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(54) Titre : DERIVES DE 1-OXYL-4-HYDROXY- OU DE 4-AMINO-2,2,6,6-TETRAMETHYLPIPERIDINE UTILISES COMME INHIBITEURS DE POLYMERISATION POUR DES MONOMERES (METH)ACRYLATE

(54) Title: DERIVATIVES OF 1-OXYL-4-HYDROXY- OR 4-AMINO-2,2,6,6-TETRAMETHYLPIPERIDINE AS POLYMERIZATION INHIBITORS FOR (METH)ACRYLATE MONOMERS

(57) Abrégé/Abstract:
Selected derivatives of 1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine and 1-oxyl-2,2,6,6-tetramethyl-4-aminopiperidine are surprisingly effective as inhibitors to prevent the premature polymerization of acrylic and methacrylic acids, their esters, their amides, vinyl acetate and acrylonitrile in the presence of water. Some of these derivatives are new compounds.

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(57) Abstract

Selected derivatives of 1–oxyl–2,2,6,6–tetramethyl–4–hydroxypiperidine and 1–oxyl–2,2,6,6–tetramethyl–4–aminopiperidine are surprisingly effective as inhibitors to prevent the premature polymerization of acrylic and methacrylic acids, their esters, their amides, vinyl acetate and acrylonitrile in the presence of water. Some of these derivatives are new compounds.

Derivatives Of 1-Oxyl-4-Hydroxy- Or 4-Amino-2,2,6,6-Tetramethylpiperidine As Polymerization Inhibitors For (Meth)Acrylate Monomers

The instant invention pertains to the use of selected derivatives of 1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine as inhibitors for preventing the premature polymerization of acrylic and methacrylic acids, their esters and amides, of vinyl acetate and of acrylonitrile in the presence of water.

Many of the industrially important ethylenically unsaturated monomers are highly susceptible to unwanted radical polymerization initiated either thermally or by adventitious impurities. Some examples of these monomers are acrylic and methacrylic acid, acrylate and methacrylate esters, acrylamide and methacrylamide, vinyl acetate and acrylonitrile. Premature polymerization may occur during manufacture, purification or storage of the monomer. Many of these monomers are purified by distillation. It is in this operation where premature polymerization is most likely to occur and to be the most troublesome. Methods to prevent or reduce the amount of such polymerization are thus highly desirable since the prevention or mitigation of such premature polymerization increases the yield of purified monomer and also insures against costly and potentially dangerous runaway polymerization in the plant.

Stable nitroxides are known in the art to be effective in preventing the premature radical polymerization of ethylenically unsaturated monomers. Some examples are seen in Japanese Hei 9-268138 which discloses the stabilization of styrene by 1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine and its lower alkyl ethers in the presence of nitrophenols. United States Patent Nos. 3,747,988 describes the use of 1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine as a polymerization inhibitor for acrylonitrile in the presence of water and oxygen. United States Patent No. 3,488,338 discloses that 1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine is an effective chain stopper in the aqueous polymerization of chloroprene. British Patent No. 1,127,127 describes the stabilization of neat acrylic acid by 1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine. Japanese Sho 60-36501 describes the stabilization of acrylate and methacrylate esters.

United States Patent Nos. 5,322,960 and 5,504,243 disclose the use of 1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine in preventing the polymerization of acrylic and methacrylic acids and their esters in the presence of water, but tout the great advantages of using said oxyl compound in combination with manganese acetate, or with hydroquinone and phenothiazine.

EP 178,168 teaches the use of 1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine or its reaction product with hexamethylene diisocyanate in stabilizing acrylic acid or methacrylic acid in the presence of water.

EP 791,573 discloses that the lower alkyl or aryl esters of 1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine are effective polymerization inhibitors alone or in combination with various coadditives for vinyl acetate in the presence of water.

Japanese Hei 5-320205 generically describes the use of 1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine, its lower alkyl ethers and lower alkanoic esters in preventing the polymerization of acrylic and methacrylic acids alone, but preferably in the presence of chelating agents for ferric salts, such as ethylenediaminetetraacetic acid. The 4-hydroxy, 4-methoxy and 4-acetoxy derivatives are specifically disclosed.

Japanese Hei 5-320217 teaches the stabilization of acrylic and methacrylic acids with 1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine, its lower alkyl ethers and lower alkanoic esters alone, but preferably in the presence of phenothiazine, an aromatic amine or phenol. The 4-hydroxy, 4-methoxy and 4-acetoxy derivatives are specifically disclosed.

German Application DE 195 10 184 A1 describes amide and formamide derivatives of 1-oxyl-2,2,6,6-tetramethyl-4-aminopiperidine as stabilizers for radically polymerizable monomers, but does not differentiate between aqueous and non-aqueous systems.

United States Patent No. 5,545,786 describes the use of selected nitroxide compounds in the prevention of the premature polymerization of vinyl aromatic monomers such as styrene especially in the presence of oxygen. There is no disclosure or suggestion that such nitroxide compounds would be particularly effective in stabilizing acrylic monomers, such as acids, esters or amides, or vinyl acetate or acrylonitrile especially in the presence of water.

United States Patent No. 5,254,760 discloses the use of selected nitroxide compounds in combination with an aromatic nitro compound for stabilizing vinyl aromatic monomers such as styrene. Again, there is no mention of aliphatic vinyl compounds or of the especial effectiveness of some selected nitroxide compounds in preventing the premature polymerization of such aliphatic vinyl monomers in the presence of water.

EP 697,386 generically discloses the use of selected nitroxyl compounds for preventing the premature polymerization of aromatic vinyl monomers such as styrene or aliphatic vinyl monomers such as acrylic monomers. Specifically, this reference teaches that 1-oxyl-4-acetylamino-2,2,6,6-tetramethylpiperidine alone or in combination with p-nitrosophenol or 2-methyl-4-nitrosophenol is effective in stabilizing styrene from premature polymerization. There is no mention that 1-oxyl-4-acetylamino-2,2,6,6-tetramethylpiperidine is used with an aliphatic vinyl monomer alone, and certainly no suggestion that said 1-oxyl-4-acetylamino-2,2,6,6-tetramethylpiperidine would be particularly effective with such aliphatic vinyl monomers in the presence of water.

EP 810,196 discloses the use inter alia of 1-oxyl-2,2,6,6-tetramethyl-4-acetylaminopiperidine in combination with a phosphine, such as triphenylphosphine, or a cobalt compound, such as cobalt acetate, as inhibitors to prevent the polymerization of (meth)acrylic acid or esters thereof. There is no teaching that 1-oxyl-2,2,6,6-tetramethyl-4-acetylaminopiperidine alone would be efficacious for that purpose.

Since, during the processes to produce and purify various ethylenically unsaturated monomers, water is often present during one of the process steps, there is a long felt need for the stable nitroxide inhibitor to be sufficiently water soluble or miscible to remain homogeneous in wet monomer streams and to prevent polymerization in the aqueous phase and yet for the inhibitor to be able to partition to such an extent that it can prevent polymerization in both the aqeuous phase and in the organic monomer phase for inhibition protection throughout the entire process.

In one aspect, this invention provides derivatives of 1-oxyl-2,2,6,6-tetramethyl-4-hydroxy-piperidine and of 1-oxyl-2,2,6,6-tetramethyl-4-aminopiperidine of sufficient water solubility and the concomitant ability to partition into an organic phase which will prevent the premature polymerization of ethylenically unsaturated monomers in the presence of water.

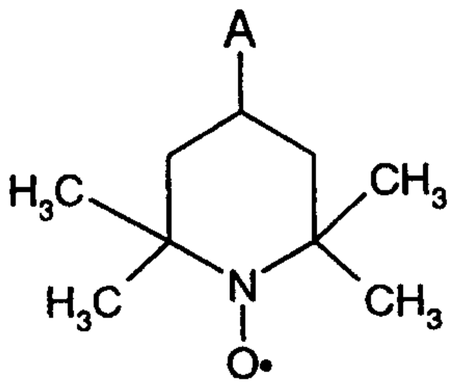
Another aspect of this invention provides novel nitroxide compounds of value in stabilizing unsaturated monomers.

In a further aspect, the instant invention provides a monomer composition stabilized against premature polymerization which comprises

(A) an ethylenically unsaturated monomer which is an unsaturated acid, an

unsaturated ester, an unsaturated amide, an unsaturated nitrile, unsaturated ether, vinyl pyridine, diethyl vinylphosphonate or sodium styrenesulfonate, and

(B) an effective stabilizing amount of a compound of formula I, II, V or VI



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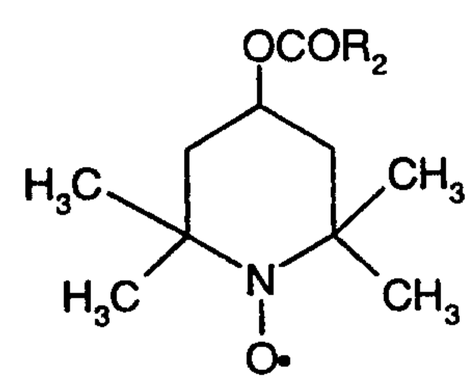

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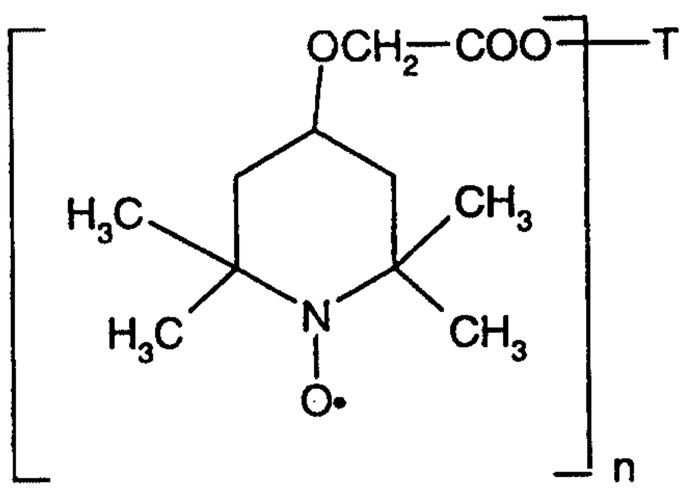

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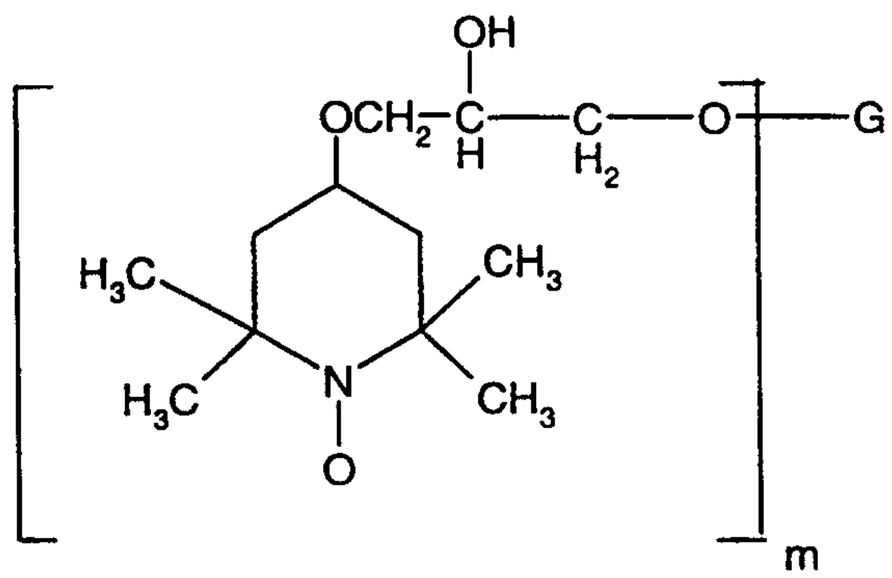


(VI)

wherein

A is OR_1 or $NR_{11}R_{12}$

R_1 is alkenyl of 2 to 4 carbon atoms, propargyl, glycidyl, alkyl of 2 to 6 carbon atoms interrupted by one or two oxygen atoms, substituted by one to three hydroxyl groups or both interrupted by said oxygen atoms and substituted by said hydroxyl groups, or R_1 is alkyl of 1 to 4 carbon atoms substituted by carboxy or by the alkali metal, ammonium or lower alkylammonium salts thereof; or R_1 is alkyl substituted by -COOE where E is methyl or ethyl,

R_2 is alkyl of 3 to 5 carbon atoms interrupted by -COO- or by -CO, or R_2 is -

$CH_2(OCH_2CH_2)_pOCH_3$ where p is 1 to 4; or

R_2 is $-NHR_3$ where R_3 is alkyl of 1 to 4 carbon atoms,

n is 2 to 4,

when n is 2, T is $-(CH_2CHR\text{-}O)_qCH_2CHR-$, where q is 0 or 1, and R is hydrogen or methyl,

when n is 3, T is glyceryl,

when n is 4, T is neopentanetetrayl,

m is 2 or 3,

when m is 2, G is $-(CH_2CHR\text{-}O)_rCH_2CHR-$, where r is 0 to 3, and R is hydrogen or methyl,

and

when m is 3, G is glyceryl;

R_{11} is hydrogen, alkyl of 1 to 4 carbon atoms, or said alkyl substituted by one or two hydroxyl, interrupted by one or two oxygen atoms, or both substituted by one hydroxyl and interrupted by one or two oxygen atoms,

R_{12} is -CO-R_{13} where R_{13} has the same meaning as R_{11}, or R_{13} is -NHR_{14} wherein R_{14} is alkyl of 1 to 4 carbon atoms, said alkyl substituted by one or two hydroxyl, substituted by alkoxy of 1 to 2 carbon atoms, or said alkyl both substituted by one hydroxyl and by one alkoxy of 1 to 2 carbon atoms, or

R_{11} and R_{12} together are -CO-CH_2CH_2-CO-, -CO-CH=CH-CO- or -$(CH_2)_6$-CO-; and

with the proviso that, when R_{13} is alkyl of 1 to 4 carbon atoms, R_{11} is not hydrogen ; and

(C) water.

The alkyl groups in the different substituents may be linear or branched.

Examples for alkyl of 1 to 6 carbon atoms are methyl ethyl propyl and its isomers, butyl and its isomers pentyl and its isomers and hexyl and its isomers.

Examples for alkenyl groups with 2 to 4 carbon atoms are ethenyl, propenyl, butenyl.

Examples for alkyl groups with 1 to 4 carbon atoms interrupted by one or two oxygen atoms are -CH_2-O-CH_3, -CH_2-CH_2-O-CH_3, -CH_2-CH_2-O-CH_2-CH_3, -CH_2-O-CH_2-CH_2-O-CH_3 or -CH_2-O-CH_2-O-CH_3.

Examples for hydroxy substituted alkyl groups with 2 to 6 carbon atoms are hydroxy ethyl, di-hydroxy ethyl, hydroxy propyl, di-hydroxy propyl, hydroxy butyl, hydroxy pentyl or hydroxy hexyl.

Preferably in the compound of formula I, R_1 is allyl, methallyl, glycidyl, 2,3-dihydroxypropyl, 2-hydroxy-4-oxapentyl or -CH_2COOH.

Preferably in the compound of formula II, R_2 is methoxymethyl, 2-methoxyethoxymethyl, 2-(2-methoxyethoxy)ethoxymethyl, -$CH_2$$COCH_3$, -$CH_2CH_2$$COOCH_3$ or butylamino.

Preferably in the compound of formula V, n is 2, T is -$(CH_2CHR\text{-}O)_qCH_2CHR$-, where q is 0, and R is hydrogen.

Preferably in the compound of formula VI, m is 2, G is -$(CH_2CHR\text{-}O)_rCH_2CHR$-, where r is 0 or 1, and R is hydrogen.

Preferably in the compound of formula I, R_{11} is hydrogen or n-butyl.

Preferably in the compound of formula I, R_{12} is -CO-R_{13} where R_{13} is hydrogen, methyl, ethyl, n-propyl, isopropyl, methoxymethyl or 2-methoxyethoxymethyl; or R_2 is N-butylcarbamoyl.

The amount of water is preferably 0.1% to 99%, more preferred 1% to 40% by weight based on the total composition.

The monomers of component (A) have at least one carbon-carbon double bond capable of undergoing free radical induced polymerization. Such monomers are well-known in commerce and comprise a wide variety of structural types. Typical examples of such monomers are the unsaturated acids such as acrylic acid, methacrylic acid and crotonic acid; unsaturated esters such as the acrylates and methacrylates exemplified by butyl acrylate, methyl methacrylate, ethyl acrylate, methyl acrylate and vinyl acetate; unsaturated amides such as acrylamide and methacrylamide; unsaturated nitriles such as acrylonitrile and methacrylonitrile; unsaturated ethers such as methyl vinyl ether; and miscellaneous vinyl monomers such as the vinyl pyridines, diethyl vinylphosphonate and sodium styrenesulfonate.

Preferably the monomer is acrylic acid, methacrylic acid, butyl acrylate, ethyl acrylate, methyl methacrylate, vinyl acetate, acrylamide or acrylonitrile; most preferably acrylic acid, vinyl acetate or acrylonitrile; most especially acrylic acid.

The effective stabilizing amount of component (B) is 1 to 10000 ppm by weight based on the weight of monomer of component (A). Preferably, the amount of component (B) is 1 to 2000 ppm by weight based on the monomer of component (A). Most preferably, the amount of component (B) is 1 to 1000 ppm by weight based on the monomer of component (A).

Preferred compounds of formula I or formula II are:

(a) 1-oxyl-2,2,6,6-tetramethyl-4-allyloxypiperidine;

(b) 1-oxyl-2,2,6,6-tetramethyl-4-(2-methoxyethoxy)piperidine;

(c) 1-oxyl-2,2,6,6-tetramethyl-4-glycidyloxypiperidine;

(d) 1-oxyl-2,2,6,6-tetramethyl-4-(2,3-dihydroxypropoxy)piperidine;
(e) 1-oxyl-2,2,6,6-tetramethyl-4-(2-hydroxy-4-oxapentoxy)piperidine;
(f) 1-oxyl-2,2,6,6-tetramethyl-4-(carboethoxymethoxy)piperidine;
(g) 1-oxyl-2,2,6,6-tetramethyl-4-(carboxymethoxy)piperidine;
(h) 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl 2-methoxyethoxyacetate;
(i) 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl 2-(2-methoxyethoxy)ethoxyacetate;
(j) 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl methoxyacetate;
(k) 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl methyl succinate;
(l) 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl acetoacetate;
(m) 1-oxyl-2,2,6,6-tetramethyl-piperidin-4-yl butylcarbamate; or
(n) N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)formamide,
(o) N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)methoxyacetamide,
(p) N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)-2-methoxyethoxyacetamide,
(q) 1-butyl-3-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)urea,
(r) N-butyl-N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)formamide,
(s) N-butyl-N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)acetamide,
(t) N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)succinimide,
(u) N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)maleimide, or
(v) N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)caprolactam.

More preferred compounds of formula I or formula II are:
(a) 1-oxyl-2,2,6,6-tetramethyl-4-allyloxypiperidine;
(c) 1-oxyl-2,2,6,6-tetramethyl-4-glycidyloxypiperidine;
(d) 1-oxyl-2,2,6,6-tetramethyl-4-(2,3-dihydroxypropoxy)piperidine;
(e) 1-oxyl-2,2,6,6-tetramethyl-4-(2-hydroxy-4-oxapentoxy)piperidine;
(f) 1-oxyl-2,2,6,6-tetramethyl-4-(carboethoxymethoxy)piperidine;
(h) 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl 2-(2-methoxyethoxy)ethoxyacetate;
(i) 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl methoxyacetate;
(k) 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl methyl succinate;
(m) 1-oxyl-2,2,6,6-tetramethyl-piperidin-4-yl butylcarbamate; or
(n) N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)formamide,
(o) N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)methoxyacetamide,
(r) N-butyl-N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)formamide, or
(s) N-butyl-N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)acetamide.

Most preferred are the following compounds of formula I or formula II:

(a) 1-oxyl-2,2,6,6-tetramethyl-4-allyloxypiperidine;

(d) 1-oxyl-2,2,6,6-tetramethyl-4-(2,3-dihydroxypropoxy)piperidine;

(e) 1-oxyl-2,2,6,6-tetramethyl-4-(2-hydroxy-4-oxapentoxy)piperidine; or

(r) N-butyl-N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)formamide.

The instant invention also pertains to a process for preventing the premature polymerization of an unsaturated monomer (A) which is an unsaturated acid, an unsaturated ester, an unsaturated amide, an unsaturated nitrile, unsaturated ether, vinyl pyridine, diethyl vinyl-phosphonate or sodium styrenesulfonate, in the presence of water by incorporating therein an effective stabilizing amount of a compound (B) of formula I, II, V or VI.

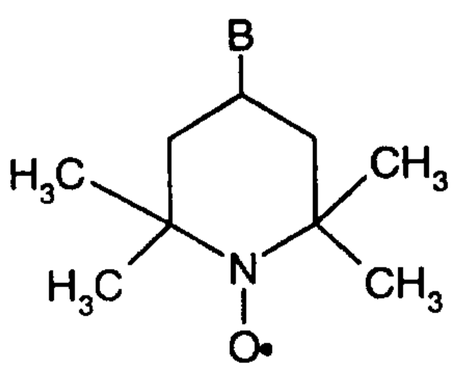
The definitions in the composition as well as their preferences apply also for the process of inhibiting premature polymerization.

The polymerization inhibitor amide, ether or ester can be introduced into the monomer to be protected by any conventional method. It may be added just upstream of the point of desired application by any suitable means. In addition, this mixture may be injected separately into the distillation train along with the incoming feed of monomer or through separate entry points providing efficient distribution of the activated inhibitor mixture. Since the inhibitor is gradually depleted during operation, it is generally necessary to maintain the appropriate amount of the inhibitor ester in the distillation system by adding additional inhibitor during the course of the distillation process. Such addition may be carried out either on a continuous basis or by intermittently charging fresh inhibitor into the distillation system if the concentration of the inhibitor is to be maintained above the minimum required level.

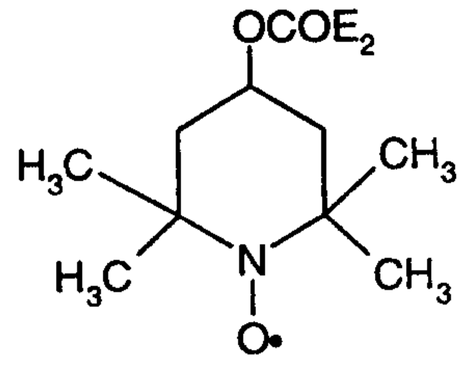
The nitroxides of this invention are highly water compatible. As many of the processes needed to produce and purify the various ethylenically unsaturated monomers may have some water present during one of the process steps, it is important that the instant stable nitroxide inhibitor be sufficiently water soluble to prevent polymerization in the aqueous phase and yet for the inhibitor to be able to partition significantly into the organic monomer phase for inhibition protection throughout the entire process. Undesired premature polymerization must be limited or mitigated throughout the purification process to insure that the reactors, tanks and pipes used to make, store and transport the purified monomer remain free from high molecular weight polymeric material. The instant amide ether or ester inhibitors are tailored to have the desirable water compatibility properties needed to bring this about.

The amount of water present will depend on the specific monomer being stabilized. In the case of monomers of limited compatibility with water such as butyl acrylate, the water content will depend on the amount needed to saturate the ester, only a few percent. On the other hand with water miscible monomers such as acrylic acid, the amount of water possible is theoretically much higher.

The instant invention pertains also to a compound of formula III or IV



(III)



(IV)

wherein

B is OE_1 or $NE_{11}E_{12}$

E_1 is alkyl of 2 to 6 carbon atoms interrupted by one or two oxygen atoms, substituted by two to three hydroxyl groups or both interrupted by said oxygen atoms and substituted by said hydroxyl groups, or E_1 is alkyl of 1 to 4 carbon atoms substituted by carboxy or by the alkali metal, ammonium or lower alkylammonium salts thereof; or E_1 is alkyl substituted by -COOE where E is methyl or ethyl, and

E_2 is alkyl of 3 to 5 carbon atoms interrupted by -COO- or by -CO-, or E_2 is -$CH_2(OCH_2CH_2)_nOCH_3$ where n is 1 to 4; or

E_2 is -NHE_3 where E_3 is alkyl of 1 to 4 carbon atoms;

E_{11} is hydrogen or alkyl of 1 to 4 carbon atoms, and

E_{12} is -CO-E_{13} where E_{13} is alkyl of 1 to 4 carbon atoms which alkyl is interrupted by one or two oxygen atoms, or E_{13} is -NHE_{14} where E_{14} is alkyl of 1 to 4 carbon atoms;

with the proviso that E_1 is not 2,3-dihydroxypropyl.

Preferred compounds are those wherein E_1 is 2-hydroxy-4-oxapentyl or -CH_2COOH

Other preferred compounds aro those where E_{11} is hydrogen or butyl, E_{13} is methoxymethyl or 2-methoxyethoxymethyl; or E_{12} is N-butylcarbamoyl.

Also preferred compounds are those wherein E_2 is methoxymethyl, 2-methoxyethoxymethyl,

2-(2-methoxyethoxy)ethoxymethyl, $-CH_2COCH_3$, $-CH_2CH_2COOCH_3$ or butylamino.

Specifically preferred compounds are:

1-oxyl-2,2,6,6-tetramethyl-4-(2-hydroxy-4-oxapentoxy)piperidine,
1-oxyl-2,2,6,6-tetramethyl-4-(carboxymethoxy)piperidine,
1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl 2-(2-methoxyethoxy)ethoxyacetate,
1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl methoxyacetate,
1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl methyl succinate,
N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)methoxyacetamide,
N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)-2-methoxyethoxyacetamide, or
1-butyl-3-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)urea.

A further subject of the invention is the use of a compound of formula I, II, V, VI for preventing the premature polymerization of an unsaturated monomer.

The compounds of formula I, II, III, IV, V and VI can be prepared with standard methods of organic chemistry. The intermediates are partially commercially available.

The following examples are meant to illustrate the instant invention.

Example 1

1-Oxyl-2,2,6,6-tetramethyl-4-allyloxypiperidine

A vigorously stirred two phase solution of 30.0 g (0.17 mol) 1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine, 29.0 g (0.24 mol) of allyl bromide, 2.6 g (8 mmol) of tetrabutylammonium bromide, 100 mL of 50% aqueous sodium hydroxide and 30 mL of toluene is heated at 70°C for 90 minutes. The mixture is partitioned between 100 mL of toluene, 100 mL of heptane and 200 mL of water. The organic phase is dried over anhydrous magnesium sulfate and concentrated to yield the title compound as a red oil after column chromatography.

Example 2

1-Oxyl-2,2,6,6-tetramethyl-4-(2-methoxyethoxy)piperidine

The title compound is synthesized using the same procedure as described in Example 1 and using 2-bromoethyl methyl ether in place of allyl bromide. The product is isolated as a red oil

after column chromatography.

Example 3

1-Oxyl-2,2,6,6-tetramethyl-4-glycidyloxypiperidine

The title compound is synthesized using the same general procedure as described in Example 1 and using epichlorohydrin in place of allyl bromide. The product is isolated as a low melting red solid after column chromatography.

Example 4

1-Oxyl-2,2,6,6-tetramethyl-4-(2,3-dihydroxypropoxy)piperidine

1.0 g of the compound of Example 3 is heated at 110°C in 50 mL of 5% aqueous sodium hydroxide for six hours. The mixture is extracted with ethyl acetate, and the organic extract is dried and concentrated. The title compound is isolated as a red oil after column chromatography.

Example 5

1-Oxyl-2,2,6,6-tetramethyl-4-(2-hydroxy-4-oxapentoxy)piperidine

1.0 g of the compound of Example 3 is heated at 60°C in a solution of 0.25 g sodium methoxide in 50 mL of methanol for six hours. The reaction mixture is then partitioned between water and ethyl acetate. The title compound is isolated as a red oil after column chromatography.

Example 6

1-Oxyl-2,2,6,6-tetramethyl-4-(carboethoxymethoxy)piperidine

0.48 g (20 mmol) of sodium hydride is added to a solution of 3.0 g (17 mmol) of 1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine in 25 mL of anhydrous tetrahydrofuran. The reaction mixture is stirred under a blanket of nitrogen for one hour. The mixture is chilled to 0°C and 2.9 g (17 mmol) of ethyl bromoacetate is added dropwise. After the addition is complete, the reaction is stirred for an additional 30 minutes during which time a white precipitate forms. The mixture is filtered and the solvent is removed under reduced pressure. The title compound is isolated as an orange solid after column chromatography and melts at 41-43°C.

Example 7

1-Oxyl-2,2,6,6-tetramethyl-4-(carboxymethoxy)piperidine

1.0 g (39 mmol) of the compound of Example 6 is added to a solution of 0.2 g sodium hydroxide in 20 mL of 1:1 water/methanol. The mixture is stirred for one hour, carefully

acidified with 1% aqueous hydrogen chloride and then extracted with ethyl acetate. The organic extract is dried over anhydrous magnesium sulfate and then contentrated to afford the title compound as an orange solid.

Example 8

1-Oxyl-2,2,6,6-tetramethylpiperidin-4-yl-2-Methoxyethoxyacetate

34.4 grams of 1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine, 29.6 grams of methyl 2-methoxyethoxyacetate and 300 mL of heptane are transferred to a 500 mL 3-necked, round-bottomed flask equipped with a mechanical stirrer, Dean-Stark trap and condenser. Trace amounts of water are removed by azeotropic distillation. 0.25 mL of tetraisopropyl orthotitanate is added to the reaction mixture. The reaction mixture is refluxed for six hours and the liberated methanol is collected in the Dean-Stark trap. The reaction mixture is allowed to cool and is then partitioned between 300 mL of ethyl acetate and 300 mL of water. The phases are separated and the organic phase is washed with water and dried over anhydrous magnesium sulfate. Evaporation of the solvent leaves the title compound as a red oil.

Example 9

1-Oxyl-2,2,6,6-tetramethylpiperidin-4-yl 2-(2-Methoxyethoxy)ethoxyacetate

The title compound is synthesized using the same procedure as described in Example 8 and using methyl 2-(2-methoxyethoxy)ethyoxyacetate in place of methyl 2-methoxy-ethoxyacetate. The title compound is isolated as a red oil after column chromatography.

Example 10

1-Oxyl-2,2,6,6-tetramethylpiperidin-4-yl Methoxyacetate

The title compound is synthesized using the same procedure as described in Example 8 and using methyl methoxyacetate in place of methyl 2-methoxyethoxyacetate. The title compound is isolated as an orange solid by crystallization from heptane and melts at 103°C.

Example 11

1-Oxyl-2,2,6,6-tetramethylpiperidin-4-yl Methyl Succinate

A solution of 6.0 g (35 mmol) of 1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine and 11.4 g (78 mmol) dimethyl succinate in 60 mL of heptane is brought to reflux. 0.05 mL of tetraisopropyl orthotitanate is added and the reaction mixture is refluxed for 16 hours while the evolved methanol is trapped in a Dean-Stark trap. The reaction mixture is then concentrated and the title compound is isolated as a red oil after column chromatography

and melts at 76°C.

Example 12

1-Oxyl-2,2,6,6-tetramethylpiperidin-4-yl Acetoacetate

The title compound is synthesized using the same procedure as described in Example 11 but using methyl acetoacetate in place of dimethyl succinate. The title compound is isolated as a red oil after column chromatography.

Example 13

1-Oxyl-2,2,6,6-tetramethyl-piperidin-4-yl Butylcarbamate

0.1 g of di-n-butyltin dilaurate is added to a solution of 1.0 g (5.8 mmol) of 1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine and 0.58 g (5.8 mmol) of butyl isocyanate in 10 mL of carbon tetrachloride. After stirring for four hours at ambient temperature, the solution is concentrated and the title compound is isolated as a red oil after column chromatography.

Example 14

N-(1-Oxyl-2,2,6,6-tetramethylpiperidin-4-yl)formamide

The title compound is prepared according to the procedure of E. J. Vlietstra et al., Macromolecules, 1990, 23, 946.

Example 15

N-(1-Oxyl-2,2,6,6-tetramethylpiperidin-4-yl)octanamide

To a stirred 0°C solution of 1.0 g of 1-oxyl-4-amino-2,2,6,6-tetramethylpiperidine and 0.65 g of triethylamine in 10 mL of methylene chloride is added dropwise a solution of 0.95 g of octanoyl chloride in 5 mL of methylene chloride. After the addition is complete, the reaction mixture is allowed to warm to ambient temperature. After two more hours, the reaction mixture is washed with 1% aqueous sodium hydroxide and finally water. The organic phase is dried over anhydrous magnesium sulfate, filtered and concentrated. The title compound is isolated as a red oil after column chromatography.

Example 16

N-(1-Oxyl-2,2,6,6-tetramethylpiperidin-4-yl)methoxyacetamide

The title compound is synthesized using the same general procedure as described in Example 15 and using methoxyacetyl chloride in place of octanoyl chloride. The title compound is isolated as an orange solid after column chromatography and melts at 124-125°C.

Example 17

N-(1-Oxyl-2,2,6,6-tetramethylpiperidin-4-yl)-2-methoxyethoxyacetamide

The title compound is synthesized using the same general procedure as described in Example 15 and using methoxyethoxyacetyl chloride in place of octanoyl chloride. The title compound is isolated as a red oil after column chromatography.

Example 18

1-Butyl-3-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)urea

To a stirred solution of 1.0 g of 1-oxyl-4-amino-2,2,6,6-tetramethylpiperidine in 75 mL of dry toluene is added dropwise 0.65 mL of butyl isocyanate. The reaction mixture is stirred for 16 hours. The solution is then concentrated to yield the title compound as a red oil.

Example 19

N-Butyl-N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)formamide

A pressure reactor is charged with 10 g of 4-butylamino-2,2,6,6-piperidine and 100 mL of ethyl formate and then purged with nitrogen. The reactor is immersed in an 100°C oil bath for three hours. A maximum pressure of 24 psi is observed. The resultant ethanol and unreacted ethyl formate are distilled off under vacuum.

The intermediate N-formyl amine product is then oxidized to corresponding nitroxide as seen below.

To a refluxing solution of the 20 g of the intermediate N-formyl amine and 0.3 g of molybdenum trioxide in 200 mL of methylene chloride is added 60 mL of 70% aqueous tert-butyl hydroperoxide in 10 mL portions over a six hour period. The molybdenum catalyst is then removed by filtration. The filtrate is washed with water, dried over anhydrous magnesium sulfate, filtered and concentrated to yield the title compound as an orange solid which melts at 77-79°C.

Example 20

N-Butyl-N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)acetamide

To a stirred solution of 95 g of 4-butylamino-2,2,6,6-tetramethylpiperidine in 500 mL of diethyl ether is added dropwise 50 mL of acetic anhydride. After the addition is complete, the

reaction mixture is stirred at 0°C for one hour and then at 20°C for three hours. The resulting precipitate is collected by filtration and washed with diethyl ether till all the orange color is removed. The free amine intermediate is isolated by partitioning the solid between aqueous sodium hydroxide and ether.

The intermediate N-acetyl amine product is then oxidized to the corresponding nitroxide as follows:

To a stirred 50°C solution of 13.3 g of N-butyl-N-(2,2,6,6-tetramethylpiperidin-4-yl)acetamide, 0.075 g of sodium tungstate-dihydrate and 0.075 g of ethylenediaminetetraacetic acid in 25 mL of methanol is added 35 mL of 30% aqueous hydrogen peroxide over a three hour period. After the addition is complete, the reaction mixture is stirred another two hours. The reaction mixture is then partitioned between diethyl ether and water. The organic phase is washed with water, 1% aqueous hydrogen chloride and then water. After drying over anhydrous magnesium sulfate and concentrating, the title compound is obtained as a red solid. After crystallization from hexane, the compound melts at 84-85°C.

Example 21

N-(1-Oxyl-2,2,6,6-tetramethylpiperidin-4-yl)caprolactam

This compound is prepared by the method of Example 14 of United States Patent No. 4,472,547.

In the Examples two different test methods are employed to determine the effectiveness of the nitroxide esters as inhibitors. The method is chosen to simulate different aspects of the purification processes.

Method 1

Acrylic acid is distilled to remove any storage stabilizer present. Stock stabilizer solutions (1.5 mg/mL) are prepared in propionic acid. This stock solution is added to the distilled acrylic acid to give a test solution having 5 ppm of total stabilizer. Aliquots of this test solution are then placed into three separate reaction tubes. Each tube is purged with a gas mixture (0.65% oxygen in nitrogen) for ten minutes. The tubes are then sealed and placed in a 110°C oil bath. The tubes are watched till the appearance of visible polymer formation is observed as a precipitate. Failure times are reported as an average of at least three tubes.

Method 2

Test solutions are prepared as in Method 1 except that the stock stabilizer solution is prepared at 0.75 mg/mL giving a test solution with 2.5 ppm of total stabilizer. Aliquots (1 mL) of the test solution are placed into three separate reaction tubes. To each tube is added 0.5 mL of toluene and 0.5 mL of distilled water. Each tube is purged as described in Method 1 and then sealed. The tubes are placed in a 90°C oil bath and heated till visible polymer is observed as a precipitate. Failure times are reported as an average of at least three tubes.

Example 22

Following the procedure of Method 1, it is seen that water miscible nitroxides and hydrophobic nitroxides each perform similarly in neat acrylic acid in the absence of water.

Table 1

Stabilization of Neat Acrylic Acid

Compound* of Example (5 ppm by weight)	Time to Onset of Polymerization (minutes)
none	5
A	220
Example 8	220

*A is bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) sebacate.

Each of the nitroxide compounds provide nearly the same stabilization efficacy to neat acrylic acid.

Example 23

Following the procedure of Method 2 where water is present in the acrylic acid, there is a clear difference in the superior stabilization performance of the instant water compatible nitroxides of formula I or formula II compared to the hydrophobic nitroxides as seen in Table 2.

Table 2

Stabilization of Aqueous Acrylic Acid

Compound* of Example (5 ppm by weight)	Time to Onset of Polymerization (minutes)
none	30
A	240
B	130
Example 1	250
Example 2	350
Example 3	490
Example 4	320
Example 5	350
Example 6	400
Example 7	230
Example 8	325
Example 9	520
Example 10	645
Example 11	600
Example 13	410

*A is bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) sebacate.
B is 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl octanoate.

Example 24

Following the procedure of Method 1, the amides of examples 14 to 21 were tested. It is seen that water miscible nitroxides and hydrophobic nitroxides each perform similarly in neat acrylic acid in the absence of water.

Table 3

Stabilization of Neat Acrylic Acid

Compound* of Example (5 ppm by weight)	Time to Onset of Polymerization (minutes)
none	8
A	147
Example 16	165
Example 19	109

*A is bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) sebacate.

Each of the nitroxide compounds provide nearly the same stabilization efficacy to neat acrylic acid.

Example 25

Following the procedure of Method 2 where water is present in the acrylic acid, there is a clear difference in the superior stabilization performance of the instant water compatible nitroxides of formula I compared to the hydrophobic nitroxides as seen in Table 4.

Table 4

Stabilization of Aqueous Acrylic Acid

Compound* of Example (2.5 ppm by weight)	Time to Onset of Polymerization (minutes)
none	29
A	241
Example 14	498
Example 15	280
Example 16	418
Example 19	503

*A is bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) sebacate.

Example 26

Following the procedure of Method 2 where water is present in the acrylic acid, there is a clear difference in the superior stabilization performance of the instant water compatible nitroxides of formula I compared to the hydrophobic nitroxide B as seen in Table 5.

Table 5

Stabilization of Aqueous Acrylic Acid

Compound* of Example (2.5 ppm by weight)	Time to Onset of Polymerization (minutes)
none	30
B	70
Example 21	365
Example 19	500

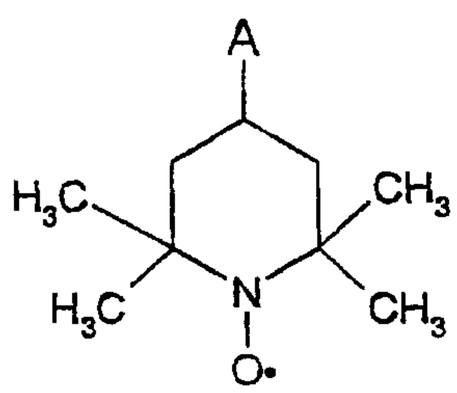
*B is N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)dodecylsuccinimide.

Claims

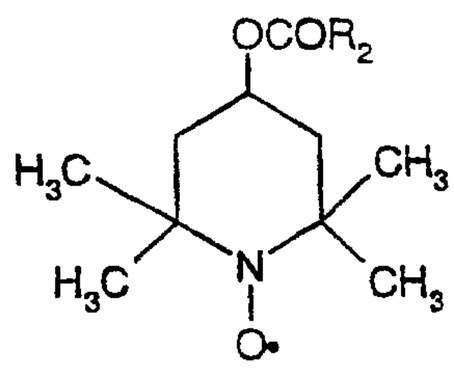
1. A monomer composition stabilized against premature polymerization which comprises

(A) an ethylenically unsaturated monomer which is an unsaturated acid, an unsaturated ester, an unsaturated amide, an unsaturated nitrile, unsaturated ether, vinyl pyridine, diethyl vinylphosphonate or sodium styrenesulfonate,

(B) an effective stabilizing amount of a compound of formula I, II, V or VI



(I)



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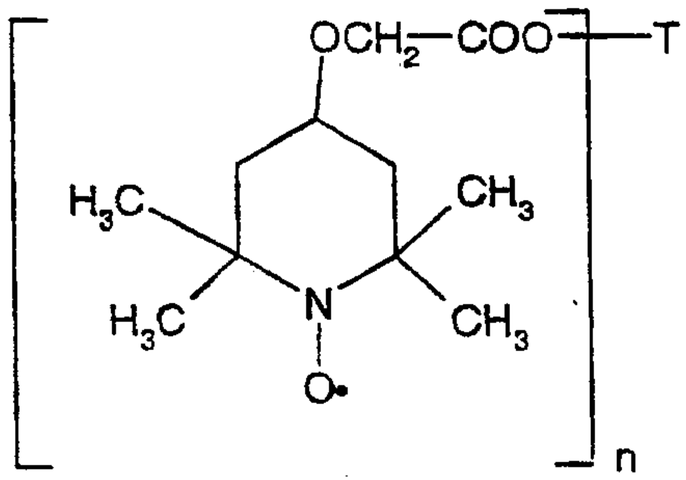

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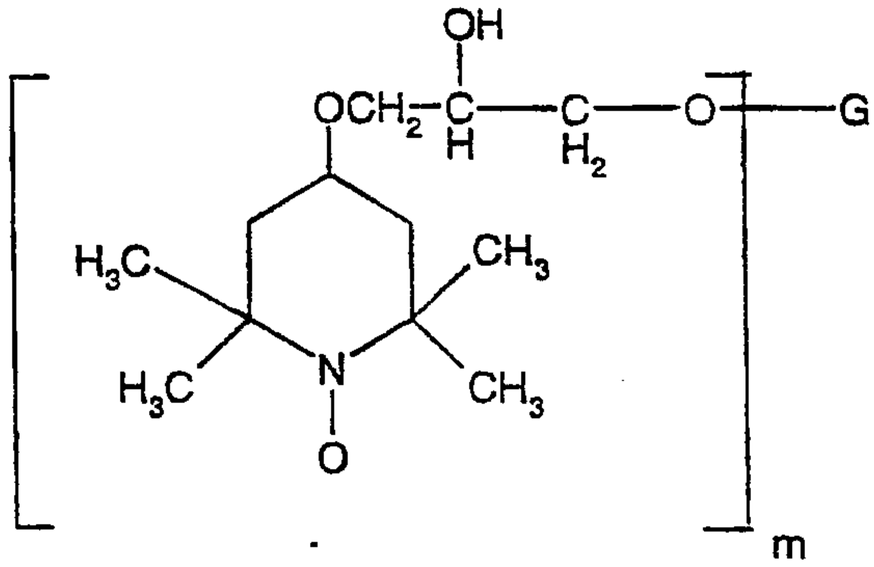

(VI)

wherein

A is OR_1 or $NR_{11}R_{12}$

R_1 is alkenyl of 2 to 4 carbon atoms, propargyl, glycidyl, alkyl of 2 to 6 carbon atoms interrupted by one or two oxygen atoms, substituted by one to three hydroxyl groups or both interrupted by said oxygen atoms and substituted by said hydroxyl groups, or R_1 is alkyl of 1 to 4 carbon atoms substituted by carboxy or by the alkali metal, ammonium or lower alkylammonium salts thereof; or R_1 is alkyl substituted by -COOE where E is methyl or ethyl, R_2 is alkyl of 3 to 5 carbon atoms interrupted by -COO- or by -CO, or R_2 is -$CH_2(OCH_2CH_2)_pOCH_3$ where p is 1 to 4; or

R_2 is -NHR_3 where R_3 is alkyl of 1 to 4 carbon atoms,

n is 2 to 4,
when n is 2, T is -(CH_2CHR-O)$_q$$CH_2CHR$-, where q is 0 or 1, and R is hydrogen or methyl,
when n is 3, T is glyceryl,
when n is 4, T is neopentanetetrayl,
m is 2 or 3,
when m is 2, G is -(CH_2CHR-O)$_r$$CH_2CHR$-, where r is 0 to 3, and R is hydrogen or methyl,
and
when m is 3, G is glyceryl;
R_{11} is hydrogen, alkyl of 1 to 4 carbon atoms, or said alkyl substituted by one or two hydroxyl, interrupted by one or two oxygen atoms, or both substituted by one hydroxyl and interrupted by one or two oxygen atoms,
R_{12} is -CO-R_{13} where R_{13} has the same meaning as R_{11}, or R_{13} is -NHR_{14} wherein R_{14} is alkyl of 1 to 4 carbon atoms, said alkyl substituted by one or two hydroxyl, substituted by alkoxy of 1 to 2 carbon atoms, or said alkyl both substituted by one hydroxyl and by one alkoxy of 1 to 2 carbon atoms, or
R_{11} and R_{12} together are -CO-CH_2CH_2-CO-, -CO-CH=CH-CO- or -$(CH_2)_6$-CO-; and
with the proviso that, when R_{13} is alkyl of 1 to 4 carbon atoms, R_{11} is not hydrogen; and
(C) water.

2. A composition according to claim 1 where in the compound of formula I, R_1 is allyl, methallyl, glycidyl, 2,3-dihydroxypropyl, 2-hydroxy-4-oxapentyl or -CH_2COOH.

3. A composition according to claim 1 where in the compound of formula II, R_2 is methoxymethyl, 2-methoxyethoxymethyl, 2-(2-methoxyethoxy)ethoxymethyl, -CH_2COCH_3, -$CH_2CH_2COOCH_3$ or butylamino.

4. A composition according to claim 1 where in the compound of formula V, n is 2, T is -(CH_2CHR-O)$_q$$CH_2CHR$-, where q is 0, and R is hydrogen.

5. A composition according to claim 1 where in the compound of formula VI, m is 2, G is -(CH_2CHR-O)$_r$$CH_2CHR$-, where r is 0 or 1, and R is hydrogen.

6. A composition according to claim 1 where in the compound of formula I, R_{11} is hydrogen or n-butyl.

7. A composition according to claim 1 or 6, where in the compound of formula I, R_{12} is -CO-R_{13} where R_{13} is hydrogen, methyl, ethyl, n-propyl, isopropyl, methoxymethyl or 2-methoxy-

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ethoxymethyl; or R_{12} is N-butylcarbamoyl.

8. A composition according to any one of claims 1 to 7, wherein the amount of water is 0.1% to 99% by weight based on the total composition.

9. A composition according to any one of claims 1 to 8, wherein the unsaturated monomer is acrylic acid, methacrylic acid, an ester of acrylic acid or methacrylic acid, an amide of acrylic acid or methacrylic acid, vinyl acetate or acrylonitrile.

10. A composition according to claim 9 wherein the unsaturated monomer is acrylic acid, methacrylic acid, butyl acrylate, ethyl acrylate, methyl methacrylate, vinyl acetate, acrylamide or acrylonitrile.

11. A composition according to any one of claims 1 to 10, wherein the effective stabilizing amount of component (B) is 1 to 10000 ppm by weight based on the weight of monomer of component (A).

12. A composition according to claim 1 wherein the compound (B) is selected from the group consisting of

(a) 1-oxyl-2,2,6,6-tetramethyl-4-allyloxypiperidine;

(b) 1-oxyl-2,2,6,6-tetramethyl-4-(2-methoxyethoxy)piperidine;

(c) 1-oxyl-2,2,6,6-tetramethyl-4-glycidyloxypiperidine;

(d) 1-oxyl-2,2,6,6-tetramethyl-4-(2,3-dihydroxypropoxy)piperidine;

(e) 1-oxyl-2,2,6,6-tetramethyl-4-(2-hydroxy-4-oxapentoxy)piperidine;

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(f) 1-oxyl-2,2,6,6-tetramethyl-4-(carboethoxymethoxy)piperidine;

(g) 1-oxyl-2,2,6,6-tetramethyl-4-(carboxymethoxy)piperidine;

(h) 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl 2-methoxyethoxyacetate;

(i) 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl 2-(2-methoxyethoxy)ethoxyacetate;

(j) 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl methoxyacetate;

(k) 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl methyl succinate;

(l) 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl acetoacetate;

(m) 1-oxyl-2,2,6,6-tetramethyl-piperidin-4-yl butylcarbamate; or

(n) N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)formamide,

(o) N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)methoxyacetamide,

(p) N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)-2-methoxyethoxyacetamide,

(q) 1-butyl-3-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)urea,

(r) N-butyl-N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)formamide,

(s) N-butyl-N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)acetamide,

(t) N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)succinimide,

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(u) N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)maleimide, and

(v) N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)caprolactam.

13. A composition according to claim 12 wherein the compound (B) is selected from the group consisting of

(a) 1-oxyl-2,2,6,6-tetramethyl-4-allyloxypiperidine;

(c) 1-oxyl-2,2,6,6-tetramethyl-4-glycidyloxypiperidine;

(d) 1-oxyl-2,2,6,6-tetramethyl-4-(2,3-dihydroxypropoxy)piperidine;

(e) 1-oxyl-2,2,6,6-tetramethyl-4-(2-hydroxy-4-oxapentoxy)piperidine;

(f) 1-oxyl-2,2,6,6-tetramethyl-4-(carboethoxymethoxy)piperidine;

(h) 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl 2-(2-methoxyethoxy)ethoxyacetate;

(i) 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl methoxyacetate;

(k) 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl methyl succinate;

(m) 1-oxyl-2,2,6,6-tetramethyl-piperidin-4-yl butylcarbamate; or

(n) N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)formamide,

(o) N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)methoxyacetamide,

(r) N-butyl-N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)formamide, and

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(s) N-butyl-N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)acetamide.

14. A composition according to claim 13 wherein the compound (B) is 1-oxyl-2,2,6,6-tetramethyl-4-allyloxypiperidine.

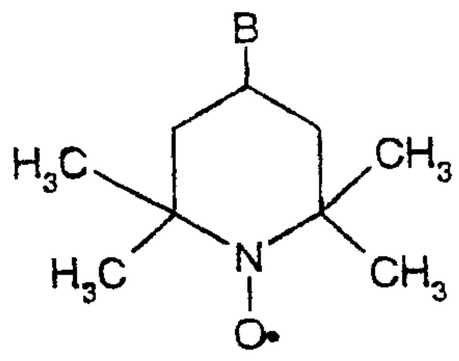
15. A composition according to claim 13 wherein the compound (B) is 1-oxyl-2,2,6,6-tetramethyl-4-(2,3-dihydroxypropoxy)piperidine.

16. A composition according to claim 13 wherein the compound (B) is 1-oxyl-2,2,6,6-tetramethyl-4-(2-hydroxy-4-oxapentoxy)piperidine.

17. A composition according to claim 13 wherein the compound (B) is N-butyl-N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)formamide.

18. A process for preventing the premature polymerization of an unsaturated monomer (A) which is an unsaturated acid, an unsaturated ester, an unsaturated amide, an unsaturated nitrile, unsaturated ether, vinyl pyridine, diethyl vinylphosphonate or sodium styrene-sulfonate, in the presence of water by incorporating therein an effective stabilizing amount of a compound (B) of formula I, II, V or VI as defined in any one of claims 1 to 7 and 12 to 17.

19. A compound of formula III or IV



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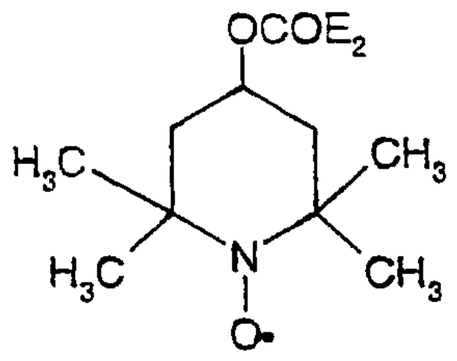

(IV)

wherein

B is OE_1 or $NE_{11}E_{12}$

E_1 is alkyl of 2 to 6 carbon atoms interrupted by one or two oxygen atoms, substituted by two to three hydroxyl groups or both interrupted by said oxygen atoms and substituted by said hydroxyl groups, or E_1 is alkyl of 1 to 4 carbon atoms substituted by carboxy or by the alkali metal, ammonium or lower alkylammonium salts thereof; or E_1 is alkyl substituted by -COOE where E is methyl or ethyl, and

E_2 is alkyl of 3 to 5 carbon atoms interrupted by -COO- or by -CO-, or E_2 is -$CH_2(OCH_2CH_2)_nOCH_3$ where n is 1 to 4; or

E_2 is -NHE_3 where E_3 is alkyl of 1 to 4 carbon atoms;

E_{11} is hydrogen or alkyl of 1 to 4 carbon atoms, and

E_{12} is -CO-E_{13} where E_{13} is alkyl of 1 to 4 carbon atoms which alkyl is interrupted by one or two oxygen atoms, or E_{13} is -NHE_{14} where E_{14} is alkyl of 1 to 4 carbon atoms;

with the proviso that E_1 is not 2,3-dihydroxypropyl.

20. A compound according to claim 19, wherein E_1 is 2-hydroxy-4-oxapentyl or -CH_2COOH.

21. A compound according to claim 19, wherein E_{11} is hydrogen or butyl, E_{13} is methoxymethyl or 2-methoxyethoxymethyl; or E_{12} is N-butylcarbamoyl.

22. A compound according to claim 19, wherein E_2 is methoxymethyl, 2-methoxyethoxy-methyl, 2-(2-methoxyethoxy)ethoxymethyl, -CH_2COCH_3, -$CH_2CH_2COOCH_3$ or butylamino.

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