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- (71) **Applicant:** THE LUBRIZOL CORPORATION
[US/US]; 29400, Lakeland Blvd., Wickliffe, Ohio 44092-2298 (US).
- (72) **Inventors:** MILLER, Cory G.; 9911, Brecksville Road, Cleveland, Ohio 44141-3247 (US). KIM, Hyungsoo; 29400, Lakeland Blvd., Wickliffe, Ohio 44092-2298 (US).
- (74) **Agents:** DEMAS, Christopher P. et al.; 29400 Lakeland Blvd., Wickliffe, Ohio 44092-2298 (US).

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(54) **Title:** WATER SOLUBLE CHAIN TRANSFER AGENTS

(57) **Abstract:** The disclosed technology relates to water soluble, or partially water soluble, chain transfer agents for preparing water soluble polymers by Reversible Addition-Fragmentation Chain Transfer ("RAFT") polymerization in an aqueous medium.



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TITLE

WATER SOLUBLE CHAIN TRANSFER AGENTS

BACKGROUND OF THE INVENTION

[0001] The disclosed technology relates to water soluble, or partially water soluble,
5 chain transfer agents for preparing water soluble polymers by Reversible Addition-Fragmentation Chain Transfer (“RAFT”) polymerization in an aqueous medium.

[0002] Many references for Reversible Addition-Fragmentation Chain Transfer (“RAFT”) polymerizations involving Chain Transfer Agents (“CTA”) teach polymerizations done in organic solvents such as toluene or 1,4-dioxane in order to prepare
10 water-based polymers (meaning either water soluble polymers or emulsions). While such organic solvents are certainly sufficient for polymerization, they pose both a health risk and a fire hazard, and thus large scale commercialization using such solvents is not desired. Further, when such organic solvent are employed for making water soluble polymers, the organic solvent must be stripped to provide a useful water-soluble polymer, which adds additional hazard as well as time and resources.

[0003] A more preferred way of synthesizing water soluble polymers is to make the polymers directly in water with a water soluble CTA. This has been demonstrated many times in the academic literature. In one report, Matsuno, Ryosuke; Goto, Yusuke; Konno, Tomohiro; Takai, Madoka; Ishihara, Kazuhiko *Journal of Nanosci-*
20 *ence and Nanotechnology* (2009), 9(1), 358-365, researchers used CTA-Na that was hydrophobically associated to a modified quantum dot (QD) in water to build a QD supported biopolymer. In this example the researchers took advantage of the surfactant properties of CTA-Na to help stabilize the QD and subsequent polymer that was grown out from the core.

[0004] What is needed is an economically feasible way to control polymerization
25 of water soluble monomers such as AMPSTM, acrylamide, acrylic acid, etc., in aqueous solutions.

SUMMARY OF THE INVENTION

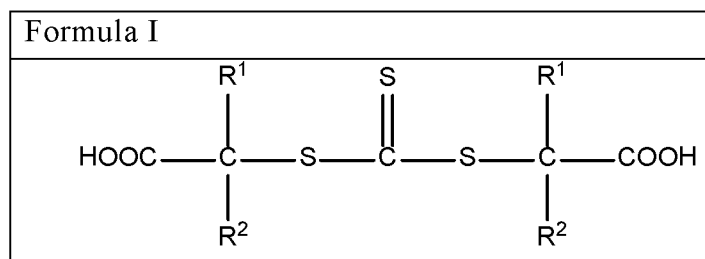
[0005] The disclosed technology, therefore, solves the problem of performing liv-
30 ing polymerizations in aqueous media by providing water soluble CTAs.

[0006] What we are proposing here, is a water soluble CTA-acid, or a water soluble CTA-acid salt made by reacting a CTA-acid with a suitable base, such as sodium

hydroxide, or an amine, to produce a water soluble RAFT agent. The molecule is then used to controllably polymerize any water-soluble monomers directly in water. The resulting polymers are of a predetermined molecular weight with a low polydispersity. Since the polymerization is living, water soluble block copolymers and other interesting geometries can be envisioned such as star and comb polymers. These materials have potential applications in any formulation that might require a water soluble polymer of defined molecular weight and shape such as for example, paints and coatings, personal and home care, energy exploration and refinery applications, including but not limited to, water treatment applications, drilling fluids, paraffin inhibiting applications, cementing applications, completion applications, and fuel transportation applications and for improving refinery and oilfield operational efficiencies.

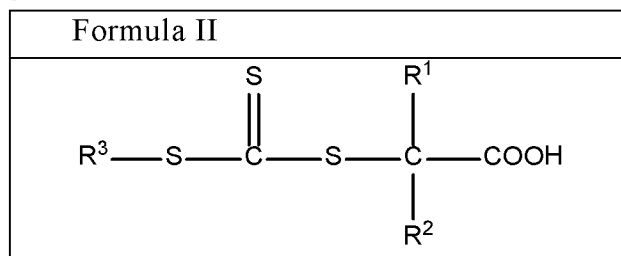
[0007] In one aspect, the disclosed technology provides a compound comprising, consisting of, or consisting essentially of a water soluble CTA-acid. In an embodiment, the water soluble CTA-acid can be in the form of a water soluble CTA-acid salt.

[0008] In an embodiment, the water soluble CTA-acid can be a thiocarbonate compound of any one of formulas I, II, III or IV:



wherein

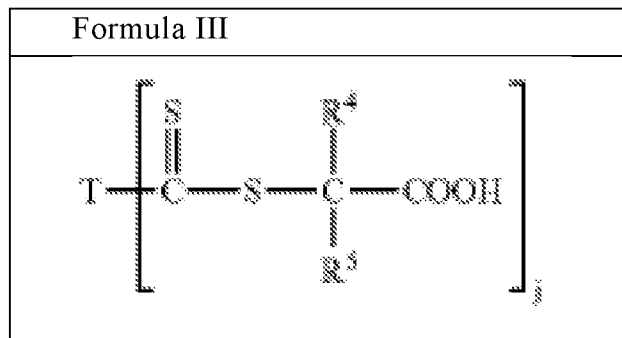
each of R^1 and R^2 is an alkyl group of four carbons or less or H, so long as the sum of the number of carbon atoms present for all R^1 , and R^2 in formula I together is less than four; or formula II



wherein

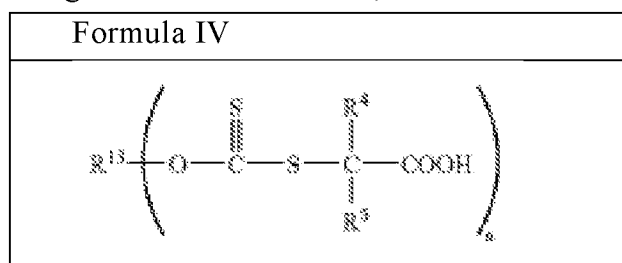
each of R^1 and R^2 is as defined above; and

R^3 is an alkyl group of four carbons or less, or H,
so long as the sum of the number of carbon atoms present for all R^1 , R^2 and R^3 in
formula II together is less than four; or formula III



wherein

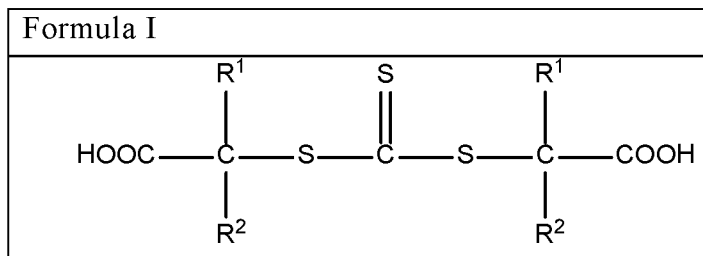
- 5 each of R^4 and/or R^5 substituents, independently, comprise an alkyl group having from 1 to 4 carbon atoms, or H;
 j is 1 or 2, with the proviso that when j is 1, T is $-(NR^6 R^7)$; and when j is 2, T is a divalent radical having a nitrogen atom directly connected to each carbon atom of the two thiocarbonyl groups present;
 10 R^6 and R^7 , independently, are the same or different, and are H or a linear or branched alkyl having from 1 to 4 carbon atoms;
 so long as the sum of the number of carbon atoms present for all R substituents in formula III together is less than four; or formula IV



wherein

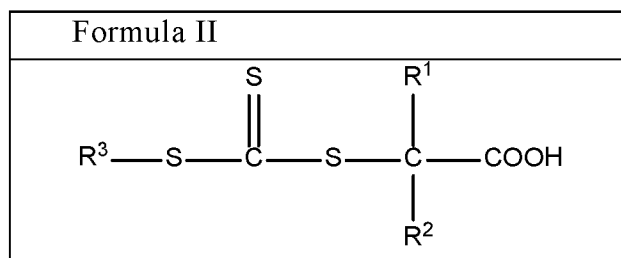
- 15 each of R^4 , and R^5 are as defined above
 R^{13} is optionally substituted, and is a linear or branched alkyl having from 1 to 4 carbon atoms; and
 a is 1 to 4;
 so long as the sum of the number of carbon atoms present for all R substituents
 20 in formula IV together is less than four.

[0009] In another embodiment, the water soluble CTA-acid can be in the form of a water soluble CTA-acid salt, and the CTA-acid portion of the water soluble CTA-acid salt can be a thiocarbonate compound having any of formulas I, II, III, or IV:



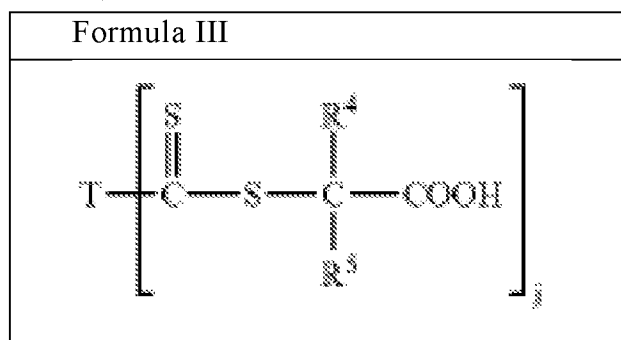
wherein

R^1 and R^2 , independently, are selected from a linear or branched alkyl having from 1 to 6 carbon atoms, a substituted alkyl having from 1 to 6 carbon atoms, substituted and unsubstituted aryl, R^1 and R^2 can form a substituted or unsubstituted cyclic ring having from 5 to 12 total carbon atoms; wherein said substituents, independently, are selected from an alkyl having from 1 to 6 carbon atoms, aryl, a halogen which can be the same or different, cyano, an ether having a total of from 2 to 20 carbon atoms, and a nitro group; or formula II



wherein

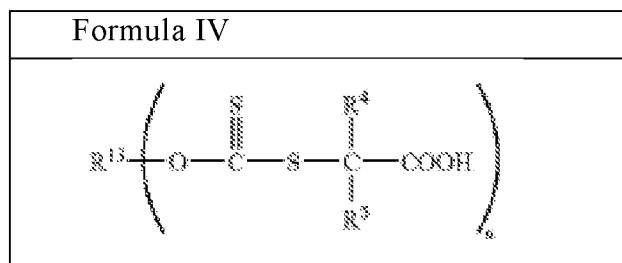
R^3 is selected from benzyl, a C_1 through C_{18} alkyl, a substituted C_1 to C_{18} alkyl, wherein said substituted group is selected from halogen, hydroxyl, alkoxy, a C_1 to C_{18} hydroxyalkyl, aralkyl, cyanoalkyl, aminoalkyl, carboxylalkyl, carboalkoxyalkyl, and mercaptoalkyl, and wherein R^1 and R^2 , independently, are as described above; or formula III



wherein

j is 1 or 2, with the proviso that when j is 1, T is $(-\text{NR}^6\text{R}^7)$, and when j is 2, T is a divalent radical having a nitrogen atom directly connected to each carbon atom of the two thiocarbonyl groups;

R^4 and R^5 , independently, are the same or different, are optionally substituted as defined for R^1 and R^2 , and are selected from a linear or branched alkyl having from 1 to 12 carbon atoms, aryl having from 6 to 18 carbon atoms, R^4 and R^5 can form a substituted or unsubstituted cyclic ring having from 3 to 12 carbon atoms, wherein said substituents, independently, are selected from an alkyl having from 1 to 6 carbon atoms, aryl, halogen, cyano, an ether having a total of from 2 to 20 carbon atoms, a nitro group, and combinations thereof; wherein R^6 and R^7 , independently, are the same or different, optionally substituted as defined for R^1 and R^2 , and are selected from hydrogen, a linear or branched alkyl having from 1 to 18 carbon atoms, aryl, aryl alkyl having from 6 to 18 carbon atoms, optionally saturated or unsaturated, arylalkyl having from 7 to 18 carbons, alkenealkyl having from 3 to 18 carbon atoms, polyalkylene glycol ether having from 3 to 200 carbon atoms, and amine, or R^6 and R^7 can form a cyclic ring with the nitrogen atom having a total of 4 to 12 carbon atoms; or formula IV



wherein

R^4 and R^5 are as defined above;

R^{13} is optionally substituted, and is selected from linear or branched alkyl having from 1 to 12 carbon atoms, aryl optionally saturated or unsaturated, arylalkyl having from 7 to 18 carbon atoms, acyl, alkene, alkenealkyl having from 3 to 18 carbon atoms, an alkylene group, an alkoxyalkyl, polyalkylene glycol, polyalkylene glycol monoalkyl ether having from 3 to 200 carbon atoms, and 2-trifluoroethyl; wherein when R^{13} is optionally substituted the substituent is selected from alkyl having from 1 to 6 carbon atoms, aryl, halogen, a cyano group, an amino group, an alkene group, an alkoxycarbonyl group, an aryloxycarbonyl group, a carboxy group, an acyloxy group, a carbamoyl group, an alkylcarbonyl group, an alkylarylcarbonyl group, an arylcarbonyl group, an arylalkylcarbonyl group, a phthalimido group, a maleimido group, a succinimido group, amidino group, guanidino group, allyl group, epoxy group, alkoxy group, an alkali metal salt, a cationic substituent, a hydroxyl group, an ether having a total of from 2 to 20 carbon atoms, nitro, sulfur, phosphorous, a carboalkoxy group, and combinations thereof; and

"a" is 1 to 4.

[0010] In an embodiment, the water soluble CTA-acid in the form of a water soluble CTA-acid salt can exclude the CTA-acid portion represented by formula II.

[0011] In embodiment of the compound, the water soluble CTA-acid can be in the form of a water soluble CTA-acid salt, and the CTA-acid portion can comprise, consists of, or consist essentially of 2-methyl-2-[(dodecylsulfanylthiocarbonyl)sulfanyl]propionic acid. In another embodiment, the water soluble CTA-acid salt can exclude 2-methyl-2-[(dodecylsulfanylthiocarbonyl)sulfanyl]propionic acid.

[0012] In embodiments, the salts of the compounds can be derived from alkali or alkali earth metal hydroxides; alkali earth carbonates; mono-, di-, and/or tri-alkyl-substituted amines; and combinations thereof.

[0013] Another aspect of the disclosed technology includes a polymer comprising, consisting of, or consisting essentially of (A) at least one water soluble CTA-acid or CTA-acid salt as described herein, or combinations thereof, and (B) monomer units derived from at least one water soluble monomer. In an embodiment, the polymer can also optionally include (C) monomer units derived from at least one water insoluble vinyl monomer. In an embodiment of the polymer, the water soluble CTA-acid can include a water soluble CTA-acid salt having a CTA-acid portion represented by formula II, and in a particular embodiment, the CTA-acid salt can be the sodium salt of 2-methyl-2-[(dodecylsulfanylthiocarbonyl)sulfanyl]propionic acid.

[0014] In an embodiment, the water soluble monomers can comprise, consist of, or consist essentially of AMPS[®], acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, citraconic acid, mesaconic acid, (alkyl) acrylamide, and derivatives or salts thereof, or any combination thereof. Water insoluble monomers can comprise, consist of, or consist essentially of any polymerizable monomer that includes an alkyl group containing 1-18 carbon atoms consisting of a simple ester, a vinyl ester, a mono-allyl ether, styrene, derivatives thereof, or any combination thereof.

[0015] In an embodiment, the polymer can comprise, consist of, or consist essentially of about 0.1 to about 50 weight percent units derived from (A) and from about 50 to about 99.9 percent by weight of the combination of (B) and optional (C).

[0016] A further aspect of the disclosed technology includes a process of producing a water soluble polymer. The process can comprise, consist of, or consist essentially of the steps of 1) combining in an aqueous solution a water soluble ethylenically substituted monomer, a CTA-Acid or CTA-acid salt as described herein, or combinations thereof, and a free radical initiator, and 2) free radically polymerizing the water soluble monomers or allowing the water soluble monomers to free radically polymerize. In an embodiment, the process can include producing a macro-CTA-Acid or macro-CTA-Acid salt, and the process can further include adding a water-insoluble monomer to form an oil-in-water emulsion, and further free radically polymerizing the water-insoluble monomer with the macro-CTA-Acid or macro-CTA-Acid salt. In an embodiment of the process, the water soluble CTA-acid can include a water soluble CTA-acid salt having a CTA-acid portion represented by formula II, and in a particular embodiment, the CTA-acid salt can be the sodium salt of 2-methyl-2-[(dodecylsulfanylthiocarbonyl)sulfanyl]propionic acid.

[0017] Another aspect of the disclosed technology contemplates the use of a CTA-Acid, CTA-acid salt or mixture thereof as a chain transfer agent. In an embodiment, the water soluble CTA-acid can be used as a chain transfer agent in the form of a water soluble CTA-acid salt having a CTA-acid portion represented by formula II, and in a particular embodiment, the CTA-acid salt can be the sodium salt of 2-methyl-2-[(dodecylsulfanylthiocarbonyl)sulfanyl]propionic acid.

[0018] These and other aspects will be described below by way of non-limiting illustration.

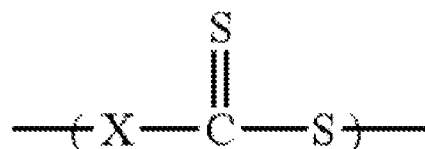
DETAILED DESCRIPTION OF THE INVENTION

[0019] An aspect of the present technology is directed to a compound comprising, consisting essentially of, or consisting of a water soluble chain transfer agent, also referred to herein as a water soluble CTA-acid. In some embodiments, the CTA-acid is inherently water soluble and in other embodiments, the CTA-acid is prepared into a water soluble salt, also referred to as a CTA-acid salt. As used herein, the term water soluble CTA-acid, or even simply CTA-acid, includes water soluble CTA-acid salts.

[0020] As used herein, water soluble means sufficiently miscible to form a 5 wt% solution.

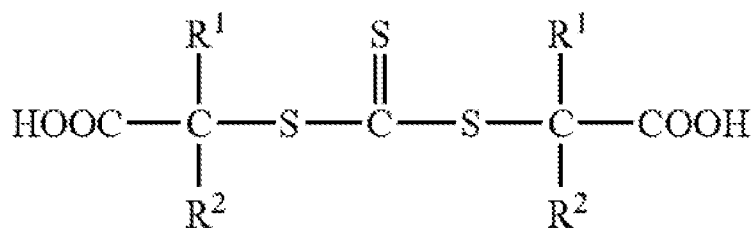
CTA-Acids

[0021] Many CTA-acids are known. There are, for example, the thiocarbonates, for example, polythiocarbonates such as dithiocarbonate or trithiocarbonate compounds and derivatives thereof. By the term "thiocarbonate", it is meant a compound
 5 having at least one segment having the formula:



wherein X comprises OR (also referred to herein as "xanthates"), SR (also referred to herein as "carbonates"), or NR₂ (also referred to herein as "carbamates"), for example with R being various hydrocarbon, heteroatom and/or hydrogen containing
 10 structures or the like preferably as illustrated hereinbelow, but not limited thereto.

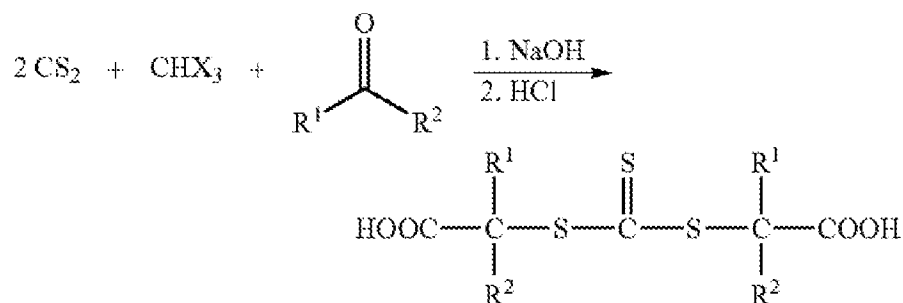
[0022] Suitable trithiocarbonate compounds for use in the present invention, include, but are not limited to, those disclosed in U.S. Pat. No. 6,596,899 to Lai, herein fully incorporated by reference. In one embodiment, di-acid trithiocarbonate compounds have the following general formula:
 15



wherein, in one embodiment, R¹ and R², independently, are the same or different, and
 20 are hydrogen ("H"), or linear or branched alkyls having from 1 to about 6 carbon atoms, or from 1 to 4 carbon atoms, or a C₁ to about C₆ alkyl having one or more substituents, or one or more aryls or a substituted aryl group having 1 to 6 substituents on the aryl ring, where the one or more substituents, independently, comprise an alkyl having from 1 to 6 carbon atoms; or an aryl; or a halogen such as fluorine or chlorine;
 25 or a cyano group; or an ether having a total of from 2 to about 20 carbon atoms such as methoxy, or hexanoxy; or a nitro; or combinations thereof. Examples of such

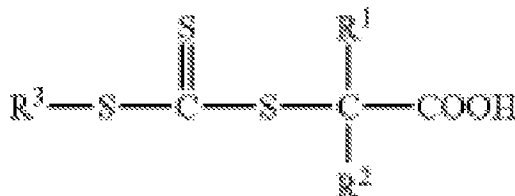
compounds include s,s'-bis-2-methyl-2-propanoic acid-trithiocarbonate and s,s'-bis-(2-phenyl-2-propanoic acid)-trithiocarbonate. R¹ and R² can also form or be a part of a cyclic ring having from 5 to about 12 total carbon atoms. R¹ and R² are preferably, independently, methyl or phenyl groups. As will be the case for all CTA-acids disclosed herein, the compound represented by the formula will be water-soluble, or at least partially water-soluble depending on the number of carbon atoms in the substituents, and in the case of the formula above specifically, R¹ and R². In a water-soluble embodiment, of the above di-acid thiocarbonate, the sum of the number of carbon atoms present for all R¹ and R² together can be less than 4, or less than 3, with any remainder substituents being H. In such a case, R¹ and R² are preferably, independently, methyl or H groups.

[0023] The abbreviated reaction formula for one method for the preparation of s,s'-bis-(α, α'-disubstituted-α''-acetic acid)-trithiocarbonates is generally written as follows:



[0024] The process utilized to form s,s'-bis-(α, α'-disubstituted-α''-acetic acid)-trithiocarbonate compounds is generally a multi-step process and includes combining the carbon disulfide and a base whereby an intermediate trithio structure is formed. A ketone can serve as solvent for the carbon disulfide/base reaction and thus can be added in the first step of the reaction. In the second step of the reaction, the haloform, or haloform and ketone, or an α-trihalomethyl-α-alkanol are added to the trithio intermediate mixture and reacted in the presence of additional base. The formed reaction product, is subsequently acidified, thus completing the reaction and forming the above described s,s'-bis-(α,α'-disubstituted-α''-acetic acid)-trithiocarbonate compound.

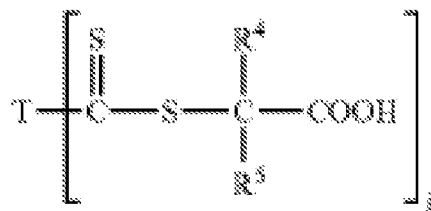
[0025] Another aspect of present invention utilizes mono-acid trithiocarbonate compounds having the following formula:



5

wherein R^3 comprises H, a benzyl group, $\text{C}_1 - \text{C}_{18}$ or $\text{C}_1 - \text{C}_4$ alkyl, or substituted alkyl such as halogen, hydroxyl, or alkoxy, $\text{C}_1 - \text{C}_{18}$ hydroxyalkyl, aralkyl, hydroxyalkyl, cyanoalkyl, aminoalkyl, carboxylalkyl, carboalkoxyalkyl or mercaptoalkyl, and R^1 and R^2 are defined hereinabove. The resulting compound is an s-substituted- s'-(α, α' -disubstituted- α'' -acetic acid)-trithiocarbonate, such as, for example, 2-methyl-2-[(dodecyl-
10 sulfanylthiocarbonyl)sulfanyl]propionic acid. Here again, the compound will be water-soluble, or at least partially water-soluble depending on the number of carbon atoms in the substituents, in this case R^1 , R^2 and R^3 . In an embodiment, of the mono-acid thiocarbonate, the sum of the number of carbon atoms present for all R^1 , R^2 and R^3 together can be less
15 than 4, or less than 3, with any remainder being H. In a water-soluble embodiment, R^1 , R^2 and R^3 are preferably, independently, methyl or H groups.

[0026] Dithiocarbonate compounds which are utilized in some embodiments of the present invention are disclosed in U.S. application Ser. No. 10/278,335 filed Oct. 23, 2002 and U.S. application Ser. No. 10/681,679 filed Oct. 8, 2003, herein fully
20 incorporated by reference. In one embodiment the dithiocarbamate compounds have the following formula:



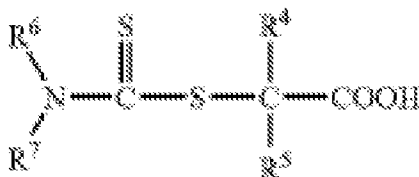
wherein j is 1 or 2, with the proviso that when j is 1, T is $\text{—}(\text{NR}^6\text{R}^7)$; and when j is 2, T is a divalent radical having a nitrogen atom directly connected to each carbon atom of the two thiocarbonyl groups present;

wherein R^4 and R^5 , independently, are the same or different, are H or optionally substituted, and are linear or branched alkyls having from 1 to about 4 carbon atoms, or 1 to about 6 or about 12 carbon atoms; or an aryl group having from 6 to about 18 carbon atoms, optionally containing heteroatoms;

wherein the R^4 and/or R^5 substituents, independently, comprise an alkyl having from 1 to 4 or 6 carbon atoms; an aryl group; a halogen; a cyano group; an ether having a total of from 2 to about 20 carbon atoms; a nitro; or combinations thereof. R^4 and R^5 can also form or be a part of a substituted or unsubstituted cyclic ring having from 3 to about 12 total carbon atoms wherein the substituents are described above. R^4 and R^5 , in an embodiment, are, independently, methyl, H, or phenyl groups;

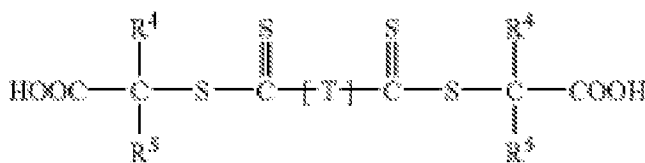
wherein R^6 and R^7 , independently, are the same or different, optionally are substituted, optionally contains heteroatoms; and are H; a linear or branched alkyl having from 1 to 4 carbon atoms, or from 1 to about 18 carbon atoms, an aryl group having from about 6 to about 18 carbon atoms optionally saturated or unsaturated; an arylalkyl having from about 7 to about 18 carbon atoms; an alkenealkyl having from 3 to about 18 carbon atoms; or derived from a polyalkylene glycol ether having from 3 to about 200 carbon atoms. R^6 and R^7 can also be derived from amines such as, but not limited to, piperazine, morpholine, pyrrolidine, piperidine, 4-alkylamino-2,2,6,6-tetramethyl piperidine, 1-alkylaminoalkyl-3,3,5,5-tetramethyl-2 piperazinone, hexamethyleneimine, phenothiazine, iminodibenzyl, phenoxazine, N,N'-diphenyl-1,4-phenylenediamine, dicyclohexylamine and derivatives thereof. R^6 and R^7 can also form a substituted or unsubstituted cyclic ring, optionally containing heteroatoms, along with the nitrogen having a total of from 4 to about 12 carbon atoms, such as benzotriazole, tolyltriazole, imidazole, 2-oxazolidone, 4,4-dimethyloxazolidone and the like. The R^6 and R^7 substituents, independently, can be the same as described herein with respect to R^{13} . R^6 and R^7 can be, in an embodiment, independently, a phenyl group or an alkyl or substituted alkyl having from 1 to about 18 carbon atoms such as a methyl group, or R^6 and R^7 , independently, can be hexamethylene. In an embodiment, R^4 , R^5 , R^6 and R^7 are, independently, methyl or H groups.

[0027] When j is 1, T of the above formula is $-(NR^6R^7)-$ and the dithiocarbamate compound is an S -(α,α' -disubstituted- α'' -acetic acid) dithiocarbamate generally having the following formula:



5 wherein R^4 , R^5 , R^6 , and R^7 are as defined hereinabove.

[0028] When j is 2, the dithiocarbamate compound is a bis- S -(α,α' -disubstituted- α'' -acetic acid) dithiocarbamate having the following formula:

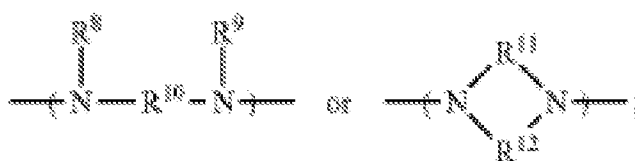


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wherein R^4 and R^5 are defined hereinabove; and

wherein T is a divalent bridging radical having a nitrogen atom directly connected to each of the thiocarbonyl groups present.

[0029] In one embodiment T is:



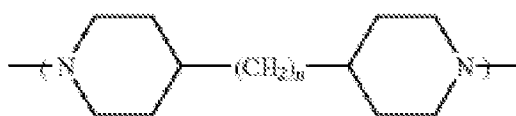
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wherein R^8 and R^9 , independently, is the same or different, is optionally substituted, and is H, a linear or branched alkyl having from 1 to 4 carbon atoms, or 1 to about 18 carbon atoms, an aryl group having from about 6 to about 18 carbon atoms, an arylalkyl having from 7 to about 18 carbon atoms, or an alkenealkyl having from 3 to about 18 carbon atoms, wherein the substituents can be the same as described herein for R^1 and R^2 ;
 20 wherein R^{10} is optionally substituted, and is non-existent, or an alkylene group having from 1 to about 18 carbon atoms with about 1 to about 4 or 6 carbon atoms preferred, or derived from a polyalkylene glycol ether having from 3 to about 200 carbon atoms, wherein the

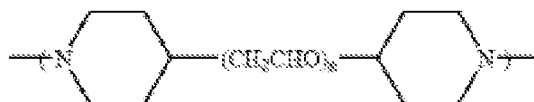
substituents can be the same as described herein for R^1 and R^2 or are heteroatoms such as oxygen, nitrogen, sulfur or phosphorous; and

wherein R^{11} and R^{12} independently, is the same or different, and is optionally substituted as described for R^1 and R^2 , and is an alkylene group having from 1 to about 4 carbon atoms, with R^{11} and R^{12} preferably having a collective total of 2 or 3 to 5 carbon atoms.

[0030] In further embodiments, T is:

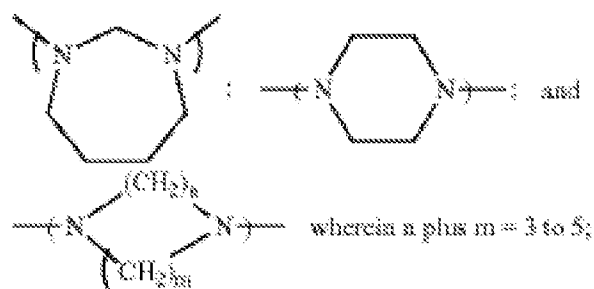


wherein n is 0 to about 18, with 0 or 1 to about 6 preferred;



wherein n is 0 to about 18, with 0 to about 6 preferred;

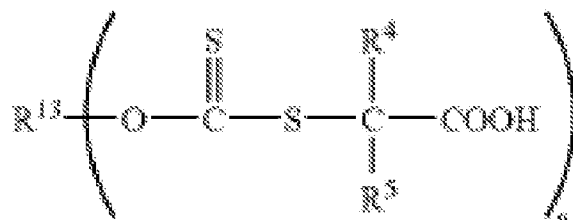
[0031] Some specific non-limiting examples of T bridging radicals are:



[0032] The S-(α, α' -disubstituted- α'' -acetic acid) or bis-S-(α, α' -disubstituted- α'' -acetic acid) dithiocarbamates are generally a reaction product of a metal salt of a dithiocarbamate, a haloform, and a ketone. A phase transfer catalyst, solvent, and a base such as sodium hydroxide or potassium hydroxide can also be utilized to form the S-(α, α' -disubstituted- α'' -acetic acid) or bis S-(α, α' -disubstituted- α'' -acetic acid) dithiocarbamates.

[0033] It is to be understood throughout the application formulas, reaction schemes, mechanisms, etc., and the specification that metals such as sodium or bases such as sodium hydroxide are referred to and the application of the present invention is not meant to be solely limited thereto. Other metals or bases such as, but not limited to, potassium and potassium hydroxide, respectively, or combinations thereof are contemplated by the disclosure of the present invention.

[0034] Alkoxy dithiocarbonate compounds are utilized in some embodiments of the present invention and having the following general formula, which may be referred to herein as a xanthate,



wherein R^4 and R^5 are as defined hereinabove;

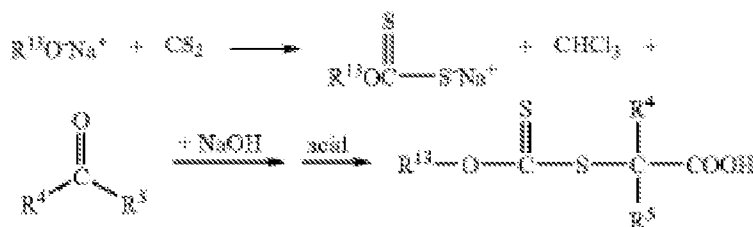
wherein R^{13} is optionally substituted, and can be a linear or branched alkyl having from 1 to 4 carbon atoms, or 1 to about 12 carbon atoms; an aryl group, optionally saturated or unsaturated; an arylalkyl having from 7 to about 18 carbon atoms; an acyl group; an alkenealkyl having from 3 to about 18 carbon atoms; an alkene group; an alkylene group; an alkoxyalkyl; derived from a polyalkylene glycol; derived from a polyalkylene glycol monoalkyl ether having from 3 to 200 carbon atoms; derived from a polyalkylene glycol monoaryl ether having from 3 to 200 carbon atoms; a polyfluoroalkyl such as 2-trifluoroethyl; a phosphorous containing alkyl; or a substituted or unsubstituted aryl ring containing heteroatoms. Alkyl and alkylene groups from 1 to 4 or 6 carbon atoms are preferred;

wherein the R^{13} substituents comprise an alkyl having from 1 to 4 or 6 carbon atoms; an aryl; a halogen such as fluorine or chlorine; a cyano group; an amino group; an alkene group; an alkoxy carbonyl group; an aryloxy carbonyl group; a carboxy group; an acyloxy group; a carbamoyl group; an alkyl carbonyl group; an alkylaryl carbonyl group; an aryl carbonyl group; an arylalkyl carbonyl group; a phthalimido

group; a maleimido group; a succinimido group; amidino group; guanidimo group; allyl group; epoxy group; alkoxy group; an alkali metal salt; a cationic substituent such as a quaternary ammonium salt; a hydroxyl group; an ether having a total of from 2 to about 20 carbon atoms such as methoxy, or hexanoxo; a nitro; sulfur; phosphorous; a carboalkoxy group; a heterocyclic group containing one or more sulfur, oxygen or nitrogen atoms, or combinations thereof; and wherein "a" is 1 to about 4, with 1 or 2 preferred.

[0035] The compounds of the above formula are generally identified as O-alkyl-S-(α, α' -disubstituted- α'' -acetic acid) xanthates. The O-alkyl-S-(α, α' -disubstituted- α'' -acetic acid) xanthates are generated as the reaction product of an alkoxylate salt, carbon disulfide, a haloform, and a ketone. Alternatively, a metal salt of xanthate can be utilized in place of the alkoxylate salt and carbon disulfide.

[0036] The general reaction mechanism for forming the O-alkyl-S-(α, α' -disubstituted- α'' -acetic acid) xanthates is as follows:



wherein R^4 , R^5 , and R^{13} are defined herein.

Salts

[0037] The foregoing CTA-acids can be salted, either to impart water-solubility or for ease of use. The salts of the CTA-acid are not particularly limited. Salts can include, for example, alkali or alkali earth metal hydroxides; alkali earth carbonates; mono-, di-, and/or tri- alkyl-substituted amines; and combinations thereof.

[0038] In an embodiment, the alkali metal hydroxides can include, but not be limited to, for example, lithium hydroxide, sodium hydroxide, potassium hydroxide. In some preferred embodiments the alkali metal hydroxide salt can comprise, consist essentially of, or consist of sodium hydroxide. In an embodiment, the alkali metal hydroxide can exclude sodium hydroxide, and the resultant polymer can exclude sodium salts.

[0039] In an embodiment, the alkali earth metal hydroxides can include, but not be limited to, for example, magnesium hydroxide or calcium hydroxide. Similarly, alkali earth carbonates can include, but not be limited to, for example, magnesium carbonate or calcium carbonate.

5 [0040] Mono, di, and/or tri alkyl substituted amines can include those having an alkyl substitute having from 1 to 12 carbon atoms, or 1 to 8 carbon atoms, or even from 1 to 4 or 6 carbon atoms. The amine can also be an alkanol amine in which the alkyl substituent includes at least one OH group. Particular alkyl amines can comprise, consist essentially of, or consist of any one or more of triethanolamine ("TEA"), ethanolamine, 2-(dimethylamino)ethanol, diethylamine, 2-(2-aminoethoxy)ethanol, 3-amino-1-propanol, N-(2-hydroxyethyl)ethylenediamine.

Polymer

[0041] A water soluble form of the CTA-acid or a water soluble CTA-acid in its salt form (i.e., a CTA-acid salt) can be employed to prepare a polymer in an aqueous medium.

15 [0042] The term aqueous medium, or aqueous solution, and the like, means a medium containing a majority of water, optionally along with other water miscible solvents, such as, for example, alcohols and the like. Preferred water miscible solvents include ethyl alcohol, isopropyl alcohol, t-butyl alcohol. Other solvents that may be partially water miscible can include, for example, ethyl acetate, methyl acetate, butyl acetate, benzene, toluene, methyl ethyl ketone, and methylene chloride. These solvents also can be used in combination with minor amounts, such as less than 10 volume%, of hydrocarbon solvents such as hexane, cyclohexane, mineral spirits, and the like. A preferred water miscible solvent is isopropyl alcohol. In an embodiment, the aqueous medium consists of water.

25 [0043] Such a polymer would comprise, consist essentially of, or consist of at least one CTA-acid or CTA-acid salt (as the end-cap of the polymer chain), monomer units derived from at least one water soluble monomer, and optionally, monomer units derived from at least one water insoluble vinyl monomer. In an embodiment, the CTA-acid polymer can be made up of about 0.1 to about 49.9 or 50 weight percent, or 0.1 to about 10 or 25 weight percent units derived from a CTA-acid, CTA-acid salt, or combination thereof, but generally from about 0.5 to about 5 weight percent, such as about 1

to about 3 weight percent units derived from a CTA-acid, CTA-acid salt, or combination thereof; and from about 50 to about 99.8 or 99.9 weight percent, or about 75 or even about 90 or 95 to about 99.8 or 99.9 weight percent, or 97 to 99 weight percent of the combination of a water soluble monomer and optional water insoluble vinyl monomer. In an embodiment, the CTA-acid polymer can have about 0.1 to about 49.9 or 50 weight percent, or 0.1 to about 10 or 25 weight percent units derived from a CTA-acid, CTA-acid salt, or combination thereof; from about 50 to about 99.9 percent by weight, or 75 or 90 to about 99.8 or 99.9 weight percent units derived from water soluble monomer, and optionally 0.1 to about 49.9 or 50 weight percent, or from about 0.5 to about 24.9 weight percent, or from about 1 to about 9.9 weight percent units derived from polymerizable water insoluble vinyl monomers.

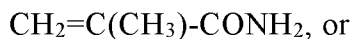
Water Soluble Monomers

[0044] Water soluble monomers that can be included in the polymer are not particularly limited and can comprise, consist essentially of, or consist of any water soluble ethylenically substituted monomer, such as, for example, 2-acrylamido-2-methylpropane sulfonic acid ("AMPSTM"), carboxylic acid monomers, (C₁ - C₁₂ alkyl) acrylamide, and derivatives or salts thereof, or any combination thereof.

[0045] Water soluble carboxylic acid monomers can include, for example, ethylenically unsaturated polymerizable carboxylic acid monomers. Suitable examples include what are often referred to as carboxylic monomers or acrylate monomers.

[0046] Additional examples of suitable sulfonic acid monomers can include: Sipomer COPS®-I, commercially available from Rhodia, which is a 40% aqueous solution of sodium allyl ether sulfonate and sodium 1-allyloxy-2-hydroxypropyl sulfonate, having a molecular weight of about 218; vinyl benzene sulfonic acids, vinyl benzene sulfonates, alkyl vinyl benzene sulfonic acids, alkyl vinyl benzene sulfonates for example SPINOMAR® NaSS, commercially available from Tosoh, which is a sodium p-styrene sulfonate having a molecular weight of about 206; 2-sulfoethylmethacrylate; alkylvinyl sulfonic acids, alkyl vinyl sulfonates for example sodium vinyl sulfonate (SVS); sodium allylsulfonate (SAS); sodium methally sulfonate (SMAS); dialkylaminoalkyl(meth)acrylate; alkyl or hydrogen halide salts of aminoalkyl(meth)acrylate; hydroxy alkyl(meth)acrylate; or any combination thereof.

[0047] In one embodiment, the unsaturated carboxylic monomers can have the following general formulae:



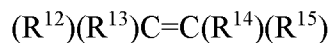
wherein X is H; a metal ion such as Li, Na, K, or Ca; an amino group such as an alkylamino or dialkylamino group having from 1 to about 6 carbon atoms or an alkyl/hydrogen halide salt thereof; or hydroxy alkyl group having from 1 to 6 carbon atoms.

[0048] Specific water-soluble monomers or co-monomers for use in the present technology include, but are not limited to, the following: acrylic acid, methacrylic acid, 2-hydroxyethyl methacrylate, hydroxypropyl methacrylate (all isomers), hydroxybutyl methacrylate (all isomers), N,N-dimethylaminoethyl methacrylate, N,N-diethylaminoethyl methacrylate, 2-dimethylaminoethyl acrylate and its alkyl/hydrogen halide salts, 2-dimethylaminoethyl methacrylate and its alkyl/hydrogen halide salts, 2-hydroxyethyl acrylate, hydroxypropyl acrylate (all isomers), hydroxybutyl acrylate (all isomers), polyethylene glycol monoacrylate, polyethylene glycol monomethacrylate, polypropylene glycol monoacrylate, polypropylene glycol monomethacrylate, N,N-diethylaminoethyl acrylate, maleic acid, fumaric acid, itaconic acid, crotonic acid, oleic acid, cinnamic acid, styrene sulfonic acid, and 2-acrylamido-2-methylpropane sulfonic acid (AMPS). Some preferred monomers are AMPSTM, acrylic acid, methacrylic acid, and acrylamide.

[0049] In some embodiments the water soluble monomers are essentially free of any acrylate monomers. In some embodiments the water soluble monomers are free of any acrylate monomers. In some embodiments the polymers described herein are essentially free of any acrylate monomers. In some embodiments the polymers described herein are free of any acrylate monomers.

[0050] In other embodiments the water soluble monomers can include acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, citraconic acid, mesaconic acid.

[0051] In some embodiments the water soluble monomers can include one or more compounds having the structural formula:



wherein: R^{12} is H or CH_3 ; R^{13} is H or COOH; R^{14} is H or COOH; and R^{15} is H, COOH or CH_2COOH ; provided that when R^{12} is H and R^{13} is COOH, R^{14} and R^{15} are different and are either H or COOH; when R^{12} and R^{13} are both H, R^{14} is COOH and R^{15} is CH_2COOH ; and when R^{12} is CH_3 , R^{13} is COOH and R^{14} and R^{15} are different and are either H or COOH. Suitable examples include maleic acid, itaconic acid, fumaric acid, citraconic acid and mesaconic acid, oleic acid, cinnamic acid or salts thereof. Unsaturated polymerizable monomers containing sulfonic acid or a salts thereof can also be included.

[0052] In some embodiments the water soluble monomers can include: (iii) one or more (C_1 - C_4 alkyl or dialkyl) amide monomers. In such embodiments the water soluble monomers may include one or more acrylamide monomers, which may also be described as ethylenically unsaturated amido functional monomers. Suitable examples include acrylamide, methyl acrylamide, methyl methacrylamide, N-alkylmethacrylamide, N,N-di-alkylmethacrylamide, N-alkylacrylamide, N,N-dialkylacrylamide, and any combination thereof.

[0053] In some embodiments the water soluble monomers can include N,N'-dimethylacrylamide, t-butylacrylamide, t-octylacrylamide, or a combination thereof.

Optional Other Monomers

[0054] In an embodiment other monomers, other than the water-soluble monomers described above, are optionally polymerized with the water soluble monomers during a polymerization reaction. Examples of monomers include, but are not limited to, polymerizable water insoluble vinyl monomers, such as any polymerizable monomer that includes an alkyl group containing 1-18 carbon atoms consisting of a simple ester, a vinyl ester, a mono-allyl ether, derivatives thereof, or any combination thereof. Some examples of other monomers include vinyl acetate; styrene; diene monomers having a total of from 4 to 12 carbon atoms with examples including, but not limited to, 1,3-butadiene, isoprene, 1,3-pentadiene, 2,3-dimethyl-1,3-butadiene, 2-methyl-1,3-pentadiene, 2,3-dimethyl-1,3-pentadiene, 2-phenyl-1,3-butadiene, and 4,5-diethyl-1,3-octadiene; α -methyl styrene; and C_1 - C_{12} alkyl styrenes with substitute groups either on the chain or on the ring or both.

Polymerization Process

[0055] A water soluble CTA-acid or a CTA-acid salt, can be employed to polymerize the above monomers in an aqueous medium by a living polymerization process as described hereinbelow to form a CTA-acid polymer.

[0056] A living polymerization is a chain polymerization which proceeds in the absence of termination and chain transfer. The following experimental criteria can be utilized to diagnose a living polymerization.

1. Polymerization proceeds until all monomer has been consumed. Further addition of monomer results in continued polymerization.

2. The number average molecular weight, M_n (or X_n , the number average degree of polymerization), is a linear function of conversion.

3. The number of polymer molecules (and active centres) is constant and independent of conversion.

4. The molecular weight can be controlled by the stoichiometry of the reaction.

5. Narrow molecular weight distribution polymers are produced.

6. Chain-end functionalized polymers can be prepared in quantitative yields.

[0057] Besides those mentioned above, other criteria can also help to determine the living character of polymerization. For radical living polymerization, one is the ability of the polymer isolated from the first step of polymerization to be used as a macroinitiator for the second step of a polymerization in which block copolymers or grafted polymers are ultimately formed. To confirm the formation of block copolymers, measurements of molecular weights and a determination of the structure of the blocks are employed. For structure measurements, the examination of NMR or IR signals for the segments where individual blocks are linked together and a determination of the end groups are both very important. In radical polymerization, only some of the criteria for living polymerizations are actually fulfilled. Due to their ability to undergo further polymerization, these types of polymers can also be called 'reactive polymers'. A more detailed description of living polymerization can be found in "Living Free-Radical Block Copolymerization Using Thio-Inifertors", by Anton Sebenik, Progress in Polymer Science, vol. 23, p. 876, 1998.

[0058] The living polymerization processes can be used to produce polymers of narrow molecular weight distribution containing one or more monomers sequences whose length and composition are controlled by the stoichiometry of the reaction and degree of conversion. Homopolymers, random copolymers or block polymers can be produced with a high degree of control and with low polydispersity. Low polydispersity polymers are those with polydispersities that are significantly less than those produced by conventional free radical polymerization. In conventional free radical polymerization, polydispersities (polydispersity is defined as the ratio of the weight average to the number average molecular weight M_w/M_n) of the polymers formed are typically greater than 2.0. Polydispersities obtained by utilizing water soluble CTA-acid or CTA-acid salt compounds and derivatives thereof as described herein can be 1.75 or 1.5, or less, often 1.3 or less, and, with appropriate choice of the chain transfer agent and the reaction conditions, can be 1.25 or less.

[0059] When the water soluble CTA-acids and CTA-acid salts are utilized only as chain-transfer agents, the polymerization can be initiated with other initiators at lower temperature while yielding polymers with similarly controlled fashion.

[0060] Free radical polymerizations utilizing the water soluble CTA-acids and CTA-acid salts as both initiators and chain transfer agents generally form telechelic polymers. When an initiator other than the water soluble CTA-acids and CTA-acid salts is also utilized, a polymer having a single functional end group is formed in proportion to the amount of said other initiator to the water soluble CTA-acids or CTA-acid salts utilized.

[0061] The free radical living polymerization process can be applied to any monomers or monomer combinations which can be free-radically polymerized.

[0062] In order to initiate the polymerization process, it is often desirable to utilize an initiator as a source for initiating free radicals. Generally, the source of initiating radicals can be any suitable method of generating free radicals such as the thermally induced homolytic scission of a suitable compound(s) (thermal initiators such as peroxides, peroxyesters, or azo compounds), the spontaneous generation from monomer, redox initiating systems, photochemical initiating systems or high energy radiation such as electron beam, X- or gamma-radiation. The initiating system is chosen such that under the reaction conditions there is no substantial adverse interaction

of the initiator or the initiating radicals with the transfer agent under the conditions of the experiment. The initiator should also have the requisite solubility in the reaction medium or monomer mixture.

[0063] Thermal initiators are chosen to have an appropriate half-life at the temperature of polymerization. The initiators can include one or more of the following compounds: 2,2'-azobis(isobutyronitrile)(AIBN), 2,2'-azobis(2-cyano-2-butane), dimethyl 2,2'-azobisdimethylisobutyrate, 4,4'-azobis(4-cyanopentanoic acid), 1,1'-azobis(cyclohexanecarbonitrile), 2-(t-butylazo)-2-cyanopropane, 2,2'-azobis[2-methyl-N-(1,1)-bis(hydroxymethyl)-2-hydroxyethyl]propionamide, 2,2'-azobis[2-methyl-N-hydroxyethyl]-propionamide, 2,2'-azobis(N,N'-dimethyleneisobutyramidine)dihydrochloride, 2,2'-azobis(2-amidinopropane)dihydrochloride, 2,2'-azobis(N,N'-dimethyleneisobutyramine), 2,2'-azobis(2-methyl-N-[1,1-bis(hydroxymethyl)-2-hydroxyethyl]propionamide), 2,2'-azobis(2-methyl N-[1,1-bis(hydroxymethyl)ethyl]propionamide), 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide], 2,2'-azobis(isobutyramide)dehydrate, 2,2'-azobis(2,2,4-trimethylpentane), 2,2'-azobis(2-methylpropane), t-butyl peroxyacetate, t-butylperoxy-2-ethylhexanoate, t-butyl peroxybenzoate, t-butyl peroxyoctoate, t-butylperoxyneodecanoate, t-butylperoxyisobutyrate, t-amyl peroxyphthalate, t-butyl peroxyphthalate, di-isopropyl peroxydicarbonate, dicyclohexyl peroxydicarbonate, dicumyl peroxide, dibenzoyl peroxide, dilauroylperoxide, potassium peroxydisulfate, ammonium peroxydisulfate, di-t-butyl hyponitrite, and dicumyl hyponitrite.

[0064] Photochemical initiator systems are chosen to have the requisite solubility in the reaction medium or monomer mixture and have an appropriate quantum yield for radical production under the conditions of the polymerization. Examples include benzoin derivatives, benzophenone, acyl phosphine oxides, and photo-redox systems production under the conditions of the polymerization. These initiating systems can include, but are not limited to, combinations of the following oxidants, potassium peroxydisulfate, hydrogen peroxide, t-butyl hydroperoxide and reductants, iron (+2), titanium (+3), potassium thiosulfite, and potassium bisulfite.

[0065] Other suitable initiating systems are known to those of ordinary skill in the art, and are described in recent texts. See, for example, Moad and Solomon "The Chemistry of Free Radical Polymerization", Pergamon, London. 1995. pp 53-95.

[0066] The preferred initiators of the present technology are 2,2'-azobis[2-methyl-N(2-hydroxyethyl)propionamide]. The amount of initiators utilized in the polymerization process can vary widely as generally from about 0.001 percent to about 99 percent, and desirably from about 0.01 percent to about 50 or 75 percent based on the total moles of CTA-acid or CTA-acid salt utilized. Preferably small amounts are utilized, such as from about 0.1 percent to about 5, 10, 15, 20, or 25 mole percent based on the total moles of CTA-acid or CTA-acid salt. In order to form polymers which are predominately telechelic, initiators other than the thiocarbonate compounds are utilized in lesser amounts, such as from about 0.001 percent to about 5 percent, desirably from about 0.01 percent to about 4.5 percent, and preferably from about 0.1 percent to about 3 percent based on the molar equivalent to the total moles of CTA-acid or CTA-acid salt utilized.

[0067] In order to form CTA-acid polymers having monomer repeat units therein, a predetermined amount of CTA-acid or CTA-acid salt, or combination thereof, can be added to a suitable reaction vessel along with a predetermined amount of monomer(s), optional solvent, and optionally initiator. The amount of CTA-acid or CTA-acid salt utilized depends on the desired molecular weight of the polymer to be formed and can be calculated as known to one of ordinary skill in the art. A formula for calculating the amount of CTA-acid or CTA-acid salt (CTA) is as follows:

$$\text{Mn of polymer} = \left(\frac{\text{Weight of monomer} \times \text{molecular weight of CTA}}{\text{Weight of CTA}} \right) + \text{molecular weight of CTA}$$

[0068] The resulting compound can be a macro-CTA-acid monomer, or a polymer or copolymer. The resulting compounds are either telechelic with identical functional groups at the ends of the chain, or a compound having a single functional end group and also an initiator terminated chain (formed by using a conventional initiator such as AIBN). As stated above, the ratios between the resulting polymers can be controlled to give desired results and generally depends on the amount of initiator utilized. The number of repeat groups from all sources, i.e., water soluble, optionally water insoluble and other monomers, or a combination thereof incorporated into each CTA-acid polymer is generally from about 1 to about 400, desirably from about 1 to about 200, and preferably from about 2 to about 80. Inasmuch as one or more water soluble monomers and optionally one or more water insoluble monomers or other

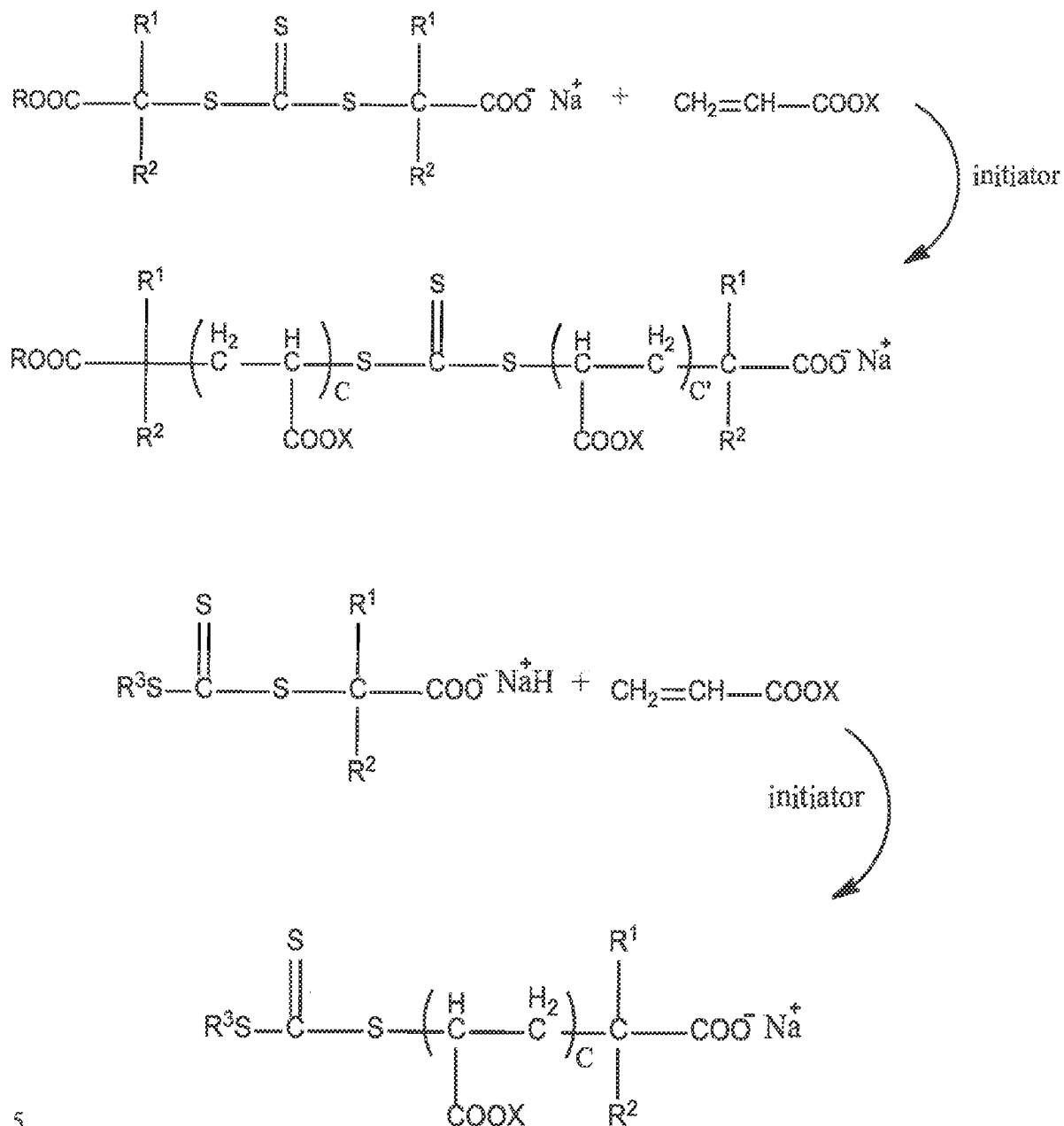
monomers which are generally neither hydrophilic or hydrophobic can be utilized, it is to be understood that repeat groups of the polymers or copolymers of the present technology can be the same or different, respectively. That is, random copolymers, terpolymers, etc., can be formed within either of the repeat groups noted, as well as
5 block copolymers which can be formed by initially adding one monomer and then subsequently adding a different monomer (e.g., an internal block copolymer).

[0069] The reaction conditions are chosen so that the temperature utilized will generate a radical in a controlled fashion, wherein the temperature is generally from about room temperature to about 200 °C. The reaction can be run at temperatures
10 lower than room temperature, but it is impractical to do so. The temperature often depends on the initiator chosen for the reaction, for example, when AIBN is utilized, the temperature generally is from about 40 °C. to about 80 °C., when azodicyanodivaleric acid is utilized, the temperature generally is from about 50 °C. to about 90 °C., when di-t-butylperoxide is utilized, the temperature generally is from about 110
15 °C. to about 160 °C., when a thiocarbonate is utilized, the temperature is generally from about 80 °C. to about 200 °C.

[0070] The polymerization process of this invention can be carried out in emulsion, solution or suspension, in either a batch, semi-batch, continuous, or feed mode. In the case of emulsion or suspension polymerization, the medium will often be pre-
20 dominately water and conventional stabilizers, dispersants and other additives can be present. For solution polymerization, the reaction medium can be chosen from a wide range of media to suit the monomer(s) being used.

[0071] Examples of polymerization mechanisms incorporating water soluble monomers into CTA-acid polymers are as follows:

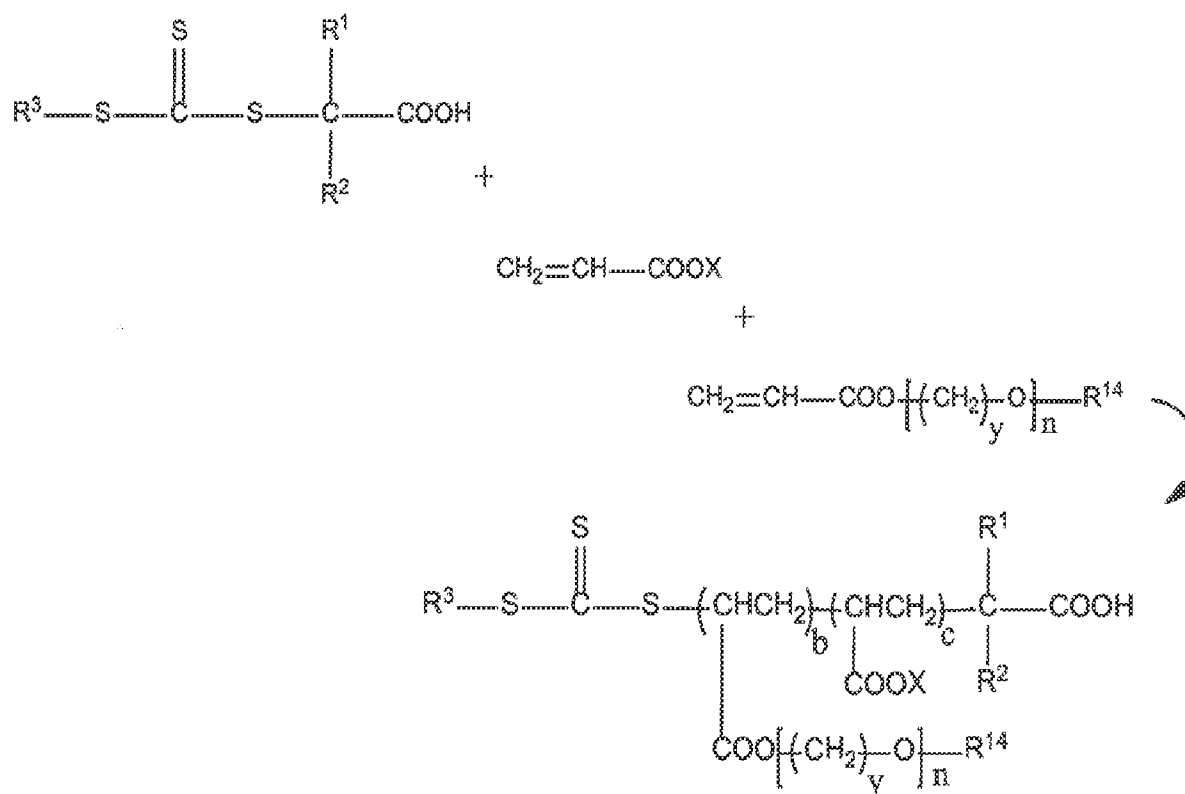
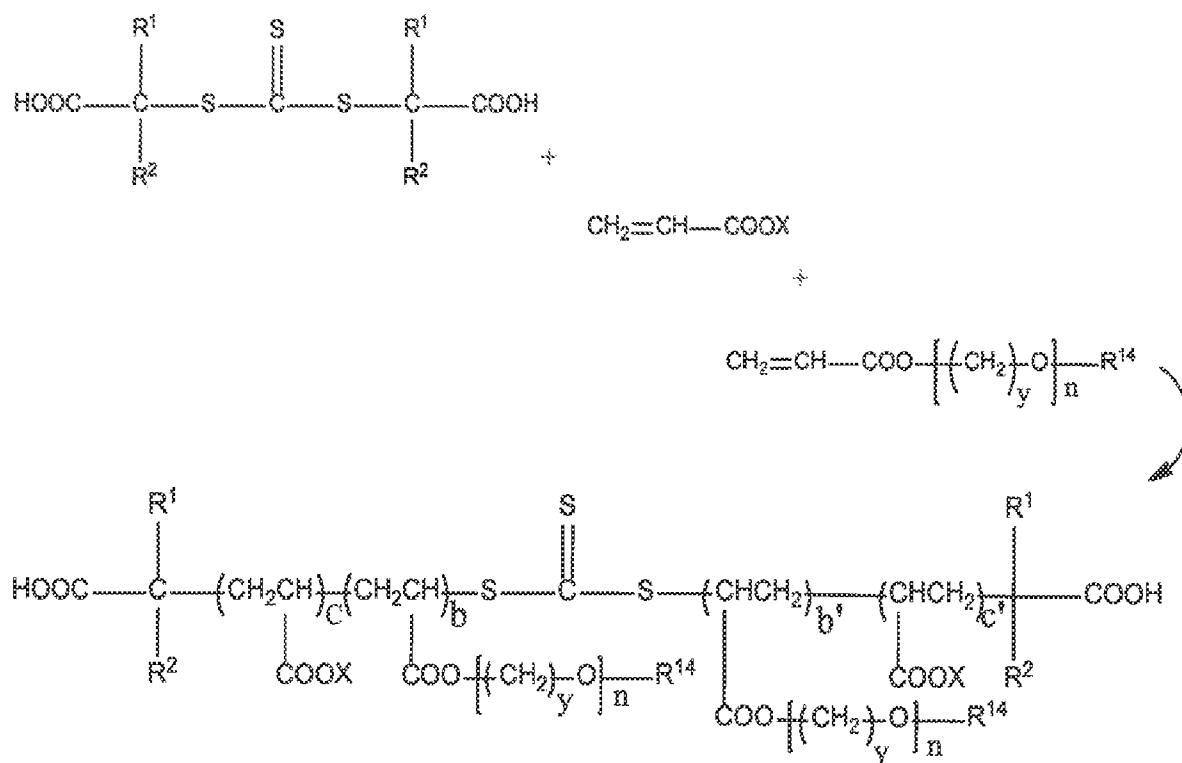
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wherein c and c' are each 1 to about 200, and R^1 , R^2 , and R^3 are defined herein.

[0072] Example reaction mechanisms for adding monomers having a hydrophobic group, as well as water soluble monomers to a CTA-acid polymer can include preparing a macro-CTA-acid monomer and adding the water insoluble monomer, as follows:



wherein b, b', c, c', n, R¹, R², R³, R¹⁴ and y are defined herein.

[0073] The process disclosed herein can be carried out in emulsion, solution or suspension in either a batch, semi-batch, continuous, or feed mode. Otherwise-conventional procedures can be used to produce narrow polydispersity polymers. For lowest polydispersity polymers, the chain transfer agent is added before polymerization is commenced. For example, when carried out in batch mode in solution, the reactor is typically charged with chain transfer agent and monomer or medium plus monomer. The desired amount of initiator is then added to the mixture and the mixture is heated for a time which is dictated by the desired conversion and molecular weight.

[0074] Polymers with broad, yet controlled, polydispersity or with multimodal molecular weight distribution can be produced by controlled addition of the CTA-acid or CTA-acid salt over the course of the polymerization process.

[0075] In the case of emulsion or suspension polymerization the medium will often be predominately water and the conventional stabilizers, dispersants and other additives can be present. For solution polymerization, the reaction medium can be chosen from a wide range of media to suit the monomer(s) being used.

[0076] As already stated, the use of feed polymerization conditions allows the use of chain transfer agents with lower transfer constants and allows the synthesis of block polymers that are not readily achieved using batch polymerization processes. If the polymerization is carried out as a feed system the reaction can be carried out as follows. The reactor is charged with the aqueous medium, the CTA-acid, CTA-acid salt or combination thereof, and optionally a portion of the monomer(s). The remaining monomer(s) is placed into a separate vessel. Initiator is dissolved or suspended in the reaction medium in another separate vessel. The medium in the reactor is heated and stirred while the monomer+aqueous medium and initiator+aqueous medium are introduced over time, for example by a syringe pump or other pumping device. The rate and duration of feed is determined largely by the quantity of solution the desired monomer/chain transfer agent/initiator ratio and the rate of the polymerization. When the feed is complete, heating can be continued for an additional period.

[0077] The water soluble CTA-acids can be employed to prepare polymers for potential applications in any formulation that might require a water soluble polymer

of defined molecular weight and shape such as for example, paints and coatings, personal and home care, energy exploration and refinery applications, including but not limited to, water treatment applications, drilling fluids, paraffin inhibiting applications, cementing applications, completion applications, and fuel transportation applications and for improving refinery and oilfield operational efficiencies.

[0078] In an embodiment, the water soluble CTA-acids can be employed to prepare improved polymers for use in a method of chelating ions of hardness (e.g., chelating or sequestering metal ions and the like) from a solution.

[0079] Typical household and I&I products that may contain polymers of the invention, include, without being limited thereto, fabric care products, such as laundry detergents (powder, liquid, gel, and unit doses) and fabric softeners (liquids or sheets), ironing sprays, dry cleaning aids, antiwrinkle sprays, stain and spot removers and the like; hard surface cleaners for the kitchen and bathroom and utilities and appliances employed or located therein, such as toilet bowl gels, tub and shower cleaners, hard water deposit removers, floor and tile cleaners, wall cleaners, floor and chrome fixture polishes, alkali-strippable vinyl floor cleaners, marble and ceramic cleaners, air freshener gels, liquid or powder cleaners for dishes (automatic and manual), and the like; disinfectant cleaners, such as toilet bowl and bidet cleaners, disinfectant hand soaps, room deodorizers, heavy duty hand soaps, cleaners and sanitizers, automotive cleaners and the like.

[0080] In an embodiment, the improved polymers or solutions thereof are employed in automatic dish detergents. Such dish detergents can be in different forms, such as, for example, liquid, powder, gels, tablets and unit dose pouches, bars, paste, hard or soft compressed monolayered tablet, hard or soft compressed multilayered tablet, single phase unidose detergent, multiphase unidose comprising, for example, any combination of powder, granulate, liquid and gel phases. In another embodiment, the improved polymers can be used in laundry detergents both in liquid, powder, gels, tablets and unit dose pouches, bars, paste, hard or soft compressed monolayered tablet, hard or soft compressed multilayered tablet, single phase unidose detergent, multiphase unidose comprising, for example, any combination of powder, granulate, liquid and gel phases.

[0081] Exemplary water treatment applications include, for example, water purification processes for potable & industrial uses, cooling water treatment, boiler water treatment, desalination (e.g., reverse osmosis, distillation), wastewater (e.g., municipal & industrial) treatment, and the like. In one preferred embodiment, the improved
5 polymers are used in water treatment applications as scale inhibitors and/or dispersants.

[0082] Exemplary deposit control applications, both scale and suspended solid dispersion, as applied to water treatment including fresh, saline, and process water, include, for example, cooling water treatment, boiler water treatment, thermal and reverse osmosis (RO) desalination, municipal and industrial wastewater, geothermal
10 exploration, oil and gas exploration and production, pulp and paper, sugar refining, as well as mining processes. Scale examples include calcium carbonate; calcium phosphates and phosphonates; calcium, barium, and strontium sulfates; magnesium hydroxide; calcium fluoride; calcium oxalates; silica; and silicates. In some cases, the improved polymers can be used as scale removing agents, rheology modifiers in
15 drilling operations as well as for slurry transport of solids suspended in water.

[0083] Exemplary personal care cleansers include but are not limited to shampoos (e.g., 2-in-1 shampoos, conditioning shampoos, bodifying shampoos; moisturizing shampoos, temporary hair color shampoos, 3-in-1 shampoos, anti-dandruff shampoos, hair color maintenance shampoos, acid (neutralizing) shampoos, salicylic acid
20 shampoos, medicated shampoos, baby shampoos, and the like), and skin and body cleansers (e.g., moisturizing body washes, antibacterial body washes; bath gels, shower gels, liquid hand soaps, bar soaps, body scrubs, bubble baths, facial scrubs, foot scrubs, and the like). Similarly, the improved polymer can be employed in pet and animal care applications. Exemplary pet and animal care cleansers include but
25 are not limited to shampoos, medicated shampoos, conditioning shampoos (e.g., detangling, antistatic, grooming), and foaming shampoos.

[0084] The amount of each chemical component described is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, that is, on an active chemical basis, unless otherwise indicated. However, unless
30 otherwise indicated, each chemical or composition referred to herein should be inter-

preted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade.

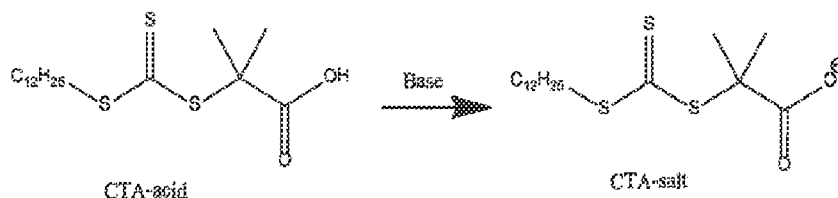
[0085] It is known that some of the materials described above may interact in the final formulation, so that the components of the final formulation may be different from those that are initially added. For instance, metal ions (of, e.g., a detergent) can migrate to other acidic or anionic sites of other molecules. The products formed thereby, including the products formed upon employing the composition of the present invention in its intended use, may not be susceptible of easy description. Nevertheless, all such modifications and reaction products are included within the scope of the present invention; the present invention encompasses the composition prepared by admixing the components described above.

[0086] The invention herein is useful for preparing RAFT polymers in an aqueous medium, which may be better understood with reference to the following examples.

[0087] EXAMPLES

[0088] Samples

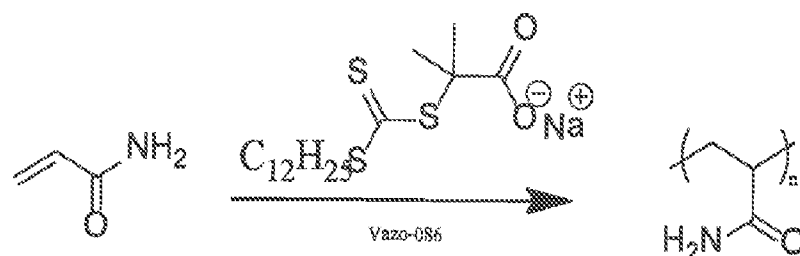
Formation of CTA-Acid Salt(s)



[0089] The following general laboratory procedure was used:

- 1.) 200g of water was added to a round bottom flask along with 9 drops of 50 wt.% NaOH in water.
- 2.) 1.94g of CTA-acid was added and the mixture gently warmed until dissolved.
- 3.) pH was adjusted to 7.5
- 4.) CTA-Na solution was poured into a 1L 3-necked flask along with 0.55g Vaso-086 initiator (a 2,2'-Azobis[2-methyl-N-(2-hydroxyethyl)propionamide] available from WAKO Chemicals)
- 5.) The solution of CTA-Na and initiator was heated to 90°C and 100 g of a 53 wt.% solution of acrylamide in water was added over 2 hours.
- 6.) The mixture thickened over time and after addition of all the monomer, solution was held at 90°C for an additional 2 hrs. before being air cooled to room temperature.

General Polymerization Illustration



- 5 [0090] A series of polymerizations was conducted using the general polymerization method listed above. In this series the amount of CTA-Na was varied to produce poly(acrylamide) polymers of different molecular weights to demonstrate the controllability of this process to produce defined and predictable molecular weight polymers. The data is shown below in Table 1.

10

Table 1: Polymerization of Acrylamide with varied CTA-Na

Sample	[CTA-Na] mol/L	[Initiator] mol/L	Conversion (%)	Residual ACM (ppm)	M_n^*	PDI
1	0.00647	0.00477	99.88	336	27,455	1.37
2	0.00938	0.00477	99.86	389	19,666	1.20
3	0.0125	0.00477	99.78	602	16,187	1.14

* M_n determined by GPC using poly(acrylamide) standards

- 15 [0091] The same general synthetic process as described above was used to polymerize AMPS-Na monomer as well. Again the CTA-Na amount was varied to demonstrate the controllability of this process to produce defined molecular weight polymers. Those results are shown below in Table 2.

Table 2: Polymerization of AMPS-Na with varied CTA-Na

Sample	[CTA-Na] mol/L	[Initiator] mol/L	Conversion (%)	M_n	PDI
4	0.00647	0.00477	99.99	13,555	1.24
5	0.00938	0.00477	99.99	11,979	1.21
6	0.0125	0.00477	100%	10,902	1.3

- 20 * M_n determined by GPC using poly(acrylamide) standards

[0092] Copolymers were produced using the above mentioned polymerization procedure with AMPS-Na (100 g) and acrylic acid (AA – 100g). Random copolymers of AMPS-Na and AA were made by dissolving sodium acrylate in a solution of AMPS-Na (50 wt.% in water). The sodium salt of acrylic acid was used in this case in order to keep the pH of the polymerization mixture above 7. If the pH dips below this value, the CTA will revert back to its acid form and precipitate out of solution leading to uncontrolled polymerization.

[0093] Block copolymers were also produced using AMPS-Na and AA. They were also synthesized according to the general polymerization process listed above by building a poly(AMPS-Na) block first, then adding acrylic acid to build a second block, producing poly(AMPS-b-acrylic acid). The results are shown below in Table 3.

Table 3: Copolymers of AMPS/Acrylic Acid

Sample	AMPS/AA (wt%)	M_n	PDI
7	30:70	22,784	1.54
8	60:40	30,544	1.64
9	50:50	19,829	1.44
10	30:70	36,316	1.64
11	20:80	37,087	1.62
12	20:80	22,962	1.50
13	60:40	19,028	1.47
14	50:50	31,464	1.65

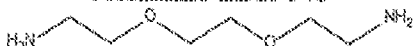
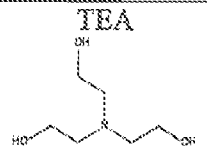
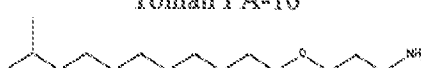

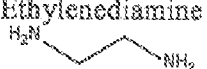
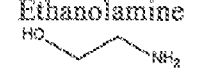

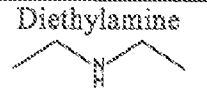
[0094] Star polymers were also produced by first forming a homopolymer of either AMPS or acrylamide using the above mentioned process, followed by a cross-linking reaction involving a difunctional monomer such as Bis-acrylamido-2-methylpropane sulfonic acid (BAMPS) or N,N-methylenebisacrylamide (NBAM). Those results are listed below in Table 4.

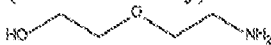


Table 4: Star Polymers of AMPS/Acrylamide

Sample	Cross-linker	Mono-mer	Linear M_n	Linear PDI	Star M_n
15	BAMPS	AMPS	15,346	1.35	209,165
16	NBAM	ACM	11,144	1.15	103,502

[0095] In addition to neutralizing CTA-acid with NaOH to generate the water-soluble chain transfer agent, various amines were used instead of NaOH. These new CTA-"bases" were made using the same procedure shown above ("Formation of CTA-Acid Salt(s)") starting with CTA-acid. The stability of several amines was tested by dispersing CTA-acid in water at 1 wt.% CTA-acid, and then dissolution by adding the amine. The resulting solutions were left at room temperature for 48 hrs. at which point the solubility was checked again. The results are shown below in Table 5.

10 Table 5: Amine Salts of CTA-Acid in Water

Salt Type	Soluble	Color
NaOH	yes	yellow
Ammonium (NH ₄)OH	yes	yellow
Jeffamine EDR 148 	no	NA
TEA 	yes	yellow
Tomah PA-16 	no	NA
1-(2-hydroxyethyl)-2-pyrrolidone 	no	NA
Ethylenediamine 	no	NA
Ethanolamine 	yes	orange
2-(Dimethylamino)ethanol 	yes	yellow
Diethylamine 	yes	yellow

2-(2-aminoethoxy)ethanol 	yes	yellow
3-amino-1-propanol 	yes	yellow
N-(2-hydroxyethyl)ethylenediamine 	yes	yellow

[0096] Two of the CTA-amine salts (CTA-TEA and CTA-diethylamine) were chosen to make poly(acrylamide) and poly(AMPS) based on the previously described general polymerization process. Those results are shown below in Table 6.

5

Table 6: Poly(acrylamide) and Poly(AMPS) Using Amine Salts of CTA-Acid

Sample	Monomer	Amine	M_n	FDI
17	AMPS-Na	TEA	14,408	1.28
18	AMPS-Na	Diethylamine	11,653	1.24
19	Acrylamide	TEA	14,285	1.19
20	Acrylamide	Diethylamine	16,037	1.16

Example 1

[0097] The calcium binding ability of the AMPS/AA block copolymers of samples 7 through 14 was tested against the comparative AMPS/AA random copolymers shown in table 7.

10

Sample	AMPS/AA (wt%)	M_w
Comp 1	25:75	<10,000
Comp 2	40:60	~20,000

[0098] Calcium binding was determined by preparing 100mL of a 1 wt% solution of the polymers in water, and adding the solutions to a burette. The polymer solution was then titrated against 100mL of a standard 0.01M CaCl_2 solution. A Ca selective electrode is used to measure the Ca ion signal present in solution (not bound to the polymer). Once the electrode measures 0.00 concentration, all of the Ca ions from the standard have been chelated to the polymer. From there, a calculation can then be performed to determine the amount of polymer needed to bind all of the Ca from the standard solution. The results of the calcium binding tests are shown in Table 8.

20

Table 8: Calcium Binding

Sample	Ca Binding, mg CaCl ₂ /g of polymer	mg Ca ²⁺ /g of polymer
Comp 1	303.6	110.6
Comp 2	310.2	113.0
7	688	250
8	453	165
9	520	189
10	691	252
11	736	268
12	786	286
13	505	184
14	490	179

[0099] The data in Table 8 shows that the sample polymers prepared with the water soluble CTA-acid bound more calcium than the random copolymers not prepared with the water soluble CTA-acid

[00100] Each of the documents referred to above is incorporated herein by reference, including any prior applications, whether or not specifically listed above, from which priority is claimed. The mention of any document is not an admission that such document qualifies as prior art or constitutes the general knowledge of the skilled person in any jurisdiction. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about." It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the invention can be used together with ranges or amounts for any of the other elements.

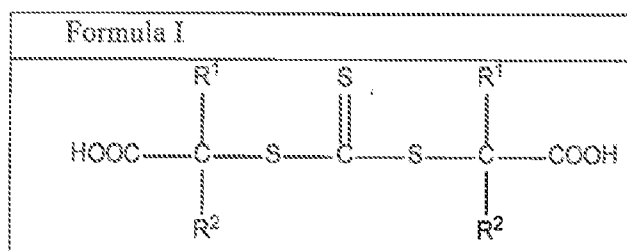
[00101] As used herein, the transitional term "comprising," which is synonymous with "including," "containing," or "characterized by," is inclusive or open-ended and does not exclude additional, un-recited elements or method steps. However, in each recitation of "comprising" herein, it is intended that the term also encompass, as alternative embodiments, the phrases "consisting essentially of" and "consisting of," where "consisting of" excludes any element or step not specified and "consisting essentially

of” permits the inclusion of additional un-recited elements or steps that do not materially affect the essential or basic and novel characteristics of the composition or method under consideration.

5 [00102] While certain representative embodiments and details have been shown for the purpose of illustrating the subject invention, it will be apparent to those skilled in this art that various changes and modifications can be made therein without departing from the scope of the subject invention. In this regard, the scope of the invention is to be limited only by the following claims.

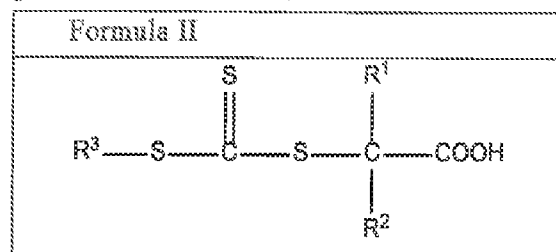
What is claimed is:

1. A compound comprising, consisting of, consisting essentially of a water soluble CTA-acid.
2. The compound of claim 1, wherein the water soluble CTA-acid is in the form of a water soluble CTA-acid salt.
3. The compound of claim 1 or 2, wherein the water soluble CTA-acid comprises, consists essentially of, or consists of a thiocarbonate compound having the formula I



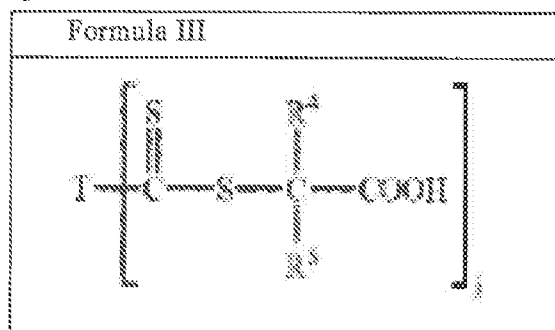
wherein

each of R^1 and R^2 is an alkyl group of four carbons or less or H, so long as the sum of the number of carbon atoms present for all R^1 , and R^2 in formula I together is less than four; or formula II



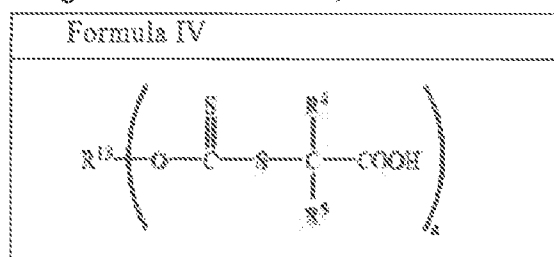
wherein

each of R^1 and R^2 is as defined above; and R^3 is an alkyl group of four carbons or less, or H, so long as the sum of the number of carbon atoms present for all R^1 , R^2 and R^3 in formula II together is less than four; or formula III



wherein

each of R^4 and/or R^5 substituents, independently, comprise an alkyl group having from 1 to 4 carbon atoms, or H;
 j is 1 or 2, with the proviso that when j is 1, T is $-\langle NR^6 R^7 \rangle$; and when j is 2, T is a divalent radical having a nitrogen atom directly connected to each carbon atom of the two thiocarbonyl groups present;
 R^6 and R^7 , independently, are the same or different, and are H or a linear or branched alkyl having from 1 to 4 carbon atoms;
 so long as the sum of the number of carbon atoms present for all R substituents in formula III together is less than four; or formula IV



wherein

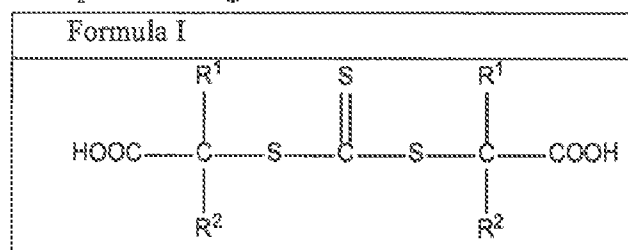
each of R^4 , and R^5 are as defined above

R^{13} is optionally substituted, and is a linear or branched alkyl having from 1 to 4 carbon atoms; and

a is 1 to 4;

so long as the sum of the number of carbon atoms present for all R substituents in formula IV together is less than four.

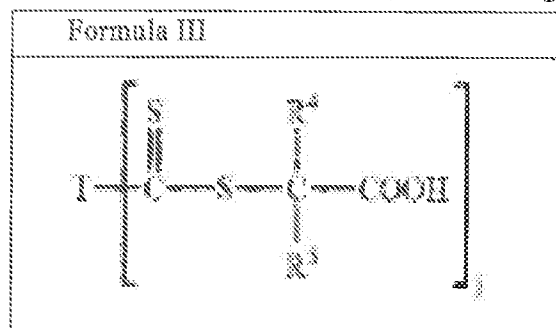
4. The compound of claim 1, 2, or 3 wherein the CTA-acid portion of the water soluble CTA-acid salt comprises, consists essentially of, or consists of a thio-carbonate compound having the formula I



wherein

R^1 and R^2 , independently, are selected from a linear or branched alkyl having from 1 to 6 carbon atoms, a substituted alkyl having from 1 to 6 carbon atoms, substituted and unsubstituted aryl, R^1 and R^2 can form a substituted or unsubstituted cyclic ring having from 5 to 12 total carbon atoms; wherein said substituents, independently, are selected from an alkyl having from 1 to 6 carbon

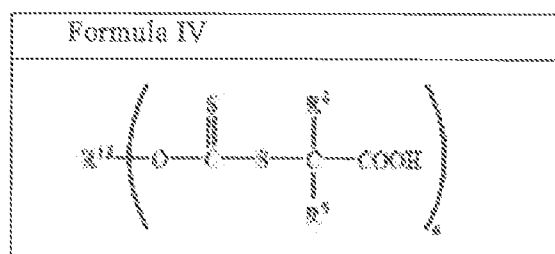
atoms, aryl, a halogen which can be the same or different, cyano, an ether having a total of from 2 to 20 carbon atoms, and a nitro group; or formula III



wherein

j is 1 or 2, with the proviso that when j is 1, T is ($--NR^6R^7$), and when j is 2, T is a divalent radical having a nitrogen atom directly connected to each carbon atom of the two thiocarbonyl groups;

R^4 and R^5 , independently, are the same or different, are optionally substituted as defined for R^1 and R^2 , and are selected from a linear or branched alkyl having from 1 to 12 carbon atoms, aryl having from 6 to 18 carbon atoms, R^4 and R^5 can form a substituted or unsubstituted cyclic ring having from 3 to 12 carbon atoms, wherein said substituents, independently, are selected from an alkyl having from 1 to 6 carbon atoms, aryl, halogen, cyano, an ether having a total of from 2 to 20 carbon atoms, a nitro group, and combinations thereof; wherein R^6 and R^7 , independently, are the same or different, optionally substituted as defined for R^1 and R^2 , and are selected from hydrogen, a linear or branched alkyl having from 1 to 18 carbon atoms, aryl, aryl alkyl having from 6 to 18 carbon atoms, optionally saturated or unsaturated, arylalkyl having from 7 to 18 carbons, alkenealkyl having from 3 to 18 carbon atoms, polyalkylene glycol ether having from 3 to 200 carbon atoms, and amine, or R^6 and R^7 can form a cyclic ring with the nitrogen atom having a total of 4 to 12 carbon atoms; or formula IV



wherein

R^4 and R^5 are as defined above;

R^{13} is optionally substituted, and is selected from linear or branched alkyl having from 1 to 12 carbon atoms, aryl optionally saturated or unsaturated, arylalkyl

having from 7 to 18 carbon atoms, acyl, alkene, alkenealkyl having from 3 to 18 carbon atoms, an alkylene group, an alkoxyalkyl, polyalkylene glycol, polyalkylene glycol monoalkyl ether having from 3 to 200 carbon atoms, and 2-trifluoroethyl; wherein when R¹³ is optionally substituted the substituent is selected from alkyl having from 1 to 6 carbon atoms, aryl, halogen, a cyano group, an amino group, an alkene group, an alkoxycarbonyl group, an aryloxy carbonyl group, a carboxy group, an acyloxy group, a carbamoyl group, an alkylcarbonyl group, an alkylarylcarbonyl group, an arylcarbonyl group, an arylalkylcarbonyl group, a phthalimido group, a maleimido group, a succinimido group, amidino group, guanidino group, allyl group, epoxy group, alkoxy group, an alkali metal salt, a cationic substituent, a hydroxyl group, an ether having a total of from 2 to 20 carbon atoms, nitro, sulfur, phosphorous, a carboalkoxy group, and combinations thereof; and

"a" is 1 to 4.

5. The compound of any of claims 1, 2, 3, or 4, wherein the salt comprises alkali or alkali earth metal hydroxide; alkali earth carbonate; mono-, di-, and/or tri-alkyl-substituted amine; and combinations thereof.
6. The compound of any previous claim wherein the salt comprises, consists of, consists essentially of sodium hydroxide.
7. The compound of any of claims 1 to 6 wherein the salt comprises, consists of, consists essentially of an alkylamine chosen from at least one of triethanolamine ("TEA"), ethanolamine, 2-(dimethylamino)ethanol, diethylamine, 2-(2-aminoethoxy)ethanol, 3-amino-1-propanol, N-(2-hydroxyethyl)ethylenediamine.
8. A polymer comprising, consisting of, consisting essentially of (A) at least one water soluble CTA-acid or CTA-acid salt according to any of claims 1 to 7 and combinations thereof, (B) monomer units derived from at least one water soluble monomer, and optionally (C) monomer units derived from at least one water insoluble vinyl monomer.
9. The polymer of claim 8, wherein the water soluble monomers comprise, consist of, consist essentially of AMPS®, acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, citraconic acid, mesaconic acid, (alkyl) acrylamide, and derivatives or salts thereof, or any combination thereof.

10. The polymer of claim 8 or 9, wherein the water insoluble monomers comprise, consist of, consist essentially of any polymerizable monomer that includes an alkyl group containing 1-18 carbon atoms consisting of a simple ester, a vinyl ester, a mono-allyl ether, styrene, derivatives thereof, or any combination thereof.
11. The polymer of claim 8 to 10 where the polymer is made up of about 0.1 to about 50 weight percent units derived from (A) and from about 50 to about 99.9 percent by weight of the combination of (B) and optional (C).
12. A process of producing a water soluble polymer comprising, consisting of, consisting essentially of the steps of 1) combining in an aqueous solution (A) a CTA-Acid or CTA-acid salt according to any of claims 1 to 7, and combinations thereof; (B) a water soluble ethylenically substituted monomer, and (D) a free radical initiator, and 2) free radically polymerizing the water soluble monomers or allowing the water soluble monomers to free radically polymerize.
13. The process of claim 12, wherein the process produces a macro-CTA-Acid or macro-CTA-Acid salt, and wherein the process further comprises 3) adding (C) a water-insoluble monomer, to form an oil-in-water emulsion, and 4) free radically polymerizing the water soluble monomers with the macro-CTA-Acid or macro-CTA-Acid salt or allowing the water soluble monomers to free radically polymerize with the macro-CTA-Acid or macro-CTA-Acid salt.
14. The use of a CTA-Acid, CTA-acid salt or mixture thereof as a chain transfer agent.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/028787

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C329/16 C08F22/02 C08F4/08
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07C C08F

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

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

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2005/095466 A1 (COATEX SAS [FR]; SUAU JEAN-MARC [FR]; JACQUEMET CHRISTIAN [FR]) 13 October 2005 (2005-10-13) abstract pages 2-5 pages 12-14 page 17, lines 8-11 examples 1-8 claims 1-26	1-14
X	US 2006/111534 A1 (SUAU JEAN-MARC [FR] ET AL) 25 May 2006 (2006-05-25) abstract paragraphs [0017] - [0047] examples 1-3 claims 1-24	1-6,8-14
A		7
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Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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

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"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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Date of the actual completion of the international search

1 July 2016

Date of mailing of the international search report

18/07/2016

Name and mailing address of the ISA/

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

Authorized officer

Dunet, Guillaume

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/028787

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	US 2014/088250 A1 (SUAU JEAN-MARC [FR] ET AL) 27 March 2014 (2014-03-27) abstract paragraphs [0011], [0020] - [0040] paragraphs [0048] - [0051], [0067] examples 1, 2 claims 1-26 -----	1-6,8-14 7
X A	US 2010/105832 A1 (CSIHONY SZILARD [DE] ET AL) 29 April 2010 (2010-04-29) abstract paragraphs [0049] - [0089] examples 1-7 tables 1, 2 claims 1-20 -----	1-6,8-14 7
X A	CN 102 070 742 B (GUANGZHOU LIBY ENTPR GROUP CO LTD) 2 January 2013 (2013-01-02) abstract page 5; compounds 8, 9 paragraph [0016] examples 1-8 claims 1-5 -----	1-12,14 13
X A	US 2006/223936 A1 (SUCH CHRISTOPHER H [AU] ET AL) 5 October 2006 (2006-10-05) abstract paragraphs [0013] - [0023], [0057], [0136] - [0138] examples 1-11 claims 1-15 -----	1-4, 8-12,14 5-7,13
X A	CN 102 504 071 B (CAS GUANGZHOU CHEMISTRY CO LTD) 4 December 2013 (2013-12-04) abstract paragraphs [0016] - [0021] examples 1-6 claims 1-5 -----	1-12,14 13
X A	US 2009/005529 A1 (LAI JOHN T [US]) 1 January 2009 (2009-01-01) abstract paragraphs [0006] - [0009], [0034] examples 1-9 claims 47-62 -----	1-6,8, 10,11,14 7,9,12, 13
X A	US 1 939 692 A (HARDMAN ALBERT F) 19 December 1933 (1933-12-19) examples 1-3 claims 1-12 page 1, right-hand column, last line ----- -/--	1-7 8-14

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2016/028787

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 860 641 A (ZENDEL HANS GEORG ET AL) 14 January 1975 (1975-01-14) abstract column 6, line 45 examples 1, 3 claims 1-12	1-7
X	----- K. A. JENSEN ET AL: "Organic Selenium Compounds. XIV. Assignment of the C=Se Stretching Frequency of Dialkyl Diselenocarbonates and Diselenothiocarbonates.", ACTA CHEMICA SCANDINAVICA., vol. 24, January 1970 (1970-01), pages 2055-2060, XP055282296, DK ISSN: 0904-213X, DOI: 10.3891/acta.chem.scand.24-2055 page 2055; compounds I, III page 2056; table 1 page 2059; table 2	1-7
X	----- E. CAMPAIGNE ET AL: "Dithiolium Derivatives. II. Some New 1,3-Dithiolium Perchlorates 1", THE JOURNAL OF ORGANIC CHEMISTRY, vol. 29, no. 7, July 1964 (1964-07), pages 1708-1710, XP055282293, US ISSN: 0022-3263, DOI: 10.1021/jo01030a011 page 1709; compounds Id, Ie	1-7
X	----- M. M. ORLINSKII ET AL: "Synthesis and biological activity of noncondensed thiazolidones-2 with polymethylene bridges", PHARMACEUTICAL CHEMISTRY JOURNAL, vol. 28, no. 4, April 1994 (1994-04), pages 243-245, XP055282304, US ISSN: 0091-150X, DOI: 10.1007/BF02219795 * Scheme with n = 2 *; page 243 ----- -/--	1-7

INTERNATIONAL SEARCH REPORT

International application No

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>CHRISTLIEB M ET AL: "The exocyclic functionalization of bis(thiosemicarbazone) complexes of zinc and copper : the synthesis of monomeric and dimeric species", DALTON TRANSACTIONS: THE INTERNATIONAL JOURNAL FOR INORGANIC, ORGANOMETALLIC AND BIOINORGANIC CHEMISTRY; [6015A], ROYAL SOCIETY OF CHEMISTRY, GB, January 2007 (2007-01), pages 5043-5054, XP008098174, ISSN: 1477-9226, DOI: 10.1039/B705087A [retrieved on 2007-10-02] * Scheme 2 *; page 5044 page 5045; compound 18 page 5049, right-hand column, paragraph 3</p>	1-7
X	<p>SHUDE XIAO ET AL: "Bifunctional 2-(alkoxycarbonothioylthio)acetic acids for the synthesis of TiO₂-poly(vinyl acetate) nanocomposites via RAFT polymerization", JOURNAL OF POLYMER SCIENCE PART A: POLYMER CHEMISTRY, vol. 52, no. 5, March 2014 (2014-03), pages 606-618, XP055282311, US ISSN: 0887-624X, DOI: 10.1002/pola.27043</p>	1-7,14
A	<p>abstract page 607, right-hand column, paragraph 2 - page 608, right-hand column, paragraph 1 * Scheme 1 *; page 609 page 610; figures 2, 3 pages 612-614</p>	8-13
X,P	<p>W0 2015/079140 A1 (COATEX SAS [FR]) 4 June 2015 (2015-06-04)</p>	1-11,14
A,P	<p>abstract pages 4-9 pages 11-12 examples 1, 2 claims 1-12</p>	12,13
X,P	<p>W0 2015/092186 A1 (COATEX SAS [FR]) 25 June 2015 (2015-06-25) abstract pages 4-8, 10 examples 1, 2 claims 1-10</p>	1-14
	----- -/--	

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/028787

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X, P	<p>US 2015/203653 A1 (RENTSCH SAMUEL [CH] ET AL) 23 July 2015 (2015-07-23)</p> <p>abstract</p> <p>paragraphs [0010] - [0044]</p> <p>paragraphs [0093] - [0096]</p> <p>examples 1, 2</p> <p>claims 1-25</p> <p>-----</p>	1-14

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2016/028787

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2005095466 A1	13-10-2005	AR 048114 A1 FR 2868068 A1 US 2007179262 A1 US 2011186773 A1 US 2012259083 A1 UY 28824 A1 WO 2005095466 A1	29-03-2006 30-09-2005 02-08-2007 04-08-2011 11-10-2012 31-10-2005 13-10-2005
US 2006111534 A1	25-05-2006	AT 455799 T AU 2003274203 A1 BR 0312903 A CA 2493395 A1 CN 1671748 A CN 101012293 A EC SP055596 A EP 1529065 A2 ES 2339005 T3 FR 2842814 A1 HR P20050180 A2 JP 2006509053 A KR 20050030640 A MA 27286 A1 MX PA05001014 A NO 333005 B1 RS 20050067 A US 2006111534 A1 US 2007106042 A1 WO 2004014967 A2 ZA 200500697 A	15-02-2010 25-02-2004 14-06-2005 19-02-2004 21-09-2005 08-08-2007 06-07-2005 11-05-2005 14-05-2010 30-01-2004 31-10-2005 16-03-2006 30-03-2005 01-04-2005 16-05-2005 11-02-2013 04-06-2007 25-05-2006 10-05-2007 19-02-2004 30-08-2006
US 2014088250 A1	27-03-2014	AU 2013322481 A1 CA 2886287 A1 CL 2015000695 A1 CN 104662051 A EP 2900708 A1 FR 2995899 A1 JP 5883546 B2 JP 2015529274 A JP 2016041815 A KR 20150052361 A US 2014088250 A1 US 2015284555 A1 WO 2014049252 A1	12-03-2015 03-04-2014 04-01-2016 27-05-2015 05-08-2015 28-03-2014 15-03-2016 05-10-2015 31-03-2016 13-05-2015 27-03-2014 08-10-2015 03-04-2014
US 2010105832 A1	29-04-2010	EP 2182011 A1 US 2010105832 A1	05-05-2010 29-04-2010
CN 102070742 B	02-01-2013	NONE	
US 2006223936 A1	05-10-2006	BR 0215285 A CA 2470522 A1 CN 1625571 A EP 1463765 A1 IL 162557 A JP 4405807 B2 JP 5173914 B2 JP 2005513252 A JP 2009173943 A	16-11-2004 10-07-2003 08-06-2005 06-10-2004 31-05-2010 27-01-2010 03-04-2013 12-05-2005 06-08-2009

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2016/028787

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		KR 20040076260 A	31-08-2004
		KR 20100109960 A	11-10-2010
		MX PA04006145 A	31-03-2005
		NZ 533519 A	27-07-2007
		US 2006223936 A1	05-10-2006
		US 2010227975 A1	09-09-2010
		WO 03055919 A1	10-07-2003

CN 102504071	B	04-12-2013	NONE

US 2009005529	A1	01-01-2009	AT 298322 T 15-07-2005
		AU 781636 B2	02-06-2005
		AU 2782601 A	27-08-2001
		CA 2399690 A1	23-08-2001
		DE 60111612 D1	28-07-2005
		DE 60111612 T2	24-05-2006
		EP 1255731 A1	13-11-2002
		JP 4914553 B2	11-04-2012
		JP 2003522816 A	29-07-2003
		KR 20030007424 A	23-01-2003
		US 6596899 B1	22-07-2003
		US 2003187138 A1	02-10-2003
		US 2003233006 A1	18-12-2003
		US 2005267274 A1	01-12-2005
		US 2008004461 A1	03-01-2008
		US 2008214773 A1	04-09-2008
		US 2009005529 A1	01-01-2009
		WO 0160792 A1	23-08-2001

US 1939692	A	19-12-1933	NONE

US 3860641	A	14-01-1975	DE 2251717 A1 02-05-1974
		FR 2203810 A1	17-05-1974
		GB 1406548 A	17-09-1975
		JP S4975527 A	20-07-1974
		US 3860641 A	14-01-1975

WO 2015079140	A1	04-06-2015	AU 2014356320 A1 28-04-2016
		CA 2927714 A1	04-06-2015
		FR 3013711 A1	29-05-2015
		WO 2015079140 A1	04-06-2015

WO 2015092186	A1	25-06-2015	CN 105722871 A 29-06-2016
		FR 3015490 A1	26-06-2015
		WO 2015092186 A1	25-06-2015

US 2015203653	A1	23-07-2015	AR 092653 A1 29-04-2015
		AU 2013322829 A1	12-03-2015
		CA 2882929 A1	03-04-2014
		CN 104685005 A	03-06-2015
		EP 2712895 A1	02-04-2014
		EP 2900760 A1	05-08-2015
		JP 2015533896 A	26-11-2015
		KR 20150060898 A	03-06-2015
		SG 11201502311S A	29-04-2015
		TW 201434923 A	16-09-2014
		US 2015203653 A1	23-07-2015
		UY 35043 A	30-04-2014

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2016/028787

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
<div> <div>W0</div> <div>2014048856 A1</div> <div>03-04-2014</div> </div>			