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(54) Title: PROCESS FOR INTERCALATING NATURAL OR SZNTHETIC CLAYS WITH BLOCK OR COMB COPOLYMERS

(57) Abstract: The instant invention relates to a process for manufacturing nanoparticles by intercalating and/or exfoliating natural or synthetic clays using block or comb copolymers having one cationic block and at least one non polar block, which are prepared by controlled free radical polymerization (CFRP). The invention also relates to improved nanocomposite compositions containing nanoparticles produced by this process and to the use of these nanocomposite compositions as, for example in, coatings, sealants, caulks, adhesives and as plastic additives.

Process for Intercalating Natural or Synthetic Clays with Block or Comb Copolymers

The instant invention relates to a process for manufacturing nanoparticles by intercalating and/or exfoliating natural or synthetic clays using block or comb copolymers having one cationic block and at least one non polar block, which are prepared by controlled free radical polymerization (CFRP). The invention also relates to improved nanocomposite compositions containing nanoparticles produced by this process and to the use of these nanocomposite compositions as, for example, in coatings, sealants, caulks, adhesives and as plastic additives.

One way of improving polymer properties is by adding a natural or synthetic clay material to polymers to form composite materials. However, incorporating clays into polymers may not provide a desirable improvement in the physical properties, particularly mechanical and optical properties of the polymer may be adversely affected.

Nanonocomposite compositions containing finely dispersed natural or synthetic clay with at least partially intercalated and/or exfoliated layers and mixtures of ethylenically unsaturated monomers and/or polymers therefrom have therefore attracted much interest in the last years. These materials combine the desired effects of dispersed clay by avoiding the negative influence on, for example, the mechanical or optical properties.

Such compositions, methods for making them and their use in polymers and coatings are for example described in WO 02/24759. Polymerization processes are described using montmorillonite clay, acrylate monomers and for example ammonium persulfate as radical initiator. This conventional polymerization process leads to polymers with broad molecular weight distributions and a high polydispersity index (PD).

Another approach is, for example described by Yang et al. in Mat. Res. Soc. Symp. Proc. Vol. 703, 2002, pages 547-552. Di-or triblock copolymers are prepared containing dimethylaminoethyl methacrylate as monomer in one block and, for example, methacrylic acid as monomer in the other block. From these copolymers cationic blocks are obtained by protonating the aminoblock in the copolymer. The protonated blockcopolymers are then used for intercalating montmorillonite. The D-spacing between the layers is typically between 1.5 and 2 nm. There is nothing disclosed, as to how the preparation of the block copolymers is carried out, in particular, the polydispersity index M_w/M_n of the individual blocks and of the total block copolymer is not known.

The instant invention provides improved nanoparticles of natural and synthetic clay, having in general higher D-spacings. The nanoparticles are prepared by intercalating and/or exfoliating natural or synthetic clays using block or comb copolymers having one cationic block and at least one non polar block, which copolymers are prepared by controlled free radical polymerization (CFRP).

Controlled free radical polymerization per se is known and can be carried out by using for example atom transfer radical polymerization (ATRP) as described in WO 96/30421. WO 96/30421 discloses a controlled or "living" polymerization process of ethylenically unsaturated monomers such as styrene or (meth)acrylates by employing the ATRP method. According to this method initiators are employed which generate a radical atom such as •Cl, in the presence of a redox system of transition metals of different oxidation states, e.g. Cu(I) and Cu(II), providing "living" or controlled radical polymerization.

Another further suitable polymerization process is disclosed in U.S. 4,581,429. 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, including block and graft copolymers. Disclosed is the use of initiators of the partial formula R'R"N-O-X. In the polymerization process the free radical species R'R"N-O• 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.

A variation of the above process is disclosed in US 5 322 912 wherein the combined use of a free radical initiator and a stable free radical agent of the basic structure R'R"N-O• for the synthesis of homopolymers and block copolymers is described.

All three processes are useful for the preparation of block-or comb copolymers wherein the block copolymers have a narrow molecular weight distribution and hence a low polydispersity index.

Surprisingly it has been found, that clay nanoparticles prepared from block- or comb copolymers obtained by CFRP are not only intercalated but in many cases exfoliated and therefore dispersions containing these nanoparticles are much more storage stable. In most cases there is no agglomeration or aggregation even after long storage periods. The nanocomposite compositions of the instant invention can be optically almost transparent, indicating the fine distribution, on the nanometer scale, of the clay.

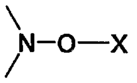
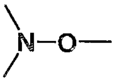
One aspect of the invention is a process for preparing a block- or comb polymer, clay nanocomposite dispersion comprising

mixing an aqueous dispersion of a natural or synthetic clay having an exchangeable cation; with

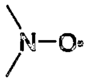
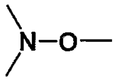
a block copolymer having a cationic block A wherein the cation is based on at least one nitrogen atom, and a nonionic block B, both blocks having a polydispersity between 1 and 3, or

a comb copolymer having a cationic backbone A wherein the cation is based on a nitrogen atom and nonionic oligomeric/polymeric chains B attached thereto, the cationic backbone A having a polydispersity between 1 and 3 and the nonionic side chains having a polydispersity of 1.0-1.8;

wherein the block copolymer is obtained

a1) by polymerizing in a first step an ethylenically unsaturated monomer 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 and adding in a second step to the resulting macromer, which has attached a labile bound  group, a further ethylenically unsaturated monomer different from that in step 1,

with the proviso that at least one monomer in the first or second step contains a cation centered on a nitrogen atom or a nitrogen atom from which a cation can be formed; or

a2) by polymerzing in a first step an ethylenically unsaturated monomer in the presence of at least one stable free nitroxyl radical  and a free radical initiator and adding in a second step to the resulting macromer, which has attached a labile bound  group, a further ethylenically unsaturated monomer different from that in step 1;
with the proviso that at least one monomer in the first or second step contains a cation centered on a nitrogen atom or a nitrogen atom from which a cation can be formed; or

a3) by polymerzing in a first step an ethylenically unsaturated monomer in the presence of a compound of formula (III) $\left[\mathrm{In}\right]_p\!-\!\left[\mathrm{Hal}\right]_q$ (III) and a catalytically effective amount
of an oxidizable transition metal complex catalyst, wherein
p represents a number greater than zero and defines the number of initiator fragments;
q represents a number greater than zero;
[In] represents a radically transferable atom or group capable of initiating polymerization and
-[Hal] represents a leaving group; and adding in a second step to the resulting macromer a further ethylenically unsaturated monomer different from that in step one;
with the proviso that at least one monomer in the first or second step contains a cation centered on a nitrogen atom or a nitrogen atom from which a cation can be formed;

wherein the comb copolymer is obtained

by polymerizing in a first step an ethylenically unsaturated monomer in the presence of a compound of formula (III) $\left[\mathrm{In}-\right]_p\left[\mathrm{Hal}\right]_q$ (III) and a catalytically effective amount of an oxidizable transition metal complex catalyst, wherein the symbols have the meanings as defined above;

exchanging the group [HAL] attached to the polymer with a group having an ethylenically unsaturated bond and subjecting the resulting macromer together with a second monomer, which contains a nitrogen based cation or a nitrogen atom from which a cation can be formed, to radical polymerization;

forming the nitrogen based cation if necessary and exchanging the cation in the natural or synthetic clay with the nitrogen based cationic block or comb copolymer and intercalating and/or exfoliating the clay at least partially.

If the clay material is a synthetic one, it may be produced by gas-phase or sol-gel processes, for example Optigel® from Süd Chemie.

Natural clay minerals are typically comprised of hydrated aluminum silicates that are fine-grained and have a platy habit. The crystalline structure of a typical clay mineral is a multi-layered structure comprised of combinations of layers of SiO_4 tetrahedra that are joined to layers of $AlO(OH)_2$ octahedra. A so called "gallery" is formed which describes the defined interlayer spaces of the layered clay minerals. Depending of the clay mineral the gallery may contain water and/or other constituents such as potassium, sodium or calcium cations. Clay minerals vary, based upon the combination of their constituent layers and cations. Isomorphic substitution of the cations of clay mineral, such as Al^{3+} or Fe^{3+} substituting for the Si^{4+} ions in the tetrahedral network, or Al^{3+}, Mg^{2+} or Fe^{2+} substituting for other cations in the octahedral network, typically occurs and may impart a net negative charge on the clay structure. Natural occurring elements within the gallery of the clay, such as water molecules or sodium or potassium cations, are attracted to the surface of the clay layers due to this net charge.

Nanocomposites are compositions in which at least one of its constituents has one or more dimensions, such as length, width or thickness in the nanometer size range. The term nanocomposite, as used herein, denotes the state of matter wherein intercalated and at least partially exfoliated clay layers are surrounded by a polymer matrix.

The term "intercalated nanocomposite", as used herein describes a nanocomposite that contains a regular insertion between the clay layers.

The term "exfoliated nanocomposite" as used herein describes a nanocomposite wherein the a few nm thick layers of clay with polymer molecules attached to it are dispersed in the matrix (oligomer/polymer) forming a composite structure on the nano/micro scale.

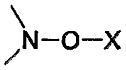
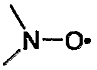
The clay minerals are items of commerce and are for example supplied by Süd-Chemie Inc., Germany or Nanocore, USA.

The natural or synthetic clay is for example a phyllosilicate.

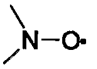
In particular the natural clay is selected from the group consisting of smectite, montmorillonite, saponite, beidellite, mica, sauconite, ledikite, montronite, hectorite, stevensite, vermiculite, kaolinite, hallosite and combinations thereof.

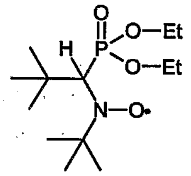
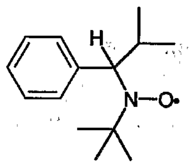
Special preference is given to montmorillonite.

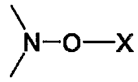
As already mentioned it is indispensable that the block copolymers are prepared by controlled free radical polymerization (CFRP). There are essentially three suitable routes:
a1) polymerization in the presence of alkoxyamine initiator/regulator compounds;
a2) polymerization in the presence of a stable nitroxyl free radical and a radical initiator (source of free radicals) and
a3) polymerization under atom transfer radical polymerization (ATRP) conditions. All three routes are known and widely described.

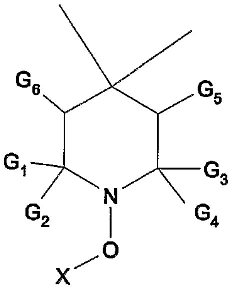
For example the structural element  or  , may be part of a cyclic ring system or substituted to form a acyclic structure.

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, WO 99/03894 and WO 00/07981, the piperidine derivatives described in WO 99/67298 and GB 2335190 or the heterocyclic compounds described in GB 2342649 and WO 96/24620. Further suitable nitroxylethers and nitroxyl radicals are described in WO 02/4805 and in WO 02/100831.

Stable free radicals having a structural element  are for example disclosed in EP-A-621 878.

Examples, such as   are for example given in WO 96/24620.

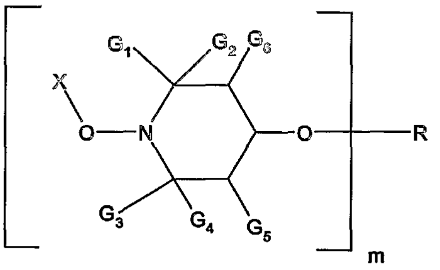
Preferably the structural element  is a structural element of formula (I)



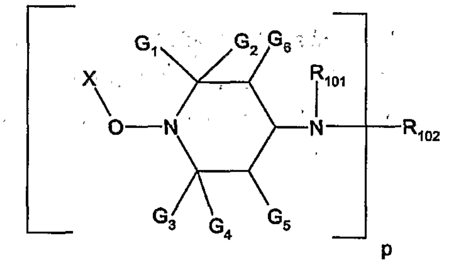
(I), wherein

G_1, G_2, G_3, G_4 are independently C_1-C_8alkyl or G_1 and G_2 or G_3 and G_4, or G_1 and G_2 and G_3 and G_4 together form a C_5-C_{12}cycloalkyl group;
G_5, G_6 independently are H, C_1-C_{18}alkyl, phenyl, naphthyl or a group $COOC_1$-C_{18}alkyl.

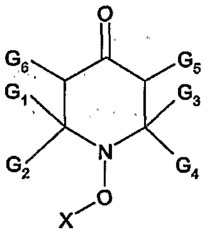
In particular the structural element of formula (I) is of formula A, B or O,



(A) ,



(B) ,



(O)

wherein

m is 1,

R is hydrogen, C_1-C_{18}alkyl 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;

p is 1;

R_{101} is C_1-C_{12}alkyl, C_5-C_7cycloalkyl, C_7-C_8aralkyl, C_2-C_{18}alkanoyl, C_3-C_5alkenoyl or benzoyl;

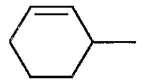
R_{102} is C_1-C_{18}alkyl, C_5-C_7cycloalkyl, C_2-C_8alkenyl unsubstituted or substituted by a cyano, carbonyl or carbamide group, or is glycidyl, a group of the formula -$CH_2CH(OH)$-Z or of the formula -CO-Z or -CONH-Z wherein Z is hydrogen, methyl or phenyl;

G_6 is hydrogen and G_5 is hydrogen or C_1-C_4alkyl,

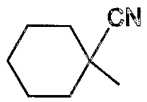
G_1 and G_3 are methyl and G_2 and G_4 are ethyl or propyl or G_1 and G_2 are methyl and G_3 and G_4 are ethyl or propyl; and

X is selected from the group consisting of

-CH_2-phenyl, CH_3CH-phenyl, $(CH_3)_2C$-phenyl, (C_5-C_6cycloalkyl)$_2$CCN, $(CH_3)_2CCN$,



,

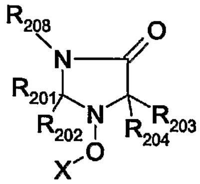


, -$CH_2CH=CH_2$, CH_3CH-$CH=CH_2$ (C_1-C_4alkyl)CR_{20}-C(O)-phenyl, (C_1-C_4)alkyl-CR_{20}-C(O)-(C_1-C_4)alkoxy, (C_1-C_4)alkyl-CR_{20}-C(O)-(C_1-C_4)alkyl, (C_1-C_4)alkyl-CR_{20}-C(O)-N-di(C_1-C_4)alkyl, (C_1-C_4)alkyl-CR_{20}-C(O)-NH(C_1-C_4)alkyl, (C_1-C_4)alkyl-CR_{20}-C(O)-NH_2, wherein

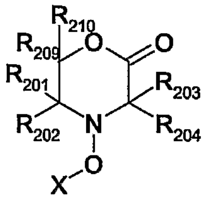
R_{20} is hydrogen or (C_1-C_4)alkyl.

The above compounds and their preparation are described in GB 2335190 and GB 2 361 235.

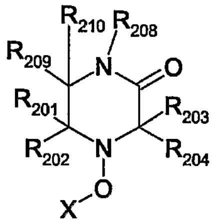
Another preferred group of nitroxylethers of step a1) are those of formula (Ic), (Id), (Ie), (If), (Ig) or (Ih)



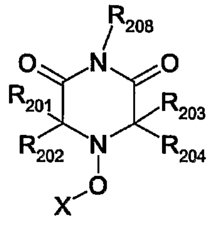
(Ic),



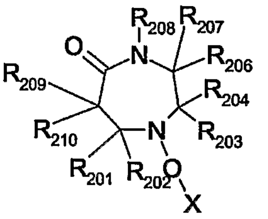
(Id),



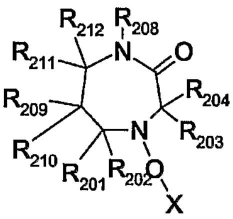
(Ie),



(If),



(Ig),



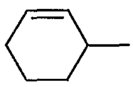
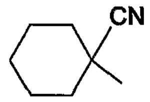
(Ih),

wherein R_{201}, R_{202}, R_{203} and R_{204} independently of each other are C_1-C_{18}alkyl, C_3-C_{18}alkenyl, C_3-C_{18}alkinyl, C_1-C_{18}alkyl, C_3-C_{18}alkenyl, C_3-C_{18}alkinyl which are substituted by OH, halogen or a group -O-C(O)-R_{205}, C_2-C_{18}alkyl which is interrupted by at least one O atom and/or NR_{205} group, C_3-C_{12}cycloalkyl or C_6-C_{10}aryl or R_{201} and R_{202} and/or R_{203} and R_{204} together with the linking carbon atom form a C_3-C_{12}cycloalkyl radical;

R_{205}, R_{206} and R_{207} independently are hydrogen, C_1-C_{18}alkyl or C_6-C_{10}aryl;

R_{203} is hydrogen, OH, C_1-C_{18}alkyl, C_3-C_{18}alkenyl, C_3-C_{18}alkinyl, C_1-C_{18}alkyl, C_3-C_{18}alkenyl, C_3-C_{18}alkinyl which are substituted by one or more OH, halogen or a group -O-C(O)-R_{205}, C_2-C_{18}alkyl which is interrupted by at least one O atom and/or NR_{205} group, C_3-C_{12}cycloalkyl or C_6-C_{10}aryl, C_7-C_9phenylalkyl, C_5-C_{10}heteroaryl, -C(O)-C_1-C_{18}alkyl, -O-C_1-C_{18}alkyl or -COOC_1-C_{18}alkyl;

R_{209}, R_{210}, R_{211} and R_{212} are independently hydrogen, phenyl or C_1-C_{18}alkyl; and

X is selected from the group consisting of -CH_2-phenyl, CH_3CH-phenyl, $(CH_3)_2$C-phenyl, (C_5-C_6cycloalkyl)$_2$CCN, $(CH_3)_2$CCN,  ,  , -$CH_2CH=CH_2$, CH_3CH-CH=CH_2 (C_1-C_4alkyl)CR_{20}-C(O)-phenyl, (C_1-C_4)alkyl-CR_{20}-C(O)-(C_1-C_4)alkoxy, (C_1-C_4)alkyl-CR_{20}-C(O)-(C_1-C_4)alkyl, (C_1-C_4)alkyl-CR_{20}-C(O)-N-di(C_1-C_4)alkyl, (C_1-C_4)alkyl-CR_{20}-C(O)-NH(C_1-C_4)alkyl, (C_1-C_4)alkyl-CR_{20}-C(O)-NH_2, wherein

R_{20} is hydrogen or (C_1-C_4)alkyl.

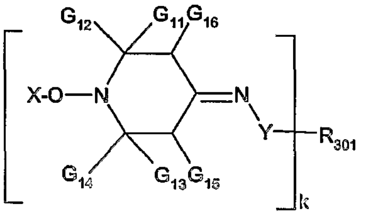
More preferably in formula (Ic), (Id), (Ie), (f), (Ig) and (Ih) at least two of R_{201}, R_{202}, R_{203} and R_{204} are ethyl, propyl or butyl and the remaining are methyl; or

R_{201} and R_{202} or R_{203} and R_{204} together with the linking carbon atom form a C_5-C_6cycloalkyl radical and one of the remaining substituents is ethyl, propyl or butyl.

Most preferably X is CH_3CH-phenyl.

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

Further suitable compounds are the 4-imino compounds of formula (II)



(II) wherein

G_{11}, G_{12}, G_{13} and G_{14} are independently C_1-C_4alkyl or G_{11} and G_{12} together and G_{13} and G_{14} together, or G_{11} and G_{12} together or G_{13} and G_{14} together are pentamethylene;

G_{15} and G_{16} are each independently of the other hydrogen or C_1-C_4alkyl;

X is as defined above;

k is 1, 2, 3, or 4

Y is O, NR_{302} or when n is 1 and R_{301} represents alkyl or aryl Y is additionally a direct bond;
R_{302} is H, C_1-C_{18}alkyl or phenyl;

if k is 1
R_{301} 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 substitued, by one or more OH, C_1-C_8alkoxy, carboxy, C_1-C_8alkoxycarbonyl;
C_5-C_{12}cycloalkyl or C_5-C_{12}cycloalkenyl;
phenyl, C_7-C_9phenylalkyl or naphthyl which may be unsubstituted or substituted by one or more C_1-C_8alkyl, halogen, OH, C_1-C_8alkoxy, carboxy, C_1-C_8alkoxycarbonyl;
-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;
$-SO_3^-Q^+$, $-PO(O^-Q^+)_2$, $-P(O)(OR_2)_2$, $-SO_2-R_2$, $-CO-NH-R_2$, $-CONH_2$, $COOR_2$, or $Si(Me)_3$, wherein Q^+ is H^+, ammnonium or an alkali metal cation;

if k is 2
R_{301} is C_1-C_{18}alkylene, C_3-C_{18}alkenylene or C_3-C_{18}alkinylene, which may be unsubstituted or substitued, by one or more OH, C_1-C_8alkoxy, carboxy, C_1-C_8alkoxycarbonyl;
or xylylene; or
R_{301} 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;

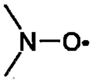
if k is 3,
R_{301} is a trivalent radical of an aliphatic, cycloaliphatic or aromatic tricarboxylic acid;
and
if k is 4, R_{301} is a tetravalent radical of an aliphatic, cycloaliphatic or aromatic tetracarboxylic acid.

Preferably G_{16} is hydrogen and G_{15} is hydrogen or C_1-C_4alkyl, in particular methyl, and

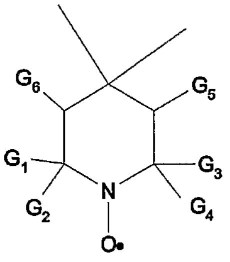
G_{11} and G_{13} are methyl and G_{12} and G_{14} are ethyl or propyl or G_{11} and G_{12} are methyl and G_{13} and G_{14} are ethyl or propyl.

The 4 imino compounds of formula V 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 .

When the polymerization process is carried out according to route a2) the structural element



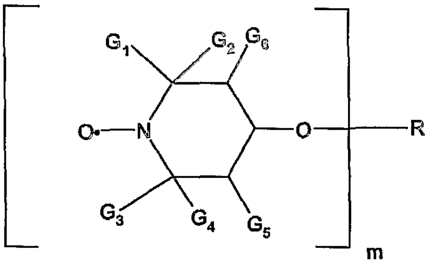
is for example a structural element of formula (I')



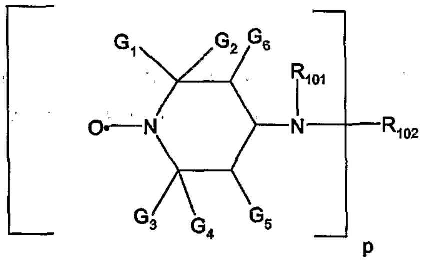
(I'), wherein

G_1, G_2, G_3, G_4 are independently C_1-C_6alkyl or G_1 and G_2 or G_3 and G_4, or G_1 and G_2 and G_3 and G_4 together form a C_5-C_{12}cycloalkyl group;
G_5, G_6 independently are H, C_1-C_{18}alkyl, phenyl, naphthyl or a group $COOC_1$-C_{18}alkyl.

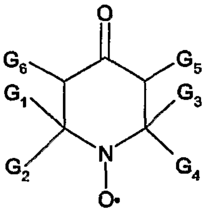
Preference is given to compounds wherein the structural element of formula (I') is of formula A', B' or O',



(A') ,



(B')



(O')

wherein

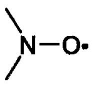
m is 1,

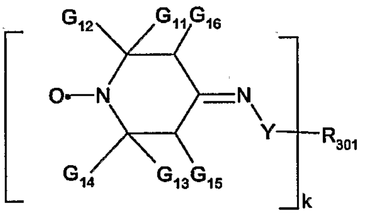
R is hydrogen, C_1-C_{18}alkyl which is uninterrupted or interrupted by one or more oxygen atoms, cyanoethyl, benzoyl, glycidyl, a monovalent radical of an aliphatic carboxylic acid having 2 to 18 carbon atoms, of a cycloaliphatic carboxylic acid having 7 to 15 carbon atoms, or an α,β-unsaturated carboxylic acid having 3 to 5 carbon atoms or of an aromatic carboxylic acid having 7 to 15 carbon atoms;

p is 1;

R_{101} is C_1-C_{12}alkyl, C_5-C_7cycloalkyl, C_7-C_8aralkyl, C_2-C_{18}alkanoyl, C_3-C_5alkenoyl or benzoyl;

R_{102} is C_1-C_{18}alkyl, C_5-C_7cycloalkyl, C_2-C_8alkenyl unsubstituted or substituted by a cyano, carbonyl or carbamide group, or is glycidyl, a group of the formula -$CH_2CH(OH)$-Z or of the formula -CO-Z or -CONH-Z wherein Z is hydrogen, methyl or phenyl;
G_6 is hydrogen and G_5 is hydrogen or C_1-C_4alkyl,
G_1 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.

Also suitable are the compounds wherein the structural element  is of formula (II')



(II') wherein

G_{11}, G_{12}, G_{13} and G_{14} are independently C_1-C_4alkyl or G_{11} and G_{12} together and G_{13} and G_{14} together, or G_{11} and G_{12} together or G_{13} and G_{14} together are pentamethylene;
G_{15} and G_{16} are each independently of the other hydrogen or C_1-C_4alkyl;

k is 1, 2, 3, or 4

Y is O, NR_{302} or when n is 1 and R_{301} represents alkyl or aryl Y is additionally a direct bond;
R_{302} is H, C_1-C_{18}alkyl or phenyl;

if k is 1
R_{301} 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 substitued, by one or more OH, C_1-C_8alkoxy, carboxy, C_1-C_8alkoxycarbonyl;
C_5-C_{12}cycloalkyl or C_5-C_{12}cycloalkenyl;
phenyl, C_7-C_9phenylalkyl or naphthyl which may be unsubstituted or substituted by one or more C_1-C_8alkyl, halogen, OH, C_1-C_8alkoxy, carboxy, C_1-C_8alkoxycarbonyl;
-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;

$-SO_3^-Q^+$, $-PO(O^-Q^+)_2$, $-P(O)(OR_2)_2$, $-SO_2-R_2$, $-CO-NH-R_2$, $-CONH_2$, $COOR_2$, or $Si(Me)_3$, wherein Q^+ is H^+, ammnonium or an alkali metal cation;

if k is 2
R_{301} is C_1-C_{18}alkylene, C_3-C_{18}alkenylene or C_3-C_{18}alkinylene, which may be unsubstituted or substitued, by one or more OH, C_1-C_8alkoxy, carboxy, C_1-C_8alkoxycarbonyl;
or xylylene; or
R_{301} 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;

if k is 3,
R_{301} is a trivalent radical of an aliphatic, cycloaliphatic or aromatic tricarboxylic acid;
and
if k is 4, R_{301} is a tetravalent radical of an aliphatic, cycloaliphatic or aromatic tetracarboxylic acid.

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, 2-butenyl, 3-butenyl, isobutenyl, n-2,4-pentadienyl, 3-methyl-2-butenyl, n-2-octenyl, n-2-dodecenyl, iso-dodecenyl, oleyl, n-2-octadecenyl oder n-4-octadecenyl.
Preferred is alkenyl with 3 bis 12, particularly preferred with 3 to 6 carbon atoms.

Alkinyl with 3 to 18 is a linear or branched radical as for example propinyl ($-CH_2-C\equiv CH$), 2-butinyl, 3-butinyl, n-2-octinyl, oder 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.

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

C_2-C_{18}alkyl interrupted by at least one O atom is for example -CH_2-CH_2-O-CH_2-CH_3, -CH_2-CH_2-O-CH_3- or -CH_2-CH_2-O-CH_2-CH_2-CH_2-O-CH_2-CH_3-. It is preferably derived from polyethlene glycol. A general description is $-((CH_2)_a-O)_b-H/CH_3$, wherein a is a number from 1 to 6 and b is a number from 2 to 10.

C_2-C_{18}alkyl interrupted by at least one NR_5 group may be generally described as $-((CH_2)_a-NR_5)_b-H/CH_3$, wherein a, b and R_5 are as defined above.

C_3-C_{12}cycloalkyl is typically, cyclopropyl, cyclopentyl, methylcyclopentyl, dimethylcyclopentyl, cyclohexyl, methylcyclohexyl or trimethylcyclohexyl.

C_6-C_{10} aryl is for example phenyl or naphthyl, but also comprised are C_1-C_4alkyl substituted phenyl, C_1-C_4alkoxy 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 for example dichlorobenzene or bromotoluene.

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

C_7-C_9phenylalkyl is benzyl, phenylethyl or phenylpropyl.

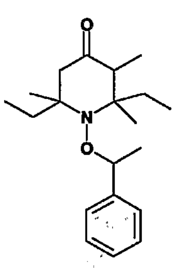
C_5-C_{10}heteroaryl is for example pyrrol, pyrazol, imidazol, 2, 4, dimethylpyrrol, 1-methylpyrrol, thiophene, furane, furfural, indol, cumarone, oxazol, thiazol, isoxazol, isothiazol, triazol, pyridine, α-picoline, pyridazine, pyrazine or pyrimidine.

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.

C_1-C_{18}alkanoyl is for example, formyl, propionyl, butyryl, octanoyl, dodecanoyl but preferably acetyl and C_3-C_5alkenoyl is in particular acryloyl.

In general the polymerization processes using nitroxylethers a1) or nitroxyl radicals together with a free radical initiator a2) are preferred. In particular polymerization process a1) is very suitable.

Particularly suitable nitroxylethers and nitroxyl radicals are those of formulae



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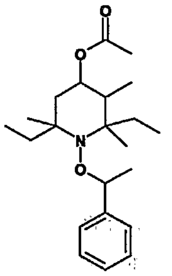

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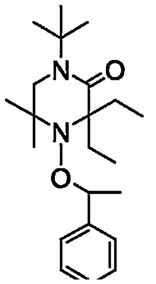

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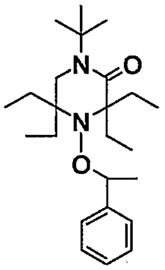

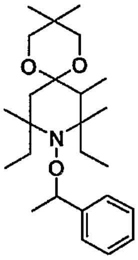

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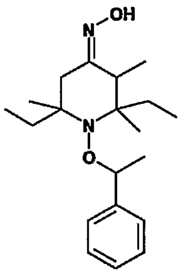

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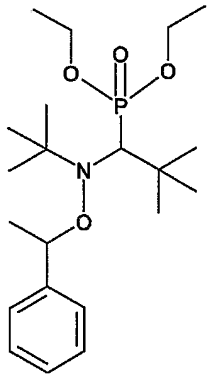

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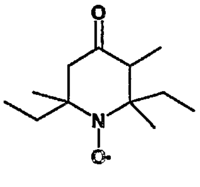

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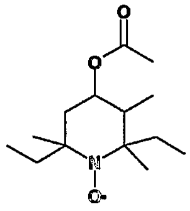

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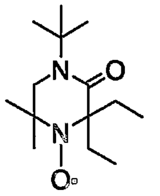

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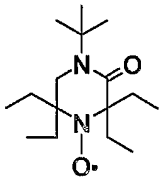

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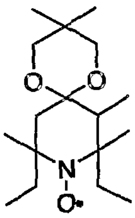

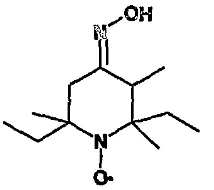

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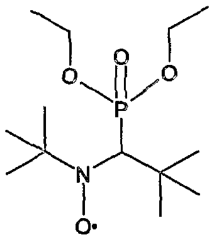


The free radical initiator of component a2) is preferably a bis-azo compound, a peroxide, perester or a hydroperoxide.

Specific preferred radical sources are 2,2'-azobisisobutyronitrile, 2,2'-azobis(2-methyl-butyronitrile), 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), 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, 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-trimethylcyclohexane, 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-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.

A suitable component a3) contains a compound of formula (III), $\left[\text{In}\right]_p\!-\!\left[\text{Hal}\right]_q$ (III) with a radically transferable atom or group •Hal as is described in WO 96/30421 and WO 98/01480. A preferred radically transferable atom or group •Hal is •Cl or •Br, which is cleaved as a radical from the initiator molecule.

Preferably [In] represents the polymerization initiator fragment of a polymerization initiator of formula (III), $\left[\text{In}\right]_p\!-\!\left[\text{Hal}\right]_q$ (III), capable of initiating polymerization of monomers or oligomers which polymerization initiator is selected from the group consisting of C_1-C_8-alkyl halides, C_6-C_{15}-aralkylhalides, C_2-C_8α-haloalkyl esters, arene sulfonyl chlorides, haloalkanenitriles, α-haloacrylates and halolactones, and
p and q represent one.

The polymerization process in the presence of a compound of formula (III) is known as ATRP (Atom Transfer Radical Polymerization) and WO 96/30421 discloses a controlled or "living" polymerization process of ethylenically unsaturated monomers such as styrene or (meth)acrylates by employing the ATRP method. According to this method initiators are employed which generate a radical atom such as •Cl, in the presence of a redox system of transition metals of different oxidation states, e.g. Cu(I) and Cu(II), providing "living" or controlled radical polymerization.

Specific initiators are selected from the group consisting of α,α'-dichloro- or α,α'-dibromoxylene, p-toluenesulfonylchloride (PTS), hexakis-(α-chloro- or α-bromomethyl)-benzene, 2-chloro- or 2-bromopropionic acid, 2-chloro- or 2-bromoisobutyric acid, 1-phenethyl chloride or bromide, methyl or ethyl 2-chloro- or 2-bromopropionate, ethyl-2-bromo- or ethyl-2-chlorisobutyrate, chloro- or bromoacetonitrile, 2-chloro- or 2-bromopropionitrile, α-bromo-benzacetonitrile and α-bromo-γ-butyrolactone (= 2-bromo-dihydro-2(3H)-furanone).

The transition metal in the oxidizable transition metal complex catalyst salt used in the process of the invention is present as an oxidizable complex ion in the lower oxidation state of a redox system. Preferred examples of such redox systems are selected from the group consisting of Group V(B), VI(B), VII(B), VIII, IB and IIB elements, such as Cu^+/Cu^{2+}, Cu^0/Cu^+, Fe^0/Fe^{2+}, Fe^{2+}/Fe^{3+}, Ru^{2+}/Ru^{3+}, Ru^{3+}/Ru^{4+}, Os^{2+}/Os^{3+}, $V^{n+}/V^{(n+1)+}$, Cr^{2+}/Cr^{3+}, Co^+/Co^{2+}, Co^{2+}/Co^{3+}, Ni^0/Ni^+, Ni^+/Ni^{2+}, Ni^{2+}/Ni^{3+}, Mn^0/Mn^{2+}, Mn^{2+}/Mn^{3+}, Mn^{3+}/Mn^{4+} or Zn^+/Zn^{2+}.

The ionic charges are counterbalanced by anionic ligands commonly known in complex chemistry of transition metals, such hydride ions (H^-) or anions derived from inorganic or organic acids, examples being halides, e.g. F^-, Cl^-, Br^- or I^-, fluoro complexes of the type BF_4^-, PF_6^-, SbF_6^- or AsF_6^-, anions of oxygen acids, alcoholates or acetylides or anions of cyclopentadiene.

Anions of oxygen acids are, for example, sulfate, phosphate, perchlorate, perbromate, periodate, antimonate, arsenate, nitrate, carbonate, the anion of a C_1-C_8carboxylic acid, such as formate, acetate, propionate, butyrate, benzoate, phenylacetate, mono-, di- or trichloro- or -fluoroacetate, sulfonates, for example methylsulfonate, ethylsulfonate, propylsulfonate, butylsulfonate, trifluoromethylsulfonate (triflate), unsubstituted or C_1-C_4alkyl-, C_1-C_4alkoxy- or halo-, especially fluoro-, chloro- or bromo-substituted phenylsulfonate or benzylsulfonate, for example tosylate, mesylate, brosylate, p-methoxy- or p-ethoxyphenylsulfonate, pentafluorophenylsulfonate or 2,4,6-triisopropylsulfonate, phosphonates, for example methylphosphonate, ethylphosphonate, propylphosphonate, butylphosphonate, phenylphosphonate, p-methylphenylphosphonate or benzylphosphonate, carboxylates derived from a C_1-C_8carboxylic acid, for example formate, acetate, propionate, butyrate, benzoate, phenylacetate, mono-, di- or trichloro- or -fluoroacetate, and also C_1-C_{12}-alcoholates, such as straight chain or branched C_1-C_{12}-alcoholates, e.g. methanolate or ethanolate.

Anionic ligands and neutral may also be present up to the preferred coordination number of the complex cation, especially four, five or six. Additional negative charges are counterbalanced by cations, especially monovalent cations such as Na^+, K^+, NH_4^+ or $(C_1$-C_4 alkyl$)_4N^+$.

Suitable neutral ligands are inorganic or organic neutral ligands commonly known in complex chemistry of transition metals. They coordinate to the metal ion through a σ-, π-, μ-, η-type bonding or any combinations thereof up to the preferred coordination number of the complex cation. Suitable inorganic ligands are selected from the group consisting of aquo (H_2O), amino, nitrogen, carbon monoxide and nitrosyl. Suitable organic ligands are selected from the group consisting of phosphines, e.g. $(C_6H_5)_3P$, $(i\text{-}C_3H_7)_3P$, $(C_5H_9)_3P$ or $(C_6H_{11})_3P$, di-, tri-, tetra- and hydroxyamines, such as ethylenediamine, ethylenediaminotetraacetate (EDTA), N,N-Dimethyl-N',N'-bis(2-dimethylaminoethyl)-ethylenediamine (Me_6TREN), catechol, N,N'-dimethyl-1,2-benzenediamine, 2-(methylamino)phenol, 3-(methylamino)-2-butanol or N,N'-bis(1,1-dimethylethyl)-1,2-ethanediamine, N,N,N',N",N"-pentamethyldiethyltriamine (PMDETA), C_1-C_8-glycols or glycerides, e.g. ethylene or propylene glycol or derivatives thereof, e.g. di-, tri- or tetraglyme, and monodentate or bidentate heterocyclic e^- donor ligands.

Heterocyclic e^- donor ligands are derived, for example, from unsubstituted or substituted heteroarenes from the group consisting of furan, thiophene, pyrrole, pyridine, bis-pyridine, picolylimine, g-pyran, g-thiopyran, phenanthroline, pyrimidine, bis-pyrimidine, pyrazine, indole, coumarone, thionaphthene, carbazole, dibenzofuran, dibenzothiophene, pyrazole, imidazole, benzimidazole, oxazole, thiazole, bis-thiazole, isoxazole, isothiazole, quinoline, bis-quinoline, isoquinoline, bis-isoquinoline, acridine, chromene, phenazine, phenoxazine, phenothiazine, triazine, thianthrene, purine, bis-imidazole and bis-oxazole.

The oxidizable transition metal complex catalyst can be formed in a separate preliminary reaction step from its ligands or is preferably formed in-situ from its transition metal salt, e.g. Cu(I)Cl, which is then converted to the complex compound by addition of compounds corresponding to the ligands present in the complex catalyst, e.g. by addition of ethylenediamine, EDTA, Me_6TREN or PMDETA.

Preferred is a composition, wherein in the step a3) the oxidizable transition metal in the transition metal complex salt is present as a transition metal complex ion in the lower oxidation state of a redox system.

More preferred is a composition, wherein the transition metal complex ion is a Cu(I) complex ion in the Cu(I)/Cu(II) system.

Route a3) is carried out when comb copolymers are prepared. The preparation of comb copolymers by the ATRP method is for example described in WO 01/51534.

The elimination of the transfer group –Y, e. g. halogen, with a polymerizable chjain terminating group –X is advantageously performed in such a way that the polymerisate is dissolved in a solvent and the monomeric compound corresponding to –X is added in the presence of a non-nucleophilic base, such as diazabicycloundecene (DBU) or similar bases, at elevated temperatures. The reaction, which is a conventional esterification reaction, takes place under conditions of a regular esterification reaction within a temperature range, for example from room temperature to 100° C.

Preferably the nitroxylether of step a1) or the nitroxyl radical of step a2) is present in an amount of from 0.001 mol-% to 20 mol-%, more preferably of from 0.002 mol-% to 10 mol-% and most preferably of from 0.005 mol-% to 5 mol-% based on the monomer or monomer mixture.

Preferably the free radical initiator is present in an amount of 0.001 mol-% to 20 mol-%, based on the monomer or monomer mixture.

The molar ratio of free radical initiator to stable free nitroxyl radical is preferably from 20:1 to 1:2, more preferably from 10:1 to 1:2.

Scission of the O-X bond of the nitroxylether may be effected by ultrasonic treatment, radiation with actinic light or heating.

The scission of the O-X bond is preferably effected by heating and takes place at a temperature of between 50°C and 180°C, more preferably from 90° C to 150° C.

The initiator of formula (III), $\left[\,\mathrm{In}\,\right]_p\!-\!\left[\boxed{\mathrm{Hal}}\right]_q$ (III) and the oxidizable transition metal are for example present in an amount of 1:10 to 1:100, relative to the monomer. The total amount of oxidizable transition metal to initiator of formula (III) is for example from 0.05:1 to 2:1, in particular from 0.2:1 to 0.5:1.

The polymerization reaction is carried out with preference under atmospheric pressure.

In the block or comb copolymer the nonionic polymer block B is composed of non-ionic repeating units of ethylenically unsaturated monomers suitable for the method of controlled or living polymerisation. These monomers are characterised by the presence of at least one group >C=C<. Representative monomers are selected from the group consisting of styrenes, acrylic and C_1-C_4alkylacrylic acid-C_1-C_{24}alkyl esters, acrylic and C_1-C_4alkylacrylic acid-C_6-C_{11}aryl-C_1-C_4alkyl esters, acrylic and C_1-C_4alkylacrylic acid-C_6-C_{11}aryloxy-C_1-C_4alkyl esters, acrylic and C_1-C_4alkylacrylic acid-hydroxy-C_2-C_6alkyl esters, acrylic and C_1-C_4alkylacrylic acid-polyhydroxy-C_3-C_6alkyl esters, acrylic and C_1-C_4alkylacrylic acid-(C_1-C_4alkyl)$_3$silyl-oxy-C_2-C_4alkyl esters; acrylic and C_1-C_4alkylacrylic acid-(C_1-C_4alkyl)$_3$silyl-C_1-C_4alkyl esters, acrylic and C_1-C_4alkylacrylic acid-heterocyclyl-C_2-C_4alkyl esters; acrylic and C_1-C_4alkylacrylic acid esters having poly-C_2-C_4alkyleneglycolester groups, wherein the ester groups may be substituted with C_1-C_{24}alkoxy groups, acrylic and methacrylic acid amides, acrylic and C_1-C_4alkylacrylic acid-(C_1-C_4alkyl)$_{1-2}$amide, acrylonitrile, esters of maleic acid or fumaric acid, maleinimide and N-substituted maleinimides.

In a preferred embodiment of the invention the nonionic polymer block B is essentially composed of repeating units of ethylenically unsaturated monomers selected from the group consisting of styrenes, acrylic and methacrylic acid-C_1-C_{24}alkyl esters, acrylic and methacrylic acid-hydroxy-C_2-C_6alkyl esters, acrylic and methacrylic acid-dihydroxy-C_3-C_4alkyl esters and acrylic and methacrylic acid esters having poly-C_2-C_4alkyleneglycolester groups, wherein the ester groups may be substituted with C_1-C_{24}alkoxy groups.

Suitable styrenes may be substituted at the phenyl group by one to three additional substituents selected from the group consisting of hydroxy, C_1-C_4alkoxy, e.g. methoxy or ethoxy, halogen, e.g. chloro, and C_1-C_4alkyl, e.g. methyl or methyl.
Suitable acrylic acid or methacrylic acid-C_1-C_{24}alkyl esters are acrylic acid or methacrylic acid esters esterified by methyl, ethyl, n-butyl, isobutyl, tert-butyl, neopentyl, 2-ethylhexyl, isobornyl, isodecyl, n-dodecyl, n-tetradecyl, n-hexadecyl or n-octadecyl.
Representative acrylic and C_1-C_4alkylacrylic acid-C_6-C_{11}aryl-C_1-C_4alkyl esters are acrylic acid or methacrylic acid esters esterified by benzyl, 2-phenylethyl, 1- or 2-naphthylmethyl or 2-(1- or 2-naphthyl)-ethyl. The phenyl or naphthyl groups may be additionally substituted with one to three additional substituents selected from the group consisting of hydroxy, C_1-C_4alkoxy, e.g. methoxy or ethoxy, halogen, e.g. chloro, and C_1-C_4alkyl, e.g. methyl or methyl.

Representative acrylic and C_1-C_4alkylacrylic acid-C_6-C_{11}aryloxy-C_1-C_4alkyl esters are acrylic acid or methacrylic acid esters esterified by phenoxyethyl or benzyloxyethyl.

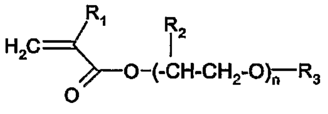
Representative acrylic acid and C_1-C_4alkylacrylic acid-hydroxy-C_2-C_4alkyl esters are acrylic acid- or methacrylic acid-2-hydroxyethylesters (HEA, HEMA) or acrylic acid- or methacrylic acid-2-hydroxypropylester (HPA, HPMA).

Representative acrylic and C_1-C_4alkylacrylic acid-polyhydroxy-C_3-C_6alkyl esters are acrylic acid- or methacrylic acid esterified by ethylene glycol or glycerol.

Representative acrylic acid- and C_1-C_4alkylacrylic acid-silyloxy-C_2-C_4alkyl ester are acrylic acid- or methacrylic acid-2-trimethylsilyloxyethylesters (TMS-HEA, TMS-HEMA).

Representative acrylic acid- or C_1-C_4alkylacrylic acid-(C_1-C_4alkyl)$_3$silyl-C_2-C_4alkyl esters are acrylic acid- or methacrylic acid-2-trimethylsilylethylesters or acrylic acid- or methacrylic acid-3-trimethylsilyl-n-propylesters.

Representative acrylic and C_1-C_4alkylacrylic acid esters having poly-C_2-C_4alkyleneglycolester groups, wherein the ester groups may be substituted with C_1-C_{24}alkoxy groups, are illustrated by the formula given below:



$$H_2C=C(R_1)-C(=O)-O-(-CH(R_2)-CH_2-O)_n-R_3$$

wherein

n represents a numeral from one to 100;

R_1 and R_2 independently of one another represent hydrogen or methyl; and

R_3 represents C_1-C_{24}alkyl, e.g. methyl, ethyl, n- or isopropyl, n-, iso-, or tert-butyl, n- or neopentyl, n-dodecyl, n-tetradecyl, n-hexadecyl, n-octadecyl, or represents aryl-C_1-C_{24}alkyl, e.g. benzyl or phenyl-n-nonyl, as well as C_1-C_{24}alkylaryl or C_1-C_{24}alkylaryl-C_1-C_{24}alkyl.

Representative acrylic acid- and C_1-C_4alkylacrylic acid-heterocyclyl-C_2-C_4alkyl esters are acrylic acid- or methacrylic acid-2-(N-morpholinyl, 2-pyridyl, 1-imidazolyl, 2-oxo-1-pyrrolidinyl, 4-methylpiperidin-1-yl or 2-oxoimidazolidin-1-yl)-ethyl esters.

Representative C_1-C_4alkylacrylic acid esters having poly-C_2-C_4alkyleneglycolester groups, wherein the ester groups may be substituted with C_1-C_{24}alkoxy groups are acrylic acid- or methacrylic acid esters of ethoxylated decanol, ethoxylated lauryl alcohol or ethoxylated stearyl alcohol, wherein the degree of ethoxylation, as expressed by the index n in the formula above, is typically in the range from 5 to 30.

Representative acrylic and C_1-C_4alkylacrylic acid-(C_1-C_4alkyl)$_{1-2}$amide are acrylic acid- or methacrylic acid N-methyl, N,N-dimethyl, N-ethyl or N,N-diethyl amide.

Representative esters of maleic acid or fumaric acid are the C_1-C_{24}alkyl esters, e.g. the methyl, ethyl, n-butyl, isobutyl, tert-butyl, neopentyl, 2-ethylhexyl, isobornyl, isodecyl, n-dodecyl, n-tetradecyl, n-hexadecyl or n-octadecyl esters, the C_6-C_{11}aryl, e.g. phenyl or naphthyl, esters or the C_6-C_{11}aryl-C_1-C_4alkyl esters, e. g. benzyl or 2-phenethyl esters. The phenyl or naphthyl groups may be additionally substituted with one to three additional substituents selected from the group consisting of hydroxy, C_1-C_4alkoxy, e.g. methoxy or ethoxy, halogen, e.g. chloro, and C_1-C_4alkyl, e.g. methyl or methyl.
Representative N-substituted maleinimides are the N-C_1-C_4alkyl, e.g. N-methyl or N-ethyl, or N-aryl, e.g. N-phenyl substituted maleinimides.

In the comb or block copolymer the polymer block A additionally contains repeating units of ethylenically unsaturated monomers substituted with cationic groups. A suitable cationic polymer block A is essentially composed of repeating units of ethylenically unsaturated monomers represented by the cationic part of a salt formed by quaternisation of an amino monomer selected from the group consisting of amino substituted styrene, (C_1-C_4alkyl)$_{1-2}$amino substituted styrene, N-mono-(C_1-C_4alkyl)$_{1-2}$amino-C_2-C_4alkyl(meth)acrylamide and N,N-di-(C_1-C_4alkyl)$_{1-2}$amino-C_2-C_4alkyl(meth)acrylamide, vinylpyridine or C_1-C_4alkyl substituted vinylpyridine, vinylimidazole and C_1-C_4alkyl substituted vinylimidazole and a compound of the formula

$CH_2=C(-R^1)-C(=O)-R^2$ (V),

wherein

R^1 represents hydrogen or C_1-C_4alkyl; and

R^2 represents amino substituted C_2-C_{18}alkoxy selected from the group consisting of amino-C_2-C_{18}alkoxy, C_1-C_4alkylamino-C_2-C_{18}alkoxy, di-C_1-C_4alkylamino-C_2-C_{18}alkoxy, hydroxy-C_2-C_4alkylamino-C_2-C_{18}alkoxy and C_1-C_4alkyl-(hydroxy-C_2-C_4alkyl)-amino-C_2-C_{18}alkoxy.

In a particularly preferred embodiment of the invention the repeating unit of an ethylenically unsaturated monomer substituted with an cationic group is represented by the cationic part of a salt formed from a compound of the formula (V), wherein
R^1 represents hydrogen or methyl; and
R^2 represents amino substituted C_2-C_{18}alkoxy selected from the group consisting of amino-C_2-C_4alkoxy, C_1-C_4alkylamino-C_2-C_4alkoxy, di-C_1-C_4alkylamino-C_2-C_4alkoxy, hydroxy-C_2C_4-alkylamino-C_2-C_{18}alkoxy and C_1-C_4alkyl-(hydroxy-C_2-C_4alkyl)amino-C_2-C_4alkoxy.

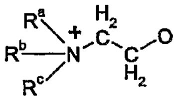
In an alternative embodiment the repeating unit of an ethylenically unsaturated monomer is the acid addition salt or the salt formed by quaternisation of an amino monomer selected from the group consisting of amino substituted styrene, (C_1-C_4alkyl)$_{1-2}$amino substituted styrene, N-mono-(C_1-C_4alkyl)$_{1-2}$aminoC_2-C_4alkyl(meth)acrylamide and N,N-di-(C_1-C_4alkyl)$_{1-2}$amino-C_2-C_4alkyl(meth)acrylamide, vinylpyridine or C_1-C_4alkyl substituted vinylpyridine, vinylimidazole and C_1-C_4alkyl substituted vinylimidazole.

Representative styrenes are substituted at the phenyl group with one or two amino groups or one or two (C_1-C_4alkyl)$_{1-2}$ amino groups, particularly one amino group in 4-position. Additional substituents are selected from the group consisting of hydroxy, C_1-C_4alkoxy, e.g. methoxy or ethoxy, halogen, e.g. chloro, or C_1-C_4alkyl, e.g. methyl or ethyl.

Representative N-mono-(C_1-C_4alkyl)$_{1-2}$amino-C_2-C_4alkyl(meth)acrylamide and N,N-di-(C_1-C_4alkyl)$_{1-2}$amino-C_2-C_4alkyl(meth)acrylamide are 2-N-tert-butylamino- or 2-N,N-dimethylaminoethylacrylamide or 2-N-tert-butylamino- or 2-N,N-dimethylaminopropylmethacrylamide.

In another preferred embodiment of the invention the repeating unit of an ethylenically unsaturated monomer substituted with an ionic group present in one of the polymer blocks A and B is the acid addition salt or the salt formed by quaternisation of an amino monomer selected from the group consisting of amino substituted styrene, (C_1-C_4alkyl)$_{1-2}$amino substituted styrene, and N,N-di-(C_1-C_4alkyl)$_2$amino-C_2-C_4alkyl(meth)acrylamide.

For example the cationic part of a salt according to formula (V) is represented by an ester group of the formula (C)



(C),

wherein

one of R^a, R^b and R^c represents 2-hydroxyethyl and the other ones represent hydrogen, methyl or ethyl; or

R^a, R^b and R^c independently of one another represent hydrogen or a substituent selected from the group consisting of C_1-C_4alkyl, aryl-C_1-C_4alkyl and (C_1-C_4alkyl)$_{1-3}$aryl.

In an especially preferred embodiment of the invention the repeating unit of an ethylenically unsaturated monomer substituted with an ionic group is represented by the cationic part of an acid addition salt or the salt formed by quaternisation of 4-aminostyrene, 4-dimethylaminostyrene and an aminoalkyl (meth)acrylate selected from the group consisting of 2-dimethylaminoethyl acrylate (DMAEA), 2-dimethylaminoethyl methacrylate (DMAEMA), 2-diethylaminoethyl acrylate (DEAEA), 2-diethylaminoethyl methacrylate (DEAEMA), 2-t-butylaminoethyl acrylate (t-BAEA), 2-t-butylaminoethyl methacrylate (t-BAEMA) and 3-dimethylaminopropylmethacrylamide, 4-vinylpyridine, 2-vinylpyridine or 1-vinylimidazole.

For example the number of repeating units of the nonionic block B is from 4-1000.

For instance the number of repeating units of the cationic block A is from 1-100.

In a specific embodiment of the invention the non-ionic block B is composed of butylacrylate (BA) and the ionic block A is composed of 2-dimethylaminoethyl acrylate (DMAEA) or 2-dimethylaminoethyl methacrylate (DMAEMA). In order to get a maximized exfoliation the length of the total blocks is for example more than 30 units. However in some cases also lower length may provide a sufficient intercalation and exfoliation.

Typical blockpolymers are for example Poly $(BA)_{16}$-block-$(DMAEA)_{4,5}$ or Poly $(BA)_{88}$-block-$DMAEA)_{19}$.

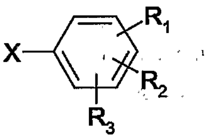
The counterion present in the salt forming component free amino group or a primary, secondary or tertiary amino group may be the anion of a carboxylic acid, phosphonic acid, sulfonic acid, mineralic acid or complex acid. Examples of the anions of mineral acids are F^-, Cl^-, Br^- or I^-. Examples for the anions of complex acids are ClO_4^-, SbF_6^- or PtF_6^-.

In a specific embodiment of the invention the counterion of the salt forming component is selected from the group consisting of mono-, bi- or tricyclic sulphonic, carboxylic or phosphonic acids and aliphatic sulphonic, carboxylic or phosphonic acids substituted with mono-, bi- or tricyclic groups alkyl halides substituted with mono-, bi- or tricyclic groups, and C_1-C_4alkyl esters of mono-, bi- or tricyclic sulphonic acids.

The mono-, bi-, or tricyclic groups present in the sulphonic, carboxylic and phosphonic acids or the mono-, bi-, or tricyclic substituents of the aliphatic sulphonic, carboxylic or phosphonic acids and alkyl halides are selected from the group consisting of saturated or unsaturated mono-, bi-, or tricycloaliphatic, heteromonocycloaliphatic or heterobicycloaliphatic, carbomonocyclic or carbobicyclic aromatic, partially saturated carbobicyclic aromatic, heteromonocyclic or heterobicyclic aromatic and partially saturated heterobicyclic aromatic groups.

Representative salt forming components which are selected from the group consisting of mono-, bi-, or tricyclic sulphonic, carboxylic and phosphonic acids or representative salt forming components which are selected from the group of aliphatic sulphonic, carboxylic or phosphonic acids substituted with monocyclic, bicyclic or tricyclic groups are illustrated by the list given below:

A preferred group of substituted mono-, bi-, or tricyclic sulphonic, carboxylic and phosphonic acids is represented by the general formula:



(IV),

wherein

X represents carboxy, sulpho or $P(=O)(OH)_2$; and

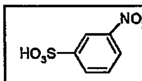
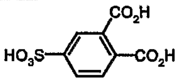
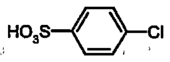
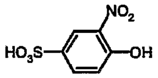
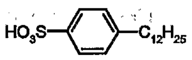
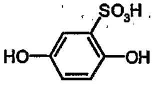
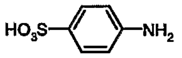
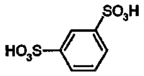
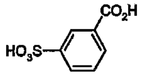
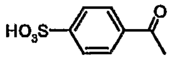
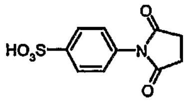
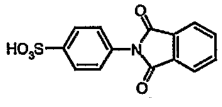
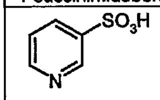
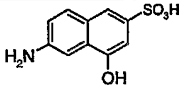
R_1, R_2 or R_3 independently of one another represent hydrogen or a substituent selected from the group consisting of functional groups or derivatised functional groups selected from the group consisting of amino, C_1-C_4alkylamino, C_1-C_4-dialkylamino, hydroxy, oxo, thio, $-NO_2$, carboxy, carbamoyl, sulpho, sulphamoyl, ammonio, amidino, cyano, formylamino, formamido and halogen; or

R_1, R_2 or R_3 independently of one another represent saturated or unsaturated aliphatic, cycloaliphatic or heterocycloaliphatic groups, carbocyclic or heterocyclic aryl groups, condensed carbocyclic, heterocyclic or carbocyclic-heterocyclic groups, which may additionally be combined with one of these groups or which may additionally be substituted with one of the functional groups or derivatised functional groups mentioned above.

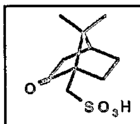
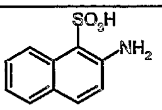
The substituent groups may additionally be interrupted with one or more bivalent groups selected from the group consisting of -O-, -S-, -C(=O)-O-, -O-C(=O)-, $-C(=O)-N(C_1$-C_4alkyl)-, $-N(C_1$-C_4alkyl)-C(=O)-, -S(=O)-, $-S(=O)_2$-, -S(=O)-O-,$-S(=O)_2$-O-, -O-S(=O)-, $-O-S(=O)_2$-, $-S(=O)-N(C_1$-C_4alkyl)-, $-S(=O)_2-N(C_1$-C_4alkyl)-, $-(C_1$-C_4alkyl)N-S(=O)-, $-(C_1$-C_4alkyl)$N-S(=O)_2$-, -P(=O)-, -P(=O)-O-, -O-P(=O)- and -O-P(=O)-O-.

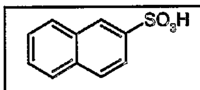
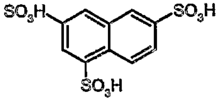
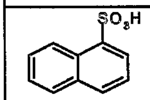
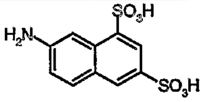
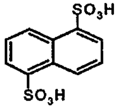
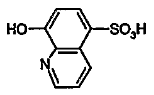
Two substituents from the group R_1 and R_2 may also represent bivalent, bridge-type C_2-C_8alkylen-, C_4-C_8alkyldiyliden- or C_4-C_8alkenyldiyliden groups which are connected with one of the above-mentioned cyclic or bicyclic groups.

Specific salt forming components, which are selected from the group consisting of mono- or bicyclic sulphonic acids, are illustrated by their structural formulae given below:

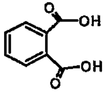
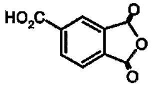
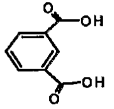
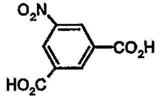
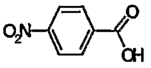
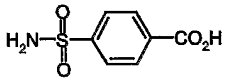
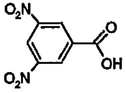
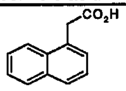
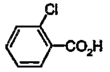
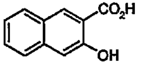
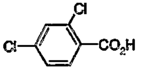
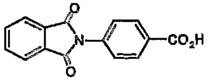
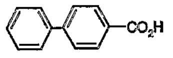
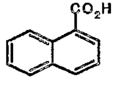
 3-nitro-benzene sulphonic acid	 4-sulphophtalic acid
 4-chlorobenzene sulphonic acid	 4-hydroxy-3-nitrobenzene sulphonic acid
 4-dodecylbenzene sulphonic acid	 2,5-dihydroxybenzene sulphonic acid
 sulphanilic acid	 benzene-1,3-disulphonic acid
 3-sulphobenzoic acid	 4-acetylsulphonic acid
 4-succinimidobenzene sulphonic acid	 4-phthalimidobenzene sulphonic acid
 pyridine-3-sulphonic acid	 7-amino-1-naphtol-3-sulphonic acid

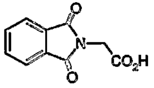
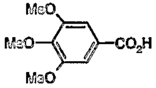
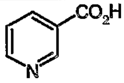
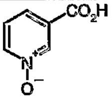
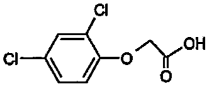
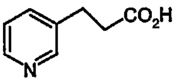
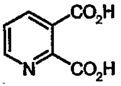
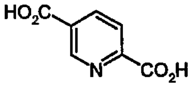
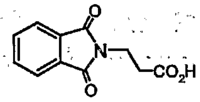
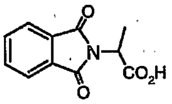
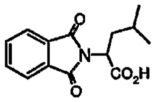
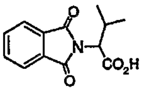
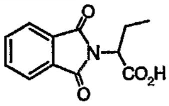
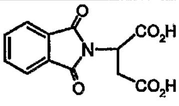
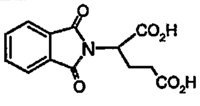
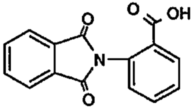
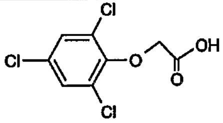
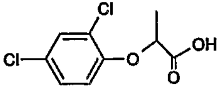
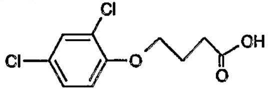
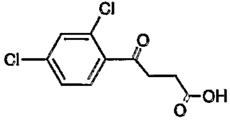
Further specific salt forming components, which are selected from the group consisting of mono- or bicyclic sulphonic acids are illustrated by their structural formulae given below:

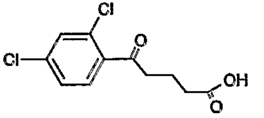
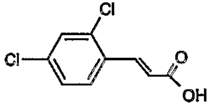
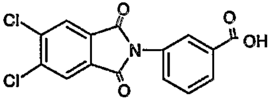
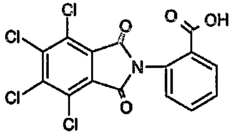
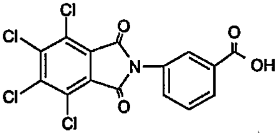
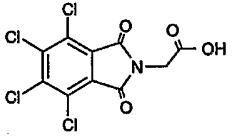
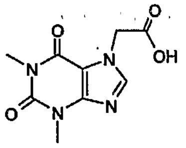
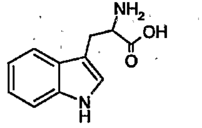
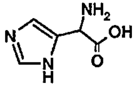
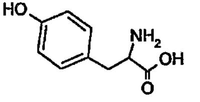
 (+-)camphor-10-sulphonic acid	 2-naphthylamine-1-sulphonic acid and isomers

 naphthalene-2-sulphonic acid	 naphthalene-trisulphonic acid, isomer mixture e.g. naphthalene 1,3,6-trisulphonic acid
 naphthalene-1-sulphonic acid	 2-naphthylamine-6,8-disulphonic acid and isomers
 naphthalene1,5-disulphonic acid and isomers	 8-hydroxyquinoline sulphonic acid

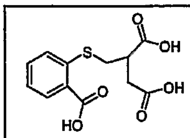
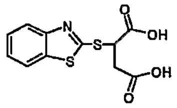
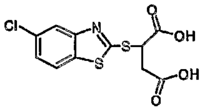
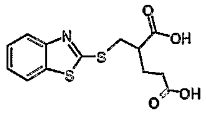
Specific salt forming components, which are selected from the group consisting of mono- or bicyclic carboxylic acids are illustrated by their structural formulae given below:

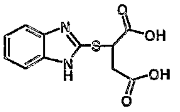
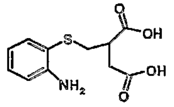
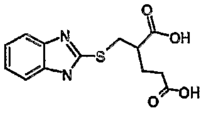
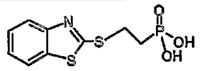
 phthalic acid	 trimellitic acid anhydride
 isophthalic acid	 5-nitro-isophthalic acid
 4-nitrobenzoic acid and isomers	 benzoic acid-4-sulphamide
 3,5-dinitrobenzoic acid and isomers	 1-naphthylacetic acid
 2-chlorobenzoic acid and isomers	 3-hydroxynaphthoic acid
 2,4-dichlorobenzoic acid and isomers	 N-(4-carboxyphenyl)phthalimide
 4-phenylbenzoic acid	 1-naphthoic acid

 phthaloyl glycine	 3,4,5-trimethoxybenzoic acid
 nicotinic acid	 nicotinic acid N-oxide
 2,4-dichlorophenoxyacetic acid	 3-pyridinepropionic acid
 quinolinic acid	 pyridine-2,5-dicarboxylic acid
 3-phthalimidopropionic acid	 2-phthalimidopropionic acid
 4-methyl-2-phthalimidovaleric acid	 2-phthalimidoisovaleric acid
 2-phthalimidobutyric acid	 phthalimidosuccinic acid
 2-phthalimidoglutaric acid	 2-phthalimidobenzoic acid
 2,4,6-trichlorophenoxyacetic acid	 2(2,4-dichlorophenoxy)-propionic acid
 4(2,4-dichorophenoxy)-butyric acid	 3(2,4-dichlorobenzoyl)-propionic acid

 3(2,4-dichlorobenzoyl)-butyric acid	 2,4-dichlorophenylacrylic acid
 3(4,5-dichlorophthalimido)-benzoic acid	 2-tetrachlorophthalimidobenzoic acid
 3-tetrachlorophthalimidobenzoic acid	 tetrachlorophthaloylglycine
 theophylline-7-acetic acid	 tryptophane
 histidine	 tyrosine

Further specific salt forming components, which are selected from the group consisting of mono- or bicyclic carboxylic acids and phosphonic acids are illustrated by their structural formulae given below:

 2(2-carboxyphenylthiomethyl)succinic acid	 2-benzothiazol-2-ylthiosuccinic acid
 2(5-chlorobenzothiazol-2-ylthio)succinic acid	 2-benzothiazol-2-ylthiomethylglutaric acid

 2-benzimidazol-2-ylthiosuccinic acid	 2(2-aminophenylthiomethyl)-succinic acid
 2-benzimidazol-2-ylthiosuccinic acid	 2-benzothiazol-2-ylthioethanephosphonic acid

Typically the block or comb copolymer is added to the natural or synthetic clay in an amount of from 1% to 1000% by weight, based on the weight of the clay, preferably of from 20% to 400% and more preferably from 50% to 400%.

Preferably the polydispersity of block A and B is between 1 and 2.

In particular the polydispersity of the blockcopolymer A-B is between 1 and 2.

A further aspect of the invention is a block or comb copolymer, clay nanocomposite dispersion obtainable by a process as described above.

The intercalated clay can, for example be isolated as a powder. The isolation process may be carried out, for example, by centrifugating the corresponding aqueous dispersion. Another possiblitiy is, to completely evaporate water and solvents and subject the solid residue to a Soxhlet extraction with a suitable organic solvent, to remove excess polymer. Suitable organic solvents are, for example, esters, ethers or aromatic solvents. The purified solid material can easily be redispersed in water to result in a clay nanocompsite dispersion.

The nanocomposite dispersions are useful for example in, coatings, sealants, caulks, adhesives and as plastic additives to modify the physical properties of the final products.

Typically scratch resistance or water vapour permeation of coatings or polymer films are advantageously influenced by the addition of the instant nanocomposite dispersions.

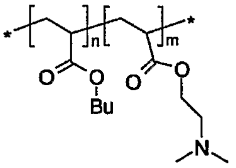
It is typical for nanocompsite dispersions, that considerable less must be added for example to a coating as compared to conventional additives to achieve the same or even a better effect. In many cases even transparency of the coating is retained.

Use of a block copolymer having one ammonium cationic block A, and at least one neutral block B or a comb copolymer having an ammonium ion containing cationic backbone A and neutral oligomeric/polymeric chains B attached thereto, wherein the block copolymer and the comb copolymer is obtained by controlled free radical polymerization as described above for the preparation of nanocomposite dispersions of natural or synthetic clay.

The following examples illustrate the invention.

Example 1

A block-copolymer of n-butyl acrylate and dimethyl aminoethyl acrylate (DMAEA) was synthesized by ATRP:



n=7.7, m=2.0; GPC: M_n=1710, M_w=2050, PDI=1.20; N-content: 1.62 wt.% (elemental analysis)

A) Preparation of the first block, poly-n-butylacrylate with terminal Br-groups: 1282 g (10.0 mol) n-butylacrylate (BASF, tech. quality), 1282 g acetone (Fluka purum), 28.45 g (0.2 mol) CuBr and 2.23 g (0.01 mol) $CuBr_2$ are added to a 4500 ml round flask equipped with a mechanical stirrer. The air is removed from the flask by stirring and evacuating and rinsing with nitrogen three times. 34.7 g (0.2 mol) PMDETA (N,N,N',N",N"-pentamethyldiethyltriamine: Fluka/purum) are added through the rubber sealing with a syringe and the mixture homogenized by stirring. After addition of 167 g (1 mol) methyl-2-bromo-propionate (MBP, = initiator) with a syringe and heating up to 60°C in the oil bath the exothermal polymerization reaction is started and is controlled by ice cooling to T=60-65°C. The mixture is polymerized for 7.5 h. The conversion (77%) is determined by ^{1}H-NMR-analysis in $CDCl_3$ (98% after 75 Min.) After cooling to room temperature 300 g neutral aluminum oxide (ALOX for chromatography, Merck) are added. After stirring the mixture for 1 h, filtration and drying in the rotary evaporator at 80°C, additional drying with a vacuum pump the polymer (slightly yellow, clear liquid) is obtained. Yield: 1192 g (98%). Elementary analysis:

	C	H	Br
calc.	60.47	8.71	6.66
found	61.24	8.78	5.28

Cu: < 10 ppm (X-ray fluorescence); GPC (THF): M_n: 1150, M_w: 1370, PDI: 1.19. (92%).

B) Preparation of the block copolymer of n-butylacrylate and 2-dimethylaminoethyl acrylate:

200 g poly-n-butylacrylate (0.18 mol Br, **Ex. 1A**) and 5.16 g (0.036 mol) CuBr (Fluka, purum) are added to a 750 ml round flask equipped with a mechanical stirrer. The air is removed from the flask by stirring and evacuating and rinsing with nitrogen three times. The mixture is stirred and 51.5 g (0.36 mol) 2-dimethylaminoethyl acrylate (DMAEA, BASF, technical quality) are added through the rubber sealing with a syringe. The air is removed again from the flask by evacuating and rinsing with nitrogen three times. 6.24 g (0.036 mol) PMDETA (Fluka/purum) are added with a syringe, and the mixture is made homogeneous by stirring. After heating up to 90°C in the oil bath the slightly exothermal polymerization reaction is started and the mixture is polymerized for 30 min. The conversion of DMAEA is quantitative, as determined by ^{1}H-NMR-analysis in $CDCl_3$. After cooling to room temperature 250 ml ethyl acetate and 110 g neutral aluminum oxide (Alox® for chromatography) are added and the mixture stirred for 1.5 h. The polymer is obtained after filtration and drying in the rotary evaporator at 80°C with a vacuum pump. Yield: 155.5 g (62 %). Elementary analysis:

	C	H	N	Br
calc.	59.98	8.72	1.95	4.20
found	61.17	9.01	1.62	3.62

GPC (THF): M_n: 1720, M_w: 2020, PDI: 1.18.

C) Protonation of the block copolymer with p-toluene sulfonic acid:

In a 500 ml round bottom flask with mechanical stirring, 145g of the copolymer is dissolved in 60.8 g 1-methoxy-2-propanol (Dowanol PM) and a solution of 31.9 g p-toluene sulfonic acid monohydrate (Fluka purum), dissolved in 200 g hot Dowanol PM, is slowly added with good stirring during 1 h at room temperature. A clear, slightly yellow solution with 40 wt.% solid content of the cationic block copolymer is obtained.

D) Intercalation of sheet silicates (Nanofil EXM 588 from Süd Chemie, Germany; sheet silicate of Montmorillonite-type) with cationic block copolymer Poly(BA-b-DMAEA) described under **C)**.

22.9 g of the above solution containing 9.15 g of the cationic block copolymer A) is put into a 100 ml round bottom flask with mechanical stirring, 30 g Dowanol PM and 5 g water are added. 3.49 g Nanofil EXM 588 (Süd Chemie, Germany) is dispersed in this mixture, homogenized and stirred for 24 h at 60°C. It is then centrifuged (IEC Centra GP8 Centrifuge) with 2000 rpm (corresponding to ca. 850 g) during 1 h, the supernatend is decanted and the solid residue at the bottom is washed with EtOH and again centrifuged for 1 h at 2000 rpm. After again decanting the supernatend, the procedure is repeated once more with a water/EtOH 1/1 (vol) mixture. The solid is dried in vacuum (0.1 mbar) at 50°C for 24 h. Yield: 4.0 g.

Analysis:

TGA: The amount of adsorbed organic material (cationic block copolymer) is determined by thermogravimetric analysis (TGA): heating rate: 10°C/min, from room temperature to 600°C. The observed weight loss of 30% corresponds to a solid content of 70 wt.%.

GPC: A direct measurement of the sample is not possible because the polymer chains are tightly attached to the sheet silicate will not pass the GPC columns. Therefore, a sample (150 mg) of this solid is refluxed with 15 ml 0.2 M LiBr solution in THF during 17 h at 65°C, to cleave off the polymer from the sheet silicate. After filtration, the molar mass (M_n) and PDI is determined by GPC in THF (relative to PS-standards): M_n=1450, M_w=2050 and PDI=1.42, correspond well to the data of the block-copolymer used for intercalation.

Powder X-ray: The product is also subjected to a powder X-ray (λ=1.54 Angström), giving an interlayer distance of 1.96 nm. Compared with the native sheet silicate (d=1.24 nm) an increase of the interlayer distance of 0.72 nm is obseved, corresponding to approximately the size of the intercalated cationic block-copolymer. The reflex at the original sheet distance has completely disappeared.

E) Intercalation of an artificial sheet silicate *Optigel SH (Süd Chemie, Germany)* with the cationic block copolymer Poly(BA_{68}-b-$DMAEMA_{19}$) with 68 BA and 19 DMAEMA units, synthesized as described under **A** and **B** and protonated as described under **C**.

770.3 g of a 30 wt.% solution of the cationic block copolymer *Poly(BA_{68}-b-$DMAEMA_{19}$)* in Dowanol PM (Fluka, puriss p.a.), 50% of the DMAEMA units neutralized with p-toluene sulfonic acid as described in **C**, are put into a 2.5 L round bottom flask with mechanical stirring. 1.4 Dowanol PM and 140 ml water are added. 120 g Optigel SH (Süd Chemie, Germany) is dispersed in this mixture, homogenized and stirred for 24 h at 60°C. The solvents are evaporated in a rotavap and the solid residue extracted in a 1 L Soxhlet extractor, first 12 h with 2 L ethyl acetate, then 4 h with 2 L ethanol and finally 14 h with 2 L ethanol/water 1:1 mixture. The gray solid is redispersed in EtOH, filtered and dried in vacuum (0.1 mbar) at 55°C for 24 h. Yield: 255.5 g of a white powder is obtained.

Analysis:

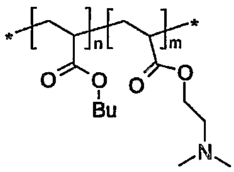
TGA: The amount of adsorbed organic material (cationic block copolymer) is determined as before, giving 54 wt.% (=46 wt.% solid content).

GPC: (Sample preparation as before) M_n=10000, M_w=14300, PDI=1.43.

Powder X-ray: Complete exfoliation with interlayer distance d > 3 nm.

Example 2

A) In analogy to Example 1, a longer block-copolymer of n-butyl acrylate and dimethyl aminoethyl acrylate (DMAEA) is synthesized.



Analysis: n=27.6, m=8.7; Mn=6270, Mw=7710, PDI=1.23

100% of the amino groups are neutralized with p-toluene sulfonic acid monohydrate Dowanol PM to a clear, slightly yellow solution with 30.5 wt.% solid content of the cationic block copolymer.

B) Intercalation of a sheet silicate with a longer cationic block copolymer Poly(BA-b-DMAEA) prepared as described under A)

300 g of above solution containing 91.5 g of the cationic block copolymer A) is put into a 1000 ml round bottom flask with mechanical stirring and 250 g Dowanol PM and 50 g water are added. 34.9 g Nanofil EXM 588 (Süd Chemie, Germany) is dispersed in this mixture with a high speed Ultraturax mixer, homogenized and stirred for 24 h at 60°C. It is then centrifuged (2000 rpm) during 1 h, the supernatend is decanted and the solid residue at the bottom dispersed in 300 ml ethyl acetate and again centrifuged for 1 h at 2000 rpm. After again decanting the supernatend, the solid is redispersed in 300 ml EtOH with an Ultraturax and centrifuged again for 1 h. The gray solid is redispersed in a water/EtOH 4/1 (vol) mixture and filtered. The solid is dried in vacuum (0.1 mbar) at 40°C for 24 h. Yield: 26.3 g.

Analysis:

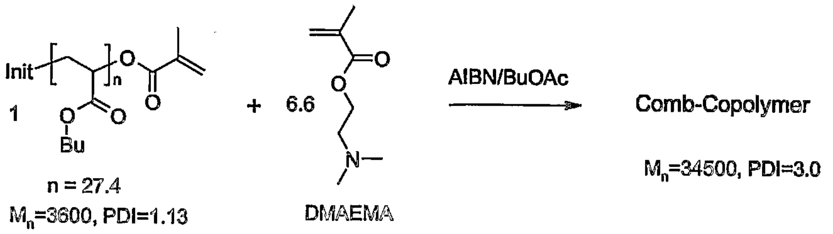
TGA: Observed weight loss: 46% corresponding to a solid content of 54 wt.%.

GPC: After refluxing with LiBr in THF at 65°C (to cleave off the polymer from the sheet silicate): M_n=3700, M_w=7240, PDI=1.82.

Powder X-ray: No reflexions above $2\Theta = 3°$, corrsponding to an interlayer distance of > 3 nm: complete exfoliation.

<u>Example 3</u>

A) A comb-copolymer of a poly(n-butyl acrylate) macromonomer (synthesized by ATRP) and dimethyl aminoethyl methacrylate (DMAEMA) is first synthesized according to known procedures (see e.g. WO-01/051534):



Synthesis of the poly(n-butyl acrylate) macromonomer (with methacrylate functional groups):

7.46 g (0.052 mol) Cu(I)Br is added into a 2.5 l reaction vessel (evacuated and rinsed with N_2 5 times) followed by the addition of 1000 g (7.80 mol) n-butyl acrylate and 350 ml acetone. The reaction mixture is homogenized by mechanical stirring. 9.0 g (0.052 mol) PMDETA are added with a syringe and a green solution is obtained. After adding 43.43 g (0.26 mol) methyl-2-bromopropionate as the initiator, the mixture is heated to 60°C. The highly exothermic reaction requires cooling with ice to maintain the temperature at about 60°C for 4 h: Conversion: 74% (^{1}H-NMR analysis). The reaction mixture is cooled to room temperature and the solvents are evaporated in the rotary evaporator. After diluting the residue with 300 ml ethylacetate 2 x 150 g SiO_2 are added. The mixture is filtered and directly converted to the macromonomer as follows:

26.86 g (0.31 mol, 1.2 eq.) methacrylic acid and 47.51 g (0.31 mol, 1.2 eq.) DBU are added to the reaction mixture which is then stirred at room temperature for 15 hours. After filtration 200 g SiO_2 are added. The reaction mixture is stirred for a half hour and filtered again. The solvents are evaporated in the rotary evaporator and the macromonomer dried at 100°C in high vacuum ($p < 0.1$ mbar). Yield: 803.3 g (97.5%) of a slightly yellow transparent viscous liquid. Analytical data:

	C	H	Br
calc.	65.06	9.30	0.00
found	64.79	9.68	<0.3

GPC (THF, PS-standards): M_n: 3600, PDI=1.13.

Radical copolymerization of this macromonomer with N,N-dimethylaminoethyl methacrylate (DMAEA):

300 g (0.081 mol, 78 wt%) of above macromonomer, 84.6 g (0.54 mol, 22 wt%) N,N-dimethylaminoethyl acrylate (DMAEMA), 640 ml 1-methoxy-2-propanol and 7.7 g (2 wt%, relative to the monomers) AIBN, are introduced into a 1.5 l reactor (evacuated and rinsed 3 times with N_2). The homogeneous mixture is polymerized at 60°C (exothermic reaction) during 24 h. This mixture containing the comb-copolymer is directly used for tests as a pigment dispersant. Analytical data of dried sample:

	C	H	N
calc.	64.26	9.39	1.95
found	63.73	9.51	2.20

GPC (THF, PS-standards): M_n=34500, PDI= 3.0.

This comb-copolymer, containing 62 wt.% n-BA units and 38 wt.% DMAEMA units (according to ^{1}H-NMR) is neutralized in Dowanol PM with p-toluene sulfonic acid monohydrate as described in Examples 1 and 2 (100% of the amino groups are quaternised). A clear, slightly yellow solution with 29.8 wt.% solid content of the cationic comb-copolymer is obtained.

B) Intercalation of a sheet silicate with a cationic comb-copolymer described under A)
513.7 g of the above solution containing 150 g of the cationic comb-copolymer A) is put into a 2 L round bottom flask with mechanical stirring and 500 g Dowanol PM and 100 g water are added. 60.3 g Nanofil EXM 588 (Süd Chemie, Germany) is dispersed in this mixture with a high speed Ultraturax mixer, homogenized and stirred for 24 h at 60°C. It is than centrifuged (2000 rpm) during 1 h, the supernatend is decanted and the solid residue at the bottom is dispersed in 600 ml ethyl acetate and again centrifuged for 1 h at 2000 rpm. After again decanting the supernatend, the solid is redispersed in 600 ml EtOH with an Ultraturax and centrifuged again for 1 h. The gray solid is redispersed in 600 ml water, filtered, washed with EtOH and filtered again. The solid is dried in vacuum (0.1 mbar) at 50°C for 24 h. Yield: 50.5 g.
Analysis:
TGA: Observed weight loss: 54% corresponding to a solid content of 46 wt.%.
GPC: After refluxing with LiBr in THF/water for 17 h at 65°C: M_n=32800, M_w=61600, PDI=1.87.
Powder X-ray: No reflexions above $2\Theta = 3°$, corrsponding to an interlayer distance of > 3 nm: complete exfoliation.

Example 4

A) The same comb-copolymer of a poly(n-butyl acrylate) macromonomer (synthesized by ATRP) and dimethyl aminoethyl methacrylate (DMAEMA) as described in example 3 A) is used, but only 50% of the amino groups are neutralized in Dowanol PM with p-toluene sulfonic acid monohydrate. A clear, slightly yellow solution with 30.0 wt.% solid content of the cationic comb-copolymer is obtained.

B) Intercalation of a sheet silicate with a cationic comb-copolymer

213.5 g of above solution containing 64.05 g of the cationic comb-copolymer is put into a 1 L round bottom flask with mechanical stirring and 175 g Dowanol PM and 35 g water are added. 24.4 g Nanofil EXM 588 (Süd Chemie, Germany) is dispersed in this mixture with a high speed Ultraturax mixture, homogenized and stirred for 24 h at 60°C. It is then centrifuged (2000 rpm) during 1 h, the supernatend is decanted and the solid residue at the bottom is dispersed in ethyl acetate and again centrifuged for 1 h at 2000 rpm. After again decanting the supernatend, the solid is redispersed in EtOH with an Ultraturax and centrifuged again for 1 h. The gray solid is redispersed in water, filtered, washed with EtOH and filtered again. The solid is dried in vacuum (0.1 mbar) at 50°C for 24 h. Yield: 27.5 g.
Analysis:
TGA: Observed weight loss: 49% corresponding to a solid content of 51 wt.%.
GPC: As in example 3, M_n=27100, M_w=45000, PDI=1.67.
Powder X-ray: No reflexions above 2Θ = 3°, corresponding to an interlayer distance of > 3 nm: complete exfoliation

C) Intercalation of another sheet silicate (*<u>Harshaw Filtrol Grade 13</u>*) with a cationic comb-copolymer

492 g of the solution according to **A)** containing 137.3 g of the cationic comb-copolymer is put into a 2.5 L round bottom flask with mechanical stirring and 1.44 L Dowanol PM and 144 ml water are added. 120 g Harshaw Filtrol Grade 13 (Engelhard Process Chemicals GmbH, Nienburg, Germany) is dispersed in this mixture with a high speed Ultraturax mixture, homogenized and stirred for 24 h at 60°C. The solvents are evaporated in a rotavap and the solid residue extracted in a 1 L Soxhlet extractor, first 12 h with 2 L ethyl acetate, then 12 h with 2 L ethanol and finally 12 h with 2 L ethanol/water 1:1 mixture. The gray solid is redispersed in EtOH, filtered and dried in vacuum (0.1 mbar) at 55°C for 24 h. Yield: 148.5 g.
Analysis:
TGA: Observed weight loss: 39 wt.% corresponding to a solid content of 61 wt.%.
Powder X-ray: No reflexions above 2Θ = 3°, corresponding to an interlayer distance of > 3 nm: complete exfoliation.

Claims

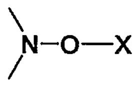
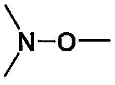
1. A process for preparing a block- or comb polymer, clay nanocomposite dispersion comprising

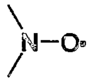
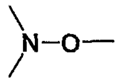
mixing an aqueous dispersion of a natural or synthetic clay having an exchangeable cation; with

a block copolymer having a cationic block A wherein the cation is based on at least one nitrogen atom, and a nonionic block B, both blocks having a polydispersity between 1 and 3, or

a comb copolymer having a cationic backbone A wherein the cation is based on a nitrogen atom and nonionic oligomeric/polymeric chains B attached thereto, the cationic backbone A having a polydispersity between 1 and 3 and the nonionic side chains having a polydispersity of 1.0-1.8;

wherein the block copolymer is obtained

a1) by polymerizing in a first step an ethylenically unsaturated monomer 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 and adding in a second step to the resulting macromer, which has attached a labile bound  group, a further ethylenically unsaturated monomer different from that in step 1,

with the proviso that at least one monomer in the first or second step contains a cation centered on a nitrogen atom or a nitrogen atom from which a cation can be formed; or a2) by polymerzing in a first step an ethylenically unsaturated monomer in the presence of at least one stable free nitroxyl radical  $>N-O\bullet$ and a free radical initiator and adding in a second step to the resulting macromer, which has attached a labile bound  $>N-O-$ group, a further ethylenically unsaturated monomer different from that in step 1;

with the proviso that at least one monomer in the first or second step contains a cation centerd on a nitrogen atom or a nitrogen atom from which a cation can be formed; or

a3) by polymerzing in a first step an ethylenically unsaturated monomer in the presence of a compound of formula (III) $\left[In\right]_p\!-\!\left[Hal\right]_q$ (III) and a catalytically effective amount

of an oxidizable transition metal complex catalyst, wherein

p represents a number greater than zero and defines the number of initiator fragments;

q represents a number greater than zero;

[In] represents a radically transferable atom or group capable of initiating polymerization and

-[Hal] represents a leaving group; and adding in a second step to the resulting macromer a further ethylenically unsaturated monomer different from that in step one;

with the proviso that at least one monomer in the first or second step contains a cation centered on a nitrogen atom or a nitrogen atom from which a cation can be formed;

wherein the comb copolymer is obtained

by polymerizing in a first step an ethylenically unsaturated monomer in the presence of a compound of formula (III) $\left[\boxed{\text{In}}\right]_p\!-\!\left[\boxed{\text{Hal}}\right]_q$ (III) and a catalytically effective amount of an oxidizable transition metal complex catalyst, wherein the symbols have the meanings as defined above;

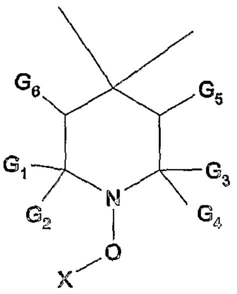
exchanging the group [HAL] attached to the polymer with a group having an ethylenically unsaturated bond and subjecting the resulting macromer together with a second monomer, which contains a nitrogen based cation or a nitrogen atom from which a cation can be formed, to radical polymerization;

forming the nitrogen based cation if necessary and exchanging the cation in the natural or synthetic clay with the nitrogen based cationic block or comb copolymer and intercalating and/or exfoliating the clay at least partially.

2. A process according to claim 1 wherein the natural or synthetic clay is a phyllosilicate.

3. A process according to claim 1 wherein the natural or synthetic clay is selected from the group consisting of smectite, montmorillonite, saponite, beidellite, mica, sauconite, ledikite, montronite, hectorite, stevensite, vermiculite, kaolinite, hallosite and combinations thereof.

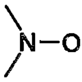
4. A process according to claim 1 wherein the structural element $>N-O-X$ is a structural element of formula (I)

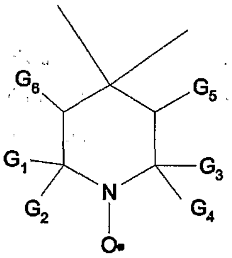


(I), wherein

G_1, G_2, G_3, G_4 are independently C_1-C_6alkyl or G_1 and G_2 or G_3 and G_4, or G_1 and G_2 and G_3 and G_4 together form a C_5-C_{12}cycloalkyl group;

G_5, G_6 independently are H, C_1-C_{18}alkyl, phenyl, naphthyl or a group COOC_1-C_{18}alkyl.

5. A process according to claim 1 wherein the structural element  is a structural element of formula (I)



(I'), wherein

G_1, G_2, G_3, G_4 are independently C_1-C_6alkyl or G_1 and G_2 or G_3 and G_4, or G_1 and G_2 and G_3 and G_4 together form a C_5-C_{12}cycloalkyl group;

G_5, G_6 independently are H, C_1-C_{18}alkyl, phenyl, naphthyl or a group COOC_1-C_{18}alkyl.

6. A process according to claim 1, wherein in step a3)

[In] represents the polymerization initiator fragment of a polymerization initiator of formula (III) capable of initiating polymerization of monomers or oligomers which polymerization initiator is selected from the group consisting of C_1-C_8-alkyl halides, C_6-C_{15}-aralkylhalides, C_2-C_8-haloalkyl esters, arene sulfonyl chlorides, haloalkanenitriles, α-haloacrylates and halolactones, and

p and q represent one.

7. A process according to claim 6 wherein in step a3) the oxidizable transition metal in the transition metal complex salt is present as a transition metal complex ion in the lower oxidation state of a redox system.

8. A process according to claim 1, wherein the nonionic polymer block B is essentially composed of repeating units of ethylenically unsaturated monomers selected from the group consisting of styrenes, acrylic and C_1-C_4alkylacrylic acid-C_1-C_{24}alkyl esters, acrylic and C_1-C_4alkylacrylic acid-C_6-C_{11}aryl-C_1-C_4alkyl esters, acrylic and C_1-C_4alkylacrylic acid-C_6-C_{11}aryloxy-C_1-C_4alkyl esters, acrylic and C_1-C_4alkylacrylic acid-hydroxy-C_2-C_6alkyl esters, acrylic and C_1-C_4alkylacrylic acid-polyhydroxy-C_3-C_6alkyl esters, acrylic and C_1-C_4alkylacrylic acid-(C_1-C_4alkyl)$_3$silyloxy-C_2-C_4alkyl esters; acrylic and C_1-C_4alkylacrylic acid-(C_1-C_4alkyl)$_3$silyl-C_1-C_4alkyl esters, acrylic and C_1-C_4alkylacrylic acid-heterocyclyl-C_2-C_4alkyl esters; acrylic and C_1-C_4alkylacrylic acid esters having poly-C_2-C_4alkyleneglycolester groups, wherein the ester groups may be substituted with C_1-C_{24}alkoxy groups, acrylic and methacrylic acid amides, acrylic and C_1-C_4alkylacrylic acid-(C_1-C_4alkyl)$_{1-2}$amide, acrylonitrile, esters of maleic acid or fumaric acid, maleinimide and N-substituted maleinimides.

9. A process according to claim 8, wherein the nonionic polymer block B is essentially composed of repeating units of ethylenically unsaturated monomers selected from the group consisting of styrenes, acrylic and methacrylic acid-C_1-C_{24}alkyl esters, acrylic and methacrylic acid-hydroxy-C_2-C_6alkyl esters, acrylic and methacrylic acid-dihydroxy-C_3-C_4alkyl esters and acrylic and methacrylic acid esters having poly-C_2-C_4alkyleneglycolester groups, wherein the ester groups may be substituted with C_1-C_{24}alkoxy groups.

10. A process according to claim 1, wherein the cationic polymer block A is essentially composed of repeating units of ethylenically unsaturated monomers represented by the cationic part of a salt formed by quaternisation of an amino monomer selected from the group consisting of amino substituted styrene, (C_1-C_4alkyl)$_{1-2}$amino substituted styrene, N-mono-(C_1-C_4alkyl)$_{1-2}$amino-C_2-C_4alkyl(meth)acrylamide and N,N-di-(C_1-C_4alkyl)$_{1-2}$amino-(C_2-C_4)alkyl(meth)acrylamide, vinylpyridine or C_1-C_4alkyl substituted vinylpyridine, vinylimidazole and C_1-C_4alkyl substituted vinylimidazole and a compound of the formula

$CH_2=C(-R^1)-C(=O)-R^2$ (V),

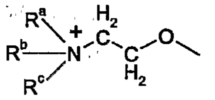
wherein

R^1 represents hydrogen or C_1-C_4alkyl; and

R^2 represents amino substituted C_2-C_{18}alkoxy selected from the group consisting of amino-C_2-C_{18}alkoxy, C_1-C_4alkylamino-C_2-C_{18}alkoxy, di-C_1-C_4alkylamino-C_2-C_{18}alkoxy, hydroxy-C_2-C_4alkylamino-C_2-C_{18}alkoxy and C_1-C_4alkyl-(hydroxy-C_2-C_4alkyl)amino-C_2-C_{18}alkoxy.

11. A process according to claim 10, wherein
R^1 represents hydrogen or methyl; and
R^2 represents amino substituted C_2-C_{18}alkoxy selected from the group consisting of amino-C_2-C_4alkoxy, C_1-C_4alkylamino-C_2-C_4alkoxy, di-C_1-C_4alkylamino-C_2-C_4alkoxy, hydroxy-C_2-C_4alkylamino-C_2-C_{18}alkoxy and C_1-C_4alkyl-(hydroxy-C_2-C_4alkyl)amino-C_2-C_4alkoxy.

12. A process according to claim 10, wherein the cationic part of a salt formed from a compound of the formula (V) is represented by an ester group of the formula (C)



(C),

wherein

one of R^a, R^b and R^c represents 2-hydroxyethyl and the other ones represent hydrogen, methyl or ethyl; or

R^a, R^b and R^c independently of one another represent hydrogen or a substituent selected from the group consisting of C_1-C_4alkyl, aryl-C_1-C_4alkyl and (C_1-C_4alkyl)$_{1-3}$aryl.

13. A process according to claim 10, wherein the cationic polymer block A is essentially composed of repeating units of an ethylenically unsaturated monomer represented by the cationic part of an acid addition salt or the salt formed by quaternisation of 4-aminostyrene, 4-dimethylaminostyrene, aminoalkyl(meth)acrylate selected from the group consisting of 2-dimethylaminoethyl acrylate (DMAEA), 2-dimethylaminoethyl methacrylate (DMAEMA), 2-diethylaminoethyl acrylate (DEAEA), 2-diethylaminoethyl methacrylate (DEAEMA), 2-t-butylaminoethyl acrylate (t-BAEA), 2-t-butylaminoethyl methacrylate (t-BAEMA) and 3-dimethylaminopropylmethacrylamide, 4-vinylpyridine, 2-vinylpyridine or 1-vinylimidazole.

14. A process according to claim 1 wherein the block or comb copolymer is added to the natural or synthetic clay in an amount of from 1% to 1000% by weight, based on the weight of the clay.

15. A process according to claim 1 wherein the polydispersity of block A and B is between 1 and 2.

16. A process according to claim 1 wherein the polydispersity of the blockcopolymer A-B is between 1 and 2.

17. A process according to claim 1 wherein the number of repeating units of the nonionic block B is from 4-1000.

18. A process according to claim 1 wherein the number of repeating units of the cationic block A is from 1-100.

19. A block or comb copolymer, clay nanocomposite dispersion obtainable by a process according to claim 1.

20. Use of a block copolymer having one ammonium cationic block A, and at least one neutral block B or a comb copolymer having an ammonium ion containing cationic backbone A and neutral oligomeric/polymeric chains B attached thereto, wherein the block copolymer and the comb copolymer is obtained by controlled free radical polymerization according to claim 1 for the preparation of nanocomposite dispersions of natural or synthetic clay.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/050184

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08K9/08 C08F2/44

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)
IPC 7 C08K C08F

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 02/24759 A (ROHM & HAAS) 28 March 2002 (2002-03-28) cited in the application claims 1-26	1-25
Y	US 4 017 452 A (SCHWARZ ECKHARD C A) 12 April 1977 (1977-04-12) claims 1-15	1-25

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

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

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

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

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

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

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

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"&" document member of the same patent family

Date of the actual completion of the international search 3 August 2004	Date of mailing of the international search report 17/08/2004
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Siemens, T

INTERNATIONAL SEARCH REPORT

Information on patent family members

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