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(71) Applicant: NOVEON IP HOLDINGS CORP. [US/US]; 9911 Brecksville Road, Cleveland, OH 44141-3247 (US).

(72) Inventor: LAI, John, Ta-Yuan; 8435 Cherry Hill Lane, Broadview Heights, OH 44147 (US).

(74) Agent: DUNLAP, Thoburn, T.; Noveon, Inc., 9911 Brecksville Road, Legal Department, Cleveland, OH 44141-3247 (US).

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(54) Title: S-(a, a' -DISUBSTITUTED-a" -ACETIC ACID) SUBSTITUTED DITHIOCARBONATE DERIVATIVES FOR CONTROLLED RADICAL POLYMERIZATIONS, PROCESS AND POLYMERS MADE THEREFROM

(57) Abstract: Dithiocarbonate derivatives are disclosed, along with a process for preparing the same. The dithiocarbonate compounds can be utilized as initators, chain transfer agents and/or terminators in controlled free radical polymerizations. The dithiocarbonates can be used to produce polymers having narrow molecular weight distribution. Advantageously, the compounds of the present invention can also introduce functional groups into the resulting polymers. The dithiocarbonate compounds have low odor and are substantially colorless.

S-(α, α'-DISUBSTITUTED-α''-ACETIC ACID) SUBSTITUTED DITHIOCARBONATE DERIVATIVES FOR CONTROLLED RADICAL POLYMERIZATIONS, PROCESS AND POLYMERS MADE THEREFROM

CROSS REFERENCE

This patent application is a continuation-in-part application based on U. S. Application Serial No. 10/278,335 filed October 23, 2002 for S-(α,α'-Disubstituted-α''-Acetic Acid) Substituted Dithiocarbonate Derivatives For Controlled Radical Polymerizations, Process And Polymer Made Therefrom, which is a continuation-in-part application based on U. S. Application Serial No. 09/505,749 filed February 16, 2000 for S,S'-Bis-(α,α'-Disubstituted-α"-Acetic Acid) - Trithiocarbonates And Derivatives As Initiator - Chain Transfer Agent - Terminator For Controlled Radical Polymerizations And The Process For Making The Same.

FIELD OF THE INVENTION

The present invention relates to s,s'-bis-(α,α'-disubstituted –α"–acetic acid) – trithiocarbonates and derivatives thereof, as well as a process for making the same. Moreover, other functional end groups can be derived from the carboxylic acid end groups. The compounds can be utilized as initiators, chain transfer agents, or terminators for controlled free radical polymerizations. Free radical polymerizations utilizing s,s'-bis-(α,α'-disubstituted –α"–acetic acid) – trithiocarbonate compounds generally form telechelic polymers. If an initiator other than the s,s'-bis-(α,α'-disubstituted –α"–acetic acid) – trithiocarbonate compound is also utilized, a polymer having a single functional end group is formed in proportion to the amount of the initiator to the s,s'-bis-(α,α'-disubstituted –α"–acetic acid) – trithiocarbonate compound utilized.

In a further embodiment, dithiocarbonate derivatives are disclosed, along with a process for preparing the same. The dithiocarbonate compounds can be utilized as initators, chain transfer agents and/or terminators in controlled free radical polymerizations. The dithiocarbonates can be used to produce polymers having narrow molecular weight distribution. Advantageously, the compounds of the present invention can also introduce functional groups into the resulting polymers. The dithiocarbonate compounds have low odor and are substantially colorless.

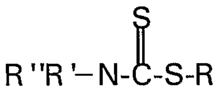
BACKGROUND OF THE INVENTION

Although several members of the class of organic thiocarbonates have been known for many years and various routes have been employed for their synthesis, the s,s'-bis-(α,α'-disubstituted –α"–acetic acid) – trithiocarbonate compounds of the present invention have not been disclosed. Trithiocarbonate compounds have been claimed for various applications, such as pesticides for agriculture, and also as lubricating oil additives.

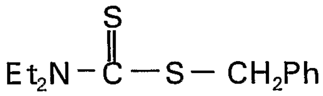
Traditional methods of producing block copolymers, such as by living polymerization or the linking of end functional polymers, suffer many disadvantages, such as the restricted type monomers which can be utilized, low conversion rates, strict requirements on reaction conditions, and monomer purity. Difficulties associated with end linking methods include conducting reactions between polymers, and problems of producing a desired pure end functional polymer. The s,s'-bis-(α,α'-disubstituted –α"–acetic acid) – trithiocarbonate compounds of the present invention can alleviate the above noted problems and difficulties when utilized in free radical polymerizations.

The prior art WO98/01478 reference discloses the use of thiocarbonates to conduct living free radical polymerizations. The reference is limited to alkyl and benzyl functional groups, and is unable to make any aryl or carboxylic acid substituted trithiocarbonates with general methods known to the art. *Synthesis*, p 894 (1986), *J. Chemical Research* (Synopsis), p 478 (1995), and *Synthetic Communications*, Vol. 18, p 1531 (1988). We have also found the conversion for the dibenzyl derivatives disclosed in their example 26 to be very slow compared to the present invention when polymerizing acrylate, as can be seen in the Example section of this application. The WO/01478 reference states in the background that experiments have shown that dithiocarbamate derivatives have low transfer constants and are substantially ineffective in conferring living characteristics to radical polymerizations.

Macromolecules, 32, p 6977-6980 (1999) states that

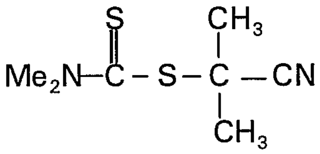


$R''R'{-}N{-}\overset{\overset{S}{\|}}{C}{-}S{-}R$ dithiocarbamate compounds:



$Et_2N-\overset{\overset{S}{\|}}{C}-S-CH_2Ph$

(2) and

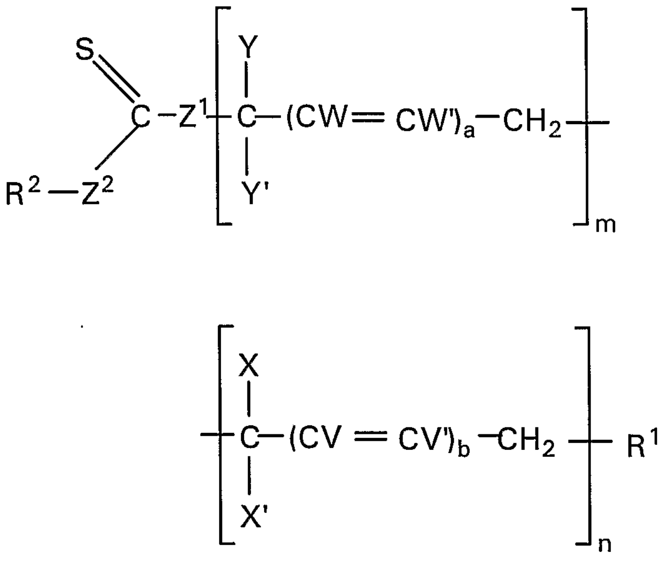


$Me_2N-\overset{\overset{S}{\|}}{C}-S-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CN$

(3)

cannot control polymerization and are not effective RAFT agents. Additionally, carboxyl end groups cannot be formed utilizing the processes disclosed. Also WO 99/35177 and Macromolecules, Rapid Communications, 21, p 1035-1039 (2001) finds that R, R^1, and R^2 need to be fine tuned to control polymerization, meaning there is no guarantee all dialkyl dithiocarbamate will work as RAFT agents. Moreover, the substituent of the single bonded sulfur atom cannot be a carboxylic acid containing group in their synthesis.

U. S. Patent No. 6,153,705 relates to a process for polymerizing block polymers of general formula (I):

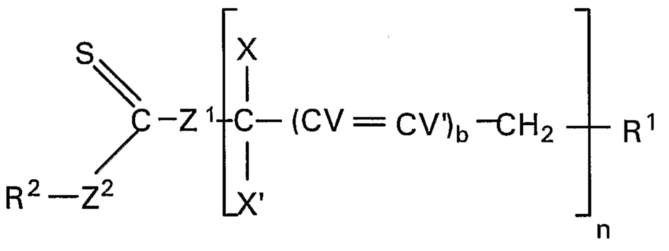


in which process the following are brought into contact with each other:

an ethylenically unsaturated monomer of formula:

$CYY'(=CW-CW')_a=CH_2$,

a precursor compound of general formula (II):



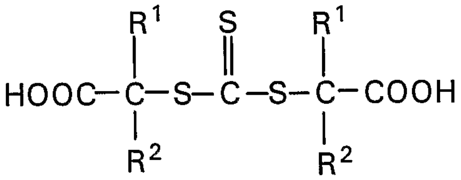
and a radical polymerization initiator.

Macromolecule Rapid Communications 2001, 22, p 1497-1503 and U. S. Patent No. 6,153,705 disclose various xanthate compounds. The references cannot prepare the xanthate compounds of the present invention utilizing the methods disclosed within the references. 1) Alkylation with tertiary alkyl halides disclosed in the '705 patent will result in elimination, not substitution. The -halo- ', ''-dialkylacetic acid disclosed by the reference cannot be alkylated. 2) The compounds of the present invention contain a tertiary carbon attached to the single bonded sulfur atom of the compound. The '705 patent preferably utilizes an R^1 group having a secondary carbon atom which results in a lower chain transfer coefficient than the present invention. Moreover, the xanthates disclosed by the references have been found to be less effective.

Unexpectedly, in view of the prior art, the compounds of the present invention are able to confer living characteristics to a free radical polymerization.

SUMMARY OF THE INVENTION

The present invention relates to s,s′-bis-(α,α′-disubstituted –α″–acetic acid) – trithiocarbonates which have the general formula:

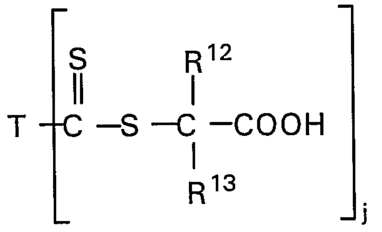


$$HOOC-\underset{R^2}{\overset{R^1}{C}}-S-\overset{S}{\overset{\|}{C}}-S-\underset{R^2}{\overset{R^1}{C}}-COOH$$

where R^1 and R^2 are set forth below, to derivatives thereof, and to a process for making the same.

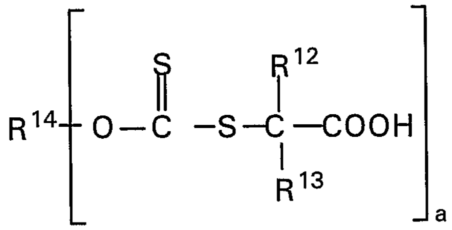
The s,s′-bis-(α,α′-disubstituted –α″–acetic acid) trithiocarbonate compounds can generally be formed from carbon disulfide, a haloform, and a ketone in a strong base, such as sodium hydroxide, followed by acidification. The s,s′-bis-(α,α′-disubstituted –α″–acetic acid) trithiocarbonate compounds can be used as inifertors, i.e. as initiators and chain transfer agents, and/or chain terminators or as a chain-transfer agent during polymerization. The compounds can thus be utilized to control free radical polymerization thermally and chemically to give narrow molecular weight distributions. Polymerization of monomers can be in bulk, in emulsion, or in solution. Block copolymers can be made if two or more monomers are polymerized in succession. The difunctional acid end groups present can further react with other reactive polymers or monomers to form block or random copolymers. Free radical polymerizations utilizing the s,s'-bis-(α,α'-disubstituted−α" −acetic acid) − trithiocarbonate compounds generally form telechelic polymers. If an initiator other than the s,s'-bis-(α,α'-disubstituted −α" − acetic acid) − trithiocarbonate compound is also utilized, a polymer having a single functional end group is formed in proportion to the amount of said other initiator to the s,s'-bis-(α,α'-disubstituted −α" − acetic acid) − trithiocarbonate compound utilized.

In a further embodiment, dithiocarbonate compounds of the present invention have the general formulae:



$$T\left[\overset{S}{\overset{\|}{C}}-S-\overset{R^{12}}{\underset{R^{13}}{C}}-COOH\right]_j$$

or

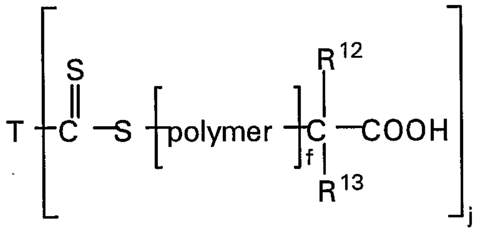


$$R^{14}\left[O-\overset{S}{\overset{\|}{C}}-S-\overset{R^{12}}{\underset{R^{13}}{C}}-COOH\right]_a$$

wherein T, R^{12}, R^{13}, R^{14}, a and j are defined hereinbelow. Preferably, the substituent T is an amine derivative, preferably a dialkylamino derivative. Thus, the dithiocarbonate compounds are xanthate and dithiocarbamate derivatives. A process for preparing the dithiocarbonate compounds is disclosed.

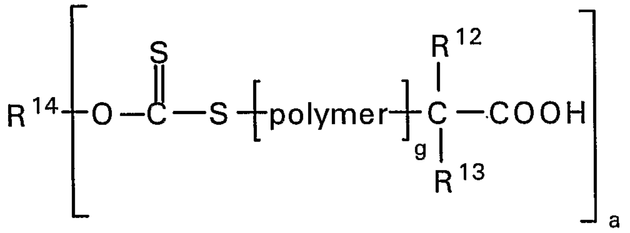
The dithiocarbonate compounds can be utilized as chain transfer agents in free radical polymerizations, as well as initiators and/or chain terminators. Narrow molecular weight distribution polymers can advantageously be produced with the dithiocarbonates of the present invention. The polymers formed in the presence of the dithiocarbonate compounds have at least one terminal carboxyl group which can be further reacted to form block or random copolymers. The monomers or polymers polymerized onto the dithiocarbonate compounds are added between the single bonded sulfur atom and the adjacent tertiary carbon atom. The polymerizations are conducted under inert atmospheres. The compounds and/or the polymers or copolymers of the present invention can be made water soluble or water dispersible through their metal or ammonium salts of the carboxylic acid group.

Accordingly, polymers having the following formulae can be produced utilizing the dithiocarbonate compounds of the present invention:



$$T\left[\overset{S}{\overset{\|}{C}}-S\left[\text{polymer}\right]_f\underset{R^{13}}{\overset{R^{12}}{C}}-COOH\right]_j$$

or

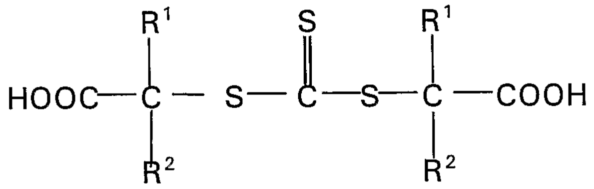


$$R^{14}\left[O-\overset{S}{\overset{\|}{C}}-S\left[\text{polymer}\right]_g\underset{R^{13}}{\overset{R^{12}}{C}}-COOH\right]_a$$

wherein, T, R^{12}, R^{13}, R^{14}, polymer, a, g, j and f are defined hereinbelow.

DETAILED DESCRIPTION OF THE INVENTION

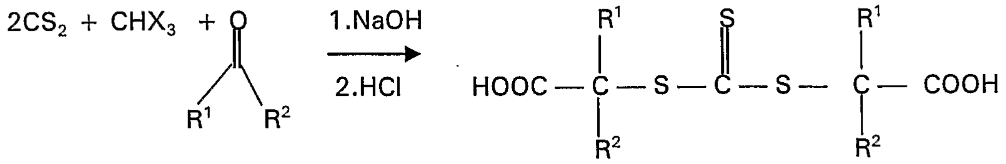
The s,s'-bis-(α,α'-disubstituted -α"-acetic acid) -trithiocarbonate and derivatives prepared by the processes disclosed later herein generally can be described by the formula:



$$HOOC-\underset{R^2}{\overset{R^1}{C}}-S-\overset{S}{\overset{\|}{C}}-S-\underset{R^2}{\overset{R^1}{C}}-COOH$$

wherein R^1 and R^2, independently, can be the same or different, and can be linear or branched alkyls having from 1 to about 6 carbon atoms, or a C_1 to about C_6 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; 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. R^1 and R^2 can also form or be a part of a cyclic ring having from 5 to about 12 total carbon atoms. R^1 and R^2 are preferably, independently, methyl or phenyl groups.

The abbreviated reaction formula for the s,s'-bis-(α,α'- disubstituted – α"–acetic acid) – trithiocarbonates of the present invention can be generally written as follows:



The process utilized to form the s,s'-bis-(α,α'-disubstituted –α"– acetic acid) – trithiocarbonate compounds of the present invention is generally a multi-step process and includes combining the carbon disulfide and a base whereby an intermediate trithio structure is formed, see I, II, III, and IV. 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 a α-trihalomethyl-α-alkanol are added to the trithio intermediate mixture and reacted in the presence of additional base, see V, VI, and VII. The formed reaction product, see IX, is subsequently acidified, thus completing the reaction and forming the above described s,s′-bis-(α,α′-disubstituted –α″–acetic acid) – trithiocarbonate compound, see X.

The reaction is carried out at a temperature sufficient to complete the interaction of the reactants so as to produce the s,s′-bis-(α,α′-disubstituted –α″– acetic acid) – trithiocarbonate compound in a desired time. The reaction can be carried out at any temperature within a wide range from about the freezing point of the reaction mass to about the reflux temperature of the solvent. The reaction temperature is generally from about minus 15° C to about 80° C, desirably from about 0° C to about 50° C, and preferably from about 15° C to about 35° C, with room temperature being preferred. The reaction can be performed at atmospheric pressure. The reaction time depends upon several factors, with the temperature being most influential. The reaction is generally complete within 20 hours and preferably within 10 hours.

A phase transfer catalyst is preferably utilized if a solvent is used in the reaction. Examples of solvents are set forth herein below. The ketone utilized in the reaction may double as a solvent, and therefore no catalyst usually is needed. The amount of phase transfer catalyst, when utilized in the present invention, is generally from about 0.1 mole percent to about 10 mole percent, desirably from about 0.5 mole percent to about 5 mole percent and preferably from about 2 mole percent to about 4 mole percent per mole of carbon disulfide. The phase transfer catalysts can be polyether, and/or an onium salt including a quaternary or tertiary organic compound of a group VA or VIA element of the Periodic Table and salts thereof. Most preferred are quaternary amines, and salts thereof.

"Onium salts" more particularly refer to tertiary or quaternary amines and salts such as are generally used in the phase transfer catalysis of heterogeneous reaction in immiscible liquids. The general requirement for the onium salt chosen is that it be soluble in both the organic and aqueous phases, when these two liquid phases are present, and usually a little more soluble in the organic phase than the aqueous phase. The reaction will also proceed with a phase transfer catalyst when there is only a single organic liquid phase present, but such a reaction is less preferable than one in which both aqueous and organic liquid phases are present. A wide variety of onium salts is effective in this ketoform synthesis.

The onium salts include the well-known salts, tertiary amines and quaternary compounds of group VA elements of the Periodic Table, and some Group VIA elements such as are disclosed in the U.S. Patent No. 3,992,432 and in a review in Angewandte Chemie, International Edition in English, 16 493-558 (August 1977). Discussed therein are various anion transfer reactions where the phase transfer catalyst exchanges its original ion for other ions in the aqueous phase, making it possible to carry our chemistry there with the transported anion, including OH-ions.

The onium salts used in this synthesis include one or more groups having the formula $(R_nY)^+X^-$, wherein Y is either a pentavalent ion derived from an element of Group VA, or a tetravalent ion derived from an element of Group VIA; R is an organic moiety of the salt molecule bonded to Y by four covalent linkages when Y is pentavalent, and three covalent linkages when Y is tetravalent; X^- is an anion which will dissociate from the cation $(R_nY)^+$ in an aqueous environment. The group $(R_nY)^+ X^-$ may be repeated as in the case of dibasic quaternary salts having two pentavalent Group VA ions substituted in the manner described.

The preferred onium salts for use in the invention have the formula

$$(R^AR^BR^CR^DY^+)X^-$$

wherein Y is N or P, and R^A – R^D are monovalent hydrocarbon radicals preferably selected from the group consisting of alkyl, alkenyl, aryl, alkaryl, aralkyl, and cycloalkyl moieties or radicals, optionally substituted with suitable heteroatom-containing functional groups. The onium salts are generally selected to be less preferentially less soluble in the less polar of the two distinct liquid phases. Any of the salts disclosed in the U.S. Patent No. 3,992,432 will be found effective, but most preferred are those in which the total number of carbon atoms in R^A,R^B,R^C, and R^D cumulatively range from about 13 to about 57, and preferably range from about 16 to about 30. Most preferred onium salts have Y =N, and hydrocarbon radicals where R^A is CH_3, and R^B, R^C, and R^D are each selected from the group consisting of n-C_2H_5, n-C_4H_5; n-C_5H_{11}; mixed C_5H_{17}; n-$C_{12}H_{25}$; n-$C_{18}H_{37}$; mixed C_8-C_{10} alkyl; and the like. However, R^A may also be selected from C_2H_5n-C_3H_7 and n-C_4H_9 benzyl.

Various counterions may be used, including Cl^-, Br^-, I^-, NO_3^-, SO_4^{-2}, HSO_4^- and $CH_2CO_2^-$. Most preferred is Cl^-.

The tertiary amines or triamines useful as phase transfer catalysts in this synthesis include the alkyl amines and the aryldialkylamines, exemplified by tributylamine and phenyldibutylamine respectively, which are commonly available, wherein each alkyl may have from 1 to about 16 carbon atoms.

The polyethers useful as catalysts in this synthesis include cyclic polyethers such as the crown ethers, disclosed in *Agenwandte Chemie*, supra, and acyclic polyethers having the formula:

$$R\text{-}O\text{-}R^E$$

wherein R and R^E are, independently, alkyls having from 1 to about 16 carbon atoms, or alkyl containing substituted functional groups such as hydroxy, sulfur, amine, ether, etc. Most preferred acyclic polyethers have the formula:

$$R - (OCH_2CH_2)_r\ OR''$$

wherein

R is an alkyl having from 1 to about 16 carbon atoms

R'' is an alkyl having from 1 to about 16 carbon atoms, or H, and

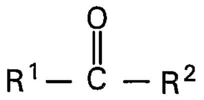
r is an integer in the range from 0 to about 300.

Most preferred are commonly available polyethers such as: tetraethylene glycol dimethyl ether; polyethylene oxide (mol wt. About 5000); poly(ethylene glycol methyl ether); 1,2-dimethoxyethane; diethyl ether, and the like.

Polyether catalysts are especially desirable in this ketoform synthesis because they are directive so as to produce a preponderance of the desired symmetrically substituted isomer, in a reaction which is remarkably free of undesirable byproducts, which reaction proceeds with a relatively mild exotherm so that the reaction is controllable.

The organic solvent may be any solvent in which the reactants are soluble and include hydrohalomethylenes, particularly hydrochloromethylenes, sulfolane, dibutyl ether, dimethyl sulfone, diisopropyl ether, di-n-propyl ether, 1,4-dioxane, tetrahydrofuran, benzene, toluene, hexane, carbon tetrachloride, heptane, mineral spirits and the like. Most preferred solvents are heptanes and mineral spirits. Solvent is generally utilized in an amount generally from about 10 to about 500 percent and preferably from about 50 percent to about 200 percent based on the total weight of the reactants.

Insofar as the reactive components are concerned, any of various ketones having the general formula:



$$R^1 - \overset{\overset{\displaystyle O}{\|}}{C} - R^2$$

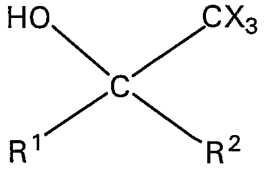
can be employed in the synthesis, wherein R^1 and R^2 are described herein above. As carbon disulfide is the controlling agent in the reaction, the ketone is generally used in an amount from about 110 mole percent to about 2,000 mole percent per mole of carbon disulfide. When the ketone is used as a solvent, it is generally utilized in an amount of from about 150 mole percent to about 300 mole percent, and preferably from about 180 mole percent to about 250 mole percent per mole of carbon disulfide.

The alkali bases suitable for use in the synthesis of the present invention include, but are not limited to, sodium hydroxide and potassium hydroxide. The base is utilized in an amount generally from about 5 times to about 15 times the number of moles of carbon disulfide and preferably from about 6 to about 10 times the number of moles of carbon disulfide utilized in the reaction.

The acids used in the acidification step include, but are not limited to, hydrochloric acid, sulfuric acid, phosphoric acid, etc. The acids are utilized in amounts suitable to make the aqueous solution acidic.

The haloform of the present invention has the general formula CHX_3 wherein X is, independently, chlorine or bromine. The amount of haloform used in the present invention is generally from about 110 mole percent to about 2000 mole percent, desirably from about 150 mole percent to about 300 mole percent, and preferably 180 mole percent to about 250 mole percent per mole of carbon disulfide. Examples of haloforms include, but are not limited to, chloroform and bromoform, and chloroform is the preferred haloform of the present invention.

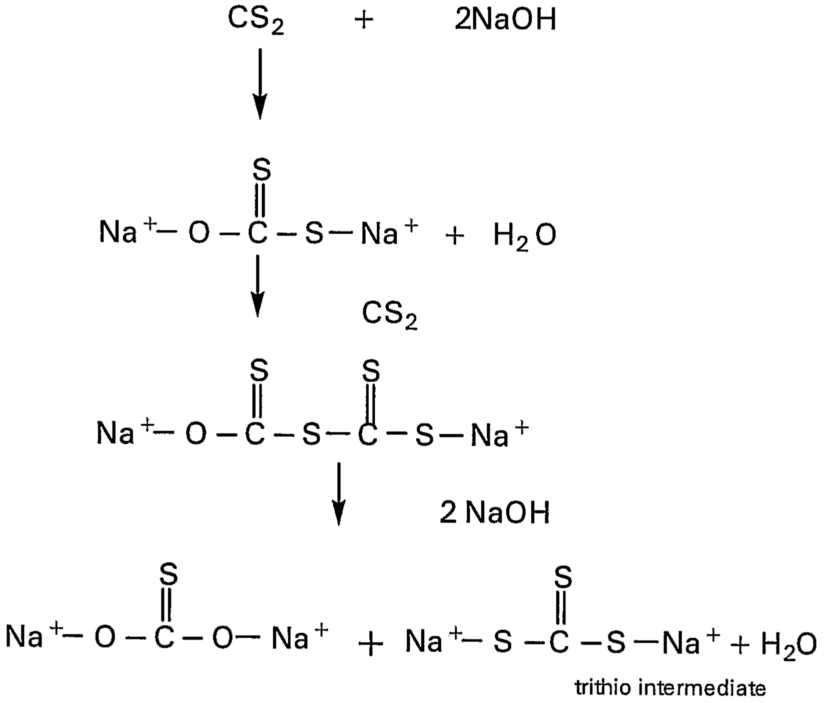
Alternatively, instead of adding both a haloform and a ketone, to the reaction mixture, an α-trihalomethyl-α-alkanol can be substituted therefore. The amount of α-trihalomethyl-α-alkanol utilized in the reaction generally is from about 110 mole percent to about 2000 mole percent, desirably is from about 150 mole percent to about 300 mole percent, and preferably is from about 180 mole percent to about 250 mole percent per mole of carbon disulfide. The general formula of the α-trihalomethyl-α-alkanol is generally represented as follows:



wherein X, R^1 and R^2 are defined above.

While not wishing to be limited to any particular mechanism, it is believed that the specific mechanism for the reaction process is as follows:

Initially, the carbon disulfide and sodium hydroxide are reacted.



$$CS_2 + 2NaOH \qquad I$$

$$\downarrow$$

$$Na^+{-}O{-}\overset{\overset{S}{\|}}{C}{-}S{-}Na^+ + H_2O \qquad II$$

$$\downarrow CS_2$$

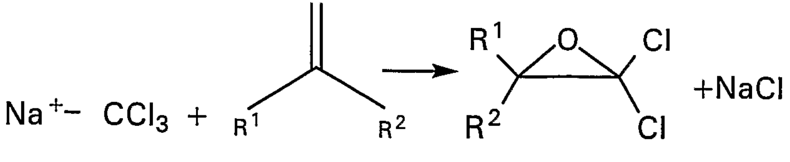
$$Na^+{-}O{-}\overset{\overset{S}{\|}}{C}{-}S{-}\overset{\overset{S}{\|}}{C}{-}S{-}Na^+ \qquad III$$

$$\downarrow 2\,NaOH$$

$$Na^+{-}O{-}\overset{\overset{S}{\|}}{C}{-}O{-}Na^+ + \underbrace{Na^+{-}S{-}\overset{\overset{S}{\|}}{C}{-}S{-}Na^+}_{\text{trithio intermediate}} + H_2O \qquad IV$$

In the subsequent step of the reaction, the chloroform is reacted with the ketone as follows:

$HCCl_3$ + NaOH $\longrightarrow$ H_2O + $Na^+{-}CCl_3$ V



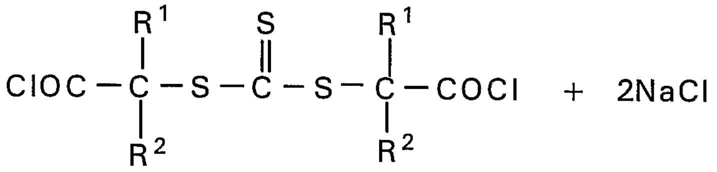
VI

(1-disubstituted-2-dichloroepoxide)

Then, the following is reacted:

$$\mathrm{Na^{+}S-\overset{\overset{S}{\|}}{C}-S^{-}Na^{+}} + 2$$

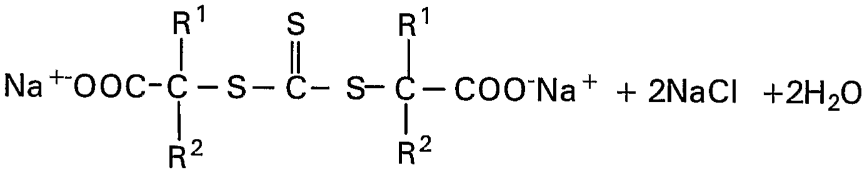
VII



$$\mathrm{ClOC-\underset{R^2}{\overset{R^1}{C}}-S-\overset{\overset{S}{\|}}{C}-S-\underset{R^2}{\overset{R^1}{C}}-COCl} + 2NaCl$$

VIII

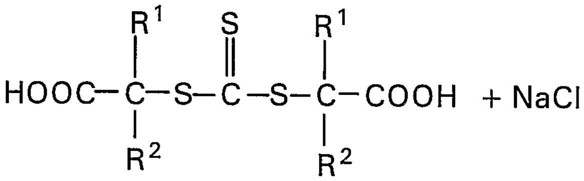
$\downarrow$ 4 NaOH



$$\mathrm{Na^{+-}OOC-\underset{R^2}{\overset{R^1}{C}}-S-\overset{\overset{S}{\|}}{C}-S-\underset{R^2}{\overset{R^1}{C}}-COO^{-}Na^{+}} + 2NaCl + 2H_2O$$

IX

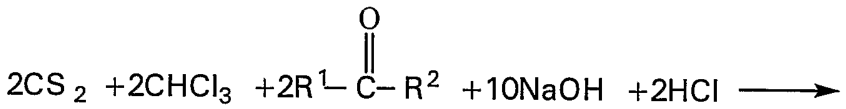
dicarboxylate salt $\downarrow$ 2HCl



$$\mathrm{HOOC-\underset{R^2}{\overset{R^1}{C}}-S-\overset{\overset{S}{\|}}{C}-S-\underset{R^2}{\overset{R^1}{C}}-COOH} + NaCl$$

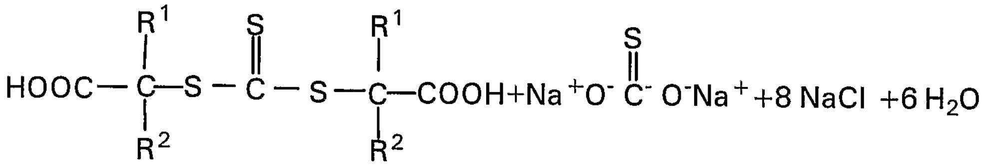
X

The overall reaction is as follows:



$$2CS_2 + 2CHCl_3 + 2\mathrm{R^1-\overset{\overset{O}{\|}}{C}-R^2} + 10NaOH + 2HCl \longrightarrow$$

XI



$$\mathrm{HOOC-\underset{R^2}{\overset{R^1}{C}}-S-\overset{\overset{S}{\|}}{C}-S-\underset{R^2}{\overset{R^1}{C}}-COOH + Na^{+}O^{-}\overset{\overset{S}{\|}}{C}{}^{-}O^{-}Na^{+}} + 8\,NaCl + 6\,H_2O$$

XII

The s,s′-bis-(α,α′-disubstituted -α″-acetic acid) -trithiocarbonate compounds produced by the present invention can generally be classified as inifertors, meaning that they act as both a chain transfer agent and an initiator. The use of other types of inifertors for block copolymers was discussed by Yagei and Schnabel in *Progress in Polymer Science* 15, 551 (1990) and is hereby fully incorporated by reference.

Thus, the compounds of the present invention can be utilized as initiators to initiate or start the polymerization of a monomer. They can also act as a chain transfer agent, which interrupts and terminates the growth of a polymer chain by formation of a new radical which can act as a nucleus for forming a new polymer chain. The compounds can also be utilized as terminators in that when most of initiating radicals and monomers are consumed, the compounds are incorporated in the polymers as a dormant species. Desirably though, another compound, such as those listed herein below, is often used as an initiator in the free radical polymerization process as described herein below, and the s,s'-bis-(α,α'-disubstituted $-\alpha''-$acetic acid) – trithiocarbonate compounds of the present invention will act as a chain-transfer agent.

The s,s'-bis-(α,α'-disubstituted $-\alpha''-$acetic acid) – trithiocarbonate compounds of the present invention can be used as chain transfer agents in a free radical polymerization process to provide polymerizations which have living characteristics and polymers of controlled molecular weight and low polydispersity, as well as for forming telechelic polymers.

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.
7. In radical polymerization, the number of active end groups should be 2, one for each end.

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.

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 stoichiometery 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 the s,s′-bis-(α,α′-disubstituted –α″–acetic acid) – trithiocarbonate compounds and derivatives thereof of the present invention are preferably 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.

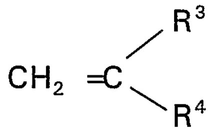
When the s,s′-bis-(α,α′-disubstituted –α″–acetic acid) – trithiocarbonates compounds are utilized only as chain-transfer agents, the polymerization can be initiated with other initiators at lower temperature while yielding polymers with similarly controlled fashion.

Free radical polymerizations utilizing the s,s′-bis-(α,α′- disubstituted – α″–acetic acid) – trithiocarbonate compounds as both initiators and chain transfer agents generally form telechelic polymers. When an initiator other than the s,s′-bis-(α,α′-disubstituted –α″–acetic acid) – trithiocarbonate compound is also utilized, a polymer having a single functional end group is formed in proportion to the amount of said other initiator to this s,s′-bis-(α,α′-disubstituted –α″–acetic acid) – trithiocarbonate compound utilized.

The free radical living polymerization process of the invention can be applied to any monomers or monomer combinations which can be free-radically polymerized. Such monomers include one or more conjugated diene monomers or one or more and vinyl containing monomers, or combinations thereof.

The diene monomers have a total of from 4 to 12 carbon atoms and examples include, but are not limited to, 1,3-butadine, isoprene, 1,3-pentadiene, 2,3-dimethyl-1-3-butadeine, 2-methyl-1,3-pentadiene, 2,3-dimethyl-1,3-pentadiene, 2-phenyl-1,3-butadiene, and 4,5-diethyl-1,3-octadiene, and combinations thereof.

The vinyl containing monomers have the following structure:



$CH_2=C(R^3)(R^4)$

where R^3 comprises hydrogen, halogen, C_1 to C_4 alkyl, or substituted C_1 - C_4 alkyl wherein the substituents, independently, comprise one or more hydroxy, alkoxy, aryloxy(OR^5), carboxy, metal carboxylate (COOM) with M being sodium, potassium, calcium, zinc or the like or an ammonium salt, acyloxy, aroyloxy(O_2CR^5), alkoxy-carbonyl(CO_2R^5), or aryloxy-carbonyl; and R^4 comprises hydrogen, R^5, CO_2H, CO_2R^5, COR^5, CN, $CONH_2$, $CONHR^5$, O_2CR^5, OR^5, or halogen. R^5 comprises C_1 to C_{18} alkyl, substituted C_1 – C_{18} alkyl, C_2 – C_{18} alkenyl, aryl, heterocyclyl, aralkyl, or alkaryl, wherein the substituents independently comprise one or more epoxy, hydroxy, alkoxy, acyl, acyloxy, carboxy (and salts), sulfonic acid (and salts), alkoxy- or aryloxy-carbonyl, dicyanato, cyano, silyl, halo and dialkylamino. Optionally, the monomers comprise maleic anhydride, N-vinyl pyrrolidone, N-alkylmaleimide, N-arylmaleimide, dialkyl fumarate and cyclopolymerizable monomers. Monomers $CH_2=CR^3R^4$ as used herein include C_1 – C_8 acrylates and methacrylates, acrylate and methacrylate esters, acrylic and methacrylic acid, styrene, α methyl styrene, C_1, - C_{12} alkyl styrenes with substitute groups both either on the chain or on the ring, acrylamide, methacrylamide, N- and N,N-alkylacrylamide and methacrylonitrile, mixtures of these monomers, and mixtures of these monomers with other monomers. As one skilled in the art would recognize, the choice of comonomers is determined by their steric and electronic properties. The factors which determine copolymerizability of various monomers are well documented in the art. For example, see: Greenley, R.Z., in *Polymer Handbook,* 3rd Edition (Brandup, J., and Immergut, E.H. Eds.) Wiley: New York, 1989 pII-53.

Specific monomers or comonomers include the following:

methyl methacrylate, ethyl methacrylate, propyl methacrylate (all isomers), butyl methacrylate (all isomers), 2-ethylhexyl methacrylate, isobornyl methacrylate, methacrylic acid, benzyl methacrylate, phenyl methacrylate, methacrylonitrile, alpha-methylstyrene, methyl acrylate, ethyl acrylate, propyl acrylate (all isomers), butyl acrylate (all isomers), 2-ethylhexyl acrylate, isobornyl acrylate, acrylic acid, benzyl acrylate, phenyl acrylate, acrylonitrile, styrene, functional methacrylates, acrylates such as glycidyl methacrylate, 2-hydroxyethyl methacrylate, hydroxypropyl methacrylate (all isomers), hydroxybutyl methacrylate (all isomers), N,N-dimethylaminoethyl methacrylate, N,N-diethylaminoethyl methacrylate, and triethyleneglycol methacrylate, itaconic anhydride, itaconic acid; metal salts such as but not limited to sodium and zinc of all monomeric acids, such as but not limited to, itaconic acid and 2-acrylamido-2-methyl-1-propanesulfonic acid, or the like; N-vinylimidazole, vinylpyridine N-oxide, 4-vinylpyridine carboxymethylbetaine, diallyl dimethylammonium chloride, p-styrenesulfonic acid, p-styrenecarboxylic acid, 2-dimethylaminioethyl acrylate and its alkyl/hydrogen halide salts, 2-dimethylaminoethyl methacrylate and its alkyl/hydrogen halide salts, N-(3-dimethylaminopropyl) acrylamide, N-(3-dimethylaminoproyl) methacrylamide, diacetone acrylamide, 2-(acetoacetoxy)ethyl methacrylate, 2-(acryloyloxy)ethyl acetoacetate, 3-trialkoxysilylpropylmethacrylate (methoxy, ethoxy, isopropoxy, etc), glycidyl acrylate, 2-hydroxyethyl acrylate, hydroxypropyl acrylate (all isomers), hydroxybutyl acrylate (all isomers), N,N-diethylaminoethyl acrylate, triethyleneglycol acrylate, methacrylamide, N-methylacrylamide, N,N-dimethylacrylamide, N-terbtbutylmethacrylamide, N-n-butylmethacrylamide, N-methylolmethacrylamide, N-ethylotmethacrylamide, N-tert-butylacrylamide, N-N-butylacrylamide, N-methylolacrylamide, N-ethylolacrylamide, vinyl benzoic acid (all isomers), dethylaminostyrene (all isomers), alpha-methylvinyl benzoic acid (all isomers), dethylamino alpha-methylstyrene (all isomers), p-vinylbenzene sulfonic acid, p-vinylbenzene sulfonic sodium salt, trimethoxysilylpropyl methacrylate, triethoxysilylpropyl methacrylate, tributoxysilyipropyl methacrylate, dimethoxymethylsilylpropyl methacrylate, diethoxymethylslylpropyl methacrylate, dibutoxymethylsilypropyl methacrylate, diisopropoxymethylsilylpropyl methacrylate, dimethoxysilylpropyl methacrylate, diethoxysilylpropyl methacrylate, dibutoxy, silylpropyl methacrylate, diisopropoxysilylpropyl methacrylate, trimethoxysilylpropyl acrylate, triethoxysifylylpropyl acrylate, tributoxysilylpropyl acrylate, dimethoxymethylsilylpropyl acrylate, diethoxymethylsilylpropyl acrylate, dibutoxymethylsilylpropyl acrylate, diisopropoxymethylsilylpropyl acrylate, dimethoxysilylpropyl acrylate, diethoxysilylpropyl acrylate, dibutoxysilylpropyl acrylate, diisopropoxysilylpropyl amiate, vinyl acetate, vinyl butyrate, vinyl benzoate, vinyl chloride, vinyl fluoride, vinyl bromide, maleic anhydride, N-phenylmaleimide, N-butylmaleimide, N-vinylpyrrolidone, N-vinylcarbazole, butadiene, isoprene, chloroprene, ethylene, and propylene, and combinations thereof.

Preferred monomers are $C_1 - C_{18}$ acrylates; $C_1 - C_8$ monoalkyl and dialkyl acrylamides; a combination of $C_1 - C_8$ acrylates and methacrylates; a combination of acrylamides and methacrylamide; $C_1 - C_8$ styrene; butadiene; isoprene and acrylonitrile.

As noted above, in order to initiate the free radical 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 (e.g., styrene), 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. The s,s′-bis-(α,α′-disubstituted –α″ – acetic acid) – trithiocarbonate compounds of the invention can serve as an initiator, but the reaction must be run at a higher temperature. Therefore, optionally it is desirable to utilize an initiator other than the s,s′-bis-(α, α′-disubstituted –α″ –acetic acid) – trithiocarbonates compounds of the present invention.

Thermal initiators are chosen to have an appropriate half-life at the temperature of polymerization. These 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(cyclohexanecarbanitrile), 2-(t-butylazo)-2-cyanopropane, 2,2′-azobis[2-methyl-N-(1,1)-bis(hydoxymethyl)-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-butyl peroxybenzoate, t-butyl peroxyoctoate, t-butylperoxyneodecanoate, t-butylperoxy isobutyrate, t-amyl peroxypivalate, t-butyl peroxypivalate, di-isopropyl peroxydicarbonate, dicyclohexyl peroxydicarbonate, dicumyl peroxide, dibenzoyl peroxide, dilauroylperoxide, potassium peroxydisulfate, ammonium peroxydisulfate, di-t-butyl hyponitrite, dicumyl hyponitrite.

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 combinations of the following oxidants and reductants:

oxidants: potassium peroxydisuffate, hydrogen peroxide, t-butyl hydroperoxide reductants: iron (11), titanium (111), potassium thiosulfite, potassium bisulfite.

Other suitable initiating systems are described in recent texts. See, for example, Moad and Solomon "The Chemistry of Free Radical Polymerization". Pergamon, London. 1995. pp 53-95.

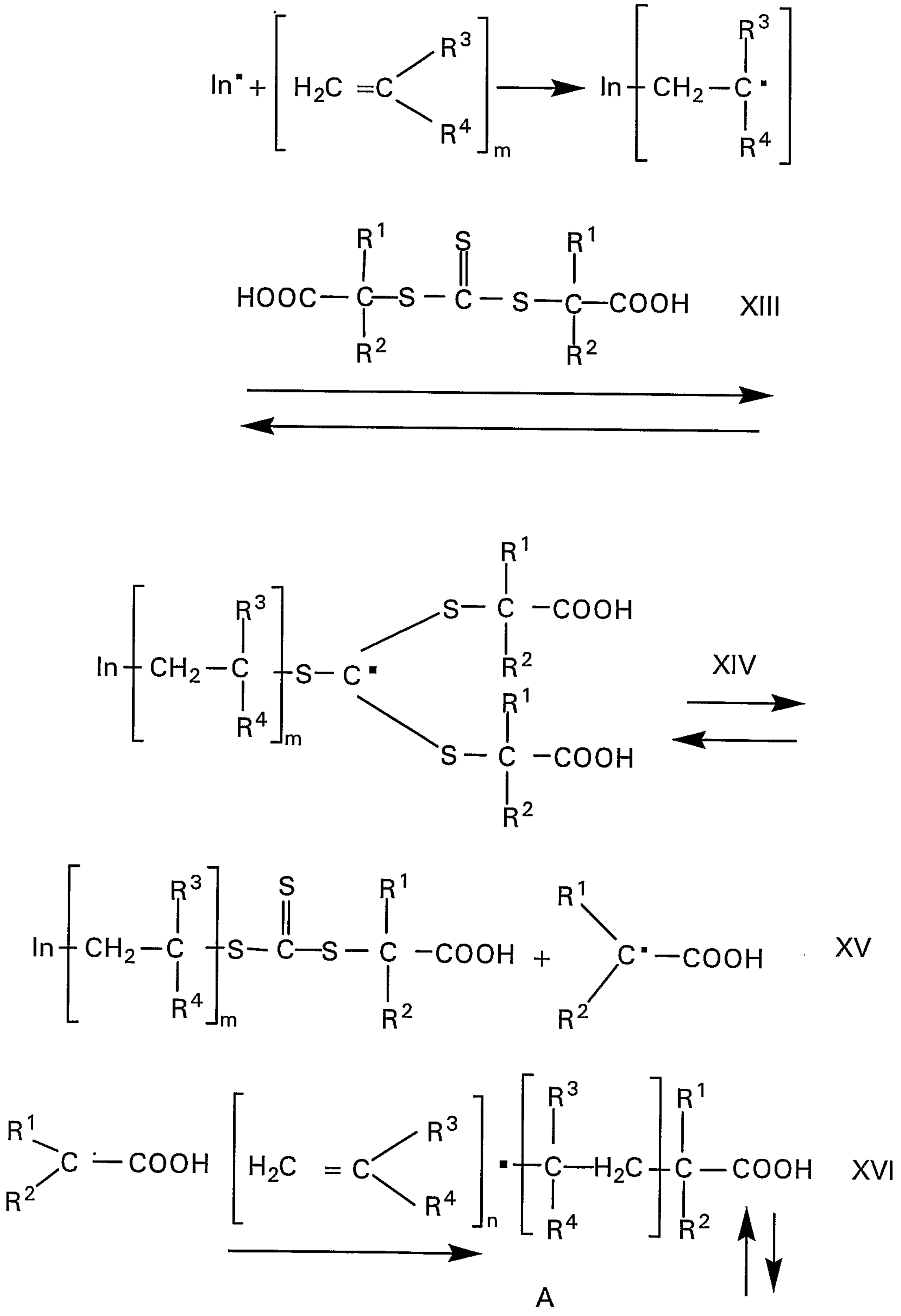
The preferred initiators of the present invention are 2,2'-azobis(isobutyronitrile)(AIBN), or 4,4'-azobis(4-cyanopentanoic acid), or 2,2'-azobis(2-cyano-2-butane), or 1,1'-azobis(cyclohexanecarbanitrile). The amount of initiators utilized in the polymerization process can vary widely as generally from about .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 chain transfer agent utilized. Preferably small amounts are utilized from about 0.1 percent to about 5, 10, 15, 20, or 25 mole percent based on the total moles of chain transfer agent utilized, i.e. said s,s'-bis-(α,α'-disubstituted -α" -acetic acid) - trithiocarbonate compounds. In order to form polymers which are predominately telechelic, initiators other than the s,s'-bis-(α,α'- disubstituted -α" -acetic acid) - trithiocarbonate 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 chain transfer agent utilized.

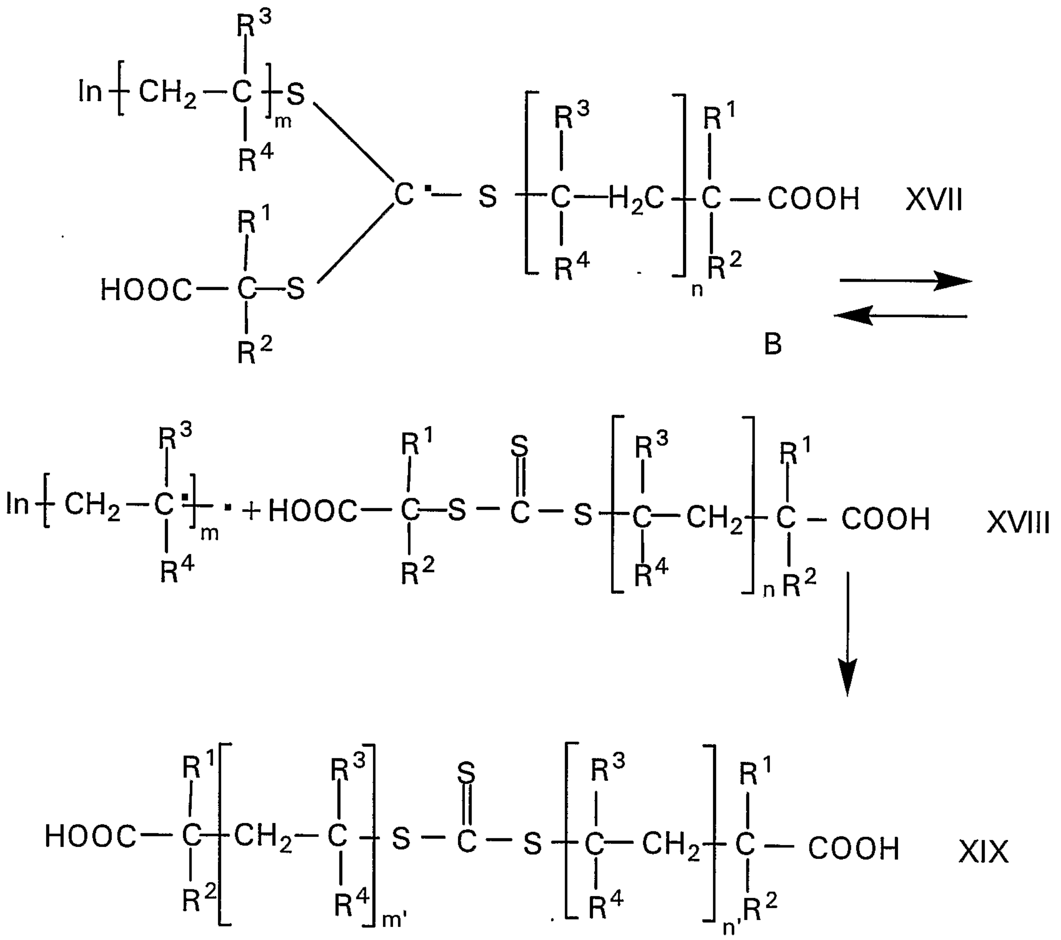
Optionally, as noted above, solvents may be utilized in the free radical polymerization process. Examples of such solvents include, but are not limited to, $C_6 - C_{12}$ alkanes, toluene, chlorobenzene, acetone, t-butyl alcohol, and dimethylformamide. The solvents are chosen so that they do not chain transfer themselves. The amount of solvent utilized in the present invention polymerization process is generally from about 10 percent to about 500 percent the weight of the monomer, and preferably from about 50 percent to about 200 percent the weight of the monomer utilized in the polymerization.

As stated above, it is preferable to utilize the s,s'-bis-(α,α'-disubstituted -α"-acetic acid) – trithiocarbonate compounds of the invention as chain transfer agents in the free radical polymerization process. The amount of chain transfer agent (CTA) utilized depends on the desired molecular weight of the polymer to be formed and can be calculated as known by one skilled in the art. A formula for calculating the amount of chain transfer agent is as follows:

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

While not wishing to be limited to any particular mechanism, it is believed that the mechanism of the free radical living polymerization process is as follows when using a vinyl monomer:


XIII
XIV
XV
XVI
A

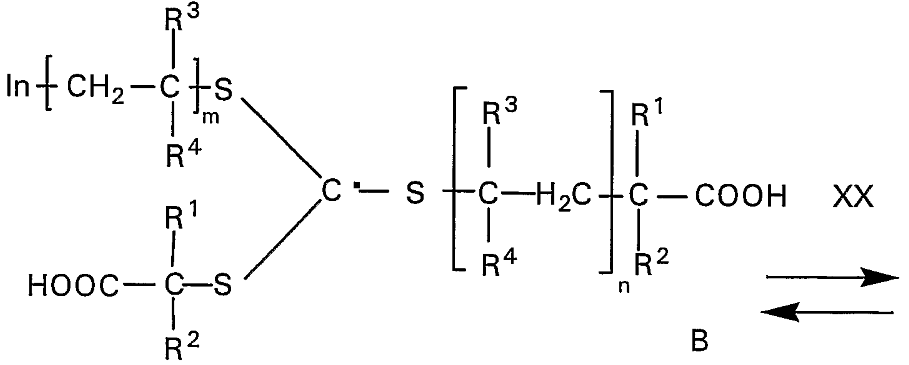


XVII

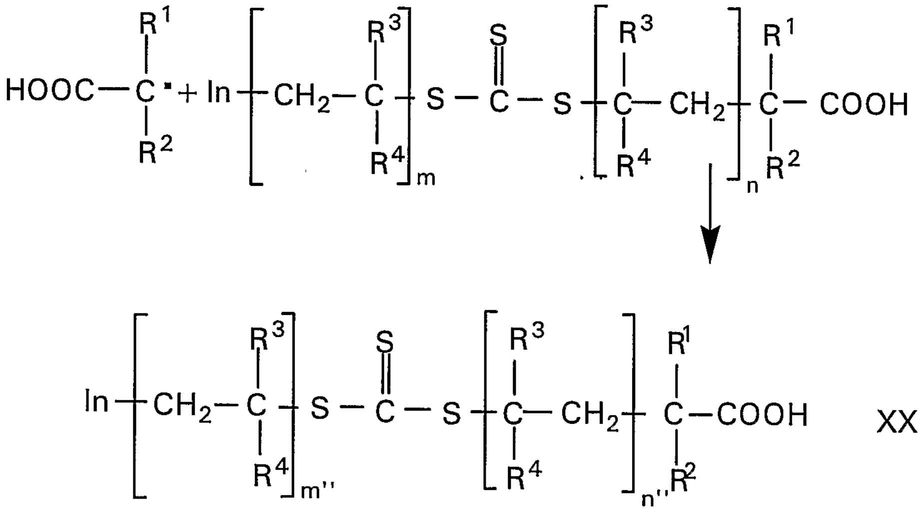
XVIII

XIX

Alternatively, the reaction can proceed as follows:



XX



XXI

$$HOOC-\overset{R^1}{\underset{R^2}{C}}{}^{\bullet} + In\left[CH_2-\overset{R^3}{\underset{R^4}{C}}\right]_m S-\overset{S}{\overset{\|}{C}}-S\left[\overset{R^3}{\underset{R^4}{C}}-CH_2\right]_n\overset{R^1}{\underset{R^2}{C}}-COOH$$

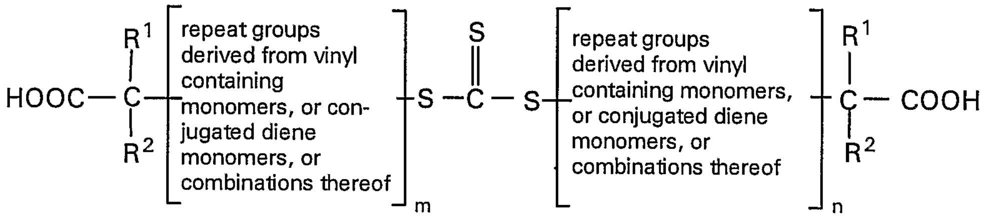
$$\downarrow$$

XXII

$$In\left[CH_2-\overset{R^3}{\underset{R^4}{C}}\right]_{m''} S-\overset{S}{\overset{\|}{C}}-S\left[\overset{R^3}{\underset{R^4}{C}}-CH_2\right]_{n''}\overset{R^1}{\underset{R^2}{C}}-COOH$$

As can be seen from the above mechanism, polymers having two different structures, see XIX and XXII, can be formed. The resulting polymers are either telechelic polymers (formed by the trithiocarbonate compounds of the present invention) with identical functional groups at the ends of the chain, or a polymer 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. Obviously, if the initiator is the only s,s'-bis-(α,α'-disubstituted -α" - acetic acid) - trithiocarbonate compound of the present invention, the resulting polymers are always telechelic. The greater the amount of the other initiator utilized, proportionally decreases the amount of telechelic polymers formed. Generally, the amount of the repeat group m, m', m", n, n', or n", is generally from about 1 to about 10,000, desirably from about 5 to about 500, and preferably from about 10 to about 200. Inasmuch as one or more vinyl monomers and/or one or more diene monomers can be utilized, it is to be understood that repeat groups of the polymers of the present invention are generally indicated by formulas XIX and XXII and can be the same or different. That is, random copolymers, terpolymers, etc., can be formed within either of the two repeat groups noted, as well as block copolymers which can be formed by initially adding one monomer and then subsequently adding a different monomer (e.g. an internal block copolymer).

The polymers formed by the present invention can be generally represented by the following formula:



$$HOOC-\overset{R^1}{\underset{R^2}{C}}-\left[\begin{array}{l}\text{repeat groups}\\\text{derived from vinyl}\\\text{containing}\\\text{monomers, or con-}\\\text{jugated diene}\\\text{monomers, or}\\\text{combinations thereof}\end{array}\right]_m-S-\overset{\overset{S}{\|}}{C}-S-\left[\begin{array}{l}\text{repeat groups}\\\text{derived from vinyl}\\\text{containing monomers,}\\\text{or conjugated diene}\\\text{monomers, or}\\\text{combinations thereof}\end{array}\right]_n-\overset{R^1}{\underset{R^2}{C}}-COOH$$

W

wherein such monomers are described herein above. Of course, the above formula can contain an initiator end group thereon as in XXII.

The reaction conditions are chosen as known to one skilled in the art 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 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 azo dicyanodivaleric 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°C to about 160°C, when s,s'-bis-(α, α' - disubstituted – α" – acetic acid) is utilized, the temperature is generally from about 80°C to about 200°C.

The low polydispersity polymers prepared as stated above by the free radical polymerization can contain reactive end groups from the monomers which are able to undergo further chemical transformation or reaction such as being joined with another polymer chain, such as to form block copolymers for example. Therefore, any of the above listed monomers, i.e.

conjugated dienes or vinyl containing monomers, can be utilized to form block copolymers utilizing the s,s'-bis-(α,α'-distributed $-\alpha''-$acetic acid) $-$ trithiocarbonate compounds as chain transfer agent. Alternatively, the substituents may be non-reactive such as alkoxy, alkyl, or aryl. Reactive groups should be chosen such that there is no adverse reaction with the chain transfer agents under the conditions of the experiment.

The process of this invention 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. Polymers with broad, yet controlled, polydispersity or with multimodal molecular weight distribution can be produced by controlled addition of the chain transfer agent over the course of the polymerization process.

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.

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 chosen medium, the chain transfer agent 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 + medium and initiator + 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.

Following completion of the polymerization, the polymer can be isolated by stripping off the medium and unreacted monomer(s) or by precipitation with a non-solvent. Alternatively, the polymer solution/emulsion can be used as such, if appropriate to its application.

The invention has wide applicability in the field of free radical polymerization and can be used to produce polymers and compositions for coatings, including clear coats and base coat finishes for paints for automobiles and other vehicles or industrial, architectural or maintenance finishes for a wide variety of substrates. Such coatings can further include pigments, durability agents, corrosion and oxidation inhibitors, rheology control agents, metallic flakes and other additives. Block and star, and branched polymers can be used as compatibilizers, thermoplastic elastomers, dispersing agents or rheology control agents. Additional applications for polymers of the invention are in the fields of imaging, electronics (e.g., photoresists), engineering plastics, adhesives, sealants, paper coatings and treatments, textile coatings and treatments, inks and overprint varnishes, and polymers in general.

As can be seen in the above shown polymerization mechanism, the s,s′-bis-(α,α'-disubstituted $-\alpha''$-acetic acid) – trithiocarbonate compound can be utilized to create telechelic polymers having two functional groups at both chain ends.

The term "telechelic polymer" was proposed in 1960 by Uraneck et al. to designate relatively low molecular weight macromolecules possessing one or more, and preferably two reactive functional groups, situated at the chain ends, thereof. The functional end groups of both the s,s'-bis-(α,α'-disubstituted –α"–acetic acid) – trithiocarbonate compound and the polymers formed therefrom, have the capacity for selective reaction to form bonds with another molecule. The functionality of a telechelic polymer or prepolymer is equal to the number of such end groups. Telechelic polymers containing a functional group, such as COOH, at each end are useful for synthesizing further chain extended copolymers and block copolymers.

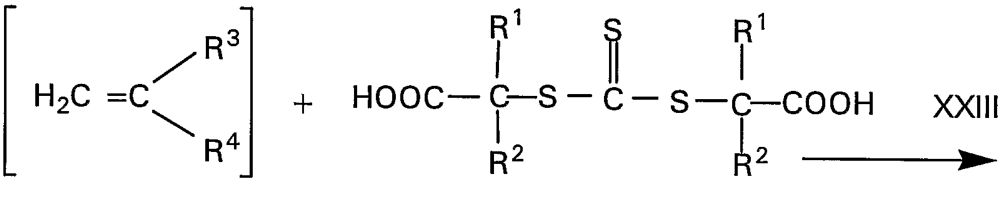
The interest in telechelic polymers resides in the fact that such polymers can be used, generally together with suitable linking agents, to carry out three important operations: (1) chain extension of short chains to long ones by means of bifunctional linking agents, (2) formation of networks by use of multifunctional linking agents, and (3) formation of (poly)block copolymers by combination of telechelics with different backbones. These concepts are of great industrial importance since they form the basis of the so-called "liquid polymer" technology exemplified by the "reaction injection molding" (RIM). Great interest has also been shown by the rubber industry because the formation of a rubber is based on network formation. In classical rubber technology, this is achieved by the cross-linking of long chains that show high viscosity. The classical rubber technology, therefore, requires an energy-intensive mixing operation. The use of liquid precursors, which can be end-linked to the desired network, offers not only processing advantages, but in some cases, also better properties of the end-product. Further information about telechelic polymers and synthesis thereof can be found in "Telechelic Polymers: Synthesis and Applications" by Eric J. Goethe, CRC Press, Boca Raton, Florida, 1989.

The reaction conditions for the reactive functional acid end groups of the telechelic polymers or s,s'-bis-(α,α'-disubstituted –α" – acetic acid) –

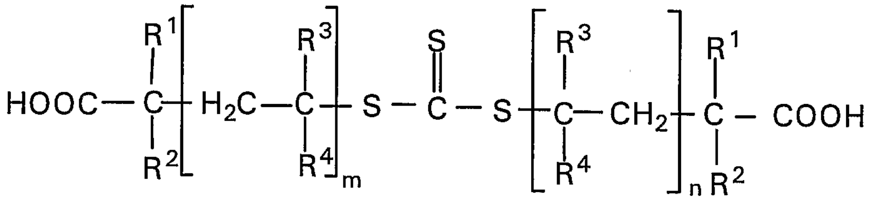
trithiocarbonate compounds of the present invention are generally the same as those for forming the above noted free radical polymers. The acid in the monomeric or in the polymeric form can be transformed to its derivatives in the conventional manner. For example, the ester can be made by refluxing the acid in alcohol with an acid catalyst with removal of water. Amides can be formed by heating the acid with an amine with the removal of water. 2-hydroxy-ethyl ester can be formed by directly reacting the acid with an epoxide with or without a catalyst such as triphenylphosphine or an acid like toluene-sulfonic acid. As seen by the examples below, any of the above noted monomers such as the one or more diene monomers or one or more vinyl containing monomers, can be utilized to form the telechelic monomers from the bis-(α,α'-distributed –α" –acetic acid) – trithiocarbonate compounds of the present invention. Any of the above noted components, such as solvent, etc., can be utilized in the herein above stated amounts.

The acid groups of the s,s'-bis-(α,α'-disubstituted –α" –acetic acid) – trithiocarbonate compound can be converted to other functional groups either before or after polymerization. Even if the s,s'-bis-(α,α'-disubstituted –α" –acetic acid) – trithiocarbonate compounds have functional end groups which have been converted from the acid end groups before polymerization, the monomers added during polymerization still add to the chain between the sulfur-tertiary carbon as shown in the mechanisms above as well as below at XXIII and XXIV. The carboxylic end groups of the s,s'-bis-(α,α'-disubstituted –α" –acetic acid) – trithiocarbonate compounds or the polymerized s,s'-bis-(α,α'-disubstituted –α" – acetic acid) – trithiocarbonate compounds can be converted or changed into other functional end groups such as esters, thioesters, amides, beta mercapto esters, beta hydroxy esters, or beta amino esters. Examples of these functional end groups are shown below.

An example reaction forming a telechelic polymer from the s,s'-bis-(α,α'-disubstituted -α" -acetic acid) – trithiocarbonate compounds of the invention when using a vinyl monomer is as follows:



$$\left[H_2C=C\begin{matrix}R^3\\R^4\end{matrix}\right] + HOOC-\underset{R^2}{\overset{R^1}{C}}-S-\overset{S}{\overset{\|}{C}}-S-\underset{R^2}{\overset{R^1}{C}}-COOH \qquad XXIII \longrightarrow$$

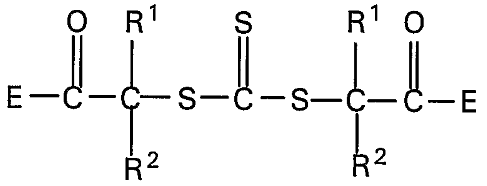


$$HOOC-\underset{R^2}{\overset{R^1}{C}}\left[H_2C-\underset{R^4}{\overset{R^3}{C}}\right]_m-S-\overset{S}{\overset{\|}{C}}-S\left[\underset{R^4}{\overset{R^3}{C}}-CH_2\right]_n\underset{R^2}{\overset{R^1}{C}}-COOH$$

XXIV

Of course, it is to be understood as indicated above, that the repeat units m and n can be derived either from conjugated diene monomers, or the indicated vinyl monomers, or combinations thereof, as generally set forth in formula W.

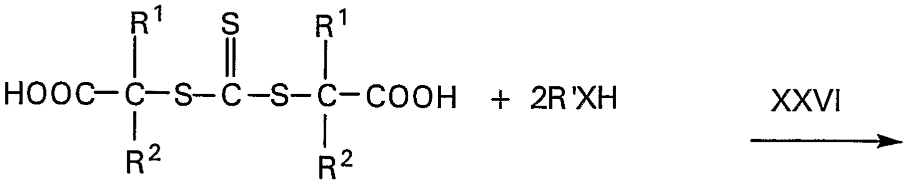
Subsequently, other functional end groups can be derived from the acid groups of the s,s'-bis-(α,α'-disubstituted -α" -acetic acid) – trithiocarbonate compound and can generally be represented by the formula:



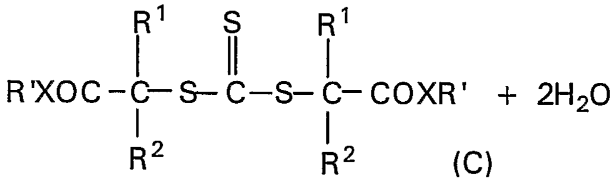
$$E-\overset{O}{\overset{\|}{C}}-\underset{R^2}{\overset{R^1}{C}}-S-\overset{S}{\overset{\|}{C}}-S-\underset{R^2}{\overset{R^1}{C}}-\overset{O}{\overset{\|}{C}}-E$$

XXV

where E is set forth below. For example,



$$HOOC-\underset{R^2}{\overset{R^1}{C}}-S-\overset{S}{\overset{\|}{C}}-S-\underset{R^2}{\overset{R^1}{C}}-COOH + 2R'XH \qquad XXVI \longrightarrow$$

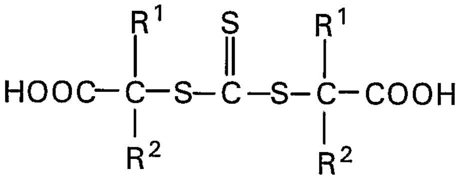


$$R'XOC-\overset{R^1}{\underset{R^2}{C}}-S-\overset{S}{\overset{\|}{C}}-S-\overset{R^1}{\underset{R^2}{C}}-COXR' \; + \; 2H_2O \quad (C)$$

XXVII

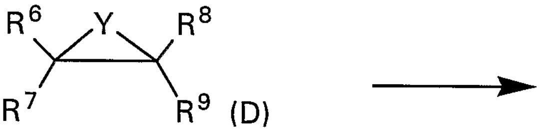
wherein E is XR′, that is R′, independently, comprises H, $C_1 - C_{18}$ alkyls which can be optionally substituted with one or more halogen, hydroxyl, or alkoxy, $C_1 - C_{18}$ hydroxyalkyls, and $C_1 - C_{18}$ aminoalkyls and X comprises oxygen, sulfur, NH, or NR′.

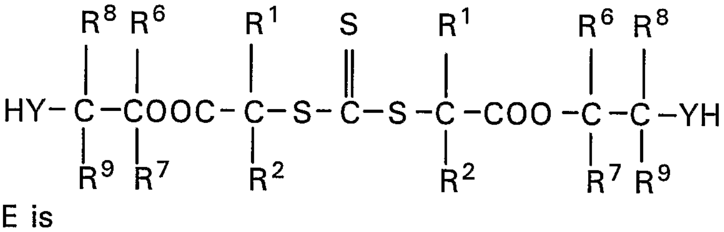
The following is still another example of functional end groups which can be derived from the acid:



$$HOOC-\overset{R^1}{\underset{R^2}{C}}-S-\overset{S}{\overset{\|}{C}}-S-\overset{R^1}{\underset{R^2}{C}}-COOH$$

XXVIII

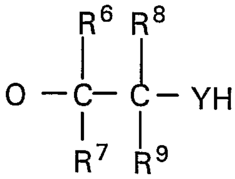




$$HY-\overset{R^8}{\underset{R^9}{C}}-\overset{R^6}{\underset{R^7}{C}}OOC-\overset{R^1}{\underset{R^2}{C}}-S-\overset{S}{\overset{\|}{C}}-S-\overset{R^1}{\underset{R^2}{C}}-COO-\overset{R^6}{\underset{R^7}{C}}-\overset{R^8}{\underset{R^9}{C}}-YH$$

XXIX

wherein E is



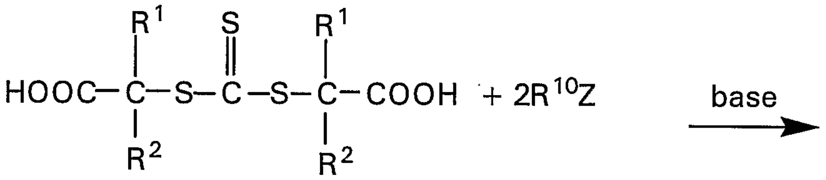
$$O-\overset{R^6}{\underset{R^7}{C}}-\overset{R^8}{\underset{R^9}{C}}-YH$$

XXX

that is where R^6 through R^9, independently comprise H, $C_1 - C_{18}$ alkyls, aryl groups or substituted aryl groups having from 1 to 6 substituents on the ring, such as halogen, hydroxyl, or alkoxy, $C_1 - C_{18}$ hydroxyalkys, $C_1 - C_{18}$

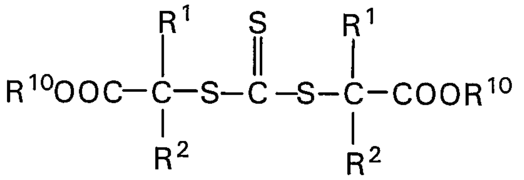
aminoalkyls, $C_1 - C_{18}$ mercapto alkyls, and the like. Y can comprise oxygen, sulfur, NH, or NR^6 to R^9.

A further example of still other functional end groups which can be derived from the acid groups of the s,s′-bis-(α,α′-disubstituted –α″ – acetic acid) – trithiocarbonate compounds is as follows:



$$HOOC-\underset{R^2}{\overset{R^1}{C}}-S-\overset{S}{\overset{\|}{C}}-S-\underset{R^2}{\overset{R^1}{C}}-COOH + 2R^{10}Z \xrightarrow{\text{base}}$$

XXXI



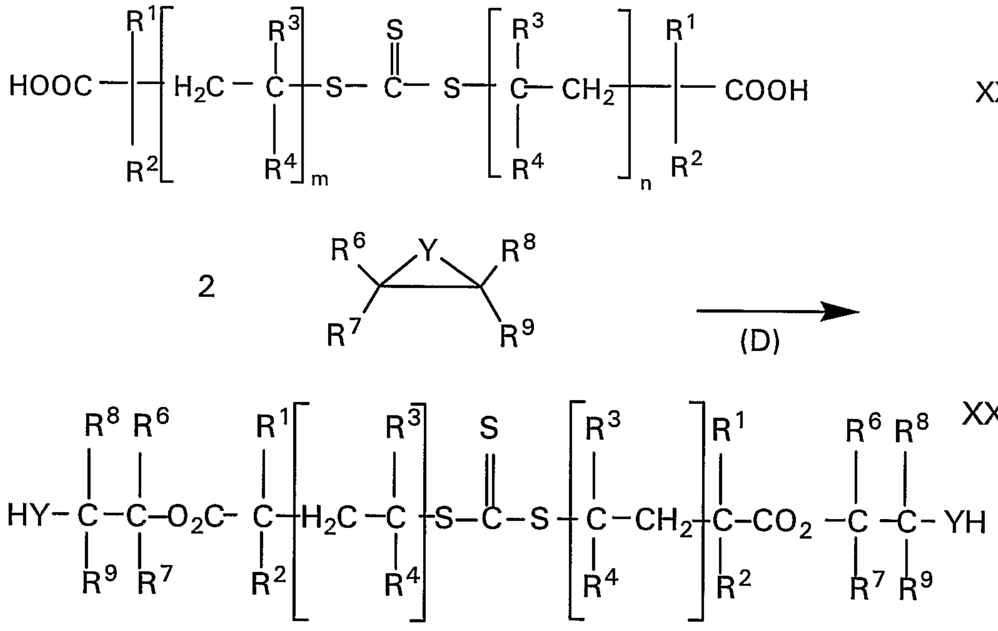
$$R^{10}OOC-\underset{R^2}{\overset{R^1}{C}}-S-\overset{S}{\overset{\|}{C}}-S-\underset{R^2}{\overset{R^1}{C}}-COOR^{10}$$

XXXII

wherein E is OR^{10}, that is where Z can comprise a leaving group, such as a halide or alkylsulfonate or aryl sulfonate. R^{10} can comprise $C_1 - C_{18}$, a alkyl or substituted alkyl wherein said substituent is halogen, hydroxyl, or alkoxy, $C_1 - C_{18}$ hydroxyalkyl or $C_1 - C_{18}$ amino alkyl and the like.

Preparation of the above shown methylesters of s,s′-bis-(2-methyl-2-propanoic acid) – trithiocarbonate is as follows: s,s′-bis-(2-methyl-2-propanoic acid) trithiocarbonate ($R^1,R^2 = CH^3$) (2.82g, 0.01 mole), Sodium carbonate powders (3.18g, 0.03 mole) and 15 ml dimethyl formamide were stirred under nitrogen at 40° C while a solution of methyliodide (3.41g, 0.024 mole) in 2 ml dimethylformamide was added dropwise over 10 minutes. The reaction was stirred at 40-50° C for 2 hours, poured into 25 ml H_2O and extracted 3 times with a total of 200 ml. ether. The etherate solution was dried over magnesium sulfate and concentrated. The yellow solid was further purified by recrystallization from hexanes. Infrared and H′NMR showed the above desired product.

An example of an already formed telechelic polymer, made from a vinyl monomer, undergoing conversion of the acid end group is as follows:

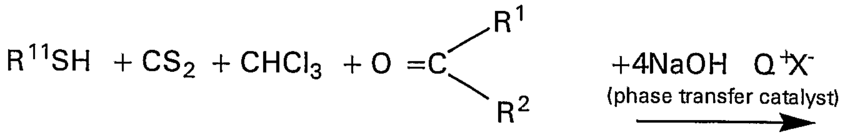

XXXIII

XXXIV

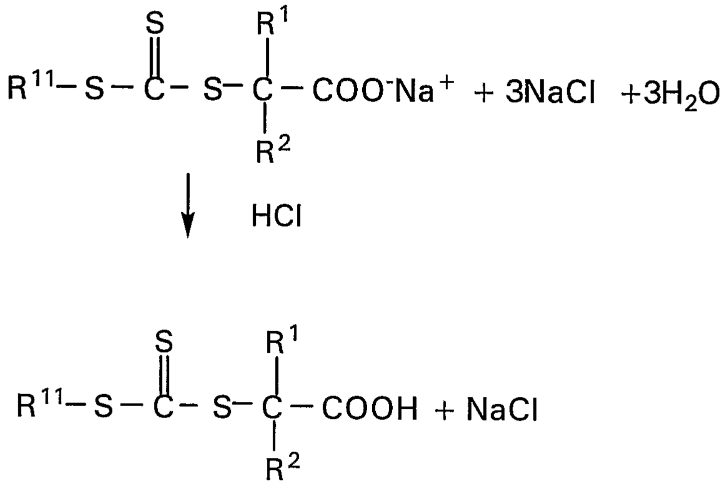
where m and n are as set forth above.

The above structure (XXXIV) was formed by reaction of epoxide with s,s'-bis-(2-methyl-2-propanoic acid) - trithiocarbonate (I)(R^1,R^2=CH_3, 0.01 mole) of the present invention and Epon® Resin 828 (Resolution Performance Products, reaction product of bisphenol A and epichlorohydrin, 80-85% diglycidyl ethers of bisphenol A) (70g) and trephenyl phosphine (0.12g) were heated to 95° C under nitrogen. The reaction was monitored for the disappearance of the carboxylic acid by titration. It was found the reaction was essentially complete in 1.5 hours. The product structure can be further confirmed by mass spectroscopy.

Another aspect of present invention further relates to forming the following compounds:


XXXV

$$R^{11}SH + CS_2 + CHCl_3 + O{=}C(R^1)(R^2) \xrightarrow[\text{(phase transfer catalyst)}]{+4NaOH\ Q^+X^-}$$



$$R^{11}-S-\overset{\overset{\displaystyle S}{\|}}{C}-S-\underset{\underset{\displaystyle R^2}{|}}{\overset{\overset{\displaystyle R^1}{|}}{C}}-COO^{-}Na^{+} + 3NaCl + 3H_2O \quad XXXVI$$

$$\downarrow HCl$$

$$R^{11}-S-\overset{\overset{\displaystyle S}{\|}}{C}-S-\underset{\underset{\displaystyle R^2}{|}}{\overset{\overset{\displaystyle R^1}{|}}{C}}-COOH + NaCl \quad XXXVII$$

wherein R^{11} comprises a benzyl group, C_1 – C_{18} alkyl, or substituted alkyl such as halogen, hydroxyl, or alkoxy, C_1 – C_{18} hydroxyalkyl, carboxylalkyl, or carboalkoxyalkyl. $Q^+ X$ is a phase transfer catalyst such as tetrabutylammoniumhydrogensulfate, or octadecyltrimethylammoniumchloride (Aliquot 336).

The resulting compound is an s – substituted alkyl – s'- (α,α' – disubstituted-α"–acetic acid) – trithiocarbonate. R^{11} is an alkyl having from 1 – 18 carbon atoms, aralkyl, hydroxyalkyl, cyanoalkyl, aminoalkyl, carboxylalkyl, or carboalkoxyalkyl, mercaptoalkyl, etc. R^1 and R^2 are as stated herein above.

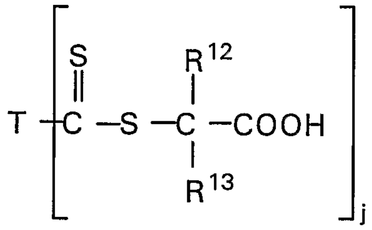
When s – substituted alkyl – s'- (α,α'–disubstituted-α"– acetic acid) – trithiocarbonate is employed either as an inifertor, or as a chain-transfer agent, unless R^{11} is carboxyl alkyl, only one end of the polymer has a carboxyl function, i.e. it is no longer a telechelic polymer.

While various polymers have been set forth herein above, it is to be understood that any of the carboxyl terminated polymers, such as W, or the E terminated polymers, and the like, can be reacted with one or more monomers and/or one or more polymers know to the art and to the literature to yield various resulting block polymers which are derived from the same monomer or from two or more different monomers. For example, each acid end group can be reacted with an excess of an epoxy compound such as a glycidyl bisphenol A and then subsequently polymerized with additional glycidyl bisphenol A to form an epoxy polymer. Naturally, other block polymers or copolymers can be reacted with the carboxylic end group or the other end groups generally denoted by E hereinabove.

Dithiocarbonates

I. Dithiocarbamates

A further embodiment of the present invention relates to dithiocarbonate compounds which have the general formula:



$$T\left[\overset{\overset{\displaystyle S}{\|}}{C}-S-\underset{\underset{\displaystyle R^{13}}{|}}{\overset{\overset{\displaystyle R^{12}}{|}}{C}}-COOH\right]_j$$

wherein j is 1 or 2, with the proviso that when j is 1, T is $-(NR^{15}R^{16})$; 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;

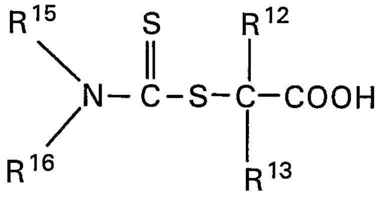
wherein R^{12} and R^{13}, independently, is the same or different, is optionally substituted, and is a linear or branched alkyl having from 1 to about 6 or about 12 carbon atoms; or an aryl group having from 6 to about 18 carbon atoms, optionally containing heteroatoms;

wherein the R^{12} and/or R^{13} substituents, independently, comprise an alkyl having from 1 to 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^{12} and R^{13} 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^{12} and R^{13} are preferably, independently, methyl or phenyl groups;

wherein R^{15} and R^{16}, independently, is the same or different, optionally is substituted, optionally contains heteroatoms; and is hydrogen; a linear or branched alkyl having 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^{15} and R^{16} can also be derived from amines such as, but not limited to, piperazine, morpholine, pyrrolidine, piperidine, 4-alkyl amino-2,2,6,6-tetramethyl piperidine, 1-alkylamioalkyl-3,3,5,5-tetramethyl-2-piperazinone, hexamethyleneimine, phenothiazine, iminodibenzyl, phenoxazine, N,N'-diphenyl-1,4-phenylenediamine, dicyclohexylamine and derivatives thereof. R^{15} and R^{16} 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^{15} and R^{16} substituents, independently, can be the same as described herein with respect to R^{14}. R^{15} and R^{16} are preferably, 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^{15} and R^{16}, independently, are hexamethylene.

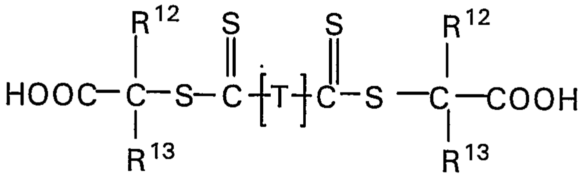
It is to be understood throughout the application formulas, reaction schemes, mechanisms, etc., and the specification that metals such as sodium or bases such as sodium hydroxide are referred to and the application of the present invention is not meant to be solely limited thereto. Other metals or bases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

When j is 1, T of above formula is $(NR^{15}R^{16})$ and the dithiocarbamate compound is a S-(α,α'-disubstituted-α''-acetic acid) dithiocarbamate generally having the following formula:



wherein R^{12}, R^{13}, R^{15}, and R^{16} are as defined hereinabove.

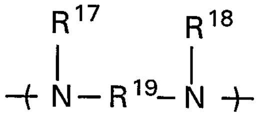
When j is 2, the dithiocarbarbamate compound is a bis-S-(α,α'-disubstituted-α''-acetic acid) dithiocarbamate having the following formula:



$$HOOC-C(R^{12})(R^{13})-S-C(=S)-[T]-C(=S)-S-C(R^{12})(R^{13})-COOH$$

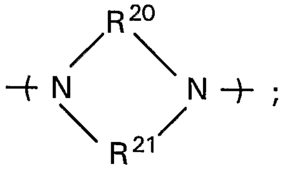
wherein R^{12} and R^{13} are defined hereinabove; and wherein T is a divalent bridging radical having a nitrogen atom directly connected to each of the thiocarbonyl groups present.

In one embodiment T is:



$$-[N(R^{17})-R^{19}-N(R^{18})]-$$

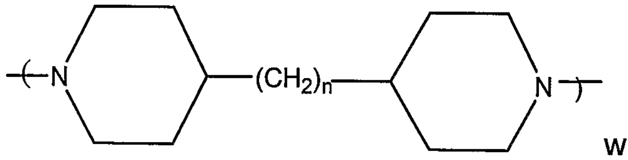
or



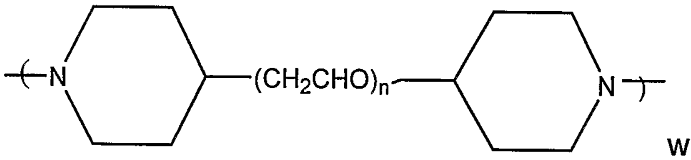
;

wherein R^{17} and R^{18}, independently, is the same or different, is optionally substituted, and is hydrogen, a linear or branched alkyl having from 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, an alkenealkyl having from 3 to about 18 carbon atoms, wherein the substitutents can be the same as described herein for R^1 and R^2; wherein R^{19} is optionally substituted, and is non-existent, or an alkylene group having from 1 to about 18 carbon atoms with about 1 to about 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^{20} and R^{21} 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^{20} and R^{21} preferably having a collective total of 3 to 5 carbon atoms.

In further embodiments, T is:

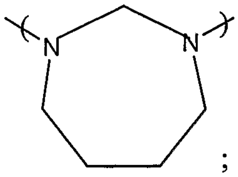


wherein n is 0 to about 18, with 0 to about 6 preferred;

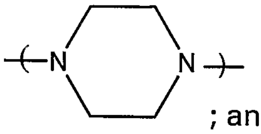


wherein n is 0 to about 18, with 0 to about 6 preferred;

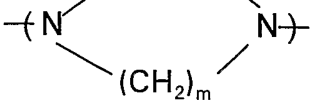
Some specific non-limiting examples of T bridging radicals are:



;



; and



wherein n plus m = 3 to 5;

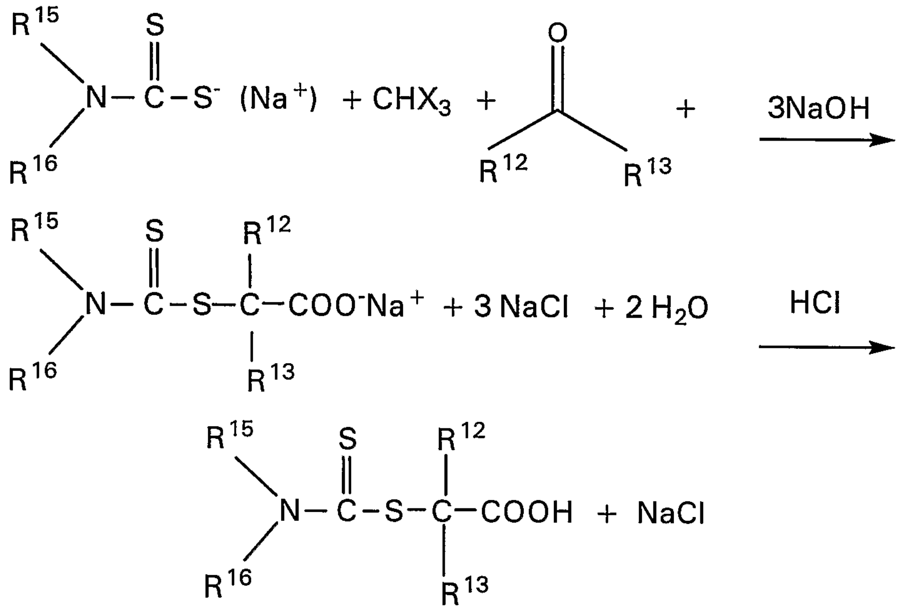
The S-(α,α'-disubstituted-α''-acetic acid) or bis S-(α,α'-disubstituted-α''-acetic acid) dithiocarbamates are generally a reaction product of a metal salt of a dithiocarbamate, a haloform, and a ketone. A phase transfer catalyst, solvent, and a base such as sodium hydroxide or potassium hydroxide can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

The metal salt of a dithiocarbamate is either prepared or purchased from a supplier such as Aldrich of Milwaukee, WI or Acros of Sommerville, NJ. Metal salts of dithiocarbamates are made in situ from amine, carbon disulfide, and a metal hydroxide as disclosed in the literature. Examples of metal salts of dithiocarbamates include sodium N,N-dimethyl dithiocarbamate and sodium N,N-diethyl-dithiocarbamate.

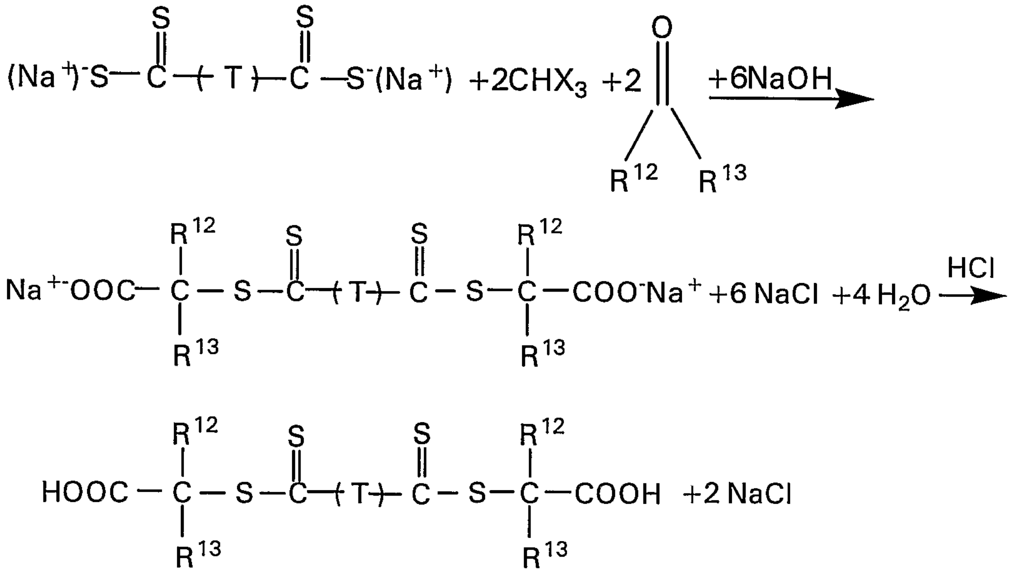
The S-(α,α'-disubstituted-α''-acetic acid) or bis S-(α,α'-disubstituted-α''-acetic acid) dithiocarbamate is formed by combining a metal salt of the dithiocarbamate with a haloform, a ketone, a base, optionally a solvent and a catalyst, in a reaction vessel preferably under an inert atmosphere. The base is preferably added to the other components over a period of time to maintain a preferred temperature range and avoid by-products. The reaction product is subsequently acidified, completing the reaction. The reaction product is isolated as a solid or liquid and is optionally purified.

The limiting agents of the reaction are usually the amine and carbon disulfide, or the metal salt of the dithiocarbamate when utilized. The haloform is utilized in the reaction in an amount from about 0 percent to about 500 percent molar excess, with about 50 percent to about 200 percent molar excess preferred. The ketone is utilized in the reaction in an amount from 0 percent to about 3000 percent molar excess, with about 100 percent to about 1000 percent molar excess preferred. The metal hydroxide when utilized, is present in an amount from 10 percent to 500 percent molar excess, with about 60 percent to 150 percent molar excess preferred.

The abbreviated reaction formula for the S-(α,α'-disubstituted-α''-acetic acid) dithiocarbamate of the present invention is generally as follows:



The abbreviated reaction formula for the bis S-(α,α'-disubstituted-α''-acetic acid) dithiocarbamate of the present invention is generally as follows:



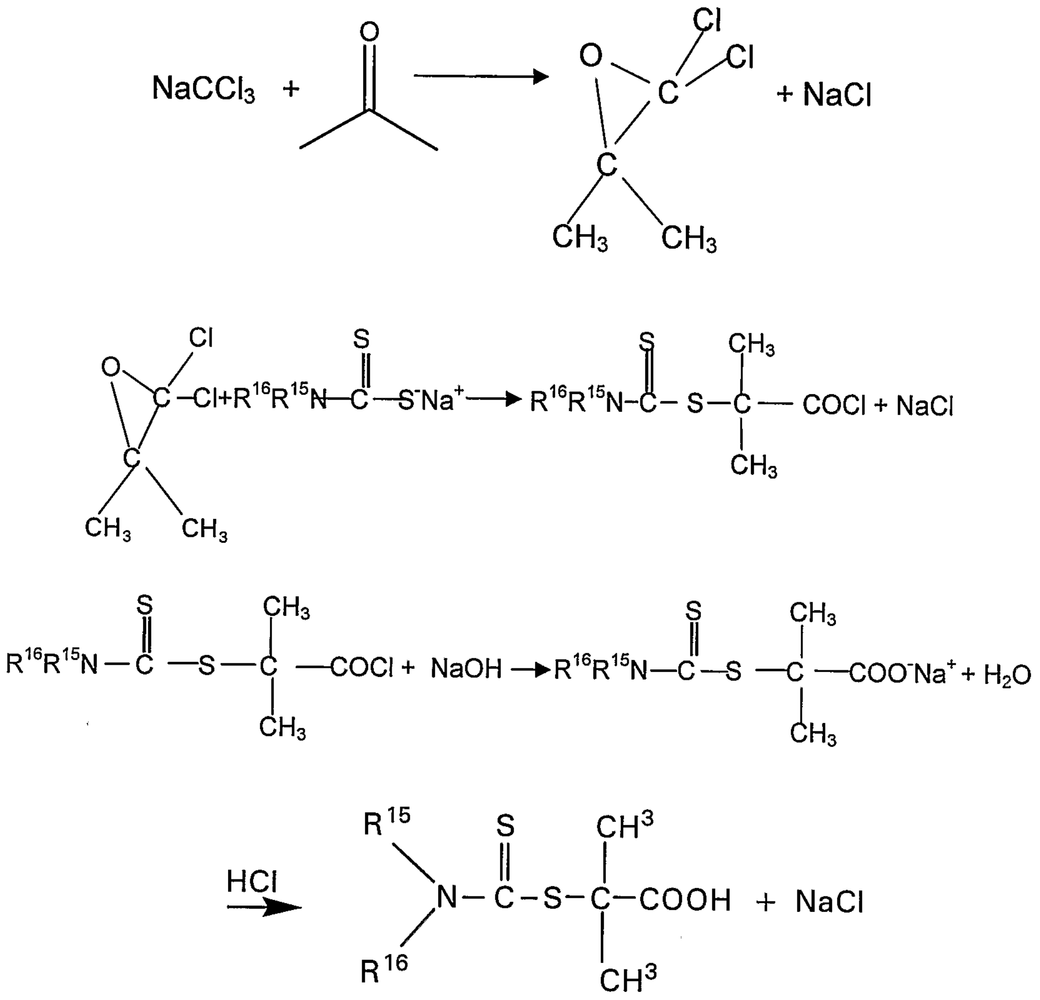
The reaction is carried out at a temperature sufficient to initiate and complete reaction of the reactants in order to produce the S-(α,α'-disubstituted-α''-acetic acid) or bis S-(α,α'-disubstituted-α''-acetic acid) dithiocarbamate compound in a desired time. The reaction can be carried out at any temperature within a wide range of from about the freezing point of the reaction mass to about the reflux temperature of the solvent. The reaction temperature is generally from about minus 15° C to about 80° C, desirably from about 0° C to about 50° C, and preferably from about 15° C to about 35° C, with about 15° C to about 25° C being preferred. The reaction can be performed at atmospheric pressure. The reaction time depends on several factors, with the temperature being most influential. The reaction is generally complete within 20 hours and preferably within about 10 hours.

A catalyst, preferably a phase transfer catalyst, is generally utilized when the optional solvent is used in the reaction. Examples of preferable catalysts and solvents are listed hereinabove and incorporated by reference. Preferred phase transfer catalysts include tricaprylmethylammonium chloride (Aliquot 336), benzyltriethylammonium chloride, and tetrabutylammonium hydrogen sulfate. The amount of catalyst and solvents utilized in the reaction to form the S-(α,α'-disubstituted-α''-acetic acid) or bis S-(α,α'-disubstituted-α''-acetic acid) dithiocarbamate compound are generally the same as set forth above and herein incorporated by reference. When the ketone is also the solvent, the catalyst is optionally eliminated from the process.

The ketones, haloforms, bases, and acids utilized in the dithiocarbamate reaction can be the same as those listed above for the trithiocarbonate synthesis and amounts thereof are herein incorporated by reference. Alternatively, an α-trihalomethyl-α-alkanol can be utilized in place of the haloform and ketone in the amounts noted hereinabove for the trithiocarbonate synthesis.

It is believed that the reaction scheme for the formation of the S-(α,α'-disubstituted-α''-acetic acid) dithiocarbamate is as follows:

$$CHCl_3 + NaOH \longrightarrow Na^{-}CCl_3 + H_2O$$

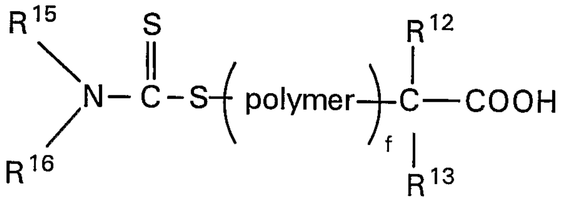


wherein R^{15} and R^{16} are defined hereinabove. The reaction scheme for the formation of the bis S-(α,α'-disubstituted-α''-acetic acid) dithiocarbonate is similar to the above reaction scheme and obvious to one of ordinary skill in the art. A phase transfer catalyst such as tetrabutylammoniumhydrogensulfate or octadecyltrimethylammoniumchloride (Aliquot 336) as mentioned above is utilized in a preferred embodiment.

The S-(α,α'-disubstituted-α''-acetic acid) or bis S-(α,α'-disubstituted-α''-acetic acid) dithiocarbamate compounds are utilized in essentially the same manner as the trithiocarbonate compounds mentioned hereinabove. That is, the S-(α,α'-disubstituted-α''-acetic acid) or bis S-(α,α'-disubstituted-α''-acetic acid) dithiocarbamate compounds in various embodiments are utilized as initiators to initiate or start the polymerization of a monomer, as a chain transfer agent which interrupts and terminates the growth of a polymer chain by formation of a new radical which can act as the nucleus for forming a new polymer chain, and/or as a terminator which are incorporated into a polymer as a dormant species. Preferably, the S-(α,α'-disubstituted-α''-acetic acid) or bis S-(α,α'-disubstituted-α''-acetic acid) dithiocarbamate compounds are utilized as chain transfer agents in free radical polymerizations having living characteristics to provide polymers of controlled molecular weight and low polydispersity.

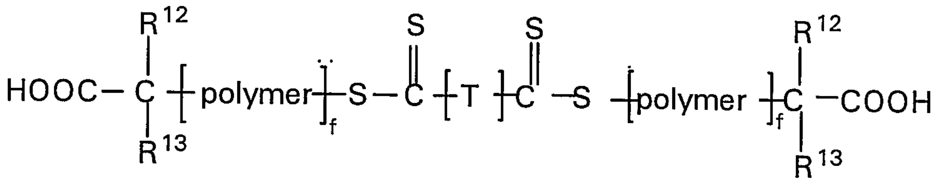
Dithiocarbamate (Co)Polymers

To this end, the present invention also relates to both a process for forming polymers or copolymer derived from the dithiocarbamate compounds having the following general formulae:



$$(R^{15})(R^{16})N-\overset{\overset{S}{\|}}{C}-S\left(\text{polymer}\right)_f\underset{R^{13}}{\overset{R^{12}}{C}}-COOH$$

or

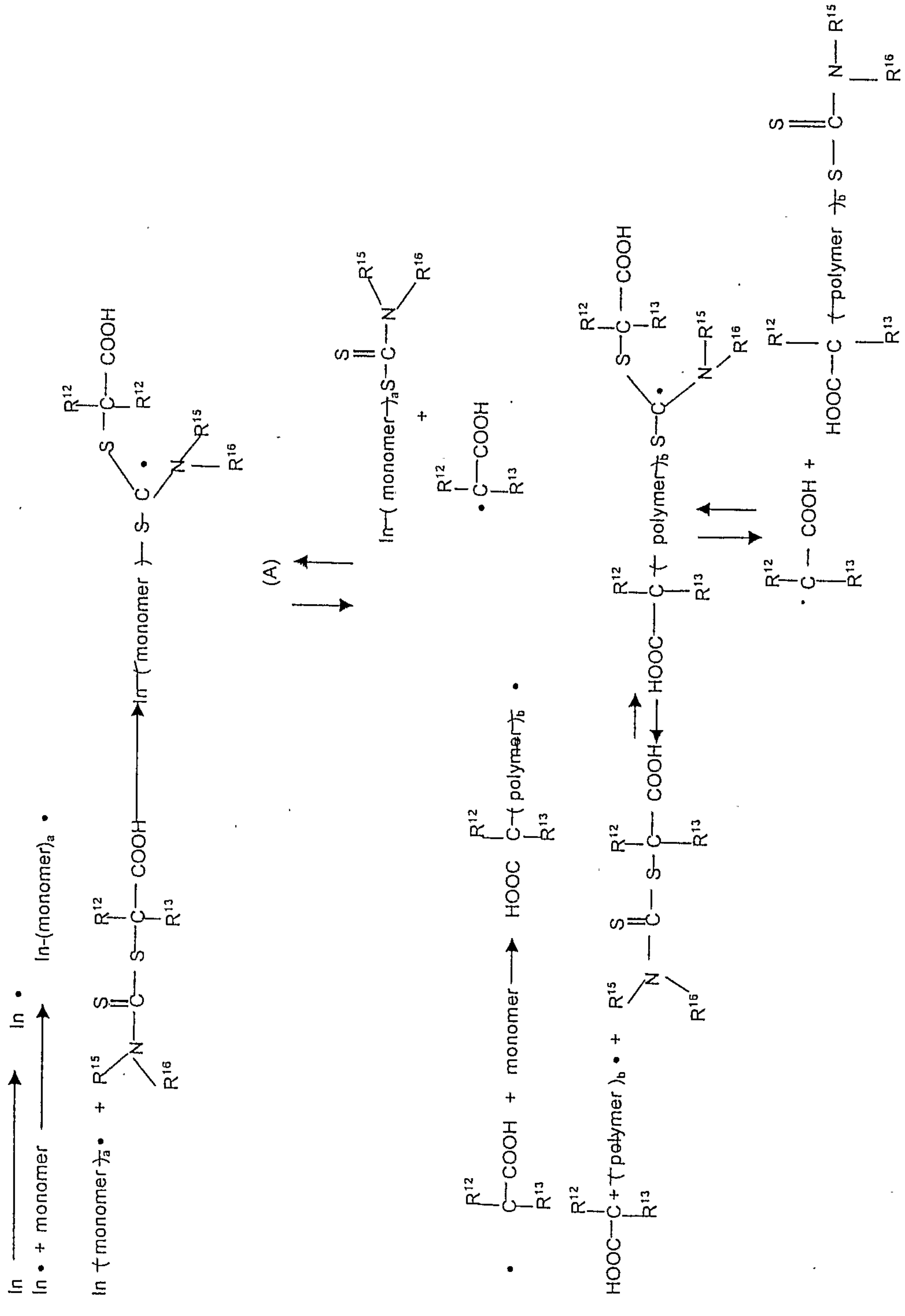


$$HOOC-\underset{R^{13}}{\overset{R^{12}}{C}}\left[\text{polymer}\right]_f S-\overset{\overset{S}{\|}}{C}\left[T\right]\overset{\overset{S}{\|}}{C}-S\left[\text{polymer}\right]_f\underset{R^{13}}{\overset{R^{12}}{C}}-COOH$$

wherein R^{12}, R^{13}, R^{15}, R^{16} and T are defined hereinabove, wherein the polymer is derived from a monomer as described herein, such as but not limited to, a conjugated diene monomer, or a vinyl containing monomer, or combinations thereof, wherein each polymer repeat unit is the same or different, and wherein f is generally from 1 to about 10,000, and preferably from about 3 to about 5,000. Preferred polymers are derived from alkyl acrylate, vinyl acetate, acrylic acid, and styrene. Of course, it is to be understood that when f is 1, the polymer is a single reacted monomer unit.

The above dithiocarbamate polymers or copolymers can be prepared by bringing into contact with each other the monomer(s) which form(s) the (polymer) repeat units and the S-(α,α'-disubstituted-α''-acetic acid) or bis S-(α,α'-disubstituted-α''-acetic acid) dithiocarbamate compounds, and optionally, a) solvent and b) a radical polymerization initiator; in suitable amounts, as described herein.

It is believed the polymer forming mechanism for the S-(α,α'-disubstituted-α''-acetic acid) dithiocarbonate compound is as follows:


In
In •
In • + monomer
In-(monomer)a •
(A)
HOOC
COOH
R12
R13
R15
R16
polymer
monomer

The mechanism for the bis S-(α,α'-disubstituted-α''-acetic acid) dithiocarbonate compound is similar to the above-noted mechanism and obvious to one of ordinary skill in the art.

As illustrated by the above reaction formulas, the monomers are polymerized into the dithiocarbamate compounds adjacent to the thiocarbonylthio linkage, between the single bonded sulfur atom and the tertiary carbon atom of the compound.

The dithiocarbamate compounds of the present invention are used to produce polymers which are substantially colorless. The polymers or copolymers of the dithiocarbamate compounds are hydrolytically stable because the electro-donating amino groups render the thiocarbonyl group less electrophilic. The polymers are also stable toward nucleophiles such as amines.

The reaction conditions are chosen as known to one ordinarily skilled in the art so that the temperature utilized will generate a radical in a controlled fashion with the temperature being generally from about room temperature to about 200°C. The reaction can be performed at temperatures 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°C to about 160°C, and when S-(α,α'-disubstituted-α''-acetic acid) or bis S-(α,α'-disubstituted-α''-acetic acid) dithiocarbamate is utilized, the temperature is generally from about 120°C to about 200°C.

The low polydispersity polymers prepared as stated above by the free radical polymerization can contain reactive end groups from the monomers which are able to undergo further chemical transformation or reaction such as being joined with another polymer chain, such as to form copolymers for example. Therefore, any of the above listed monomers, i.e. conjugated dienes or vinyl containing monomers, are utilized to form copolymers utilizing the S-(α,α'-disubstituted-α''-acetic acid) or bis S-(α,α'-disubstituted-α''-acetic acid) dithiocarbamate compounds as chain transfer agent. Moreover, in one embodiment the polymers are crosslinked using a crosslinker during polymerization. Suitable crosslinkers include, but are not limited to, polyallyl pentaerythritol, polyallyl sucrose, trimethylol propane diacrylate, trimethylol propane triacrylate, glycerol triacrylate, methylene bis-acrylamide and ethylene-glycol diacrylate. Alternatively, the substituents may be non-reactive such as alkoxy, alkyl, or aryl. Reactive groups should be chosen such that there is no adverse reaction with the chain transfer agents under the conditions of the experiment.

The process of this invention is carried out in emulsion, solution or suspension in either a batch, semi-batch, continuous, or feed mode. Bulk polymerization (no solvent) is also achieved because propagation is slower. 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. The polydispersity of polymers or copolymers produced from the dithiocarbamates is generally less than about 3.0. 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. Polymers with broad, yet controlled, polydispersity or with multimodal molecular weight distribution can be produced by controlled addition of the chain transfer agent over the course of the polymerization process.

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.

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 chosen medium, the chain transfer agent 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 still another separate vessel. The medium in the reactor is heated and stirred while the monomer + medium and initiator + 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.

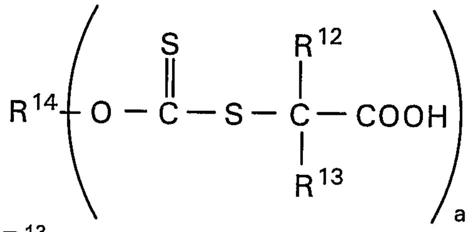
Following completion of the polymerization, the polymer can be isolated by stripping off the medium and unreacted monomer(s) or by precipitation with a non-solvent. Alternatively, the polymer solution/emulsion can be used as such, if appropriate to its application. The applications for the S-(α,α'-disubstituted-α''-acetic acid) dithiocarbamate compounds include any of those listed hereinabove with regard to the trithiocarbonate compounds.

Derivatives of the dithiocarbamate polymers or copolymers can also be formed including esterification products from the alcohol and/or diol end groups present. Thioesters can be formed utilizing mercaptan, and amides can be formed from amines, etc. Ammonium salts can be formed from primary, secondary, and tertiary amines. Metal salts can be formed from alkaline or alkaline earth hydroxides, oxides and the like.

The invention has wide applicability in the field of free radical polymerization and can be used to produce polymers and compositions for coatings, including clear coats and base coat finishes for paints for automobiles and other vehicles or industrial, architectural or maintenance finishes for a wide variety of substrates. Such coatings can further include conventional additives such as pigments, durability agents, corrosion and oxidation inhibitors, rheology control agents, metallic flakes and other additives. Block, star, and branched polymers can be used as compatibilizers, thermoplastic elastomers, dispersing agents or rheology control agents. Additional applications for polymers of the invention are in the fields of imaging, electronics (e.g., photoresists), engineering plastics, adhesives, sealants, paper coatings and treatments, textile coatings and treatments, inks and overprint varnishes, and polymers in general.

II. Alkoxy Dithiocarbonates

Yet another embodiment of the present invention relates to alkoxy dithiocarbonate compounds having the following formulae:



$$R^{14}\left(O - \overset{\overset{S}{\|}}{C} - S - \underset{R^{13}}{\overset{R^{12}}{C}} - COOH \right)_a$$

wherein R^{12} and R^{13} are as defined hereinabove;

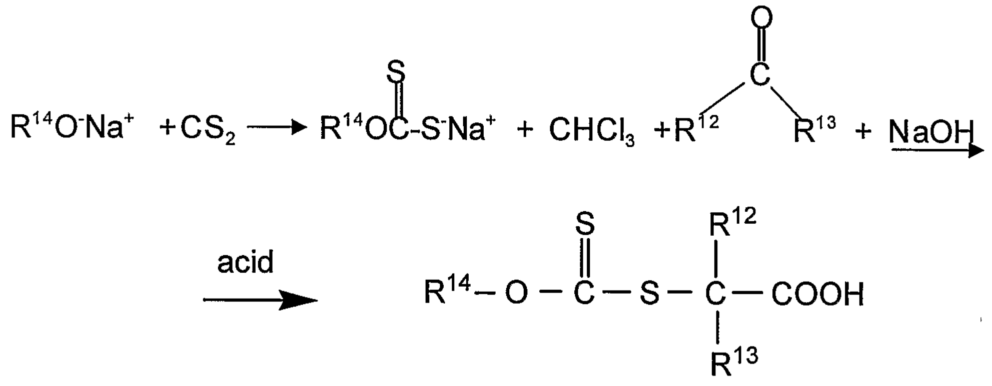
wherein R^{14} is optionally substituted, and can be a linear or branched alkyl having from 1 to about 12 carbon atoms; an aryl group, optionally saturated or unsaturated; an arylalkyl having from 7 to about 18 carbon atoms; an acyl group; an alkenealkyl having from 3 to about 18 carbon atoms; an alkene 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 6 carbon atoms are preferred;

wherein the R^{14} substituents comprise an alkyl having from 1 to 6 carbon atoms; an aryl; a halogen such as fluorine or chlorine; 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; guanidimo group; allyl group; epoxy group; alkoxy group; an alkali metal salt; a cationic substitutent 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 hexanoxy; 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.

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.

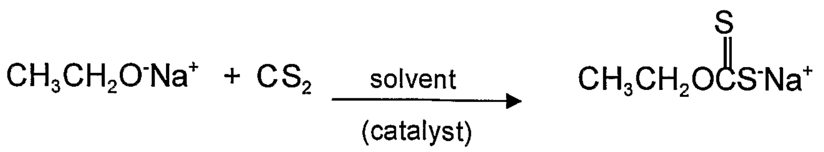
The alkoxylate salt or carbon disulfide, or alternatively the metal salt of xanthate are typically the limiting agents for the reaction. The haloform is utilized in the reaction in an amount generally from 0 percent to about 500 percent molar excess, and preferably from about 50 to about 200 percent molar excess. The ketone is utilized in the reaction in an amount generally from 0 percent to about 3000 percent molar excess, and preferably from about 100 percent to about 1000 percent molar excess. The metal hydroxide when utilized, is present in an amount from 10 percent to 500 percent molar excess, with about 60 percent to 150 percent molar excess preferred.

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



The preparation of the O-alkyl-S-(α,α'-disubstituted-α"-acetic acid) xanthates begins with the addition of a xanthate, i.e., a salt of xanthic acid to a reaction vessel, preferably equipped with an agitating device, thermometer, addition funnel, and a condenser. The xanthate can be prepared from an alkoxylate salt and carbon disulfide as known in the art.

For example, the sodium salt of O-ethyl xanthate, $CH_3CH_2OC(S)S^-Na^+$, can be prepared from sodium ethoxide and carbon disulfide in the presence of a solvent such as an acetone, and optionally a catalyst, such as Aliquot 336 or other catalyst stated herein or known in the art, in a reaction vessel, preferably at about 0° to about 25°C. The general reaction is:



$$CH_3CH_2O^-Na^+ + CS_2 \xrightarrow[\text{(catalyst)}]{\text{solvent}} CH_3CH_2O\overset{\overset{S}{\|}}{C}S^-Na^+$$

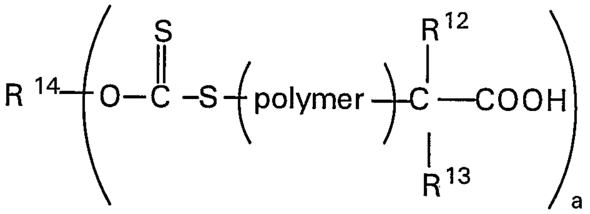
The metal salt of O-ethyl xanthate is also commercially available from sources such as Aldrich Chemical of Milwaukee, WI.

In a further step, a ketone, a haloform, optionally a solvent, and a catalyst, all as described hereinabove, are added to the reaction vessel containing the xanthate metal salt. When the ketone is used as the solvent, the catalyst is optionally eliminated from the process. A strong base as noted hereinabove is added to the mixture, preferably over an extended period of time. The reaction components are preferably mixed throughout the reaction. The reaction product is subsequently acidified with an acid as noted hereinabove, completing the reaction and forming the O-alkyl-S-(α,α'-disubstituted-α"-acetic acid) xanthate. The reaction is conducted at a temperature generally from about 0° C to about 80° C, and preferably from about 15° C to about 50° C, with room temperature being preferred. The reaction can be performed at atmospheric pressure under an inert atmosphere. The reaction time generally depends on temperature, and generally is complete within 20 hours, and preferably within 10 hours. An α-trihalomethyl-α-alkanol can be utilized in place of a haloform and ketone, as noted hereinabove with regard to the trithiocarbonate compounds.

The O-alkyl-S-(α,α'-disubstituted-α"-acetic acid) xanthates can be utilized as an initiator to initiate or start the polymerization of a monomer, as a chain transfer agent which interrupts and terminates the growth of a polymer chain by formation of a new radical which can act as the nucleus for forming a new polymer chain, and/or as a terminator which are incorporated into a polymer as a dormant species. Preferably, the O-alkyl-S-(α,α'-disubstituted-α"-acetic acid) xanthates are utilized as chain transfer agents in free radical polymerizations having living characteristics to provide polymers of controlled molecular weight and low polydispersity.

Xanthate (Co)Polymers

Polymers or copolymers of the following formulas can be prepared from the O-alkyl-S-(α,α'-disubstituted-α"-acetic acid) xanthates:

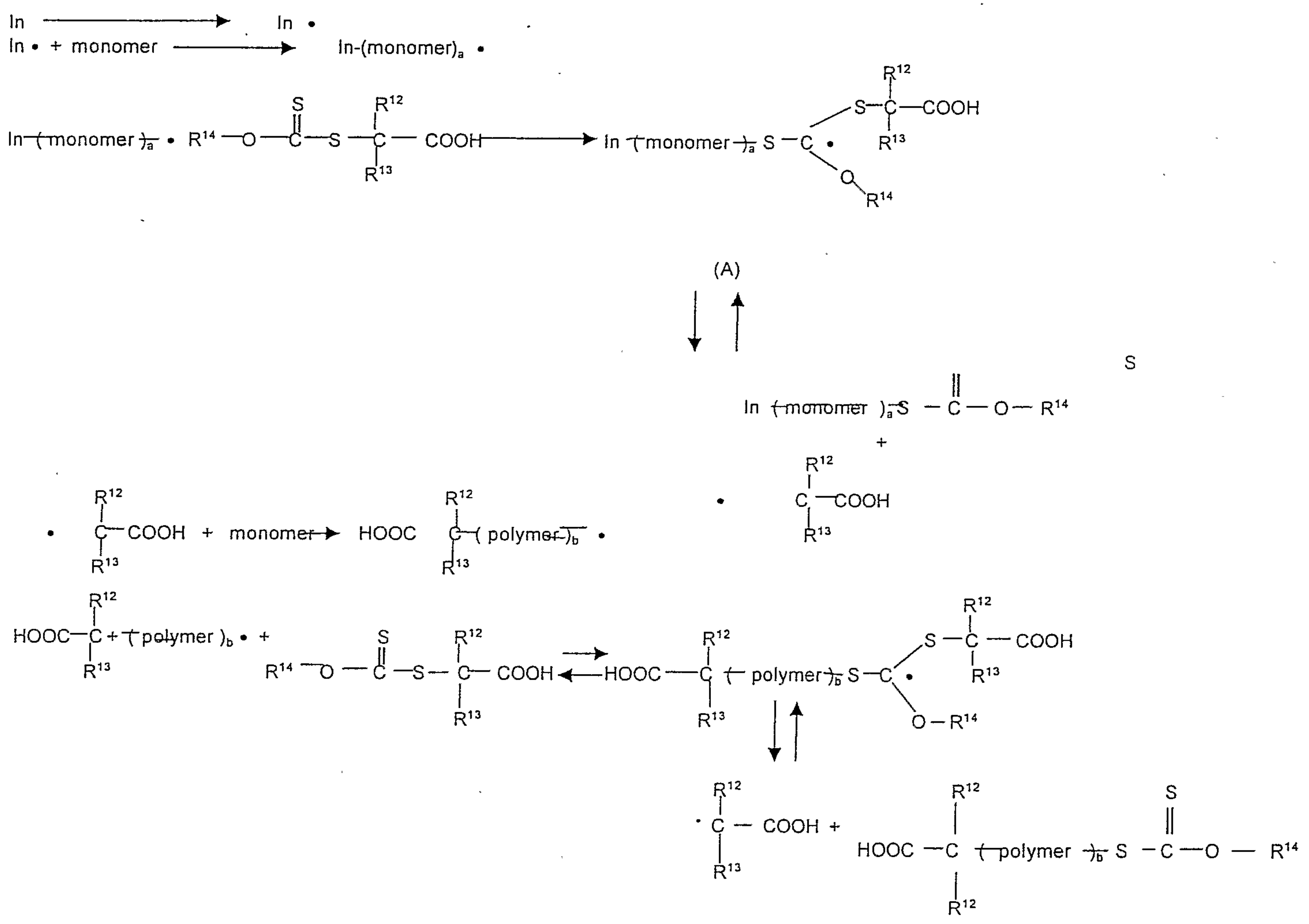


$$R^{14}\left(O-\overset{\overset{\displaystyle S}{\|}}{C}-S\left(\text{polymer}\right)\underset{\underset{\displaystyle R^{13}}{|}}{\overset{\overset{\displaystyle R^{12}}{|}}{C}}-COOH\right)_a$$

wherein a, R^{12}, R^{13}, and R^{14} are as defined hereinabove, wherein the polymer is derived from a conjugated diene monomer, or a vinyl containing monomer, or combinations thereof, as defined hereinabove and incorporated by reference, and wherein each g repeat unit, independently, is the same or different and is generally from 1 to about 10,000, and preferably from about 5 to about 500. Preferred monomers are alkyl acrylates, acrylic acid, and styrene. Of course, it is to be understood that when g is 1, the polymer is a single reacted monomer unit.

The above polymers or copolymers can be prepared by bringing into contact with each other the monomer(s) which form O-alkyl-S-(α,α'-disubstituted-α"-acetic acid) xanthate compound, and optionally a) solvent, and b) a radical polymerization initiator; in suitable amounts, as described hereinabove.

It is believed the mechanism is as follows:



As illustrated by the above mechanism, the monomers are polymerized into the xanthate compounds adjacent to the thiocarbonylthio linkage, between the single bonded sulfur atom and the tertiary carbon atom of the compound.

The O-alkyl dithiocarbonate compounds of the present invention can be used to produce polymers which are substantially colorless. The polymers or copolymers of the O-alkyl dithiocarbanate compounds are more hydrolytically stable because the electro-donating amino groups render the thiocarbonyl group less electrophilic and the polymers are stable toward nucleophiles such as amines.

The reaction conditions are chosen as known to one skilled in the art 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 performed at temperatures 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°C to about 160°C, and when O-alkyl-S-(α,α'-disubstituted-α''-acetic acid) xanthate is utilized, the temperature is generally from about 80°C to about 200°C.

As noted above with respect to the dithiocarbamate compounds, the polymers or copolymers prepared from the O-alkyl-S-(α,α'-disubstituted-α''-acetic acid) xanthate contain reactive end groups which are able to further undergo chemical transformation or reaction in order to be joined with another polymer chain, in order to form extended copolymers for example. The process of the invention can be carried out, for example, in emulsion solution or suspension in either a batch, semi-batch, continuous, bulk or feed mode.

Conventional procedures can be used to produce narrow polydispersity polymers. For lowest polydispersity polymers, the chain transfer agent is added before polymerization is commenced. The polydispersity of the xanthate polymers or copolymers is generally less than about 3.0. 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. Polymers with broad, yet controlled, polydispersity or with multimodal molecular weight distribution can be produced by controlled addition of the chain transfer agent over the course of the polymerization process.

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.

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 chosen medium, the chain transfer agent 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 + medium and initiator + 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.

Following completion of the polymerization, the polymer can be isolated by stripping off the medium and unreacted monomer(s) or by precipitation with a non-solvent. Alternatively, the polymer solution/emulsion can be used as such, if appropriate to its application. The applications for the O-alkyl-S-(α,α'-disubstituted-α''-acetic acid) xanthate dithiocarbonate compounds include any of those listed hereinabove with regard to the trithiocarbonate and dithiocarbamate compounds.

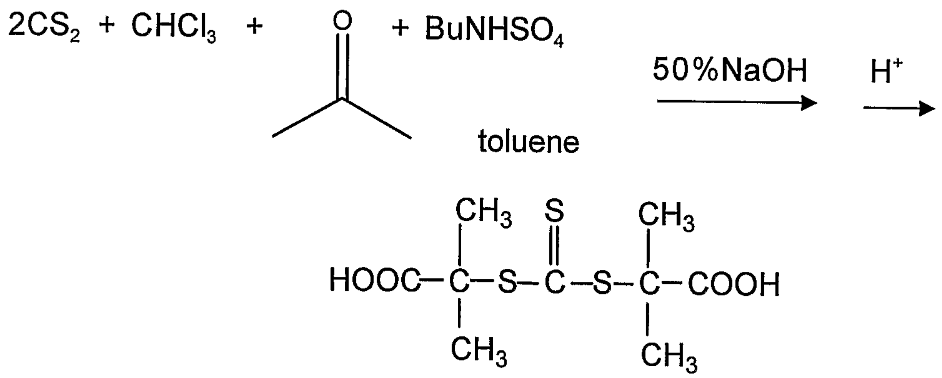
The dithiocarbonate compounds of the invention have wide applicability in the field of free radical polymerization and can be used as thickeners and to produce polymers and compositions for coatings, including clear coats and base coat finishes for paints for automobiles and other vehicles or industrial, architectural or maintenance finishes for a wide variety of substrates. Such coatings can further include pigments, durability agents, corrosion and oxidation inhibitors, rheology control agents, metallic flakes and other additives. Block and star, and branched polymers can be used as compatibilizers, thermoplastic elastomers, dispersing agents or rheology control agents. Additional applications for polymers of the invention are composites, potting resins, foams, laminate, in the fields of imaging, electronics (e.g., photoresists), engineering plastics, adhesives, sealants, paper coatings and treatments, textile coatings and treatments, inks and overprint varnishes, and polymers in general, and the like.

The present invention will be better understood by reference to the following examples which serve to describe, but not to limit, the present invention.

EXAMPLES:

EXAMPLE 1

Synthesis of s,s'-bis-(α, α' - disubstituted – α" – acetic acid) – trithiocarbonate, ($R^1 = R^2 = CH_3$)

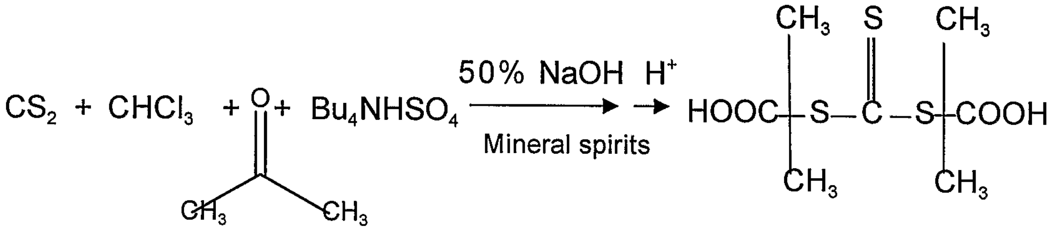


Procedure:

In a 500 ml jacketed flask equipped with a mechanical stirrer, a thermometer, a reflux condenser and an addition funnel added 22.9 grams of carbon disulfide, 2.0 gram of tetrabutylammonium bisulfate and 100 ml toluene. The solution was stirred at 20°C under nitrogen and 168 grams of 50% sodium hydroxide solution was added dropwise to keep the temperature between 20-30°C. 30 min. after the addition, a solution of 43.6 grams of acetone and 89.6 grams of chloroform was added at 20-30°C. The reaction was then stirred at 15-20°C overnight. 500 ml water was added to the mixture, the layers were separated. The organic layer was discarded and the aqueous layer was acidified with concentrated HCl to precipitate the product as yellow solid. 50 ml toluene was added to stir with the mixture. Filtered and rinsed the solid with toluene to collect 22.5 grams of product after drying in the air to constant weight.

EXAMPLE 2

Synthesis of s,s'-bis-(α, α' - disubstituted – α" – acetic acid) – trithiocarbonates. ($R^1 = R^2 = CH_3$)

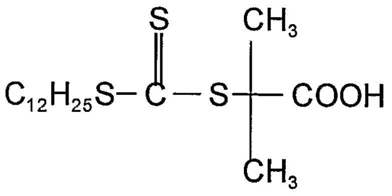


The procedure was essentially the same as in example 1, except that mineral spirits replaced toluene as solvent. 40.3 grams of product was obtained as yellow solid.

EXAMPLE 3

Synthesis of s-alkyl-s'-(-(α, α' - disubstituted – α" – acetic acid) – trithiocarbonates

$$C_{12}H_{25}SH + CS_2 + CHCl_3 + (CH_3)_2CO + R_4N^{+}Cl^{-} \xrightarrow{NaOH} \xrightarrow{H^+}$$



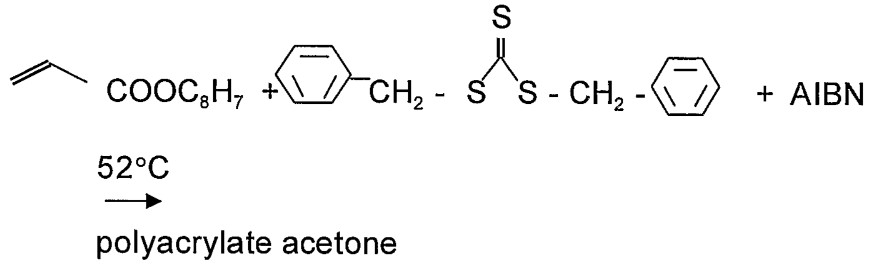
$$C_{12}H_{25}S-\overset{\overset{\displaystyle S}{\|}}{C}-S-\underset{CH_3}{\overset{CH_3}{C}}-COOH$$

Procedure:

Dodecylmercaptan (0.1 mole), and Aliquot 336 (0.004 mole) was dissolved in 48g acetone. 50% sodium hydroxide solution (0.105 mole) was added, followed by dropwise addition of carbon disufide (0-1 mole) in 10g acetone solution. The media turned from colorless to yellow. After 20 min., chloroform (0.15 mole) was added followed by dropwise addition of 50% NaOH (0.5 mole) and 5 g NaOH beads. The rxn was stirred at 15-20°C overnight, filtered and the sol. was rinsed with acetone. The acetone layer was concentrated to dryness. The mass was dissolved in water, acidified with concentrated HCl to precipitate the product, rinsed with water to collect the yellow solid. The solid was dissolved in 350 ml hexanes. The solution was dried over magnesium sulfate and filtered. The organic solution was cooled to precipitate the product as yellow flakes. Yield is 85%.

EXAMPLE 4

Polymerization of Prior Art Compounds



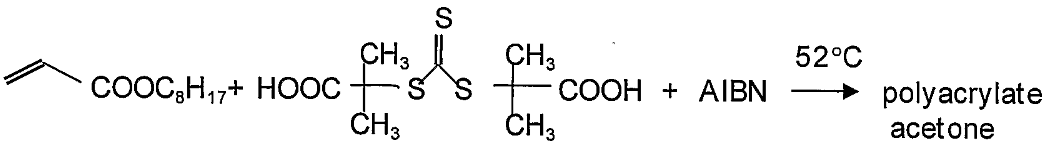
Procedure:

Dibenzyltrithiocarbonate (1.54 g, 5.3 mmole), 2-ethylhexylacrylate (25grams 135.7 mmole), AIBN (0.05g, 0.3mmole) and acetone (25ml) were mixed. 1 ml of undecane was added as GC internal standard for calculating the conversion. The solution was purged with nitrogen for 15 min. before heating to 52°C under nitrogen. No exotherm was detected throughout the reaction. Aliquots of the sample were taken for GC and GPA analyses during the course of the polymerization. The following table showed the progress of the polymerization in 7 hours.

Sample	Time (mins.)	Mn	Mw	Conv. %
1				
2	120	866	970	3.7
3	270	1180	1428	13.2
4	420	1614	2059	26.9

EXAMPLE 5

Polymerization with s,s'-bis-(α, α' - disubstituted – α'' – acetic acid) – trithiocarbonates



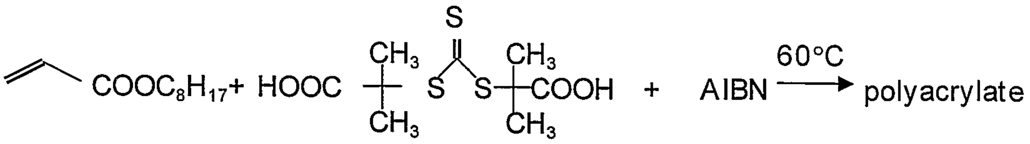
Procedure:

Following the same procedure as in example 4, the novel tricarbonate (1.50g, 5.3mmole), 2-ethylhexylacrylate (25g, 135.7 mmole), AIBN (0.05g, 0.3mmole) and acetone (25ml) were mixed. 1 ml of undecane was added as internal standard The reaction was stirred at 52°C for 7 hours. The following table showed the conversion and the molecular weights of the resulting polymer.

Sample	Time (mins.)	Mn	Mw	Conv. %
1	45	669	724	3.5
2	120	1433	1590	25.8
3	240	3095	3621	79.8
4	300	3345	3898	87.9
5	420	3527	4136	93.9

EXAMPLE 6

Polymerization with s,s'-bis-(α, α' - disubstituted – α'' – acetic acid) trithiocarbonates.



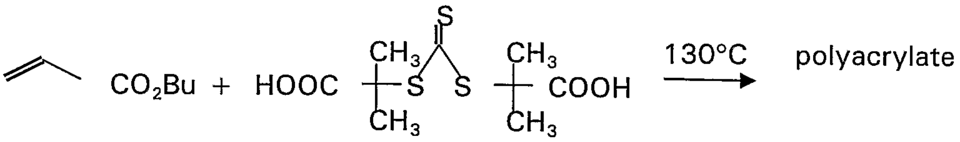
Procedure:

This is a bulk polymerization with the trithiocarbonate as chain-transfer agent The trithiocarbonate (1.0g, 3.5mmole), 2-ethylhexylacrylate (25g, 135.7mmole), AIBN (0.05g, 0.3mmole) and 1 ml undecane (internal standard) were purged with nitrogen, then heated to 60°C for 3 hours. The following table showed the conversion and the molecular weight of the polymer.

Sample	Time (mins.)	Mn	Mw	Conv. %
1	30	2229	2616	35.6
2	90	4501	5526	91.9
3	180	4672	5780	97.8

EXAMPLE 7

Polymerization with s,s'-bis-(α, α' - disubstituted – α" – acetic acid) trithiocarbonates.



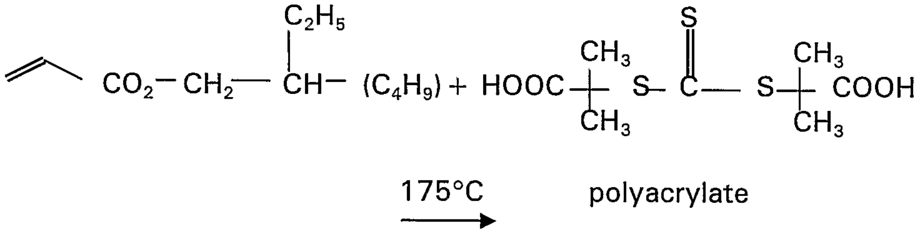
Procedure:

The trithiocarbonate was used as inifertor. Trithiocarbonate (1.0g, 3.5 mmole), n-butylacrylate (20g, 156.1 mmole) with 1 ml decane as internal standard were purged with nitrogen for 15 min., then polymerized at 130°C under nitrogen for 6 hours. The following table showed the conversion and the molecular weights of the polymer.

Sample	Time (mins.)	Mn	Mw	Conv. %
1	60	1118	1242	16.0
2	120	1891	2199	32.5
3	240	2985	3337	52.5
4	360	3532	4066	65.7

EXAMPLE 8

Free Radical Polymerization utilizing s,s′-bis-(α, α' - disubstituted – α" – acetic acid) – trithiocarbonates as inifertor.



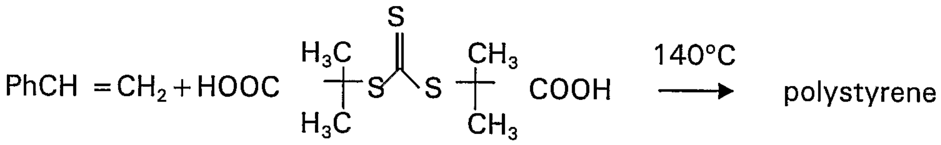
Procedure:

The trithiocarbonate (2.0g, 7.1mmole) and 2-ethylhexylacrylate (25.0g, 135.7mmole) were purged with nitrogen for 15 min then heated to 175°C for 10 hours. The following table showed the conversion and molecular weighs of the polymer.

Sample	Time (mins.)	Mn	Mw	Conversion
1	40	1006	1117	24.2
2	90	1446	1699	42.0
3	150	1750	2241	51.9
4	600	2185	3115	98.9

EXAMPLE 9

Polymerization with s,s′-bis-(α, α' - disubstituted – α" – acetic acid) trithiocarbonates.



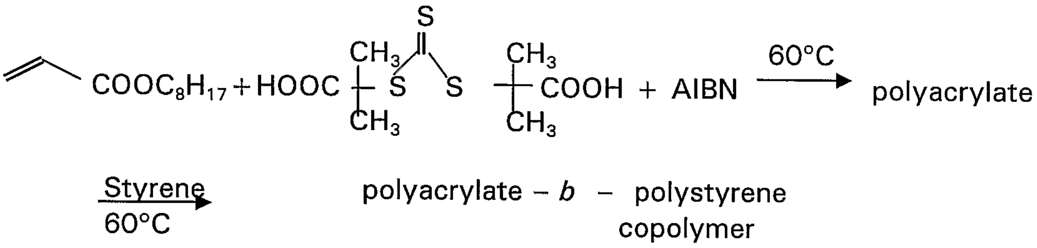
Procedure:

The trithiocarbonate was used as inifertor to make polystyrene. The trithiocarbonate (2.0g, 7.1mmole) and styrene (25g, 240.4mmole) with 1 ml decane as internal standard were polymerized at 140°C under nitrogen for 6 hours. The following table showed the progress of the polymerization.

Sample	Time (mins.)	Mn	Mw	Conv. %
1	30	613	648	9.5
2	60	779	831	16.9
3	120	1829	2071	53.9
4	300	2221	2559	72.3
5	360	2537	2956	84.5

EXAMPLE 10

Polymerization with s,s′-bis-(α, α' - disubstituted – α" – acetic acid) trithiocarbonates.



Procedure:

The trithiocarbonate was used as chain-transfer agent to make block copolymers of 2-ethylhexylacrylate and styrene. The trithiocarbonate (1.5g, 5.3mmole), 2-ethylhexylacrylate (30g, 162.8mmole) and AIBN (0.03g, 0. 18mmole) with 1 ml undecane as the internal standard were polymerized at 60°C under nitrogen as before. 6.5 hours later, styrene (15g, 144.2mmole) and AIBN (0.03g, 0.18mmole) was added. The polymerization continued and the following shows the progress.

Sample	Time (mins.)	Mn	Mw	Conv. %
1	70	1922	2459	32.5
2	135	3556	4204	80.8
3	270	4095	4874	95.0
4	330*	4407	5025	96.6
5	1290	4834	5969	-

*Styrene added

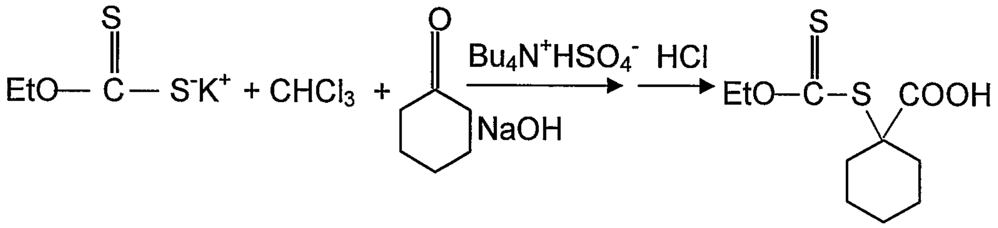
EXAMPLE 11

Polymerization with the trithiocarbonate from example 3. The trithiocarbonate (1.82g. 5mmole), n-butyl acrylate (25g, 195.1mmole) and

AIBN (0.04g, 0.25mmole) with 1 ml undecane as the internal standard were polymerized under nitrogen atmosphere for 7 hours. It showed 97.5% conversion by GC as depicted in the following table:

Sample	Time (min)	Mn	Mw	Pd	% Conv.
1	60	2177	2792	1.26	46.2
2	120	2758	3865	1.40	67.1
3	420	3786	5439	1.44	97.5

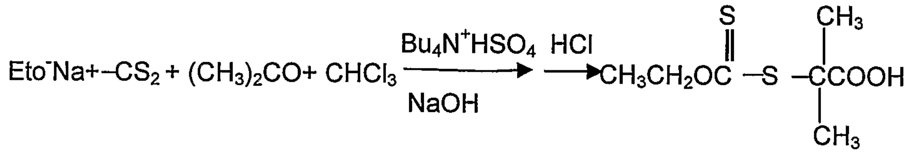
EXAMPLE 12



Procedure:

In a 300 ml jacketed flask equipped with a mechanical stirrer, thermometer, addition funnel and nitrogen-inlet tube (for inerting) 16.3 grams potassium O-ethylxanthate, 17.9 grams chloroform, 1.36 grams tetrabutylammonium hydrogen sulfate and 88.1 grams cyclohexanone were placed and cooled to between 15-20°C. 40 grams of sodium hydroxide beads were added in portions to keep the temperature below 25°C. After the addition, the reaction was stirred at about 20°C for 12 hours. 100 ml of water was added and the aqueous layers were acidified with concentrated hydrochloric acid. 100 ml toluene was added to extract the product. After drying the toluene solution with magnesium sulfate, it was filtered and concentrated to afford 20 grams of yellow solid which was further purified by recrystallizing from hexanes.

EXAMPLE 13

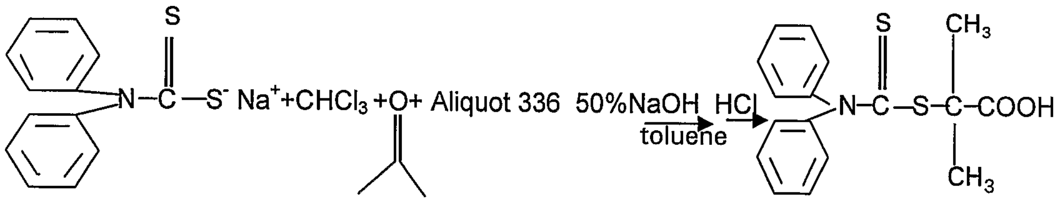


$$Eto^{-}Na+-CS_2 + (CH_3)_2CO + CHCl_3 \xrightarrow[NaOH]{Bu_4N^{+}HSO_4} \xrightarrow{HCl} CH_3CH_2O\overset{\overset{S}{\|}}{C}-S-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}COOH$$

In this example, sodium O-ethylxanthate was formed in situ. 7.6 grams carbon disulfide, 1 gram tetrabutylammonium hydrogen sulfate and 58.1 grams acetone were stirred in a reaction vessel as equipped above in Example 12. 7.1 grams sodium ethoxide (96%, Aldrich) was added in portions at room temperature. 30 minutes after the addition, 17.9 grams chloroform was added followed by 20 grams sodium hydroxide beads in portions to keep the temperature below 25°C . Stirred at 15° C for 12 hours. The mixture was filtered and rinsed thoroughly with acetone. The acetone solution was concentrated and dissolved in water. 20 ml concentrated HCl was added. The oil formed was extracted into two 50 ml portions of toluene, dried over magnesium sulfate, and concentrated into an oil. The oil was extracted with two 50 ml portions of boiling hexane. Beige-colored solid was produced from the solution.

EXAMPLE 14

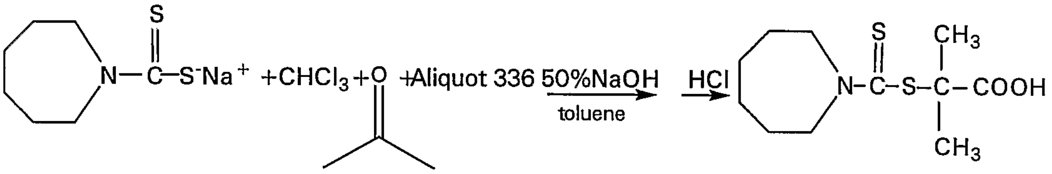
Synthesis of S-(methyl, methyl, acetic acid) dithiocarbamate



Procedure:

10.7 grams sodium N,N-diphenyldithiocarbamate, 7.2 grams chloroform, 4.6 grams acetone, 0.8 gram Aliquot 336 and 50 ml toluene were stirred at 15-20°C under nitrogen while 16 grams 50% sodium hydroxide was added dropwise to keep the reaction temperature below 20° C. The reaction was stirred for 12 hours. Water was added to dissolve the solid. The layers were separated and the aqueous layer was acidified with concentrated hydrochloric acid. The solid was washed with water and recrystallized from toluene to afford light-yellow colored solid.

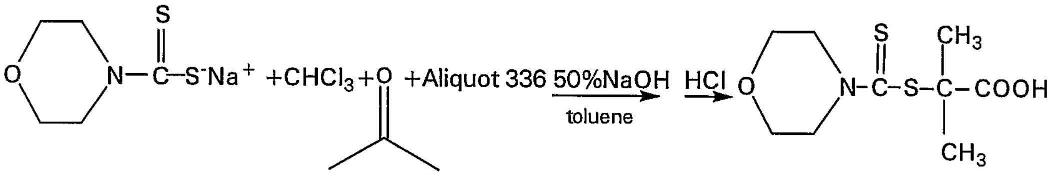
EXAMPLE 15



Procedure:

Sodium N,N-diphenyldithiocarbamate was replaced by sodium N,N-hexamethylenedithiocarbamate and the reaction was conducted as explained in Example 14. The product was a white solid.

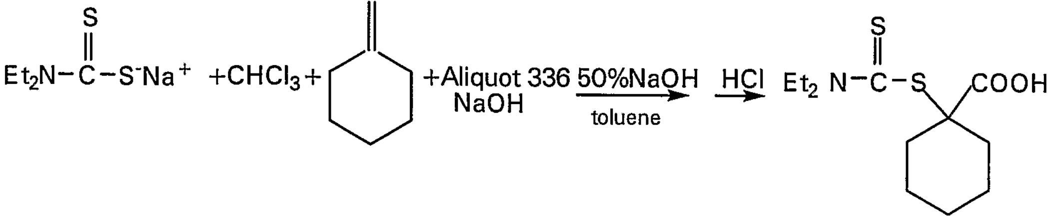
EXAMPLE 16



Procedure:

The sodium dithiocarbamate utilized in this example was sodium morpholinodithiocarbamate. The reaction was conducted as explained in Example 14. The product was afforded in good yield as white powders.

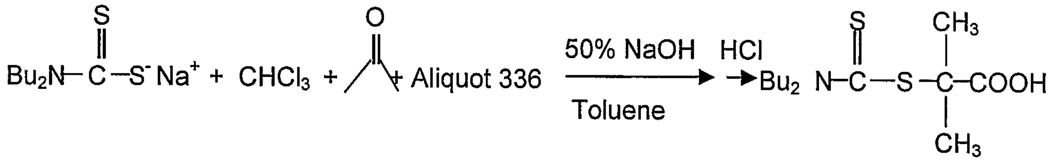
EXAMPLE 17



Procedure:

The sodium dithiocarbamate utilized in this example was sodium N,N-diethyl dithiocarbamate. The reaction was conducted as explained in Example 14 and acetone was replaced by cyclohexanone. The product was afforded in good yield as white powders.

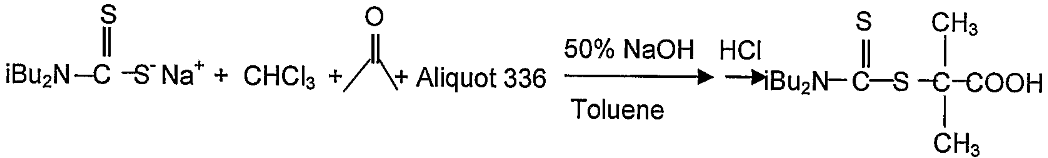
EXAMPLE 18



Procedure:

Sodium N,N-dibutyldithiocarbamate was utilized in this example. The reaction was conducted as described in Example 14. The product was isolated as white powder.

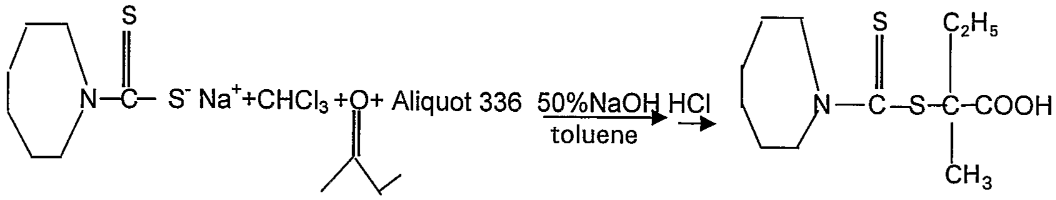
EXAMPLE 19



Procedure:

Sodium N,N-di-isobutyldithiocarbamate was utilized in this example. The reaction was conducted as described in Example 14. The product was isolated as yellow solid.

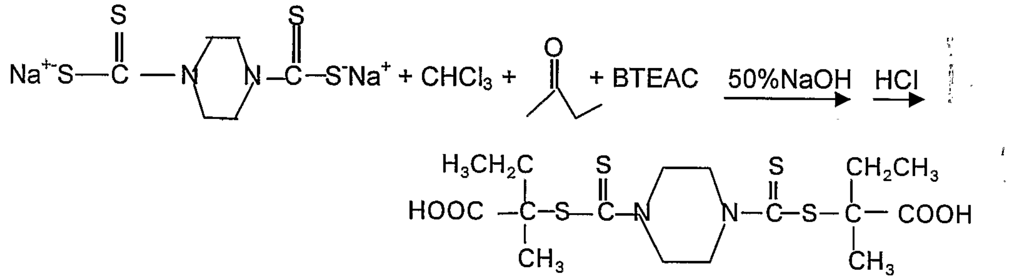
EXAMPLE 20



Procedure:

Sodium N,N-hexamethylene dithiocarbamate, 2-butanone was utilized in this example. The reaction was conducted as explained in Example 14 and was replaced by acetone. The product was afforded in good yield as white powder after recrystallization from hexane/toluene.

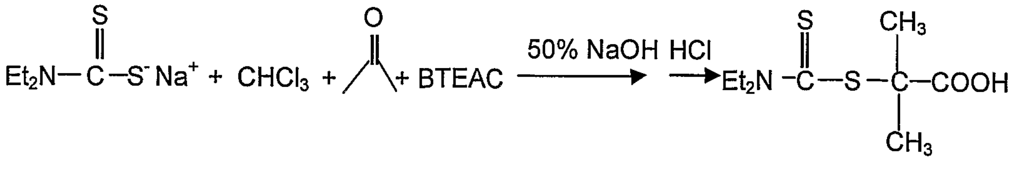
EXAMPLE 21



Procedure:

14.1 grams of S,S'-disodium salt of the piperazine bis-(dithiocarbamic acid), 100 ml 2-butanone, 17.9 grams chloroform and 1.13 grams benzyltriethylammonium chloride were mixed and stirred at 15-20° C under nitrogen atmosphere. 40 grams 50% sodium hydroxide solution was added in portions to keep the reaction temperature under 20° C. After the addition, the reaction was allowed to stir at 20° C for 12 hours. The mixture was filtered and the solid was rinsed with 2-butanone and then stirred with 100 ml water. Concentrated HCl was added until water turned acidic. The solid was collected and rinsed with water, to yield off-white colored powders. The powder was crystallized with methanol to afford white powder.

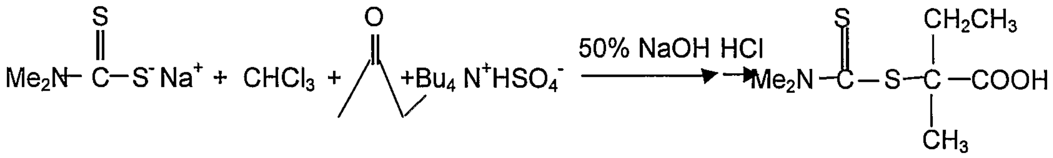
EXAMPLE 22



As in the above procedure of Example 21 the disodium salt of piperizine bis-(dithiocarbamic acid) was replaced with sodium diethyldithiocarbamate, and

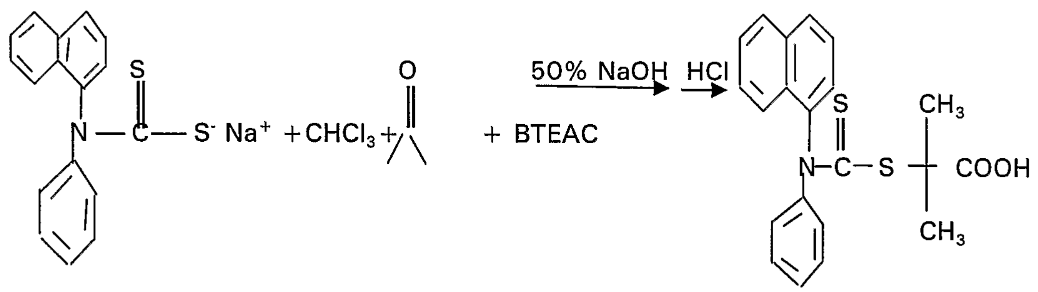
2-butanone with acetone. The desired product was obtained as white powders in high yield.

EXAMPLE 23



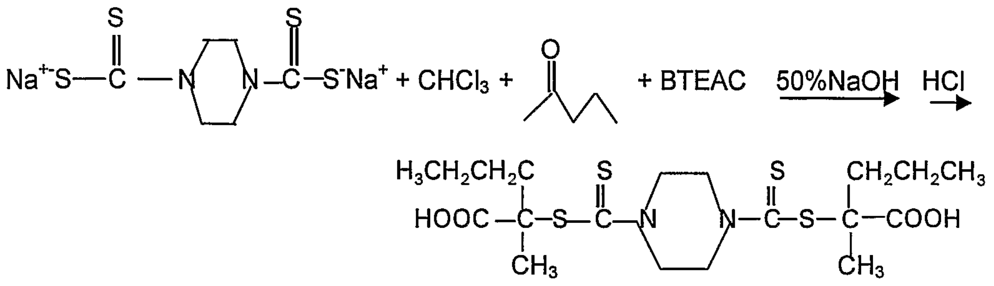
The procedure of Example 21 was utilized and the disodium salts of piperizine bis-(dithiocarbamic acid) was replaced by sodium dimethyldithiocarbamate, and BTEAC was replaced by tetrabutylammonium hydrogensulfate, the desired product was obtained as white powders.

EXAMPLE 24



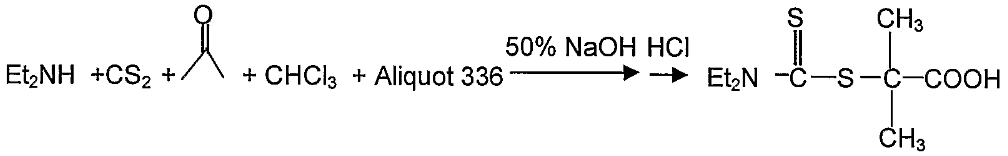
The reaction was performed as in Example 21, but the dithiocarbamate salt was sodium N-phenyl-N-1-naphthyl dithiocarbamate, and the ketone was acetone. The product was obtained as beige-colored powders after recrystallization from a mixture of toluene and heptane.

EXAMPLE 25



The reaction was performed in a similar manner as in Example 21, but 2-butanone was replaced by 2-pentanone, the product was white powders after recrystallization from hexanes.

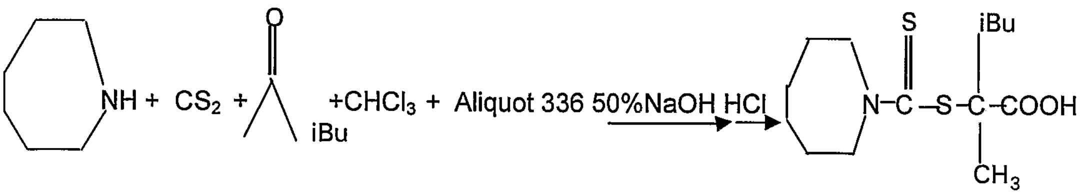
EXAMPLE 26



Procedure:

7.38 grams diethylamine and 80 ml acetone and 2.0 grams Aliquot 336 were mixed and stirred under nitrogen atmosphere at 15° C. 7.6 grams carbon disulfide in 20 ml acetone was added dropwise to keep the temperature below 20° C. 30 minutes after the addition, 8.8 grams 50% sodium hydroxide was added. 30 minutes later, 17.9 grams chloroform was added followed by 31.2 grams 50% sodium hydroxide. The reaction was allowed to stir at 15-20° C for 12 hours. The mixture was concentrated and then dissolved in water. 15 ml concentrated HCl was added to precipitate a beige-colored solid which was washed thoroughly with water (20 grams). Recrystallization from toluene afforded white solid.

EXAMPLE 27

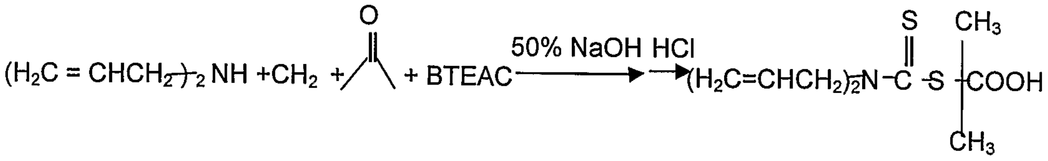


Procedure:

The diethylamine of the procedure of Example 26 was replaced by hexamethyleneimine and acetone was replaced by methyl isobutyl ketone.

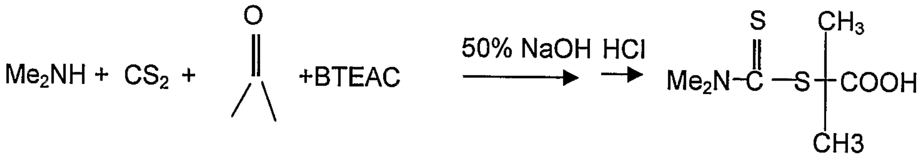
The product was recrystallized from hexane/toluene to afford white powders.

EXAMPLE 28



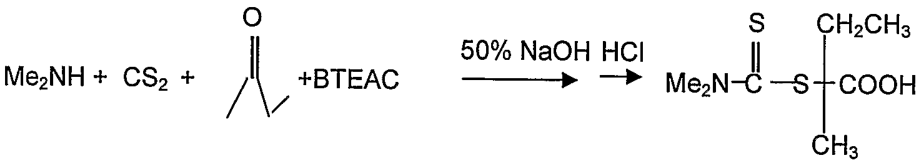
The diethylamine of the procedure of Example 26 was replaced by diallylamine and Aliquot® 336 was replaced by BTEAC. The product was white crystalline solid after recrystallization from hexane/toluene.

EXAMPLE 29



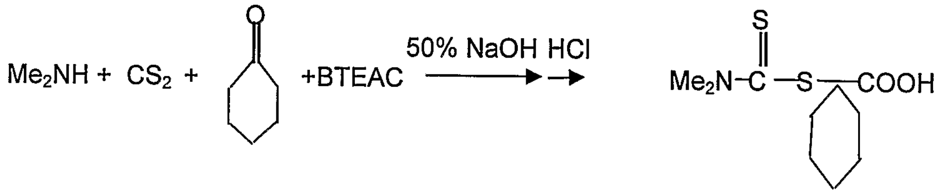
The diethylamine of the procedure of Example 26 was replaced by dimethyl-amine (40% in water). The product was white crystals after recrystallization from toluene.

EXAMPLE 30



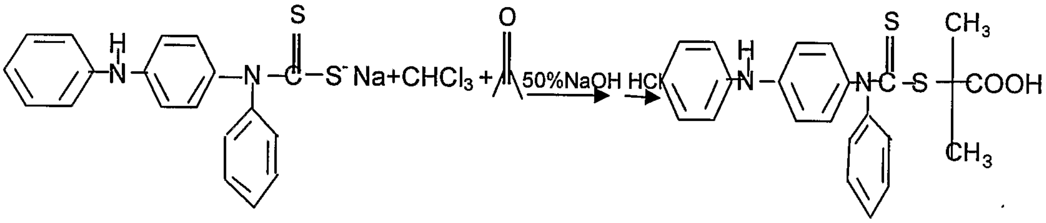
The acetone of the procedure of Example 27 was replaced by 2-butanone. The produce was a white solid after recrystallization from toluene.

EXAMPLE 31



The acetone of the procedure of Example 26 was replaced by cyclohexanone. The product was white solid after recrystallization from toluene.

EXAMPLE 32



In this example, 22.8 grams of sodium N-phenyl-N-4-anlinophenyl dithiocarbamate, 17.9 grams chloroform and 100 ml acetone were mixed and stirred at 15°C under nitrogen. 40 grams 50% sodium hydroxide was added dropwise in to keep the temperature under 20°C. The reaction was allowed to stir overnight (approximately 12 hours) at 15°C. Solvent was removed in a rotary evaporator and the residue was dissolved in water. The aqueous solution was acidified with concentrated hydrochloric acid to collect a green-colored solid. The dried solid was recrystallized from toluene to afford grayish-colored solid. The structure was confirmed by H-NMR.

EXAMPLE 33

Controlled Radical Polymerization with novel dithiocarbonate derivatives

The theoretical number-averaged molecular $(Mn)_{theo}$ weight for each polymer or copolymer was calculated from the formula XII (a) assuming 100% conversion.

$(Mn)_{ex}$ is the Mn measured by GPC from polymerization products. In bulk polymerization, 20-25 grams of monomer, 0.01-0.05 grams of an initiator such as

AIBN and the amount of the dithiocarbonate as needed to give desired Mn (calculated using formula XII(a)) are purged with nitrogen gas, then heated to temperature gradually. Sometimes air or water-cooling is necessary to keep the temperature under 83°C. The resulting polymers were subjected to MALDI mass spectrum measurement. The spectrum clearly showed the carboxyl-terminating group in every polymer chain.

Block copolymerization was performed by making the first polymer in bulk, then add the second monomer and same amount of initiator, then polymerizing in the same manner. Random copolymerization could have been performed if both monomers were added at the same time.

The results of the polymerizations and block polymerizations are listed in the following table.

Dithiocarbonate Polymers

Dithiocarbonate Example	Monomer	Solvent	Temp.	$(Mn)_{ex}$	$(Mn)_{theo}$	PD	Time/ Hour
Control	Butyl acrylate	--		>100,000		>3	1
12	Butyl acrylate	MEK	80	3777	5000	1.78	5
26	Styrene	none-bulk polym.	140	7830	5000	2.05	5
17	Butyl acrylate	MEK	80	1645	2000	2.07	5
14	Butyl acrylate	MEK	75	4656	5000	1.31	5
21	Butyl acrylate	MEK	80	3049	3000	1.32	6
19	Butyl acrylate	MEK	80	3683	3000	2.03	6
13	Ethyl acrylate	none-bulk polym.	65	5564	10000	1.83	5
29	Vinyl acetate	none-bulk polym.	70	4367	5000	1.47	5
15	t-butylacrylamide	THF	70	3622	5000	1.91	5
24	Butyl acrylate	none-bulk polym.	80	5093	5000	1.36	6.5
32	Butyl acrylate	MEK	80	2061	5000	1.61	2.5

Block Copolymers

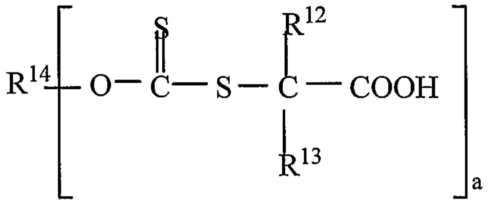
Dithiocarbonate Example	Monomer-1	$(Mn)_{ex}$	$(Mn)_{theo}$	PD	Monomer-2	$(Mn)_{ex}$	$(Mn)_{theo}$	PD
30	Butyl acrylate	1695	1798	1.92	Vinyl acetate	1873	2540	1.87
31	Butyl acrylate	1631	1798	2.23	Vinyl acetate	2014	2444	1.96

While in accordance with the patent statutes the best mode and preferred embodiment have been set forth, the scope of the invention is not limited thereto, but rather by the scope of the attached claims.

WHAT IS CLAIMED IS:

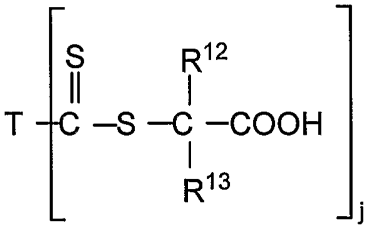
1. A dithiocarbonate composition, comprising:

a compound having the formula:



$$R^{14}\left[-O-\overset{\overset{\displaystyle S}{\|}}{C}-S-\underset{\underset{\displaystyle R^{13}}{|}}{\overset{\overset{\displaystyle R^{12}}{|}}{C}}-COOH\right]_a$$

, or



$$T\left[-\overset{\overset{\displaystyle S}{\|}}{C}-S-\underset{\underset{\displaystyle R^{13}}{|}}{\overset{\overset{\displaystyle R^{12}}{|}}{C}}-COOH\right]_j$$

wherein R^{12} and R^{13}, independently, is the same or different, is a linear or branched alkyl having from 1 to about 12 carbon atoms; or an aryl group having from 6 to about 18 carbon atoms, optionally containing heteroatoms; or R^{12} and R^{13} forms or is a part of a substituted or unsubstituted cyclic ring having from 3 to about 12 carbon atoms;

wherein R^{14} is optionally substituted, and is a linear or branched alkyl having from 1 to about 12 carbon atoms, an aryl group optionally saturated or unsaturated; an arylalkyl having from about 7 to about 18 carbon atoms; an acyl group; an alkene group; an alkenealkyl having from 3 to about 18 carbon atoms; an alkylene group; an alkoxyalkyl; derived from a polyalkylene glycol; derived from a polyalkylene glycol monoalkyl ether having from about 3 to about 200 carbon atoms; derived from a polyalkylene glycol monoaryl ether having from about 3 to about 200 carbon atoms, a polyfluoroalkyl; a phosphorous containing alkyl; or a substituted or unsubstituted aryl ring containing heteroatoms;

wherein "a" is 1 to about 4;

wherein j is 1 or 2;

with the proviso that when j is 1, T is $-(NR^{15}R^{16})$, 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; and

wherein R^{15} and R^{16}, independently, is the same or different, optionally substituted, optionally contains heteroatoms, and is hydrogen; or a linear or branched alkyl having from 1 to about 18 carbons; or an aryl group or an aryl alkyl group having from 6 to about 18 carbon atoms, optionally saturated or unsaturated; or an arylalkyl having from 7 to about 18 carbons; or an alkenealkyl having from 3 to about 18 carbon atoms; or derived from polyalkylene glycol ether; or derived from an amine; or R^{15} and R^{16} are in the form of a substituted or unsubstituted cyclic ring with the nitrogen atom having a total of 4 to about 12 carbon atoms.

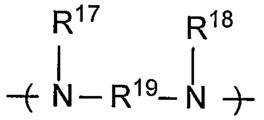
2. A composition according to claim 1, wherein R^{12} and R^{13}, independently, is a phenyl group, or an alkyl group having 1 to about 10 carbon atoms, or wherein R^{12} and R^{13} are part of said cyclic ring.

3. A composition according to any of the previous claims, wherein R^{14} is an alkyl having from 1 to about 8 carbon atoms, wherein j is 1, and wherein R^{15} and R^{16}, independently, is a phenyl group, or an alkyl group having from 1 to about 10 carbon atoms, or hexamethylene, or wherein R^{15} and R^{16} are part of said cyclic ring.

4. A composition according to any of the previous claims, wherein said "a" is 1 or 2, wherein R^{14} is an alkyl having from 1 to about 4 carbon atoms, and wherein R^{12} and R^{13} independently, is an alkyl having from 1 to about 4 carbon atoms, or wherein R^{12} and R^{13} are part of said cyclic ring.

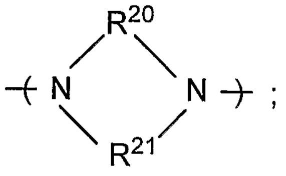
5. A composition according to claim 1, wherein said "a" is 2 and wherein R^{12} and R^{13}, independently, are a phenyl group, or an alkyl group

having 1 to about 10 carbon atoms, or wherein R^{12} and R^{13} are part of a cyclic ring, wherein R^{14} is an alkyl having from 1 to about 8 carbon atoms, wherein j is 2 and T is:



$$-\!\left(\!-N(R^{17})-R^{19}-N(R^{18})-\!\right)\!-$$

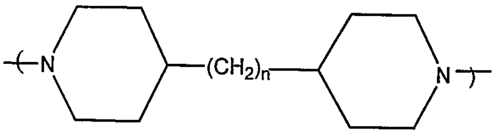
or



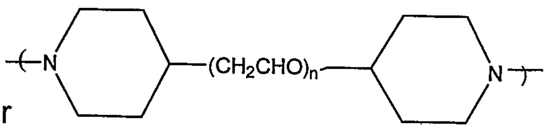
wherein R^{17} and R^{18}, independently, is the same or different, is optionally substituted, and is hydrogen; a linear or branched alkyl having from 1 to about 18 carbon atoms; or an aryl group having from about 6 to about 18 carbon atoms; or an arylalkyl having from 7 to about 18 carbon atoms; or a alkenealkyl having from 3 to about 18 carbon atoms;

wherein R^{19} is optionally substituted, or is non-existent; or an alkylene group having from 1 to about 18 carbon atoms; or derived from a polyalkylene glycol either having from 3 to about 200 carbon atoms; and wherein R^{20} and R^{21}, independently, is the same or different, and is optionally substituted, and is an alkylene group having from 1 to about 4 carbon atoms.

6. A composition according to claim 1, wherein said "a" is 2, wherein j is 2, and wherein T is:



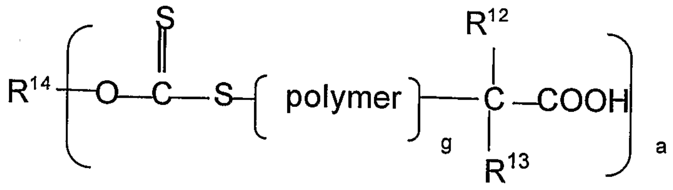
or



wherein n is 0 to about 18, and wherein R^{12} and R^{13}, independently, is a phenyl group, or an alkyl group having 1 to about 10 carbon atoms, or R^{12} and R^{13} are part of a cyclic ring having from 3 to about 12 carbon atoms.

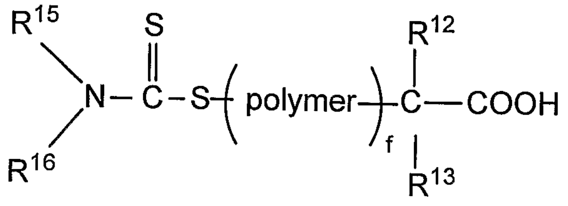
7. A composition, comprising:

a polymer or copolymer having the formula:

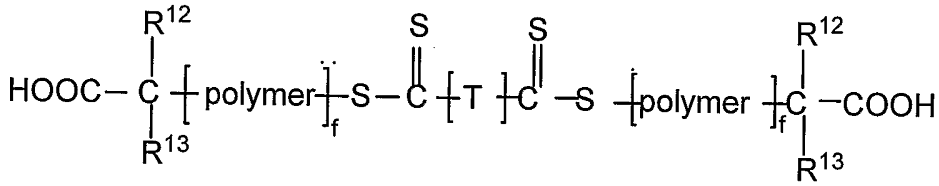


$$R^{14}\left[O-\overset{S}{\overset{\|}{C}}-S-\left(\text{polymer}\right)_g-\underset{R^{13}}{\overset{R^{12}}{C}}-COOH\right]_a$$

,



, or



$$HOOC-\underset{R^{13}}{\overset{R^{12}}{C}}-[\text{polymer}]_f-S-\overset{S}{\overset{\|}{C}}-[T]-\overset{S}{\overset{\|}{C}}-S-[\text{polymer}]_f-\underset{R^{13}}{\overset{R^{12}}{C}}-COOH$$

wherein R^{12} and R^{13}, independently, can be the same or different, can be a linear or branched alkyl having from 1 to about 12 carbon atoms; or an aryl group having from 6 to about 18 carbon atoms, optionally containing heteroatoms; or R^{12} and R^{13} can form or be a part of a substituted or unsubstituted cyclic ring having from 3 to about 12 carbon atoms;

wherein R^{14} is optionally substituted, and can be a linear or branched alkyl having from 1 to about 12 carbon atoms, an aryl group optionally saturated or unsaturated; an arylalkyl having from about 7 to about 18 carbon atoms; an acyl group; an alkene group; an alkenealkyl having from 3 to about 18 carbon atoms; an alkylene group; an alkoxyalkyl; derived from a polyalkylene glycol; derived from a polyalkylene glycol monoalkyl ether having from about 3 to about 200 carbon atoms; derived from a polyalkylene glycol monoaryl ether having from about 3 to about 200 carbon atoms, a polyfluoroalkyl; a phosphorous containing alkyl; or a substituted or unsubstituted aryl ring containing heteroatoms;

wherein R^{15} and R^{16}, independently, is the same or different, optionally substituted, optionally contains heteroatoms, and is hydrogen; or a linear or branched alkyl having from 1 to about 18 carbons; or an aryl group having from 6 to about 18 carbon atoms, optionally saturated or unsaturated; or an arylalkyl having from 7 to about 18 carbons; or an alkenealkyl having from 3 to about 18 carbon atoms; or derived from polyalkylene glycol ether; or derived from an amine; or R^{15} and R^{16} are in the form of a substituted or unsubstituted cyclic ring with the nitrogen atom having a total of 4 to about 12 carbon atoms;

wherein T is a divalent radical having a nitrogen atom directly connected to each carbon atom of the two thiocarbonyl groups;

wherein said polymer repeat units are derived from at least one conjugated diene monomer, or a vinyl containing monomer, or combinations thereof, with the proviso that each repeat unit can be the same or different; and

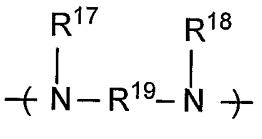
wherein the number of said repeat units f, independently, is from 1 to about 10,000.

wherein said g is from about 1 to about 10,000; and

wherein said "a" is 1 to about 4.

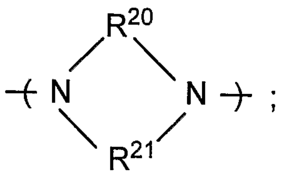
8. A composition according to claim 7, wherein R^{12} and R^{13}, independently, is a phenyl group, or an alkyl group having 1 to about 10 carbon atoms, or wherein R^{12} and R^{13} are part of a cyclic ring having from 3 to about 12 carbon atoms; and wherein R^{15} and R^{16}, independently, is a phenyl group, or an alkyl group having from 1 to about 10 carbon atoms, or hexamethylene, or wherein R^{15} and R^{16} are part of a cyclic ring having from 3 to about 12 carbon atoms

9. A composition according to any of claims 7 or 8, wherein R^{12} and R^{13} independently, is a phenyl group or an alkyl group having from 1 to about 8 carbon atoms, or wherein R^{12} and R^{13} are part of a cyclic ring having from 3 to about 12 carbon atoms, and wherein T is:



$$-\!\left(\overset{R^{17}}{\underset{}{N}}-R^{19}-\overset{R^{18}}{\underset{}{N}}\right)\!-$$

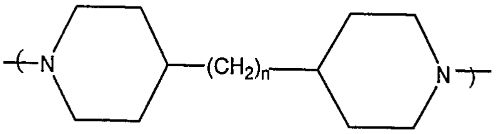
or



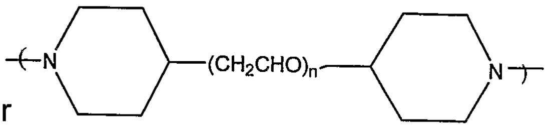
;

wherein R^{17} and R^{18}, independently, is the same or different, is optionally substituted, and is hydrogen; or a linear or branched alkyl having from 1 to about 18 carbon atoms; or an aryl group having from about 6 to about 18 carbon atoms; or an arylalkyl having from 7 to about 18 carbon atoms; or a alkenealkyl having from 3 to about 18 carbon atoms; wherein R^{19} is optionally substituted, or is non-existent; or an alkylene group having from 1 to about 18 carbon atoms; or derived from a polyalkylene glycol either having from 3 to about 200 carbon atoms; wherein R^{20} and R^{21}, independently, is the same or different, and is optionally substituted, and is an alkylene group having from 1 to about 4 carbon atoms, or

wherein T is:

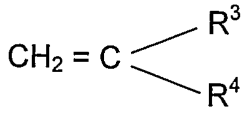


or



, wherein n is 0 to about 18.

10. A composition according to any of claims 7 to 9, wherein said conjugated diene monomer has from 4 to 12 carbon atoms, and wherein said vinyl containing monomer has the formula:



$$CH_2 = C \begin{array}{l} R^3 \\ R^4 \end{array}$$

wherein R^3 comprises hydrogen, halogen, $C_1 - C_4$ alkyl, or substituted C_1 - C_4 alkyl wherein said substituents, independently, comprise one or more hydroxy, alkoxy, aryloxy(OR^5), carboxy, metal carboxylate (COOM) with M being sodium, potassium, calcium, zinc or an ammonium salt, acyloxy, aroyloxy(O_2CR^5), alkoxy-carbonyl(CO_2R^5), aryloxy-carbonyl; or N-pyrrolidonyl;

wherein R^4 comprises hydrogen, R^5, CO_2H, CO_2R^5, COR^5, CN, $CONH_2$, $CONHR^5$, O_2CR^5, OR^5 or halogen; and

wherein R^5 comprises $C_1 - C_{18}$ alkyl, substituted $C_1 - C_{18}$ alkyl, $C_2 - C_{18}$ alkenyl, aryl, heterocyclyl, aralkyl, or alkaryl, and

wherein said substituents, independently, comprise one or more epoxy, hydroxy, alkoxy, acyl, acyloxy, carboxy, carboxy salts, sulfonic acid, sulfonic salts, alkoxy- or aryloxy-carbonyl, dicyanato, cyano, silyl, halo or dialkylamino.

11. A composition according to any of claims 7 to 10, wherein said polymer repeat unit is derived from alkyl acrylate, vinyl acetate, acrylic acid, or styrene, N-vinyl pyrrolidone or a combination thereof, and wherein said number of repeat units f or g is from about 3 to about 5,000.

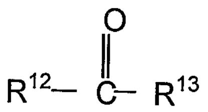
12. A composition according to any of claims 7 to 11, wherein R^{12} and R^{13}, independently, are a phenyl group or an alkyl group having from 1 to about 4 carbon atoms.

13. A method for forming a dithiocarbonate compound, comprising the steps of:

reacting a) an alkoxylate salt of a xanthate compound or a metal salt of a dithiocarbamate compound, b) carbon disulfide, c) a haloform, and d) a ketone in the presence of a base, and optionally a solvent and a catalyst, to form a reaction product; and

acidifying the reaction product to form said dithiocarbonate compound.

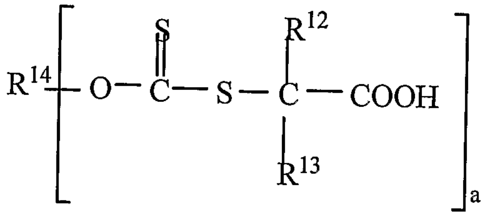
14. A method according to claim 13, wherein said haloform is chloroform or bromoform, or a blend thereof, and wherein said ketone has the formula:



$$R^{12}-\overset{\overset{\displaystyle O}{\|}}{C}-R^{13}$$

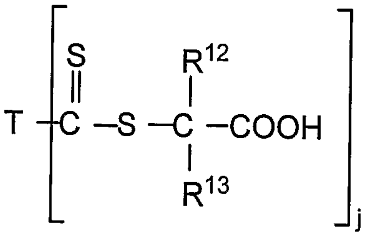
wherein R^{12} and R^{13}, independently, is the same or different, is optionally be substituted, and is a linear or branched alkyl having from 1 to about 12 carbon atoms; or an aryl group having from 6 to about 18 carbon atoms, optionally containing heteroatoms; or R^{12} and R^{13} forms and is part of a substituted or unsubstituted cyclic ring having from 3 to about 12 carbon atoms.

15. A method according to any of claims 13 or 14, wherein said dithiocarbonate compound has a formula:



$$R^{14}\left[-O-\overset{\overset{\displaystyle S}{\|}}{C}-S-\underset{R^{13}}{\overset{R^{12}}{\underset{|}{\overset{|}{C}}}}-COOH\right]_a$$

, or



$$T\left[-\overset{\overset{\displaystyle S}{\|}}{C}-S-\underset{R^{13}}{\overset{R^{12}}{\underset{|}{\overset{|}{C}}}}-COOH\right]_j$$

wherein said "a" is 1 to about 4

wherein j is 1 or 2;

wherein R^{12} and R^{13}, independently, is the same or different, is optionally substituted, and is a linear or branched alkyl having from 1 to about 8 carbon atoms; or an aryl group having from 6 to about 18 carbon atoms, optionally containing heteroatoms; or R^{12} and R^{13} can form and be part of a substituted or unsubstituted cyclic ring having from 3 to about 12 carbon atoms;

wherein R^{14} is optionally substituted, and is a linear or branched alkyl having from 1 to about 12 carbon atoms, an aryl group optionally saturated or unsaturated; an arylalkyl having from about 7 to about 18 carbon atoms; an acyl group; an alkene group; an alkenealkyl having from 3 to about 18 carbon atoms; an alkylene group; an alkoxyalkyl; derived from a polyalkylene glycol; derived from a polyalkylene glycol monoalkyl ether having from about 3 to about 200 carbon atoms; derived from a polyalkylene glycol monoaryl ether having from about 3 to about 200 carbon atoms, a polyfluoroalkyl; a phosphorous containing alkyl; or a substituted or unsubstituted aryl ring containing heteroatoms; and

with the proviso that when j is 1, T is $-(NR^{15}R^{16})$, 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; and

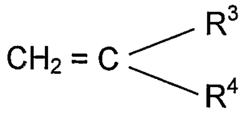
wherein R^{15} and R^{16}, independently, is the same or different, optionally substituted, optionally contains heteroatoms, and is hydrogen; or a linear or branched alkyl having from 1 to about 18 carbons; or an aryl group or an aryl alkyl group having from 6 to about 18 carbon atoms, optionally saturated or unsaturated; or an arylalkyl having from 7 to about 18 carbons; or an alkenealkyl having from 3 to about 18 carbon atoms; or derived from polyalkylene glycol ether; or derived from an amine; or R^{15} and R^{16} are in the form of a substituted or unsubstituted cyclic ring with the nitrogen atom having a total of 4 to about 12 carbon atoms.

16. A method according to any of claims 13 through 15, including said catalyst, and wherein said reaction is conducted at a temperature of from about -15°C to about 80°C.

17. A method according to claims 13 through 16, wherein said haloform is utilized in an amount from 0 percent to about 500 percent molar excess and said ketone is used in an amount from 0 percent to about 300 percent molar excess, based on the molar amount of said metal salt of said dithiocarbamate.

18. A method according to claims 13 through 17, further including the step of reacting at least one vinyl containing monomer, or at least one conjugated diene monomer with said dithiocarbonate compound to form a dithiocarbonate copolymer.

19. A method according to claims 13 through 18, wherein said conjugated diene monomer has from 4 to 12 carbon atoms, and wherein said vinyl containing monomer has the formula:



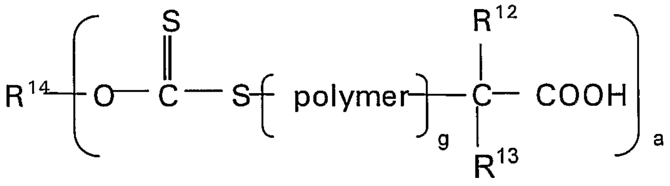
$$CH_2 = C(R^3)(R^4)$$

wherein R^3 comprises hydrogen, halogen, $C_1 - C_4$ alkyl, or substituted $C_1 - C_4$ alkyl wherein said substituents, independently, comprise one or more hydroxy, alkoxy, aryloxy(OR^5), carboxy, metal carboxylate (COOM) with M being sodium, potassium, calcium, zinc or an ammonium salt, acyloxy, aroyloxy(O_2CR^5), alkoxy-carbonyl(CO_2R^5), aryloxy-carbonyl; or N-pyrrolidonyl;

wherein R^4 comprises hydrogen, R^5, CO_2H, CO_2R^5, COR^5, CN, $CONH_2$, $CONHR^5$, O_2CR^5, OR^5 or halogen; and

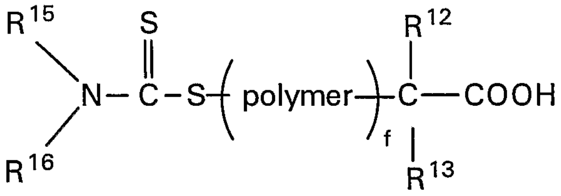
wherein R^5 comprises $C_1 - C_{18}$ alkyl, substituted $C_1 - C_{18}$ alkyl, $C_2 - C_{18}$ alkenyl, aryl, heterocyclyl, aralkyl, or alkaryl, and wherein said substituents, independently, comprise one or more epoxy, hydroxy, alkoxy, acyl, acyloxy, carboxy, carboxy salts, sulfonic acid, sulfonic salts, alkoxy- or aryloxy-carbonyl, dicyanato, cyano, silyl, halo or dialkylamino.

20. A method according to claims 18 or 19, wherein said dithiocarbonate copolymer has the formula:



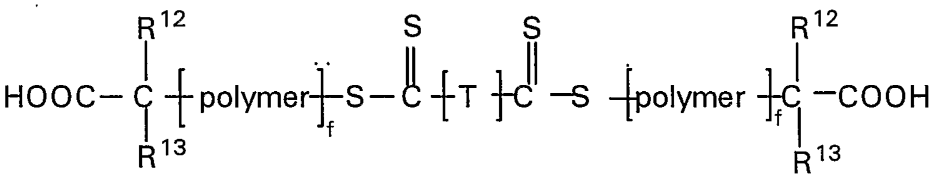
$$R^{14}\left[O-\overset{S}{\overset{\|}{C}}-S\left[\text{polymer}\right]_g-\underset{R^{13}}{\overset{R^{12}}{C}}-COOH\right]_a$$

,



$$\begin{matrix}R^{15}\\ \\ R^{16}\end{matrix}\!\!>N-\overset{S}{\overset{\|}{C}}-S\left(\text{polymer}\right)_f-\underset{R^{13}}{\overset{R^{12}}{C}}-COOH$$

,or



$$HOOC-\underset{R^{13}}{\overset{R^{12}}{C}}-\left[\text{polymer}\right]_f-S-\overset{S}{\overset{\|}{C}}-\left[T\right]-\overset{S}{\overset{\|}{C}}-S-\left[\text{polymer}\right]_f-\underset{R^{13}}{\overset{R^{12}}{C}}-COOH$$

wherein said polymer repeat units are derived from at least one said conjugated diene monomer, or said vinyl containing monomer, or combinations thereof, with the proviso that each repeat unit can be the same or different; and

wherein the number of said repeat units f, independently, is from 1 to about 10,000.

wherein said g is from about 1 to about 10,000.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 03/33476

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07C329/16 C07C329/18 C07C333/20 C07C333/22 C07C333/24
C07D295/21 C08F2/38

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07C C07D C08F

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

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

EPO-Internal, BEILSTEIN Data, WPI Data, PAJ, 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	DE 22 51 717 A (AKZO) 2 May 1974 (1974-05-02)	1-4
A	example 1a	[illegible]-13

X	C.W. PLUIJGERS, ET AL.: "Plant growth-regulating activity of S-carboxy-methyl-N,N-dimethyldithiocarbamate and related compounds" RECUEIL DES TRAVAUX CHIMIQUES DES PAYS-BAS, vol. 80, no. 9/10, 9 September 1961 (1961-09-09), pages 1089-1100, XP0002085775 ELSEVIER SCIENCE PUBLISHERS, AMSTERDAM, NL ISSN: 0165-0513	1-3
A	compounds 10,21,23	13

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

☒ Patent family members are listed in annex.

° Special categories of cited documents :

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search 4 March 2004	Date of mailing of the international search report 25/03/2004
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer English, R

International Application No
PCT/US 03/33476

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	L. FIELD, ET AL.: "Preparation and chlorinolysis of alpha-mercaptodiethylacetic acid" JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 74, no. 18, 20 September 1952 (1952-09-20), pages 4707-4708, XP002270060 AMERICAN CHEMICAL SOCIETY, WASHINGTON, DC, US compound III	1,2,4
X	R.J. STOODLEY: "Studies related to penicillins. Part II. The rearrangement of 6-beta-aminopenicillanic acid to 2,3-dihdro-6-methoxycarbonyl-2,2-dimethyl-1,4-thiazin-3-one" JOURNAL OF THE CHEMICAL SOCIETY, SECTION C: ORGANIC CHEMISTRY, no. 23, 1968, pages 2891-2894, XP002270061 ROYAL SOCIETY OF CHEMISTRY, LETCHWORTH, GB page 2893, left-hand column, line 13 - line 14	1,2,4
X	GB 1 223 524 A (LAAKETHADAS ORION) 24 February 1971 (1971-02-24)	1,2
A	compounds of formula II page 5, line 20 - line 23	13
X	A. BISTRZYCKI, ET AL.: "Synthese von Abkömmlingen des 1,3-Oxthiophans" HELVETICA CHIMICA ACTA, vol. 3, 1920, pages 447-467, XP0008027599 VERLAG HELVETICA CHIMICA ACTA, BASEL, CH	1,2
A	page 466	13
A	WO 99/31144 A (E.I. DU PONT DE NEMOURS, ET AL.) 24 June 1999 (1999-06-24) compounds 63,64,66,69,71,72 page 2 - page 3; examples 24,26-28,30,33,34,36,40,41,50	1-20
A	WO 98/01478 A (E.I. DU PONT DE NEMOURS) 15 January 1998 (1998-01-15) cited in the application page 4 - page 5	1-20

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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.
A	R.T.A. MAYADUNNE, ET AL.: "Living radical polymerisation with reversible addition-fragmentation chain transfer (RAFT polymerisation) using dithiocarbamates as chain transfer agents" MACROMOLECULES, vol. 32, no. 21, 19 October 1999 (1999-10-19), pages 6977-6980, XP000866676 AMERICAN CHEMICAL SOCIETY, WASHINGTON, DC, US ISSN: 0024-9297 cited in the application the whole document	1-20
A	US 6 153 705 A (P. CORPART, ET AL.) 28 November 2000 (2000-11-28) cited in the application column 4 - column 5; claims 1,11,12; examples 1.1,1.9,2,3	1-20
A	D. TATON, ET AL.: "Direct synthesis of double hydrophilic statistical di- and triblock copolymers comprised of acrylamide and acrylic acid units via the MADIX process" MACROMOLECULAR RAPID COMMUNICATIONS, vol. 22, no. 18, December 2001 (2001-12), pages 1497-1503, XP002270318 WILEY VCH, WEINHEIM, DE cited in the application the whole document	1-20
A	M. DESTARAC, ET AL.: "Dithiocarbamates as universal reversible addition-fragmentation chain transfer agents" MACROMOLECULAR RAPID COMMUNICATIONS, vol. 21, no. 15, October 2000 (2000-10), pages 1035-1039, XP002270319 WILEY VCH, WEINHEIM, DE cited in the application table 1	1-20
A	F. ANDREANI, ET AL.: "New alpha-substituted aryl thioacetic derivatives forming analogues of clofibrate" IL FARMACO, EDIZIONE SCIENTIFICA, vol. 30, no. 10, October 1975 (1975-10), pages 847-858, XP002271975 SOCIETA CHIMICA ITALIANA, PAVIA, IT page 853, paragraph 2	13

International application No.
PCT/US 03/33476

INTERNATIONAL SEARCH REPORT

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

As a result of the prior review under R. 40.2(e) PCT,
null additional fees are to be refunded.

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-12, 13,14 (in part), 15, 16-19 (in part), 20

   Disubstituted S-carboxymethyldithiocarbonate and -dithiocarbamate derivatives of claim 1, polymers of claim 7 terminated by a dithiocarbonate or dithiocarbamate group and by a disubstituted carboxymethyl group, and the preparation of both groups of compounds.

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2. claims: 13,14,16-19 (in part)

   Process for the preparation of dithiocarbonate and dithiocarbamate derivatives not included in claim 1 and of polymers not included in claim 7.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 03/33476

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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