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(54) **ANTIFOULANT COMPOSITIONS FOR VAPOR-SPACE APPLICATIONS**

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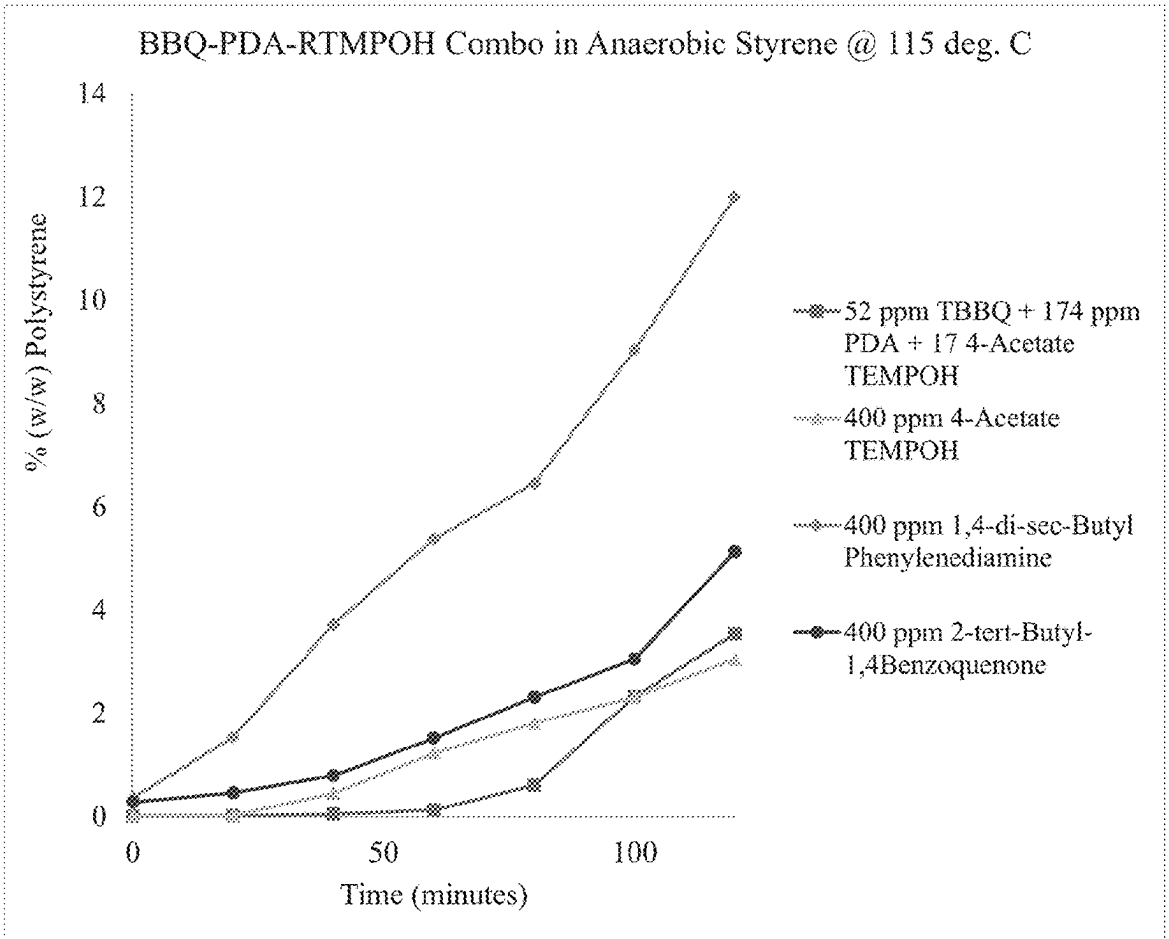
(57) **ABSTRACT**

Polymerization inhibitor compositions are provided. The polymerization inhibitor compositions include at least a first inhibitor compound including a hydroxylamine, a second inhibitor including phenylenediamine, and a third inhibitor including a benzoquinone or naphthoquinone. Methods of inhibiting the polymerization of monomers using the compositions of the disclosure are also provided. The methods of inhibiting polymerization of monomers include a step of adding a composition of the disclosure to the monomer. In some instances, the monomer is an ethylenically unsaturated monomer. Such ethylenically unsaturated monomers include, but are not limited to, vinyl acetate, acrylonitrile, acrylates, methacrylates, 1,3-butadiene, styrene, isoprene, (meth)acrylic acid, and combinations thereof. Methods of preparing the polymerization inhibitors and compositions of the disclosure are also provided.



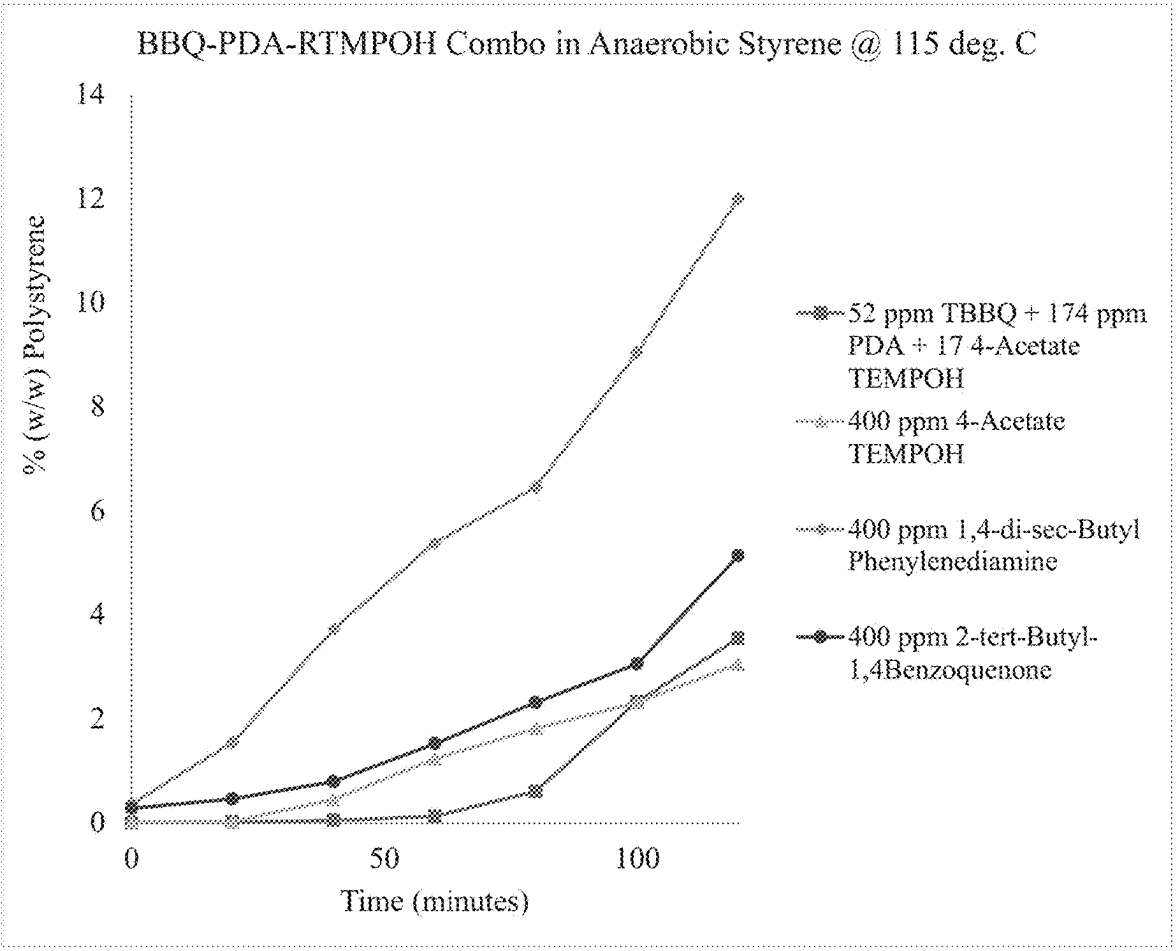

BBQ-PDA-RTMPOH Combo in Anaerobic Styrene @ 115 deg. C
% (w/w) Polystyrene
14
12
10
8
6
4
2
0
0
50
100
Time (minutes)
52 ppm TBBQ + 174 ppm PDA + 17 4-Acetate TEMPOH
400 ppm 4-Acetate TEMPOH
400 ppm 1,4-di-sec-Butyl Phenylenediamine
400 ppm 2-tert-Butyl-1,4Benzoquenone

FIG. 1

ANTIFOULANT COMPOSITIONS FOR VAPOR-SPACE APPLICATIONS

FIELD OF THE INVENTION

[0001] The present disclosure generally relates to compositions that include a blend of polymerization inhibitors and methods of using the same to inhibit unwanted polymerization in vapor-space areas. More particularly, the present disclosure relates to compositions that include at least one compound having a hydroxylamine of stable nitroxide radical, a quinone and a phenylenediamine, useful for inhibiting polymerization of ethylenic unsaturated monomers.

BACKGROUND

[0002] Ethylenically unsaturated monomers are typically manufactured in a three-stage process consisting of (i) reaction, (ii) recovery, and (iii) purification. Distillation operations at elevated temperatures are often involved in the recovery and purification stages. The processes include fractional distillation of the monomers. In the top sections of the distillation columns, purified monomer vapor condenses into liquid pools prior to transfer into storage facilities. Some of the condensed monomer streams cascade down the column. In the vapor space areas of the distillation column, the liquid monomer pools are likely to generate spontaneous or peroxide-initiated free-radicals. Current polymer inhibitor technologies are confined to liquid streams in the bottom sections of the process columns. The inhibitors are typically non-volatile so that they are confined to the bottom section of the distillation column, and no inhibitor reaches highly reactive monomer pools in the vapor-space sections. With conventional inhibitors, the pooled monomers are not treated to abate unwanted polymerization. For this reason, reactive monomers undesirably polymerize through radical polymerization especially at elevated temperature or when in contact with rust on the surfaces of the process equipment such as distillation column trays.

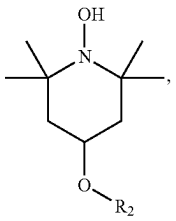
[0003] In the presence of polymerization initiators such as organic peroxides, which are ubiquitous in recycled streams previously exposed to atmospheric oxygen, this polymerization is particularly acute. Conventional polymerization inhibitors, such as 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (HTEMPO) and 4-oxo-2,2,6,6-tetramethylpiperidin-1-oxyl (OTEMPO) are generally effective. The premature polymerization of these monomers is generally controlled by directly dosing polymerization inhibitors into liquid hydrocarbon streams to reduce the premature polymerization of the monomers. However, these polymerization inhibitors (HTEMPO and OTEMPO) are not volatile. In the field, the process is accelerated when liquid monomer condenses on the trays, far above the bulk liquid that is treated with non-volatile polymerization inhibitors. The problem is acute if the trays have rust or when there are residual polymers in cracks and nooks. Equally important, preexisting polymers in equipment cracks, dead legs and stagnant pools of liquid monomer cause the rapid accumulation of foulant polymer due to the Norris-Trommsdorf effect. Due to accelerated polymerization, the growing polymer foulant causes mechanical damage and potential release of vast quantities of heat resulting in fires or explosions. The complete inhibition of tray corrosion or the complete removal of polymer from hard-to-reach locations in purification towers means that preventing unwanted polymerization in vapor spaces is difficult. It is in this regard that there is a pressing need for antipolymerants that are effective in the vapor-space sections of distillation columns.

BRIEF SUMMARY

[0004] A composition for inhibiting monomer polymerization is provided. The composition includes a first inhibitor compound comprising a hydroxylamine; a second inhibitor compound comprising a phenylenediamine; and a third inhibitor compound comprising a benzoquinone or naphthoquinone.

[0005] In some aspects, the first inhibitor compound is of formula (II):

(II)



wherein R_2 is C_1-C_{22} alkyl, C_1-C_{22} alkenyl, C_1-C_{22} alkynyl, C_1-C_{22} cycloalkyl, aryl, —C_1-C_{22} alkylene, —C(O)(C_1-C_{22} alkyl), —C(O)(C_1-C_{22} alkenyl), —C(O)(C_1-C_{22} alkynyl), —C(O)(C_1-C_{22} cycloalkyl), —C(O)(aryl), or —C(O)(C_1-C_{22} alkylene), wherein the alkyl, alkylene, cycloalkyl, and aryl are optionally substituted with one or more C_1-C_{22} alkyl, C_1-C_{22} alkenyl, C_1-C_{22} alkynyl, or aryl.

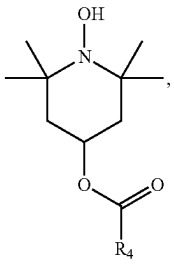
[0006] In some aspects, R_2 is —C(O)(C_1-C_{22} alkyl), —C(O)(C_1-C_{22} alkenyl), —C(O)(C_1-C_{22} alkynyl), —C(O)(C_1-C_{22} cycloalkyl), —C(O)(aryl), or —C(O)(C_1-C_{22} alkylene), wherein the alkyl, alkylene, cycloalkyl, and aryl are optionally substituted with one or more C_1-C_{22} alkyl, C_1-C_{22} alkenyl, C_1-C_{22} alkynyl, or aryl.

[0007] In some aspects, the first inhibitor is selected from the group consisting of: 2,2,6,6-tetramethylpiperin-1,4-diol; 4-methoxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-ethoxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-propoxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-butoxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-pentoxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-hexyloxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-heptyloxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-octyloxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-nonyloxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-decyloxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-undecyloxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-dodecyloxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-tridecyloxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-tetradecyloxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-pentadecyloxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-hexadecyloxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-heptadecyloxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-octadecyloxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-nodecyloxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-decyloxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-icosyloxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-henicosyloxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-docosyloxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-(phenoxy)-2,2,6,6-tetramethylpiperidin-1-ol; 4-(benzyloxy)-2,2, 6,6-

tetramethylpiperidin-1-ol; 2,2,6,6-tetramethyl-4-(naphthalen-2-yloxy)piperidin-1-ol; and any combination thereof.

[0008] In some aspects, the first inhibitor is a compound of formula IIa:

(IIa)

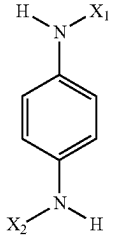


wherein R_4 is H, C_1-C_{22} alkyl, C_1-C_{22} alkenyl, C_1-C_{22} alkynyl, C_1-C_{22} cycloalkyl, aryl, —C_1-C_{22} alkylene, —C(O)(C_1-C_{22} alkyl), —C(O)(C_1-C_{22} alkenyl), —C(O)(C_1-C_{22} alkynyl), —C(O)(C_1-C_{22} cycloalkyl), —C(O)(aryl), or —C(O)(C_1-C_{22} alkylene), wherein the alkyl, alkylene, cycloalkyl, and aryl are optionally substituted with one or more C_1-C_{22} alkyl, C_1-C_{22} alkenyl, C_1-C_{22} alkynyl, or aryl.

[0009] In some aspects, the first inhibitor is selected from the group consisting of: 1-hydroxy-2,2,6,6-tetramethylpiperidin-4-yl acetate, 1-hydroxy-2,2,6,6-tetramethylpiperidin-4-yl propanoate, 1-hydroxy-2,2,6,6-tetramethylpiperidin-4-yl butyrate, 1-hydroxy-2,2,6,6-tetramethylpiperidin-4-yl pentanoate, 1-hydroxy-2,2,6, 6-tetramethylpiperidin-4-yl hexanoate, 1-hydroxy-2,2,6,6-tetramethylpiperidin-4-yl heptanoate, 1-hydroxy-2,2,6,6-tetramethylpiperidin-4-yl octanoate, 1-hydroxy-2,2,6,6-tetramethylpiperidin-4-yl nonanoate, 1-hydroxy-2,2,6,6-tetramethylpiperidin-4-yl decanoate, 1-hydroxy-2,2,6, 6-tetramethylpiperidin-4-ylundecanoate, 1-hydroxy-2,2,6,6-tetramethylpiperidin-4-yl dodecanoate, 1-hydroxy-2,2,6,6-tetramethylpiperidin-4-yl 2-ethylhexanoate, 1-hydroxy-2,2,6, 6-tetramethylpiperidin-4-yl stearate, 1-hydroxy-2,2,6,6-tetramethylpiperidin-4-yl benzoate, 1-hydroxy-2,2,6,6-tetramethylpiperidin-4-yl palmitoate, 1-hydroxy-2,2,6,6-tetramethylpiperidin-4-yl behenoate, 1-hydroxy-2,2,6,6-tetramethylpiperidin-4-yl 4-tert-butylbenzoate, or any combination thereof.

[0010] In some aspects, the second inhibitor compound is a phenylenediamine of formula (IV) or formula (V):

(IV)



para-phenylenediamine

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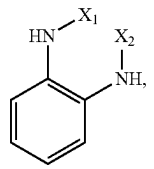
(V)



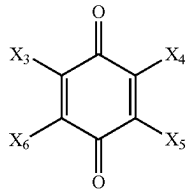
ortho-phenylenediamine

wherein X_1 and X_2 are independently C_1-C_{22} alkyl, or aryl, wherein the alkyl and aryl are optionally substituted with one or more C_1-C_{22} alkyl or aryl.

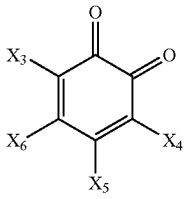
[0011] In some aspects, the second inhibitor is selected from the group consisting of: 1,2-phenylenediamine, 1,4-phenylenediamine, N,N'-di-methyl-p-phenylenediamine, N,N'-di-sec-butyl-1,4-phenylenediamine, N,N'-di-1,4-dimethylpentyl-1,4-phenylenediamine, N, N'-di-ethyl-1,4-phenylenediamine, N-tert-butyl-N'-phenyl-1,4-phenylenediamine, N,N'-di-phenyl-1,4-phenylenediamine, and any combination thereof.

[0012] In some aspects, the third inhibitor compound is a benzoquinone of formula (VI) or formula (VII):

(VI)



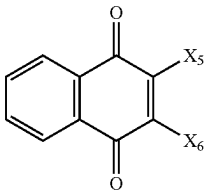
(VII)



wherein X_3, X_4, X_5, and X_6 are independently H, C_1-C_{22} alkyl, or aryl, wherein the alkyl and aryl are optionally substituted with one or more C_1-C_{22} alkyl or aryl.

[0013] In some aspects, the third inhibitor compound is a naphthoquinone of formula (VII) or formula (VIII):

(VII)



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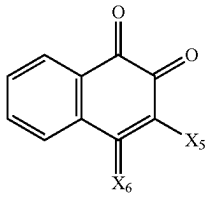
(VIII)



wherein X_5 and X_6 are independently H, C_1-C_{22} alkyl, aryl, wherein the alkyl and aryl are optionally substituted with one or more C_1-C_{22} alkyl or aryl.

[0014] In some aspects, the first inhibitor compound is present in the composition at a concentration of about 0.01% by weight to about 80% by weight, and the second inhibitor compound is present in the composition at a concentration of about 0.01% by weight to about 50% by weight.

[0015] In some aspects, the composition further comprises an organic solvent.

[0016] In some aspects, the composition further comprises an ethylenic unsaturated monomer selected from the group consisting of vinyl acetate, acrylonitrile, an acrylate, a methacrylate, 1,3-butadiene, styrene, isoprene, acrylic acid, methacrylic acid and any combination thereof.

[0017] A method of inhibiting polymerization of a monomer is provided. The method includes adding the composition described herein to the monomer.

[0018] In some aspects, the monomer is provided within a solution.

[0019] In some aspects, the solution further comprises one or more additional components selected from: an acid, an organic solvent, and water.

[0020] In some aspects, the monomer is an ethylenic unsaturated monomer.

[0021] In some aspects, the composition is added to the monomer such that a concentration of the first inhibitor compound is about 0.1 ppm to about 10,000 ppm.

[0022] In some aspects, the composition is added to the monomer such that a concentration of the second inhibitor compound is about 0.1 ppm to about 10,000 ppm.

[0023] In some aspects, the monomer is selected from the group consisting of vinyl acetate, acrylonitrile, an acrylate, a methacrylate, 1,3-butadiene, styrene, isoprene, acrylic acid, methacrylic acid and any combination thereof.

[0024] The foregoing has outlined rather broadly the features and technical advantages of the present disclosure in order that the detailed description that follows may be better understood. Additional features and advantages of the disclosure will be described hereinafter that form the subject of the claims of this application. It should be appreciated by those skilled in the art that the conception and the specific aspects disclosed may be readily utilized as a basis for modifying or designing other aspects for carrying out the same purposes of the present disclosure. It should also be realized by those skilled in the art that such equivalent aspects do not depart from the spirit and scope of the disclosure as set forth in the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0025] A detailed description of the invention is hereafter described with specific reference being made to the drawings.

[0026] FIG. **1** shows kinetic curves showing the effectiveness of the combination of 4-Acetate TEMPO and N,N'-di-sec-butyl-1,4-phenylenediamine as an antipolymerant compared to the performance of a 25 ppm dose of composition of N,N'-di-sec-butyl-1,4-phenylenediamine and 2,6-di-tert-butylphenol for styrene polymerization at about 135° C. using the static method.

DETAILED DESCRIPTION

[0027] Various aspects of the present disclosure are described below. The relationship and functioning of the various elements of the aspects may better be understood by reference to the following detailed description. However, aspects are not limited to those explicitly described herein and it should be understood that, in certain instances, details may have been omitted that are not necessary for an understanding of the aspects disclosed herein, such as-for example-conventional synthesis and/or formulation.

[0028] The present disclosure relates to compositions that include a blend of polymerization inhibitors and methods of using the same to inhibit the polymerization of ethylenic unsaturated monomers. Polymerization inhibitor compositions of the present disclosure include a hydroxylamine, a phenylenediamine, and a benzoquinone or naphthoquinone.

[0029] A "polymerization inhibitor," in the presence of polymerizable monomers, inhibits the formation of a polymer from those monomers during the induction time. After the induction time has lapsed, the polymer's formation occurs at substantially the same rate that it would form at in the absence of the polymerization inhibitor.

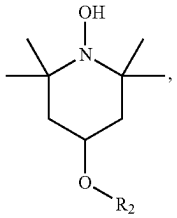
[0030] Polymerization inhibitors and polymerization retarders can be considered generally as "antipolymerants" which are compounds that can inhibit or reduce the formation of polymers from one or more radically polymerizable compounds.

[0031] The term "fouling" refers to the formation of polymers, prepolymers, oligomer and/or other materials, which would become insoluble in and/or precipitate from a stream and deposit on equipment under the conditions of operation of the equipment. In turn, the inhibitor, retarder, and amine stabilizer components and compositions of the disclosure can be referred to as "antifouling" as they inhibit or reduce such formation.

Compositions of the Disclosure

[0032] The present disclosure relates to compositions for inhibiting monomer polymerization where the compositions include a first inhibitor compound includes a hydroxylamine, a second inhibitor compound comprising a phenylenediamine, and a third inhibitor compound comprising a benzoquinone or naphthoquinone. In some aspects, the compositions are for inhibiting monomer polymerization, where the monomer is an ethylenic unsaturated monomer. For example, the compositions of the disclosure are useful for inhibiting polymerization of ethylenic unsaturated monomers including, but not limited to, vinyl acetate, acrylonitrile, acrylates, methacrylates, 1,3-butadiene, styrene, isoprene, (meth)acrylic acid, and combinations thereof.

[0033] In some aspects, the first inhibitor compound is of formula (II):



(II)

where R_2 is selected from H, C_1-C_{22} alkyl, C_1-C_{22} alkenyl, C_1-C_{22} alkynyl, C_1-C_{22} cycloalkyl, aryl, —C_1-C_{22} alkylene, —C(O)(C_1-C_{22} alkyl), —C(O)(C_1-C_{22} alkenyl), —C(O)(C_1-C_{22} alkynyl), —C(O)(C_1-C_{22} cycloalkyl), —C(O)(aryl), and —C(O)(C_1-C_{22} alkylene), wherein the alkyl, alkylene, cycloalkyl, and aryl are optionally substituted with one or more C_1-C_{22} alkyl, C_1-C_{22} alkenyl, C_1-C_{22} alkynyl, or aryl.

[0034] The term "aryl" refers to monocyclic, bicyclic (fused), and tricyclic (fused or spiro) hydrocarbon ring systems having a total of five to fourteen ring carbon atoms, wherein at least one ring in the system is aromatic and wherein each ring in the system contains 3 to 7 ring carbon atoms. The term "aryl" may be used interchangeably with the term "aryl ring."

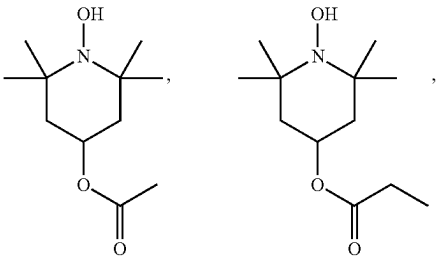
[0035] In certain aspects, R_2 is —C(O)(C_1-C_{22} alkyl), —C(O)(C_1-C_{22} alkenyl), —C(O)(C_1-C_{22} alkynyl), —C(O)(C_1-C_{22} cycloalkyl), —C(O)(aryl), and —C(O)(C_1-C_{22} alkylene), where the alkyl, alkylene, cycloalkyl, and aryl are optionally substituted with one or more C_1-C_{22} alkyl, C_1-C_{22} alkenyl, C_1-C_{22} alkynyl, or aryl.

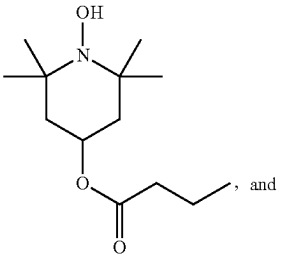
[0036] In some aspects, R_2 is H. In some aspects, R_2 is C_1-C_{22} alkyl. In some aspects, R_2 is C_1-C_{22} alkenyl. In some aspects, R_2 is C_1-C_{22} alkynyl. In some aspects, R_2 is C_1-C_{22} cycloalkyl, where the cycloalkyl is optionally substituted with one or more C_1-C_{22} alkyl, C_1-C_{22} alkenyl, C_1-C_{22} alkynyl, or aryl. In some aspects, R_2 is aryl, where the aryl is optionally substituted with one or more C_1-C_{22} alkyl, C_1-C_{22} alkenyl, C_1-C_{22} alkynyl, or aryl. In some aspects, R_2 is —C_1-C_{22} alkylene, where the alkylene is optionally substituted with aryl that is optionally substituted with one or more C_1-C_{22} alkyl, C_1-C_{22} alkenyl, C_1-C_{22} alkynyl, or aryl. In some aspects, R_2 is —C(O)(C_1-C_{22} alkyl). In some aspects, R_2 is —C(O)(C_1-C_{12} alkyl). In some aspects, R_2 is —C(O)(C_1-C_6 alkyl). In some aspects, R_2 is —C(O)(methyl). In some aspects, R_2 is —C(O)(ethyl). In some aspects, R_2 is —C(O)(propyl). In some aspects, R_2 is —C(O)(butyl). In some aspects, R_2 is —C(O)(C_1-C_{22} alkenyl). In some aspects, R_2 is —C(O)(C_1-C_{22} alkynyl). In some aspects, R_2 is —C(O)(C_1-C_{22} cycloalkyl), where the cycloalkyl is optionally substituted with one or more C_1-C_{22} alkyl, C_1-C_{22} alkenyl, C_1-C_{22} alkynyl, or aryl. In some aspects, R_2 is —C(O)(aryl), where the aryl is optionally substituted with one or more C_1-C_{22} alkyl, C_1-C_{22} alkenyl, C_1-C_{22} alkynyl, or aryl. In some aspects, R_2 is —C(O)(C_1-C_{22} alkylene), where the alkylene is optionally substituted with aryl that is optionally substituted with one or more C_1-C_{22} alkyl, C_1-C_{22} alkenyl, C_1-C_{22} alkynyl, or aryl.

[0037] In some aspects, the compound of formula (II) is 2,2,6,6-tetramethylpiperin-1,4-diol; 4-methoxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-ethoxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-propoxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-butoxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-pentoxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-hexyloxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-heptyloxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-octyloxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-nonyloxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-decyloxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-undecyloxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-dodecyloxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-tridecyloxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-tetradecyloxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-pentadecyloxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-hexadecyloxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-heptadecyloxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-octadecyloxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-nodecyloxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-decyloxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-icosyloxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-henicosyloxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-docosyloxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-(phenoxy)-2,2,6,6-tetramethylpiperidin-1-ol; 4-(benzyloxy)-2,2, 6,6-tetramethylpiperidin-1-ol; or 2,2,6,6-tetramethyl-4-(naphthalen-2-yloxy)piperidin-1-ol.

[0038] In certain aspects, the compositions of the disclosure include compounds of formula (I) and (II), respectively, where R_1 and R_2 are the same. For example, in some aspects, the compositions of the disclosure include compounds of formula (I) and (II), respectively, where R_1 and R_2 are each, independently, —C(O)(C_1-C_{22} alkyl). In certain aspects, the compositions of the disclosure include first and second inhibitor compounds of formula (I) and (II), respectively, where R_1 and R_2 are different.

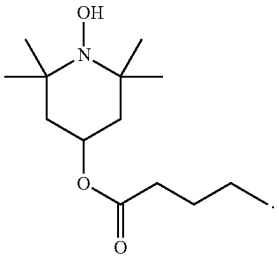
[0039] In some aspects, the second inhibitor compound having a hydroxylamine is selected from the group consisting of:



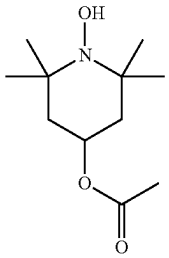


, and

-continued

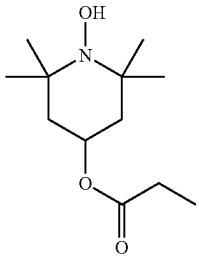


In some aspects, the second inhibitor compound having a hydroxylamine is:



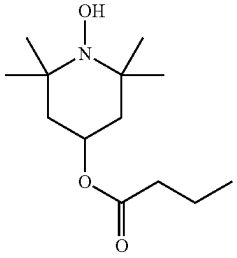
4-acetoxy-2,2,6,6-tetramethylpiperidin-1-ol.

In some aspects, the second inhibitor compound having a hydroxylamine is:



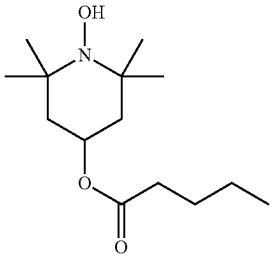
4-propionoxy-2,2,6,6-tetramethylpiperidin-1-ol.

In some aspects, the second inhibitor compound having a hydroxylamine is:



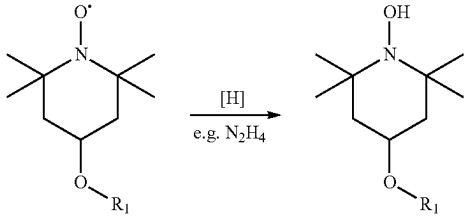
4-butyroxy-2,2,6,6-tetramethylpiperidin-1-ol.

In some aspects, the second inhibitor compound having a hydroxylamine is:

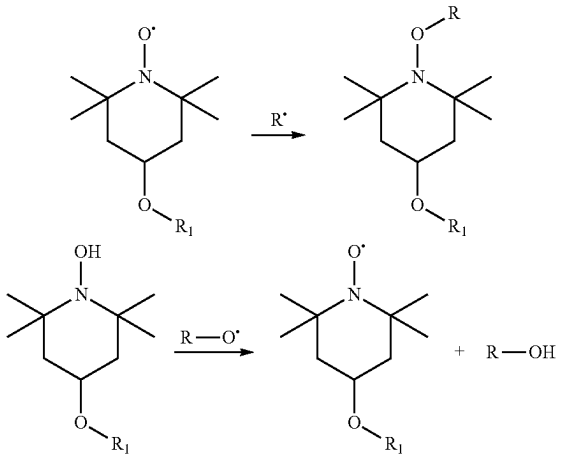


4-valeroxy-2,2,6,6-tetramethylpiperidin-1-ol.

[0040] The presently disclosed compound of formula (II) having a hydroxylamine has benefits over the corresponding nitroxide (compound of formula (I)), such as the capability to provide additional polymerization inhibition, as will be more fully explained below. A general synthetic route to produce a hydroxylamine of a nitroxide is to reduce its corresponding nitroxide with a reducing reagent as follows:



[0041] A hydroxylamine of a nitroxide has the potential to provide additional polymerization inhibition as compared to the corresponding nitroxide when carbon-centered and oxygen-centered radical initiators are present. This is explained as follows:



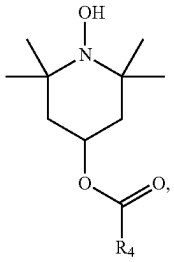
[0042] The hydroxylamine of a nitroxide is an excellent hydrogen donor due to its weak NO—H bond in the compound, and thus it is an efficient antioxidant. As an antioxidant, the hydroxylamine of a nitroxide easily reacts with

oxygen-centered radicals, such as peroxide radicals, while it's converted to its corresponding nitroxide. Nitroxides are generally known as the most effective inhibitors because of their superior inhibiting capabilities through scavenging carbon-centered free radicals at a nearly diffusion controlled rate. This rate is several orders of magnitude faster than phenolic compounds. However, their kinetic superiority is not always advantageous. For instance, it may lose its superiority when oxygen-centered radicals are present as the predominant free radicals. Another issue of concern with a nitroxide is its consumption through non-inhibition and unwanted reactions with process stream components or other inhibitor additives. As a result, high nitroxide inhibitor dosages are often required for a given inhibition efficacy, thereby making their use economically unattractive or even infeasible.

[0043] In essence, each hydroxylamine of a nitroxide is equivalent to one hydrogen donor plus one nitroxide anti-polymerant when oxygen-centered radicals and carbon-centered radicals are both present, which is an attractive incentive offered by the hydroxylamines of nitroxides. That is, one hydroxylamine of a nitroxide is able to eliminate one oxygen-centered radical and one carbon-centered radical whereas a nitroxide is only capable to eliminate a carbon-centered radical.

[0044] In some aspects, the first inhibitor is a compound of formula IIa:

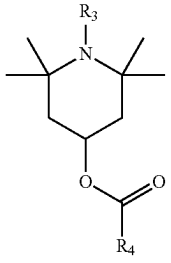
(IIa)



wherein R_4 is H, C_1-C_{22} alkyl, C_1-C_{22} alkenyl, C_1-C_{22} alkynyl, C_1-C_{22} cycloalkyl, aryl, —C_1-C_{22} alkylene, —C(O)(C_1-C_{22} alkyl), —C(O)(C_1-C_{22} alkenyl), —C(O)(C_1-C_{22} alkynyl), —C(O)(C_1-C_{22} cycloalkyl), —C(O)(aryl), or —C(O)(C_1-C_{22} alkylene), wherein the alkyl, alkylene, cycloalkyl, and aryl are optionally substituted with one or more C_1-C_{22} alkyl, C_1-C_{22} alkenyl, C_1-C_{22} alkynyl, or aryl.

[0045] In some aspects, the first inhibitor is a compound of formula III:

(III)



wherein R_3 is —O• or —OH; and R_4 is C_1-C_{22} alkyl or aryl, wherein the alkyl and aryl are optionally substituted with one or more C_1-C_{22} alkyl or aryl.

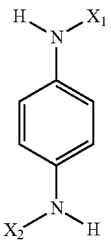
[0046] In some aspects, R_3 is —O•. In some aspects, R_3 is —OH.

[0047] In some aspects with regard to formulae (IIa) and (III), R_4 is C_1-C_{22} alkyl that is optionally substituted with one or more C**1**-C_{22} alkyl or aryl. In some aspects with regard to formulae (IIa) and (III), R_4 is C_1-C_5 alkyl that is optionally substituted with one or more C_1-C_{22} alkyl or aryl. In some aspects with regard to formulae (IIa) and (III), R_4 is C_1-C_4 alkyl that is optionally substituted with one or more C_1-C_{22} alkyl or aryl. In some aspects with regard to formulae (IIa) and (III), R_4 is C_1-C_{10} alkyl that is optionally substituted with one or more C_1-C_{22} alkyl or aryl. In some aspects with regard to formulae (IIa) and (III), R_4 is C_1-C_8 alkyl that is optionally substituted with one or more C_1-C_{22} alkyl or aryl. In some aspects, R_4 is aryl that is optionally substituted with one or more C_1-C_{22} alkyl or aryl. In some aspects, R_4 is methyl. In some aspects, R_4 is propyl. In some aspects, R_4 is butyl. In some aspects, R_4 is a C_5 alkyl group. In some aspects, R_4 is a C_6 alkyl group. In some aspects, R_4 is a C_7 alkyl group. In some aspects, R_4 is a C_8 alkyl group. In some aspects, R_9 is a C_5 alkyl group. In some aspects, R_4 is a C_{10} alkyl group. In some aspects, R_4 is a C_{22} alkyl group. In some aspects, R_4 is a C_{21} alkyl group. In some aspects, R_4 is a C_{11} alkyl group. In some aspects, R_4 is a benzyl group.

[0048] Examples of a compound of formulae (IIa) or (III) include, but are not limited to, 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl acetate; 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl propanoate; 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl butyrate; 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl pentanoate; 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl hexanoate; 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl heptanoate; 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl octanoate; 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl nonanoate; 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl decanoate; 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl undecanoate; 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl dodecanoate; 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl 2-ethylhexanoate; 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl stearate; 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl benzoate; 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl palmitoate; 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl behenoate; or 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl 4-tert-butylbenzoate.

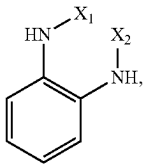
[0049] In some aspects, the compound of formulae (IIa) or (III) is 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl acetate; 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl propanoate; or 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl butyrate. In some aspects, the compound of formulae (IIa) or (III) is 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl acetate. In some aspects, the compound of formulae (IIa) or (III) is 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl propanoate. In some aspects, the compound of formulae (IIa) or (III) is 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl butyrate.

[0050] In some aspects, the second inhibitor compound is a phenylenediamine of formula (IV) or formula (V):



(IV)

para-phenylenediamine



(V)

ortho-phenylenediamine

wherein X_1 and X_2 are independently C_1-C_{22} alkyl, or aryl, wherein the alkyl and aryl are optionally substituted with one or more C_1-C_{22} alkyl or aryl.

[0051] In some aspects, the second inhibitor compound is a phenylenediamine of formula (IV). In some aspects, the second inhibitor compound is a phenylenediamine of formula (V).

[0052] Examples of phenylenediamines include, but are not limited to, 1,2-phenylenediamine, 1,4-phenylenediamine, N,N'-di-methyl-p-phenylenediamine, N,N'-di-sec-butyl-1,4-phenylenediamine, N,N'-di-1,4-dimethylpentyl-1,4-phenylenediamine, N,N'-di-ethyl-1,4-phenylenediamine, N-tert-butyl-N'-phenyl-1,4-phenylenediamine, and N,N'-diphenyl-1,4-phenylenediamine.

[0053] In some aspects, the phenylenediamine is N,N'-di-sec-butyl-1,4-phenylenediamine, N,N'-di-1,4-dimethylpentyl-1,4-phenylenediamine, N,N'-di-ethyl-1,4-phenylenediamine, N-tert-butyl-N'-phenyl-1,4-phenylenediamine, or N,N'-di-phenyl-1,4-phenylenediamine.

[0054] In some aspects, the phenylenediamine is N,N'-di-sec-butyl-1,4-phenylenediamine.

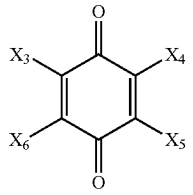
[0055] In some aspects, the phenylenediamine is N,N'-di-1,4-dimethylpentyl-1,4-phenylenediamine.

[0056] In some aspects, the phenylenediamine is N,N'-di-ethyl-1,4-phenylenediamine.

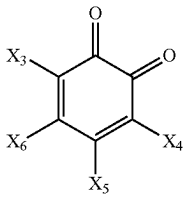
[0057] In some aspects, the phenylenediamine is N-tert-butyl-N'-phenyl-1,4-phenylenediamine.

[0058] In some aspects, the phenylenediamine is N,N'-diphenyl-1,4-phenylenediamine.

[0059] In some aspects, the third inhibitor compound is a benzoquinone of formula (VI) or formula (VII):



(VI)

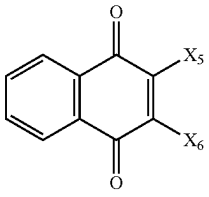


(VII)

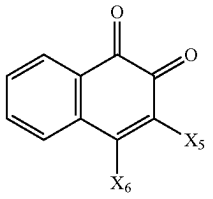
wherein X_3, X_4, X_5, and X_6 are independently H, C_1-C_{22} alkyl, or aryl, wherein the alkyl and aryl are optionally substituted with one or more C_1-C_{22} alkyl or aryl.

[0060] In some aspects, the third inhibitor compound is a benzoquinone of formula (VI). In some aspects, the third inhibitor compound is a benzoquinone of formula (VII).

[0061] In some aspects, the third inhibitor compound is a naphthoquinone of formula (VII) or formula (VIII):



(VII)



(VIII)

wherein X_5 and X_6 are independently H, C_1-C_{22} alkyl, aryl, wherein the alkyl and aryl are optionally substituted with one or more C_1-C_{22} alkyl or aryl.

[0062] In some aspects, X_5 and X_6 are independently H or C_1-C_{22} alkyl.

[0063] In some aspects, X_5 and X_6 are independently H or C_1-C_{15} alkyl.

[0064] In some aspects, X_5 and X_6 are independently H or C_1-C_{10} alkyl.

[0065] In some aspects, X_5 and X_6 are independently H or C_1-C_5 alkyl.

[0066] In some aspects, the third inhibitor compound is a naphthoquinone of formula (VII). In some aspects, the third inhibitor compound is a naphthoquinone of formula (VIII).

[0067] In some aspects, X_3, X_4, X_5, and X_6 are independently H or C_1-C_{22} alkyl. In some aspects, at least one of X_3, X_4, X_5, and X_6 is C_1-C_{22} alkyl. In some aspects, X_3, X_4, and X_5 are H and X_6 is C_1-C_{22} alkyl. In some aspects, X_3, X_4, and X_5 are H and X_6 is C_1-C_{10} alkyl. In some aspects, X_3, X_4, and X_5 are H and X_6 is tert-butyl.

[0068] Examples of benzoquinones include, but are not limited to, 2-tert-butyl-1,4-benzoquinone, 2-tert-butyl-5-methylbenzoquinone, 2-sec-butyl-5-methylbenzoquinone, 2-n-butyl-5-methylbenzoquinone, 2-sec-butyl-5-methylbenzoquinone, 2-iso-propyl-5-methylbenzoquinone, 2,5-di-sec-butylbenzoquinone, 2,5-di-tert-butylbenzoquinone, 2,5-di-iso-popylbenzoquinone, 2,6-di-sec-butylbenzoquinone, 2,6-di-tert-butylbenzoquinone, 2,6-di-iso-popylbenzoquinone, 2,6-di-methylbenzoquinone, 2,5-di-methylbenzoquinone, 2,6-di-ethylbenzoquinone, 2,5-di-ethylbenzoquinone, 2,6-di-proylbenzoquinone, 2,5-di-propylbenzoquinone, 2,6-di-n-butylbenzoquinone, 2,5-di-n-buylbenzoquinone, 2,6-di-tert-butylbenzoquinone, 2,6-di-iso-propylbenzoquinone, 2-n-pentylbenzoquinone, 2,6-di-n-pentylbenzoquinone, 2,6-di-n-pentylbenzoquinone, 2-n-hexylbenzoquinone, 2,6-di-hexylbenzoquinone, 2,6-di-hexylbenzoquinone, 2-n-heptylbenzoquinone, 2,6-di-heptylbenzoquinone, 2,6-di-heptylbenzoquinone, 2-n-octylbenzoquinone, 2,6-di-octylbenzoquinone, 2,6-di-octylbenzoquinone, 2-n-nonylbenzoquinone, 2,6-di-nonylbenzoquinone, 2,6-di-nonylbenzoquinone, 2-n-decylbenzoquinone, 2,6-di-decylbenzoquinone, 2,6-di-decylbenzoquinone, 2-n-undecylbenzoquinone, 2,6-di-undecylbenzoquinone, 2,6-di-undecylbenzoquinone, 2-n-dodecylbenzoquinone, 2,6-di-dodecylbenzoquinone, and 2,6-di-dodecylbenzoquinone

[0069] In some aspects, the benzoquinone is 2-tert-butyl-1,4-benzoquinone.

[0070] Examples of naphthoquinones include, but are not limited to, 1,4-naphthoquinone, 1,2-naphthoquinone, 1-methyl-1,4-naphthoquinone, 1-ethyl-1,4-naphthoquinone, 1-n-propyl-1,4-naphthoquinone, 1-isopropyl-1,4-naphthoquinone, 1-n-butyl-1,4-naphthoquinone, 1-sec-butyl-1,4-naphthoquinone, 1-tert-butyl-1,4-naphthoquinone, 1-methyl-1,2-naphthoquinone, 1-ethyl-1,2-naphthoquinone, 1-n-propyl-1,2-naphthoquinone, 1-isopropyl-1,2-naphthoquinone, 1-n-butyl-1,2-naphthoquinone, 1-sec-butyl-1,2-naphthoquinone, and 1-tert-butyl-1,2-naphthoquinone

[0071] In some aspects, the composition consists essentially of a first inhibitor compound, a second inhibitor compound, and a third inhibitor compound. In other aspects, the composition consists of an organic solvent, a first inhibitor, a second inhibitor, and a third inhibitor compound. In some aspects, the composition does not include 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl.

[0072] In some aspects, the first inhibitor compound is present in the composition at a concentration of about 0.01% by weight to about 80% by weight. In some aspects, the first inhibitor compound is present in the composition at a concentration of about 0.01% by weight to about 70% by weight. In some aspects, the first inhibitor compound is present in the composition at a concentration of about 0.01% by weight to about 60% by weight. In some aspects, the first inhibitor compound is present in the composition at a concentration of about 0.01% by weight to about 50% by weight. In some aspects, the first inhibitor compound is present in the composition at a concentration of about 0.01% by weight to about 40% by weight. In some aspects, the first inhibitor compound is present in the composition at a concentration of about 0.01% by weight to about 30% by weight. In some aspects, the first inhibitor compound is present in the composition at a concentration of about 0.01% by weight to about 20% by weight. In some aspects, the first inhibitor compound is present in the composition at a concentration of about 0.01% by weight to about 10% by weight.

[0073] For example, in certain aspects, the first inhibitor compound is present in the composition at a concentration of about 0.01% by weight, about 0.1% by weight, about 1% by weight, about 5% by weight, about 10% by weight, about 15% by weight, about 20% by weight, about 25% by weight, about 30% by weight, about 35% by weight, about 40% by weight, about 45% by weight, about 50% by weight, about 55% by weight, about 60% by weight, about 65% by weight, about 70% by weight, about 75% by weight, or about 80% by weight.

[0074] In some aspects, the second inhibitor compound is present in the composition at a concentration of about 0.01% by weight to about 50% by weight. In some aspects, the second inhibitor compound is present in the composition at a concentration of about 0.01% by weight to about 40% by weight. In some aspects, the second inhibitor compound is present in the composition at a concentration of about 0.01% by weight to about 30% by weight. In some aspects, the second inhibitor compound is present in the composition at a concentration of about 0.01% by weight to about 20% by weight. In some aspects, the second inhibitor compound is present in the composition at a concentration of about 0.01% by weight to about 10% by weight.

[0075] For example, in certain aspects, the second inhibitor compound is present in the composition at a concentration of about 0.01% by weight, about 0.1% by weight, about 1% by weight, about 5% by weight, about 10% by weight, about 15% by weight, about 20% by weight, about 25% by weight, about 30% by weight, about 35% by weight, about 40% by weight, about 45% by weight, or about 50% by weight.

[0076] In some aspects, the third inhibitor compound is present in the composition at a concentration of about 0.01% by weight to about 80% by weight. In some aspects, the third inhibitor compound is present in the composition at a concentration of about 0.01% by weight to about 70% by weight. In some aspects, the third inhibitor compound is present in the composition at a concentration of about 0.01% by weight to about 60% by weight. In some aspects, the third inhibitor compound is present in the composition at a concentration of about 0.01% by weight to about 50% by weight. In some aspects, the third inhibitor compound is present in the composition at a concentration of about 0.01% by weight to about 40% by weight. In some aspects, the third inhibitor compound is present in the composition at a concentration of about 0.01% by weight to about 30% by weight. In some aspects, the third inhibitor compound is present in the composition at a concentration of about 0.01% by weight to about 20% by weight. In some aspects, the third inhibitor compound is present in the composition at a concentration of about 0.01% by weight to about 10% by weight.

[0077] For example, in certain aspects, the third inhibitor compound is present in the composition at a concentration of about 0.01% by weight, about 0.1% by weight, about 1% by weight, about 5% by weight, about 10% by weight, about 15% by weight, about 20% by weight, about 25% by weight,

about 30% by weight, about 35% by weight, about 40% by weight, about 45% by weight, about 50% by weight, about 55% by weight, about 60% by weight, about 65% by weight, about 70% by weight, about 75% by weight, or about 80% by weight.

[0078] In some aspects, a mole ratio of the first inhibitor compound to the second inhibitor compound is about 100:1 to about 1:100. In some aspects, a mole ratio of the first inhibitor compound to the second inhibitor compound is about 90:1 to about 1:90. In some aspects, a mole ratio of the first inhibitor compound to the second inhibitor compound is about 80:1 to about 1:80. In some aspects, a mole ratio of the first inhibitor compound to the second inhibitor compound is about 70:1 to about 1:70. In some aspects, a mole ratio of the first inhibitor compound to the second inhibitor compound is about 60:1 to about 1:60. In some aspects, a mole ratio of the first inhibitor compound to the second inhibitor compound is about 50:1 to about 1:50. In some aspects, a mole ratio of the first inhibitor compound to the second inhibitor compound is about 40:1 to about 1:40. In some aspects, a mole ratio of the first inhibitor compound to the second inhibitor compound is about 30:1 to about 1:30. In some aspects, a mole ratio of the first inhibitor compound to the second inhibitor compound is about 20:1 to about 1:20. In some aspects, a mole ratio of the first inhibitor compound to the second inhibitor compound is about 10:1 to about 1:10. In some aspects, a mole ratio of the first inhibitor compound to the second inhibitor compound is about 1:1.

[0079] In some aspects, the composition also includes one or more additional compounds selected from the group consisting of 2,2,6,6-tetramethylpiperidin-1-oxyl; 2,2,6,6-tetramethylpiperidin-1-ol; 4-hydroxyl-2,2,6,6-tetramethylpiperidin-1-oxyl; 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-oxo-2,2,6,6-tetramethylpiperidin-1-oxyl; 4-oxo-2,2,6,6-tetramethylpiperidin-1-ol; 4-acetoxy-2,2,6,6-tetramethylpiperidin-1-oxyl; 4-acetoxy-2,2,6,6-tetramethylpiperidin-1-ol; 4-propionoxy-2,2,6,6-tetramethylpiperidin-1-oxyl; 4-propionoxy-2,2,6,6-tetramethylpiperidin-1-ol; and bis((2,2,6,6-tetramethylpiperidin-1-oxyl)-4-yl) oxalate. In some aspects, the composition also includes 2,2,6,6-tetramethylpiperidin-1-oxyl. In some aspects, the composition also includes 2,2,6,6-tetramethylpiperidin-1-ol. In some aspects, the composition also includes 4-hydroxyl-2,2,6,6-tetramethylpiperidin-1-oxyl. In some aspects, the composition also includes 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-ol. In some aspects, the composition also includes 4-oxo-2,2,6,6-tetramethylpiperidin-1-oxyl. In some aspects, the composition also includes 4-oxo-2,2,6,6-tetramethylpiperidin-1-ol. In some aspects, the composition also includes 4-acetoxy-2,2,6,6-tetramethylpiperidin-1-oxyl. In some aspects, the composition also includes 4-acetoxy-2,2,6,6-tetramethylpiperidin-1-ol. In some aspects, the composition also includes 4-propionoxy-2,2,6,6-tetramethylpiperidin-1-oxyl. In some aspects, the composition also includes 4-propionoxy-2,2,6,6-tetramethylpiperidin-1-ol. In some aspects, the composition also includes bis((2,2,6,6-tetramethylpiperidin-1-oxyl)-4-yl) oxalate.

[0080] The composition may optionally also include one or more organic solvents. One of ordinary skill in the art will appreciate that there are many organic solvents that are compatible with the compositions of the disclosure. For example, in some aspects, the one or more organic solvents are selected from vinyl acetate, dimethyl phthalate, dimethylformamide, toluene, xylene, highly aromatic naphtha, acetonitrile, ethyl acetate, acetone, dichloromethane, tetrahydrofuran, hexanes, dimethyl sulfoxide, N-methyl-2-pyrrolidone, and combinations thereof. In certain aspects, the composition also includes vinyl acetate. In certain aspects, the composition also includes dimethyl phthalate. In certain aspects, the composition also includes dimethylformamide. In certain aspects, the composition also includes toluene. In certain aspects, the composition also includes xylene. In certain aspects, the composition also includes highly aromatic naphtha. In certain aspects, the composition also includes acetonitrile.

[0081] In some aspects, the composition also includes one or more ethylenic unsaturated monomers. One of ordinary skill in the art will appreciate that there are many ethylenic unsaturated monomers that are compatible with the compositions of the disclosure. For example, in some aspects, the one or more ethylenic unsaturated monomers are selected from vinyl acetate, acrylonitrile, acrylate esters, methacrylate esters, 1,3-butadiene, styrene, isoprene, (meth)acrylic acid, and combinations thereof. In certain aspects, the composition also includes vinyl acetate. In certain aspects, the composition also includes acrylonitrile. In certain aspects, the composition also includes acrylates. In certain aspects, the composition also includes methacrylates. In certain aspects, the composition also includes 1,3-butadiene. In certain aspects, the composition also includes styrene. In certain aspects, the composition also includes isoprene. In certain aspects, the composition also includes acrylic acid and (meth)acrylic acid.

Methods of Using the Compositions of the Disclosure

[0082] The present disclosure also relates to methods of inhibiting polymerization of monomers that include adding a composition of the disclosure to the monomer. In some aspects, an effective amount of the composition of the disclosure is added to the monomer, where an effective amount is any amount sufficient to inhibit the polymerization of the monomer.

[0083] In some aspects, the monomer is an ethylenic unsaturated monomer. In some aspects the monomer is an ethylenic unsaturated monomer selected from vinyl acetate, acrylonitrile, acrylate esters, methacrylate esters, 1,3-butadiene, styrene, isoprene, (meth)acrylic acid, and combinations thereof are disclosed. In some aspects, the methods disclosed herein are useful in inhibiting the polymerization of vinyl acetate. In some aspects, the methods disclosed herein are useful in inhibiting the polymerization of acrylonitrile. In some aspects, the methods disclosed herein are useful in inhibiting the polymerization of acrylates. In some aspects, the methods disclosed herein are useful in inhibiting the polymerization of methacrylates. In some aspects, the methods disclosed herein are useful in inhibiting the polymerization of 1,3-butadiene. In some aspects, the methods disclosed herein are useful in inhibiting the polymerization of styrene. In some aspects, the methods disclosed herein are useful in inhibiting the polymerization of isoprene. In some aspects, the methods disclosed herein are useful in inhibiting the polymerization of (meth)acrylic acid.

[0084] The composition of the disclosure can be added manually or automatically to the fluid. The composition can also be added continuously and/or intermittently. Automatic addition may be accomplished through the use of chemical

injection pumps. The chemical injection pumps may be programmed to add particular amounts of the polymerization inhibitor composition, or any components thereof, at certain time intervals to the fluid. In alternate aspects, the chemical injection pumps can be manually controlled to add particular amounts of the polymerization inhibitor composition, or any components thereof, to the fluid. Addition of the presently disclosed polymerization inhibitor compositions to the monomer will thereby inhibit polymerization of the monomer.

[0085] In some aspects, the monomer is provided as a neat liquid. In other aspects, the monomer is provided within a solution, hereafter referred to as "the monomer solution."

[0086] In some aspects, the monomer solution also includes one or more additional components selected from an acid, an organic solvent, water, and combinations thereof. For example, in some aspects, the monomer solution includes one or more organic solvents selected from vinyl acetate, dimethyl phthalate, dimethylformamide, toluene, xylene, highly aromatic naphtha, acetonitrile, ethyl acetate, acetone, dichloromethane, tetrahydrofuran, hexanes, dimethyl sulfoxide, N-methyl-2-pyrrolidone, and combinations thereof.

[0087] In some aspects, the composition is added to the monomer such that a concentration of the first inhibitor compound is about 0.1 ppm to about 10,000 ppm. In some aspects, the composition is added to the monomer such that a concentration of the first inhibitor compound is about 0.1 ppm to about 5,000 ppm. In some aspects, the composition is added to the monomer such that a concentration of the first inhibitor compound is about 0.1 ppm to about 1,000 ppm. In some aspects, the composition is added to the monomer such that a concentration of the first inhibitor compound is about 0.1 ppm to about 500 ppm.

[0088] In some aspects, the composition is added to the monomer such that a concentration of the second inhibitor compound is about 0.1 ppm to about 10,000 ppm. In some aspects, the composition is added to the monomer such that a concentration of the second inhibitor compound is about 0.1 ppm to about 5,000 ppm. In some aspects, the composition is added to the monomer such that a concentration of the second inhibitor compound is about 0.1 ppm to about 1,000 ppm. In some aspects, the composition is added to the monomer such that a concentration of the second inhibitor compound is about 0.1 ppm to about 500 ppm.

[0089] In some aspects, the composition is added to the monomer such that a concentration of the third inhibitor compound is about 0.1 ppm to about 10,000 ppm. In some aspects, the composition is added to the monomer such that a concentration of the third inhibitor compound is about 0.1 ppm to about 5,000 ppm. In some aspects, the composition is added to the monomer such that a concentration of the third inhibitor compound is about 0.1 ppm to about 1,000 ppm. In some aspects, the composition is added to the monomer such that a concentration of the third inhibitor compound is about 0.1 ppm to about 500 ppm.

[0090] The methods of the disclosure are useful for inhibiting the premature polymerization of monomers during manufacturing process, particularly those that are performed under acidic conditions. For example, the methods of the disclosure are useful for preventing polymerization of acrylates, which may include, but are not limited to, acrylonitrile, acrylic acid, methyl methacrylic acid and its esters, and vinyl acetate.

[0091] The methods of the disclosure are also useful for preventing the premature polymerization of styrene during manufacturing and purification processes.

[0092] The methods of the disclosure are also useful in butadiene extraction processes. This utility stems from the balanced partition coefficients between polar organic phases and organic phases.

[0093] In some aspects, the compositions disclosed herein are used in distillative purification of olefins. For example, the composition can be added to the process stream before entering the distillation unit or the composition can be added to the process stream in the distillation unit.

Examples

Example 1—Polymerization Inhibition with N,N-di-sec-butylphenylenediamine (PDA)

[0094] The ability of compositions of the disclosure to inhibit the polymerization of polystyrene was assessed via the following protocol. Styrene was used as the reactive monomer for the polymerization kinetics studies and screening of the proposed antipolymerant products. To prevent polymerization during storage and transportation, styrene is stabilized with tert-butylcatechol (TBC). For each run of experiments, the stabilizer was removed, and the styrene thus freshly cleaned was used immediately. Styrene was used as the reactive monomer for the polymerization kinetics studies and screening of the proposed antipolymerant products. To prevent polymerization during storage and transportation, styrene is stabilized with TBC. For each run of experiments, the stabilizer was removed, and the styrene thus freshly cleaned was used immediately.

[0095] As a precaution, styrene that was cleaned and stored overnight, even under sub-zero refrigeration conditions, had to be discarded, since there was notable polymerization under storage. Alumina was used to remove the TBC using a chromatography column. The alumina column was prepared on the day of the scheduled set of experiments.

[0096] Into a 500 mL round bottom flask, about 300 mL of neat neat styrene treated with about 400 ppm of N, N-di-sec-butylphenylenediamine, the prototype PDA, were charged. A thermocouple was inserted directly into the reaction solution and the reaction temperature of the solution set for 115° C. To prevent the loss of the reaction solution due to evaporation, the flask was armed with a reflux equipment before being placed on a heating block. Through another port, a stream of nitrogen was flowed through the reaction solution while under vigorous stirring during the course of the kinetics study. The moment in time when the solution temperature reached 115° C. was designated as the beginning of the study, or time zero. A sample of the reaction solution was taken from the reactor after which the solution was immediately diluted with toluene. The concentration of polystyrene in the diluted solution was analyze using a proprietary procedure. From that point in time, a sample was collected every 20 minutes and the reaction solution similarly diluted and analyzed for the concentration of polystyrene.

Example 2—Polymerization Inhibition with 4-Acetoxy TEMPOH

[0097] The polymerization reactor was charged with 300 mL of styrene freshly cleaned and treated with 400 ppm of 4-Acetoxy TEMPOH. The reaction kinetics study was conducted as illustrated in Example 1.

Example 3—Polymerization Inhibition with 2-tert-Butylbenzoquinone

[0098] Using the procedure in the above examples, the antipolymerant performance of 400 ppm of 2-tert-butylbenzoquinone was carried out.

Example 4—Polymerization Inhibition with a Synergistic Composition of 2-tert-Butylbenzoquinone, 4-Acetoxy TEMPOH and PDA

[0099] A freshly prepared solution of styrene, 300 mL, was treated with 52 ppm of TBBQ, 174 ppm of PDA and 174 ppm of 4-Acetoxy TEMPOH. The solution was transferred into polymerization reactor followed by the kinetics study using the procedure in the foregoing examples.

[0100] The samples tested and the results of the assay are shown in FIG. **1** and summarized in Table 1 below.

TABLE 1

Percent (w/w) concentration of polystyrene under anaerobic conditions.

Time	400 ppm 4-acetate TEMPOH	400 ppm PDA	400 ppm TBBQ	52 ppm TBBQ + 174 ppm PDA + 174-Acetate TEMPOH
0	0.0213	0.362	0.279	0.00825
20	0.0266	1.54	0.461	0.0183
40	0.450	3.72	0.794	0.0480
60	1.23	5.38	1.52	0.128
80	1.81	6.45	2.31	0.605
100	2.31	9.03	3.05	2.32
120	3.05	12.0	5.13	3.54

[0101] All of the compositions and methods disclosed and claimed herein can be made and executed without undue experimentation in light of the present disclosure. While this invention may be embodied in many different forms, there are described in detail herein specific preferred aspects of the invention. The present disclosure is an exemplification of the principles of the invention and is not intended to limit the invention to the particular aspects illustrated. In addition, unless expressly stated to the contrary, use of the term "a" is intended to include "at least one" or "one or more." For example, "a compound" is intended to include "at least one compound" or "one or more compounds."

[0102] Any ranges given either in absolute terms or in approximate terms are intended to encompass both, and any definitions used herein are intended to be clarifying and not limiting. Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard deviation found in their respective testing measurements. Moreover, all ranges disclosed herein are to be understood to encompass any and all subranges (including all fractional and whole values) subsumed therein.

[0103] Any composition disclosed herein may comprise, consist of, or consist essentially of any element, component and/or ingredient disclosed herein or any combination of two or more of the elements, components or ingredients disclosed herein.

[0104] Any method disclosed herein may comprise, consist of, or consist essentially of any method step disclosed herein or any combination of two or more of the method steps disclosed herein.

[0105] The transitional phrase "comprising," which is synonymous with "including," "containing," or "characterized by," is inclusive or open-ended and does not exclude additional, un-recited elements, components, ingredients and/or method steps.

[0106] The transitional phrase "consisting of" excludes any element, component, ingredient, and/or method step not specified in the claim.

[0107] The transitional phrase "consisting essentially of" limits the scope of a claim to the specified elements, components, ingredients and/or steps, as well as those that do not materially affect the basic and novel characteristic(s) of the claimed invention.

[0108] As used herein, the term "about" refers to the cited value being within the errors arising from the standard deviation found in their respective testing measurements, and if those errors cannot be determined, then "about" may refer to, for example, within 5% of the cited value.

[0109] Furthermore, the invention encompasses any and all possible combinations of some or all of the various aspects described herein. It should also be understood that various changes and modifications to the presently preferred aspects described herein will be apparent to those skilled in the art. Such changes and modifications can be made without departing from the spirit and scope of the invention and without diminishing its intended advantages. It is therefore intended that such changes and modifications be covered by the appended claims.

What is claimed is:

1. A composition for inhibiting monomer polymerization, comprising:

a first inhibitor compound comprising 4-acetoxy TEMPO;

a second inhibitor compound comprising 2-tert-butylbenzoquinone; and

a third inhibitor compound comprising N,N'-di-sec-butyl phenylenediamine.

2. The composition of claim **1**, wherein the first inhibitor compound is present in the composition at a concentration of about 0.01% by weight to about 80% by weight and the second inhibitor compound is present in the composition at a concentration of about 0.01% by weight to about 50% by weight.

3. The composition of claim **1**, further comprising an organic solvent.

4. The composition of claim **1**, further comprising an ethylenic unsaturated monomer selected from the group consisting of vinyl acetate, acrylonitrile, an acrylate, a methacrylate, 1,3-butadiene, styrene, isoprene, acrylic acid, methacrylic acid and any combination thereof.

5. A method of inhibiting polymerization of a monomer, comprising:

adding a composition to the monomer, the composition comprising a first inhibitor compound comprising 4-acetoxy TEMPO, a second inhibitor compound comprising 2-tert-butylbenzoquinone, and a third inhibitor compound comprising N,N'-di-sec-butyl phenylenediamine.

6. The method of claim **5**, wherein the monomer is provided within a solution.

7. The method of claim **6**, wherein the solution further comprises an additional component selected from the group consisting of an acid, an organic solvent, water, and any combination thereof.

8. The method of claim **5**, wherein the monomer is an ethylenic unsaturated monomer.

9. The method of claim **5**, further comprising adding from about 0.1 ppm to about 10,000 ppm of the first inhibitor compound.

10. The method of claim **5**, further comprising adding from about **0.1** ppm to about 10,000 ppm of the second inhibitor compound.

11. The method of claim **5**, the wherein the monomer is selected from the group consisting of vinyl acetate, acrylonitrile, an acrylate, a methacrylate, 1,3-butadiene, styrene, isoprene, acrylic acid, methacrylic acid and any combination thereof.

12. A method of inhibiting polymerization of a monomer, comprising:

adding a composition to the monomer, the composition consisting essentially of a first inhibitor compound comprising a hydroxylamine, a second inhibitor compound comprising a phenylenediamine, and a third inhibitor compound comprising a benzoquinone or naphthoquinone.

13. The method of claim **12**, wherein the monomer is provided within a solution.

14. The method of claim **13**, wherein the solution further comprises an additional component selected from the group consisting of an acid, an organic solvent, water, and any combination thereof.

15. The method of claim **12**, wherein the monomer is an ethylenic unsaturated monomer.

16. The method of claim **12**, further comprising adding from about 0.1 ppm to about 10,000 ppm of the first inhibitor compound.

17. The method of claim **12**, further comprising adding from about 0.1 ppm to about 10,000 ppm of the second inhibitor compound.

18. The method of claim **12**, the wherein the monomer is selected from the group consisting of vinyl acetate, acrylonitrile, an acrylate, a methacrylate, 1,3-butadiene, styrene, isoprene, acrylic acid, methacrylic acid and any combination thereof.

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