** independently are H, C₁-C₁₈alkyl, phenyl, naphthyl or a group COOC₁-C₁₈alkyl.

7. A color filter composition according to claim 1 wherein the structural element of formula (I) is a compound of formula (O1)



10

(01).

8. A color filter composition according to claim 1 wherein the monomer in step a1 or a2 is selected from isoprene, 1,3-butadiene, α -C₅-C₁₈alkene, 4-vinyl-pyridine or pyridinium-ion, 2-vinyl-pyridine or pyridinium-ion, vinyl-imidazole or imidazolinium-ion, dimethylacrylamide, 3-dimethylaminopropylmethacrylamide, styrene, α -methyl styrene, p-methyl styrene, p-tert-butyl-styrene or a compound of formula $\text{CH}_2=\text{C}(\text{R}_a)-(\text{C}=\text{Z})-\text{R}_b$, wherein R_a is hydrogen or methyl, R_b is NH₂, O⁻(Me⁺), unsubstituted C₁-C₁₈alkoxy, C₂-C₁₀₀alkoxy interrupted by at least one N and/or O atom, or hydroxy-substituted C₁-C₁₈alkoxy, unsubstituted C₁-C₁₈alkylamino, di(C₁-C₁₈alkyl)amino, hydroxy-substituted C₁-C₁₈alkylamino or hydroxy-substituted di(C₁-C₁₈alkyl)amino, -O-CH₂-CH₂-N(CH₃)₂ or -O-CH₂-CH₂-N⁺H(CH₃)₂ An⁻;

20 An⁻ is a anion of a monovalent organic or inorganic acid;

Me is a monovalent metal atom or the ammonium ion.

Z is oxygen or sulfur.

25

- 57 -

9. A color filter composition according to claim 1 wherein in step b the alcohol is an unsubstituted linear or branched C₈-C₃₆alkyl mono alcohol or mixtures thereof or a mono alcohol derived from ethylenoxide, propylenoxide or mixtures thereof with up to 100 C atoms.

5

10. A method for producing a color filter, which comprises coating the color filter composition according to claim 1 on a substrate, followed by exposure and development.

10 **11.** The use of a dispersant according to claim 1d as dispersant in color filters

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2007/056622

A. CLASSIFICATION OF SUBJECT MATTER
INV. G03F7/00 C09B67/00

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)
G03F C09B

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

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

EPO-Internal, WPI Data, INSPEC

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Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2004/090030 A (CIBA SC HOLDING AG [CH]; VOGEL THOMAS [DE]; SODER SIBYLLE [CH]; SIMMEN) 21 October 2004 (2004-10-21) page 10, line 13 - page 18, line 27; claims 1,13,14 page 44, lines 5-7 page 49, line 15 - page 50, line 13 -----	1-3,5-11
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Further documents are listed in the continuation of Box C.



See patent family annex.

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& document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

28 August 2007

12/09/2007

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Thiele, Norbert

INTERNATIONAL SEARCH REPORT

International application No PCT/EP2007/056622

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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