

METHODS AND COMPOSITIONS FOR STYRENE INHIBITION VIA IN SITU GENERATION OF QUINONE METHIDES

FIELD OF THE INVENTION

[0001] The invention pertains to methods and compositions for inhibiting the undesired polymerization of vinyl aromatic monomers, such as styrene monomers, during processes such as monomer preparation, and purification, and during storage and shipment of products containing such monomers.

BACKGROUND OF THE INVENTION

[0002] Common industrial methods for producing styrene typically include separation and purification processes such as distillation to remove unwanted impurities. Unfortunately, purification processes carried out at elevated temperatures result in an increased rate of undesired polymerization. Distillation is generally carried out under vacuum to minimize loss of monomer.

[0003] Furthermore, it is well known that styrene monomers readily polymerize when heated. Heat polymerization is rapid. In fact, polymerization increases with increasing temperature. This polymerization is undesirable during many stages of the manufacturing, processing, handling, storage and use of styrene monomers, as it results not only in the loss of desired monomer end-product, but also in the uses of production efficiency caused by polymer formation and/or agglomeration of polymer on process equipment.

[0004] To minimize this problem, free radical inhibitors consisting of nitrated phenol-based retarders have been used to inhibit the polymerization. These reagents are typically added prior to the distillation. However, these nitrated phenol-based retarders can be toxic. Thus, there exists a strong need for a green inhibitor that provides an effective means of preventing polymerization.

SUMMARY OF THE INVENTION

[0005] In one exemplary embodiment of the invention, a composition is provided for inhibiting the polymerization of a variety of vinyl aromatic monomers. The composition comprises (1) an hydroxybenzyl alcohol and (2) a dehydration catalyst. In further aspects of the invention, (1) and (2) are present in an amount of 1-99 wt% (1) : 99-1 wt% (2). In another exemplary embodiment, the weight ratio of (1):(2) is about 2:1 to about 20:1.

[0006] The vinyl aromatic monomer may be chosen from a variety of members such as those selected from the group consisting of styrene, bromostyrene, divinyl benzene, α -methylstyrene, and vinyl toluene.

[0007] In further exemplary embodiments, the dehydration catalyst is an organic acid and may be chosen from i) alkyl, aryl, and alkaryl sulfonic acids and C₆-C₂₂ saturated or unsaturated carboxylic acids. In one exemplary embodiment, the organic acid is dodecyl benzene sulfonic acid. In other exemplary embodiments, the hydroxyl benzyl alcohol compound is di-tert butyl hydroxy benzyl alcohol.

[0008] In further exemplary embodiments, an hydroxyl amine compound (3) may be conjointly utilized with the hydroxy benzyl alcohol (1) and dehydration catalysts (2). In further exemplary embodiments, a stable free radical, such as a nitroxyl compound, may be conjointly used with the components (1) and (2).

[0009] In other aspects of the invention, methods are provided for inhibiting the polymerization of vinyl monomers wherein a quinone methide compound is added to the monomer. In one embodiment, the quinone methide is formed in situ via reaction of a hydroxy benzyl alcohol (1) and a dehydration catalyst (2). In other embodiments of the invention, from about 10-10,000 ppm, collectively, of the components (1) and (2) are added to the vinyl monomer based upon one million parts of the vinyl monomer.

[0010] The optional hydroxyl amine compound may be added to the vinyl monomer in an amount of about 1-10,000 ppm hydroxylamine based upon one million parts of the vinyl monomer. Further, in other embodiments, the optional nitroxyl compound may be added to the vinyl monomer in an amount of about 1-10,000 ppm based on one million parts of the vinyl monomer.

[0011] The present invention and its advantages over the prior art will become apparent upon reading the following detailed description and the appended claims with reference to the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] These and other aspects of the invention will be understood from the description and claims herein, taken together with the drawings showing details of construction and illustrative embodiments, wherein:

[0013] Fig. 1 is a graph depicting the percentage of polymer produced when di-tertbutyl hydroxybenzyl alcohol (i.e., DTBHBA) plus dodecylbenzenesulfonic acid (i.e., DDBSA) is added to the styrene solution and when a quinone methide is added to the styrene solution in the present invention; and

[0014] Fig. 2 is a graph depicting multiple ratios of DTBHBA plus DDBSA and the resultant percentage of polymer that is produced in the present invention.

DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS

[0015] Approximating language, as used herein throughout the specification and claims, may be applied to modify any quantitative representation that could permissibly vary without resulting in a change in the basic function to which it is related. Accordingly, a value modified by a term or terms, such as “about”, is not limited to the precise value specified. In at least some instances, the approximating language may correspond to the precision of an instrument for measuring the value. Range limitations may be combined and/or interchanged, and such ranges are identified and include all the sub-ranges stated herein unless context or language indicates otherwise. Other than in the operating examples or where otherwise indicated, all numbers or expressions referring to quantities of ingredients, reaction conditions and the like, used in the specification and the claims, are to be understood as modified in all instances by the term “about”.

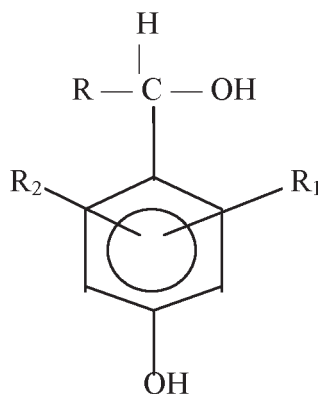
[0016] “Optional” or “optionally” means that the subsequently described event or circumstance may or may not occur, or that the subsequently identified material may or may not be present, and that the description includes instances where the event or circumstance occurs or where the material is present, and instances where the event or circumstance does not occur or the material is not present.

[0017] As used herein, the terms “comprises”, “comprising”, “includes”, “including”, “has”, “having”, or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a process, method, article or apparatus that comprises a list of elements is not necessarily limited to only those elements, but may

include other elements not expressly listed or inherent to such process, method, article, or apparatus.

[0018] The singular forms “a”, “an”, and “the” include plural referents unless the context clearly dictates otherwise.

[0019] In accordance with one aspect of the invention, a quinone methide polymerization inhibitor is added to the vinyl monomer. Although applicant is not bound to any particular theory of operation, the quinone methide is in situ generated by the dehydrating action of a strong acid catalyst on a hydroxybenzyl alcohol. As to the hydroxybenzyl alcohols (1) that may be used, these may generally be of the type given in Formula I:



(I)

wherein R is H, or C₁-C₁₀ alkyl, or C₆-C₂₀ alkylaryl, R₁ and R₂ may or may not be present and are independently selected from C₁-C₁₀ alkyl groups, preferably C₁-C₆ alkyl groups. At present, the preferred hydroxybenzyl alcohol is 3,5-di-tertbutyl 4-hydroxybenzyl alcohol (i.e., di-tertbutyl hydroxybenzyl alcohol).

[0020] The dehydrating catalyst (2) is a strong acid catalyst and, in certain exemplary embodiments, may be chosen from alkyl, aryl, and alkylaryl sulfonic acids (the number of C atoms being between about 1-40), and C₂-C₃₆ saturated or unsaturated carboxylic acids. For example, alkyl benzene sulfonic acids such as dodecylbenzene sulfonic acid and toluene sulfonic acid such as para toluene sulfonic acid may be mentioned as exemplary. Further, stearic acid is an example of a C₂-C₃₆ saturated carboxylic acid that may be mentioned.

[0021] In accordance with one exemplary embodiment, an hydroxylamine inhibitor can be conjointly used with (1) and (2) above. Hydroxylamines have the functional groups —NOH— and may be represented by the general Formula II:



(II)

wherein R_3 and R_4 may be the same or different and are selected from hydrogen, alkyl, aryl, alkaryl, or hydroxyalkyl groups and preferably have about three to about 20 carbon atoms. In one exemplary embodiment, the hydroxylamine is 2-propanol, 1,1'—(hydroxyimino)bis. Details pertaining to the hydroxylamines can be seen in U.S. Patent 6,024,894 (Arhancet) – incorporated herein by reference.

[0022] In still other embodiments, the hydroxybenzyl alcohol (1) and dehydrating catalyst (2) may be employed as a polymerization inhibitor conjointly with a stable free radical, such as the nitroxyl compounds. Exemplary nitroxyl compounds that may be mentioned are 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxy, or tetramethylpiperidino-N-oxyl, or 1-oxyl-2,2,6,6-tetramethyl-4-piperidinol. Details about the nitroxyl free radicals can be seen for example in U.S. Patent 5,254,760 (Winter et al.) – incorporated by reference herein.

[0023] The compositions and methods of the present invention are effective at inhibiting polymerization of vinyl aromatic monomers under processing and storage conditions. Exemplary processing conditions include but are not limited to preparation, purification, distillation and vacuum distillation processes.

[0024] Styrene, for example, is typically processed at temperatures between 75 °C and 125 °C. In one aspect of the invention, the compositions and methods of the present invention are effective at inhibiting the polymerization of styrene over this range of temperatures.

[0025] The vinyl aromatic monomers that are treated by the compositions and methods of the present invention include but are not limited to styrene, bromostyrene, divinylbenzene, and α -methylstyrene. The compositions and methods of the present invention are particularly efficacious at inhibiting the polymerization of styrene monomer.

[0026] The total amount of hydroxybenzyl alcohol (1) and dehydration catalyst (2) used in the methods of the present invention is that amount which is sufficient to inhibit polymerization of vinyl aromatic monomers. This amount will vary according to the conditions under which the vinyl aromatic monomer is being processed, contaminants in the system and the temperature of the system. At higher processing

temperatures and higher monomer contamination, larger amounts of the inhibiting composition are required.

[0027] For purposes of the present invention, the term "effective inhibiting amount" is that amount which is effective at inhibiting vinyl aromatic monomer polymerization. In one embodiment, this amount ranges from about 1 part to about 10,000 parts of hydroxybenzyl alcohol (1) and dehydration catalyst, collectively, per 1 million parts of monomer. In another embodiment, this amount will range from about 1 to about 1,500 parts per million parts monomer.

[0028] Accordingly, it is possible to produce a more effective vinyl aromatic monomer polymerization inhibiting treatment than is obtained by the use of either compound by itself when measured at comparable treatment levels. This synergism or enhanced activity between components allows for the concentration of each of the components to be lowered and the total quantity of polymerization inhibitor required, particularly at higher temperatures, may be lowered while achieving a commensurate level of polymerization inhibition.

[0029] As such, one exemplary weight ratio of hydroxybenzyl alcohol (1) to dehydration catalyst (2) will generally range from about 2:1 to about 4:1. In one embodiment, the weight ratio is about 2:1 to about 20:1.

[0030] The compositions of the present invention can be introduced into the vinyl aromatic monomer by any conventional method at any point of the processing system, either as separate and individual ingredients or as a combination of ingredients.

[0031] The compositions of the present invention may be added to the vinyl aromatic monomer as either a dispersion or as a solution using a suitable liquid carrier or solvent. Any solvent that is compatible with the individual ingredients of the composition and the vinyl aromatic monomer to be treated may be employed. It is often desirable to dissolve the inhibitors in the monomer to which the inhibitor is being added to avoid introducing additional impurities in the monomer. Exemplary liquid carriers include organic solvents, such as ethyl benzene, water, glycols, and glycol ethers.

[0032] The method of the present invention can control the fouling of processing equipment, such as the equipment used in separation and purification processes of styrene monomer, which is due to or caused by the polymerization of the monomer. The instant invention may be used as both a process inhibitor, which is employed during preparation and processing (e.g., employing heat) of the styrene

monomer, and as a product inhibitor, which is combined with the styrene monomer in order to inhibit polymerization during storage and handling.

[0033] The invention will now be described in conjunction with the following examples which should be viewed as being illustrative of the invention and should not be deemed to limit the invention in any manner.

EXAMPLES

[0034] The effect of a combined treatment of di-tertiary butyl hydroxybenzyl alcohol (DTBHBA) and dodecylbenzene sulfonic acid (DDBSA) on the thermal polymerization of styrene at 120 °C was evaluated by comparing polymer formation utilizing the following procedure.

[0035] Uninhibited styrene (5 mL) was placed in a test tube and the appropriate amount of polymerization inhibitor(s) was added, either a known inhibitor compound 4-benzylidene-2,6-ditert-butyl-2,5 cyclohexadien-1-one (CAS 7078-98-0) as a comparative inhibitor, or the claimed inhibitor composition [DTBHBA/DDBSA]. The tube was capped with a rubber septum and argon was bubbled through the liquid at 10 mL/min. for 3 minutes. The tubes were then placed in an oil bath heated to 120 °C. Once the temperature reached 120 °C, the stop clock was started and this time was considered as time zero. About 5 ml of the sample was removed from the test tube at varying time intervals for up to 4 hours and measured precisely before pouring into about 40 ml methanol to precipitate out the styrene polymer. The precipitated polystyrene was filtered with a gas membrane filter, dried at 100 °C and weighed. The results of this testing are presented in Table I.

Table I: Styrene Polymerization Results

Mg 2.5 mL	Time in Minutes	CAS 7078-98-0 600 ppmA	DTBHBA 600 ppmA	DTBHBA/ DDBSA 600/600 ppmA	DDBSA 600 ppmA
	0	0	0	0	0
	60	4.7	193.4	0.8	53
	120	15.6		3.2	109.2
	180	27.2		10.1	
	240	46.1		15.8	
(%) Polymer	Time in Minutes	CAS 7078-98-0 600 ppmA	DTBHBA 600 ppmA	DTBHBA/ DDBSA 600/600 ppmA	DDBSA 600 ppmA

	0	0	0	0	0
	60	0.21	8.50	0.04	2.33
	120	0.69		0.14	4.80
	180	1.20		0.44	
	240	2.03		0.69	

ppmA = ppm actives basis

[0036] The results presented in Table I demonstrate that the invention composition is more effective than either ingredient by itself. (See Fig. 1).

[0037] Uninhibited styrene (5 mL) was placed in a test tube and varying ratios of DTBHBA/DDBSA were added. The tube was capped with a rubber septum and argon was bubbled through the liquid at 10 mL/min. for 3 minutes. The tubes were then placed in an oil bath heated to 120 °C. Once the temperature reached 120 °C, the stop clock was started and this time was considered as time zero. About 5 ml of the sample was removed from the test tube at varying time intervals for up to 4 hours and measured precisely before pouring into about 40 ml methanol to precipitate out the styrene polymer. The precipitated polystyrene was filtered with a gas membrane filter, dried at 100 °C and weighed. The results of this testing are presented in Table II.

Table II: Styrene Polymerization Results at 120 °C with different ratios of DTBHBA/DDBSA.

Mg 2.5 mL	Time in Minutes	DTBHBA/ DDBSA 600/600 ppmA	DTBHBA/ DDBSA 600/300 ppmA	DTBHBA/ DDBSA 600/150 ppmA	DTBHBA/ DDBSA 600/50 ppmA	DTBHBA/ DDBSA 600/25 ppmA
	0	0	0	0	0	0
	60	1.2	1	0.6	1.5	1.8
	120	4.1	3.2	4.2	4.4	8.1
	180	8.9	6.5	12.3	20.4	36.1
	240	16.2	10.1	24.9	59.2	124.2
(%) Polymer	Time in Minutes	DTBHBA/ DDBSA 600/600 ppmA	DTBHBA/ DDBSA 600/300 ppmA	DTBHBA/ DDBSA 600/150 ppmA	DTBHBA/ DDBSA 600/50 ppmA	DTBHBA/ DDBSA 600/25 ppmA
	0	0	0	0	0	0
	60	0.05	0.04	0.03	0.07	0.08
	120	0.18	0.14	0.18	0.19	0.36
	180	0.39	0.29	0.54	0.90	1.59
	240	0.71	0.44	1.09	2.60	5.46

[0038] The results presented in Table II demonstrate that the invention composition is more effective at a DTBHBA/DDBSA 600/300 ppm ratio, than at the other ratios. (See Fig. 2).

[0039] While this invention has been described in conjunction with the specific embodiments described above, it is evident that many alternatives, combinations, modifications and variations are apparent to those skilled in the art. Accordingly, the preferred embodiments of this invention, as set forth above are intended to be illustrative only, and not in a limiting sense. Various changes can be made without departing from the spirit and scope of this invention. Therefore, the technical scope of the present invention encompasses not only those embodiments described above, but also all that fall within the scope of the appended claims.

[0040] What is claimed is:

CLAIMS

1. A composition for inhibiting the polymerization of a vinyl aromatic monomer comprising:
 - (1) a hydroxybenzyl alcohol; and
 - (2) a dehydrating catalyst.
2. A composition as recited in claim 1 wherein said (1) and (2) are present in an amount of about 1-99 wt% (1) : 99-1 wt% (2).
3. A composition as recited in claim 2, wherein the weight ratio of (1):(2) is about 2:1 to about 20:1.
4. A composition as recited in claim 1, wherein said vinyl aromatic monomer is a member selected from the group consisting of styrene, bromostyrene, divinylbenzene, and α -methylstyrene.
5. A composition as recited in claim 1 wherein said dehydrating catalyst (2) is an acid chosen from i) alkyl, aryl, and alkylaryl sulfonic acids and ii) C₂-C₃₆ saturated or unsaturated carboxylic acids.
6. A composition as recited in claim 5 wherein said dehydrating catalyst is an alkyl, aryl, or alkylaryl sulfonic acid.
7. A composition as recited in claim 1, wherein said hydroxybenzyl alcohol is di-tert butyl hydroxybenzyl alcohol.
8. A composition as recited in claim 1 wherein said dehydrating catalyst is dodecyl benzene sulfonic acid or para toluene sulfonic acid.

9. A composition as recited in claim 1 further comprising a 3) hydroxylamine compound wherein said hydroxylamine is present in an amount of 1-99 wt% based on the total weight of (1) and (2).

10. A composition as recited in claim 1 further comprising (4) a nitroxyl compound, said 4) being present in an amount of 1-99 wt% based on the total weight of (1) and (2).

11. A method for inhibiting the polymerization of a vinyl monomer comprising adding to said monomer (1) a hydroxybenzyl alcohol and (2) a dehydrating catalyst.

12. A method as recited in claim 11 wherein said (1) and (2) are present in an amount of about 1-99 wt% (1) : 99-1 wt% (2).

13. A method as recited in claim 11 wherein the weight ratio of (1):(2) is about 2:1 to about 20:1 and wherein about 10-10,000 ppm of said (1) and (2) combined is added to said vinyl monomer, based upon one million parts of said vinyl monomer.

14. A method as recited in claim 11 wherein said dehydrating catalyst is an acid chosen from i) alkyl, aryl, and alkylaryl sulfonic acids and ii) C₆-C₂₂ saturated or unsaturated carboxylic acids.

15. A method as recited in claim 11 wherein said hydroxybenzyl alcohol is di-tert butyl hydroxybenzyl alcohol.

16. A method as recited in claim 14 wherein said acid is dodecyl benzene sulfonic acid or para toluene sulfonic acid.

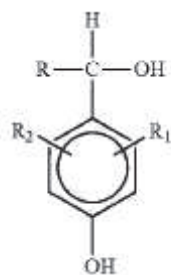
17. A method as recited in claim 11 further comprising adding to said vinyl monomer a (3) hydroxylamine compound, said hydroxylamine being added in an amount of about 1-10,000 ppm hydroxylamine based on 1 million parts of said vinyl monomer.

18. A method as recited in claim 11 further comprising adding to said vinyl monomer a (4) nitroxyl compound, said nitroxyl compound being added in an amount of about 1-10,000 ppm based on 1 million parts of said vinyl monomer.

19. A method for inhibiting the polymerization of a vinyl monomer comprising adding to said vinyl monomer an effective amount of the composition of claim 1.

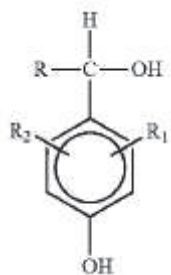
20. A method as recited in claim 19 wherein said composition comprises di-tertbutyl hydroxybenzyl alcohol and dodecyl benzene sulfonic acid or para toluene sulfonic acid.

21. A composition as recited in claim 1 wherein said hydroxybenzyl alcohol has the formula



wherein R is H, or C₁-C₁₀ alkyl, or C₆-C₂₀ alkylaryl, R₁ and R₂ may or may not be present and are independently selected from C₁-C₁₀ alkyl groups.

22. A method as recited in claim 11 wherein said hydroxybenzyl alcohol has the formula



wherein R is H, or C₁-C₁₀ alkyl, or C₆-C₂₀ alkylaryl, R₁ and R₂ may or may not be present and are independently selected from C₁-C₁₀ alkyl groups.