

Polymerization inhibitor for stabilizing olefinically unsaturated monomers

The invention relates to the use of a polymerization
5 inhibitor for stabilizing olefinically unsaturated monomers, and to a monomer composition which comprises both olefinically unsaturated monomers and this polymerization inhibitor.

10 During the preparation of olefinically unsaturated monomers, for example ethene, butadiene, vinyl acetate, (meth)acrylic acid, (meth)acrylate, acrylonitrile or styrene, these olefinically unsaturated monomers are subjected to a purification process step, for example
15 distillation or extraction, in order to remove undesired by-products or impurities.

These olefinically unsaturated monomers can polymerize as early as during the preparation and/or purification
20 process. Some of these olefinically unsaturated monomers, for example butadiene, tend to polymerize spontaneously even in the course of storage or in the course of transport.

25 This premature and undesired polymerization of these olefinically unsaturated monomers leads firstly to a reduction in the amount of usable olefinically unsaturated monomers, and secondly to undesired deposition of undesired polymer. This deposition of the undesired
30 polymer can lead under some circumstances to reduced heat transfer in individual plant parts. Moreover, surfaces which are coated with the undesired polymer, or plant parts, for example filters, which are blocked by the undesired polymer, can lead to interruption of
35 production.

Consequently, additives are generally added to the olefinically unsaturated monomers as early as in the

preparation process, which are referred to either as polymerization inhibitors or as polymerization retardants, which are capable either of preventing the undesired polymerization process or at least of
5 retarding it.

A multitude of polymerization inhibitors is known for olefinically unsaturated monomers, for example styrene. Examples of compounds used for the purpose include
10 sulfur, p-benzoquinone, 4-tert-butylpyrocatechol, phenothiazine or sterically hindered phenols. However, some of these compounds have considerable disadvantages, for example their toxicity, instability at relatively high temperatures or insufficient activity
15 under the appropriate process conditions of the preparation or purification process. Some of the polymerization inhibitors mentioned even require oxygen to be able to display their action, which can lead to considerable problems with regard to the explosion
20 protection for use in industrial scale processes.

Polymerization inhibitors frequently described in the literature are so-called stable free nitroxyl radicals, for example 2,2,6,6-tetramethylpiperidine N-oxyl
25 (frequently abbreviated as TEMPO). For example, US 3,747,988 describes the addition of a nitroxyl radical, especially of 2,2,6,6-tetramethyl-4-hydroxypiperidine N-oxyl, to acrylonitrile before the distillation. These stable free radicals are also described in US
30 3,488,338, except as chain terminators for 2-chloro-1,3-butadiene. US 4,670,131 describes the use of these stable free nitroxyl radicals as a polymerization inhibitor for stabilizing olefinically unsaturated monomers, for example ethene, propene, butene or
35 butadiene.

The use of stable free nitroxyl radicals is described, inter alia, by the following publications "Inhibition

of Radical Polymerization by Nitroxide Mono- and Biradicals" (Vysokomol, Soyed. 8: 1966, No. 9, 1642-1646) by L. V. Ruban et al., "A Re-Examination of Some Stabilized Radicals as Inhibitors of Polymerization" (J. Polym. Mater. 19 (2002), 113-120) and "Stabilized Radicals as Inhibitors of Polymerization - Reactions of Alkoxyamines with Growing Polymer Radicals" (J. Macrom. Science 2002, Vol. A39, No. 11, 1295-1303) by Bevington et al.

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Numerous publications describe the use of compositions which comprise, inter alia, stable free nitroxyl radicals. For instance, US 6,525,146, WO 2002/088055 and EP 1 077 245 describe a composition composed of stable free nitroxyl radicals and phenol derivatives as a polymerization inhibitor. Further examples of a composition for the stabilization of olefinically unsaturated monomers which have stable free nitroxyl radicals are described, for example, by US 2003/080318, WO 2002/094884, WO 2002/033026, WO 2002/008161, EP 1 077 206 and DE 199 56 509.

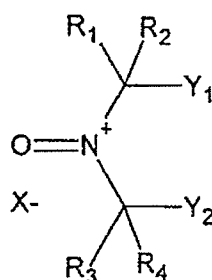
It is therefore an object of the present invention to provide a polymerization inhibitor for olefinically unsaturated monomers with improved action over the prior art. In particular, a polymerization inhibitor shall be provided which has improved properties in the stabilization of olefinically unsaturated monomers with respect to premature polymerization during the preparation and purification process or during storage.

It has been found that, surprisingly, compounds of the formula (1) and/or (2) are suitable as polymerization inhibitors for olefinically unsaturated monomers. The preparation of these compounds has been known for some time, but it has not been recognized that these compounds can be used as polymerization inhibitors. It was also surprising that these compounds which do not

possess a stable free radical can display this action as a polymerization inhibitor. The solution to this problem was all the more surprising given that it was found that the action of these compounds as polymerization inhibitors is improved over prior art polymerization inhibitors which have a stable free radical in their structure. With the same molar amount of polymerization inhibitor in the olefinically unsaturated monomers, a lower polymer content in the olefinically unsaturated monomers can be obtained by the inventive use compared to the prior art. Alternatively, the same polymer fraction in the olefinically unsaturated monomers can be achieved by a smaller molar amount of polymerization inhibitor.

The invention provides for the use of a polymerization inhibitor for stabilizing olefinically unsaturated monomers, the polymerization inhibitor comprising

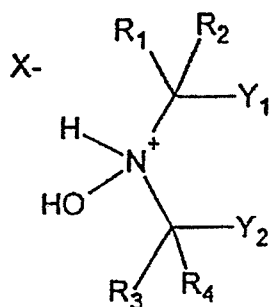
- from 0 to 100% by weight of a compound of the formula (1)



(1)

and

- from 100 to 0% by weight of a compound of the formula (2)



(2)

where:

R_1, R_2, R_3 and R_4 = alkyl group having from 1 to 4 carbon atoms and

Y_1, Y_2 = alkyl group having from 1 to 4 carbon atoms, or Y_1 and Y_2 together form a ring system,

X^- = inorganic or organic anion,

where the substituents of the R_1, R_2, R_3, R_4, Y_1 and Y_2 type are the same or different, either the substituents of the Y_1 and Y_2 type or the ring system based on the substituents of the Y_1 and Y_2 type may be unsubstituted or substituted, and the sum of the percentages by weight of the compounds of the formula (1) and (2) adds up to 100% by weight, and being mixed with an olefinically unsaturated monomer or monomer mixture which comprises at least one olefinically unsaturated monomer.

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The invention further provides a monomer composition, the monomer composition comprising a polymerization inhibitor which comprises

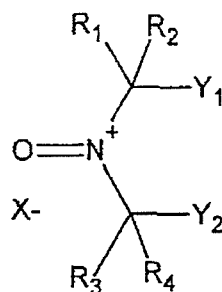
- from 40 to 60 % by weight of a compound of the formula (1) and
- from 60 to 40% by weight of a compound of the formula (2),

and comprising at least one olefinically unsaturated monomer, selected from alke-1-enes or alka-1, 3-dienes which may be either substituted or unsubstituted.

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In the inventive use of a polymerization inhibitor for stabilizing olefinically unsaturated monomers, the polymerization inhibitor comprises

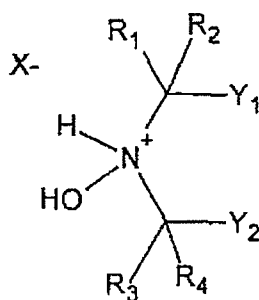
- from 0 to 100% by weight of a compound of the formula (1)



(1)

and

- from 100 to 0% by weight of a compound of the formula (2)



(2)

15 where:

R_1 , R_2 , R_3 and R_4 = alkyl group having from 1 to 4 carbon atoms and

Y_1 , Y_2 = alkyl group having from 1 to 4 carbon atoms, or Y_1 and Y_2 together form a ring system,

X^- = inorganic or organic anion,

where the substituents of the R_1 , R_2 , R_3 , R_4 , Y_1 and Y_2 type are the same or different, either the substituents of the Y_1 and Y_2 type or the ring system based on the substituents of the Y_1 and Y_2 type may be unsubstituted or substituted, and the sum of the percentages by weight of the compounds of the formula (1) and (2) adds up to 100% by weight, and is mixed with an olefinically unsaturated monomer or monomer mixture which comprises at least one olefinically unsaturated monomer.

In the inventive use of these polymerization inhibitors, either compounds of the formula (1) or of the formula (2) may be used. However, preference is given in the inventive use to using a composition as the polymerization inhibitor which comprises both compounds of the formula (1) and of the formula (2). In particular, a polymerization inhibitor is used which comprises

- from 40 to 60% by weight of a compound of the formula (1)

and

- from 60 to 40% by weight of a compound of the formula (2).

Particular preference is given to using a polymerization inhibitor which comprises

- from 45 to 55% by weight of a compound of the formula (1)

and

- from 55 to 45% by weight of a compound of the formula (2).

The polymerization inhibitors used in the use according to the invention can be prepared in a process as described by Merbouh et al. in "Preparation of tetramethylpiperidine-1-oxoammonium salts and their use as oxidants in organic chemistry. A review" (Organic Preparations and Procedures International, 2004, 36(1), 3-31) or Golubev et al. in "Some reactions of free

iminoxyl radicals with the participation of the unpaired electron" (Seriya Khimicheskaya, No. 11, 1965, 1927-1936).

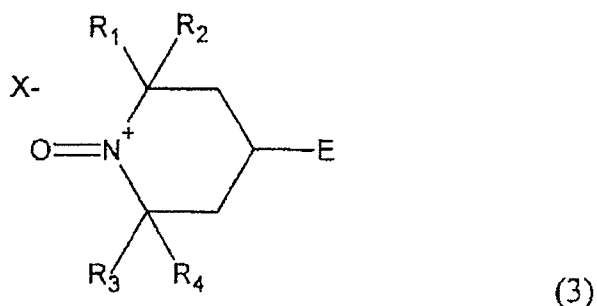
5 In a preferred process for preparing these compounds of the formula (1), generally both compounds of the formula (1) and of the formula (2) are formed; in this process, the appropriate nitroxyl radical is reacted in solution with a strong inorganic or organic acid. The
10 disproportionation of the nitroxyl radical forms an approx. 1:1 mixture of the corresponding oxoammonium salt of the formula (1) and of the corresponding hydroxylamine compound of the formula (2). Therefore, when a composition of these compounds of the formula
15 (1) and (2) is used in the use according to the invention, a complicated separation of the two compounds after the preparation process can be dispensed with.

In a particular embodiment of the use of these
20 polymerization inhibitors according to the invention, they are prepared in situ.

In a particular embodiment of the use according to the invention, the substituents of the Y_1 and Y_2 type are
25 substituted, the substituent or these substituents of the substituents of the Y_1 and Y_2 type being selected from alkyl, ester, ether, hydroxyl, oxo, cyano, cyano-hydrin, amino, amide, carboxyl, halogen, hydantoin, ketal, acetal or urethane group.

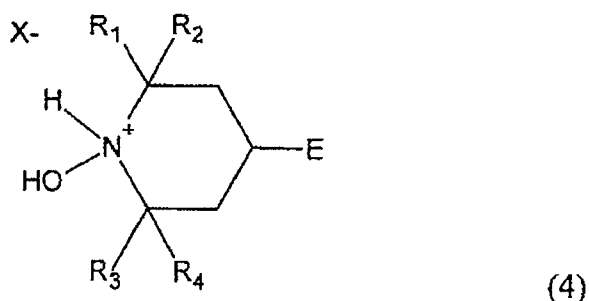
30 The two substituents of the Y_1 and Y_2 type of the polymerization inhibitor together preferably form a ring system. In the use according to the invention, particular preference is given to using a polymeriza-
35 tion inhibitor which comprises

- from 0 to 100% by weight of a compound of the formula (3)



and

- from 100 to 0% by weight of a compound of the formula (4)



where:

- 10 R_1, R_2, R_3 and R_4 = alkyl group having from 1 to 4 carbon atoms,
- E = alkyl, ester, ether, hydroxyl, oxo, cyano, cyanohydrin, amino, amide, carboxyl,
- 15 halogen, hydantoin, ketal, acetal or urethane group and
- X^- = inorganic or organic anion,

where the substituents of the R_1, R_2, R_3 and R_4 type are the same or different. In the use according to the invention, very particular preference is given to using

20 a polymerization inhibitor which comprises compounds of the formula (3) and/or (4) where R_1, R_2, R_3 and R_4 = methyl group.

In particular, in the use according to the invention, polymerization inhibitors are used which have an inorganic or an organic anion in the compounds of the formulae (1) to (4); the polymerization inhibitors used preferably have inorganic anions. In the use according to the invention, particular preference is given to using polymerization inhibitors which have, as the anion X^- in the compounds of the formulae (1) to (4), a halogen anion, preferably chlorine or bromine anion.

In the context of this invention, a polymerization inhibitor is understood to mean a compound which is capable of preventing polymerization of the olefinically unsaturated monomer for a certain period. The period until polymerization occurs in the case of an olefinically unsaturated monomer without a polymerization inhibitor is therefore shorter than the period for an olefinically unsaturated monomer with a polymerization inhibitor.

Moreover, in the context of this invention, olefinically unsaturated monomers are understood to mean compounds which have at least one C-C double bond and are capable of entering into a polymerization reaction.

In the use of the polymerization inhibitor according to the invention, preference is given to using at least one olefinically unsaturated monomer selected from alk-1-enes or alka-1,3-dienes which may be either unsubstituted or substituted. Preference is given to using olefinically unsaturated monomers selected from ethene, propene, butadiene, vinyl acetate, (meth)acrylic acid, (meth)acrylate, acrylonitrile, acrolein, N-vinylformamide, chloroprene, isoprene, divinylbenzene or styrene.

In the context of this invention, (meth)acrylic acid means both acrylic acid and methacrylic acid, and (meth)acrylate means both acrylic esters and methacrylic esters, these olefinically unsaturated monomers
5 being substituted or unsubstituted.

In the use according to the invention, it is possible to use either one compound of olefinically unsaturated monomers or a mixture of different olefinically
10 unsaturated monomers.

In the use according to the invention, the polymerization inhibitors may be added to the olefinically unsaturated monomers as a solid, solution or as a
15 suspension. In this case, the polymerization inhibitors may also be added to the olefinically unsaturated monomers during a process, for example preparation or purification process. It is advantageous, in the use of these polymerization inhibitors according to the
20 invention, to ensure a suitable solvent or dispersant which is compatible firstly with the olefinically unsaturated monomer and also with these polymerization inhibitors, and that there can be no undesired reactions.

25 These polymerization inhibitors can be added to the unsaturated monomers or monomer mixtures by common prior art methods. Advantageously, in the use according to the invention, the polymerization inhibitors can be added to the feed stream of a distillation column, into
30 the inlet and outlet of a heat exchanger or of an evaporator ("boiler") or into the inlet and outlet of a condenser. In addition, in the use according to the invention, the polymerization inhibitors may also be added to the olefinically unsaturated monomers in
35 storage tanks.

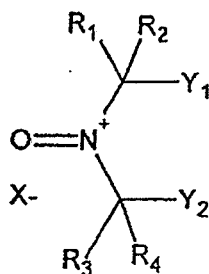
In the context of this invention, the term "effective amount of the inventive polymerization inhibitor" is

understood to mean the amount of polymerization inhibitor which is needed to prevent the premature polymerization of the olefinically unsaturated monomers. This effective amount of the polymerization inhibitor is dependent upon the conditions under which the olefinically unsaturated monomer is stored or handled. For example, in the case of distillation of the unsaturated monomer, a relatively high amount of the polymerization inhibitor is needed owing to the relatively high temperatures and the relatively high concentration of impurities.

In the use of the polymerization inhibitor according to the invention, from 100 ppb (m/m) to 10 000 ppm (m/m), more preferably from 1 ppm (m/m) to 1000 ppm (m/m) and most preferably from 10 ppm (m/m) to 100 ppm (m/m) of polymerization inhibitor is preferably added to the olefinically unsaturated monomer or to the monomer mixture, based on the olefinically unsaturated monomer.

The inventive monomer composition comprises a polymerization inhibitor which comprises

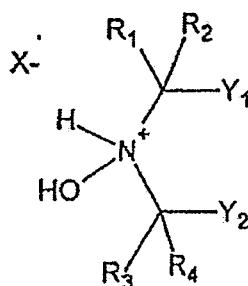
- from 40 to 60 % by weight of a compound of the formula (1)



(1)

and

- from 60 to 40% by weight of a compound of the formula (2)



(2)

where:

- $\text{R}_1, \text{R}_2, \text{R}_3$ and R_4 = alkyl group having from 1 to 4 carbon atoms and
 Y_1, Y_2 = alkyl group having from 1 to 4 carbon atoms, or Y_1 and Y_2 together form a ring system,
 X^- = inorganic or organic anion,
- where the substituents of the $\text{R}_1, \text{R}_2, \text{R}_3, \text{R}_4, \text{Y}_1$ and Y_2 type are the same or different, either the substituents of the Y_1 and Y_2 type or the ring system based on the substituents of the Y_1 and Y_2 type may be unsubstituted or substituted, and the sum of the percentages by weight of the compounds of the formula (1) and (2) adds up to 100% by weight, and comprises at least one olefinically unsaturated monomer, selected from alke-1-enes or alka-1, 3-dienes which may be either substituted or unsubstituted.
- The inventive monomer composition may comprise either compounds of the formula (1) or of the formula (2) as polymerization inhibitors. The inventive monomer composition preferably comprises both compounds of the formula (1) and of the formula (2) as polymerization inhibitors. The inventive monomer composition comprises a polymerization inhibitor which
- from 40 to 60% by weight of a compound of the formula (1)
- and

- from 60 to 40% by weight of a compound of the formula (2).

The monomer composition more preferably comprises a polymerization inhibitor which comprises

- 5 • from 45 to 55% by weight of a compound of the formula (1)

and

- from 55 to 45% by weight of a compound of the formula (2).

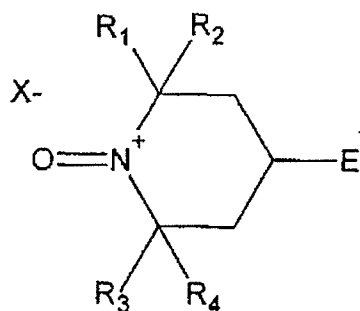
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In a particular embodiment of the inventive monomer composition, the substituents of the Y_1 and Y_2 type in the compounds of the formulae (1) and (2) of the polymerization inhibitor are substituted, the
15 substituent or these substituents of the substituents of the Y_1 and Y_2 type being selected from alkyl, ester, ether, hydroxyl, oxo, cyano, cyanohydrin, amino, amide, carboxyl, halogen, hydantoin, ketal, acetal or urethane group.

20

The two substituents of the Y_1 and Y_2 type of the compounds of the formulae (1) and (2) of the polymerization inhibitor together preferably form a ring system. More preferably, the inventive monomer
25 composition comprises a polymerization inhibitor which comprises

- from 0 to 100% by weight of a compound of the formula (3)



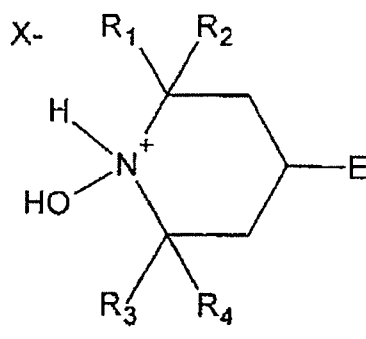
(3)

30

and

- from 100 to 0% by weight of a compound of the formula (4)

5



(4)

where:

- 10 R₁, R₂, R₃ and R₄ = alkyl group having from 1 to 4 carbon atoms,
- E = alkyl, ester, ether, hydroxyl, oxo, cyano, cyanohydrin, amino, amide, carboxyl, halogen, hydantoin, ketal, acetal or urethane group and
- 15 X⁻ = inorganic or organic anion,

where the substituents of the R₁, R₂, R₃ and R₄ type are the same or different. Most preferably, the inventive monomer composition comprises compounds of the formula

20 (3) and/or (4) where R₁, R₂, R₃ and R₄ = methyl group as polymerization inhibitor.

In particular, the inventive monomer composition has an inorganic or an organic anion in the compounds of the

25 formulae (1) to (4); it preferably has inorganic anions. The inventive monomer composition more preferably has, as the anion X⁻ in the compounds of the formulae (1) to (4), a halogen anion, preferably chlorine or bromine anion.

The inventive monomer composition preferably has at least one olefinically unsaturated monomer selected from alk-1-enes or alka-1,3-dienes which may be either substituted or unsubstituted. It preferably comprises olefinically unsaturated monomers selected from ethene, propene, butadiene, vinyl acetate, (meth)acrylic acid, (meth)acrylate, acrylonitrile, acrolein, N-vinylformamide, chloroprene, isoprene, divinylbenzene or styrene.

The inventive monomer composition may comprise either one compound of olefinically unsaturated monomers or a mixture of different olefinically unsaturated monomers.

The inventive monomer compositions preferably comprise from 100 ppb (m/m) to 10 000 ppm (m/m), more preferably from 1 ppm (m/m) to 1000 ppm (m/m) and most preferably from 10 ppm (m/m) to 100 ppm (m/m) of polymerization inhibitor, based on the olefinically unsaturated monomer.

The examples which follow are intended to illustrate the use according to the invention in detail, without any intention that the invention be restricted to these embodiments.

Preparation of the polymerization inhibitors:

Example 1:

In Example 1, no polymerization inhibitor was used.

Example 2:

In Example 2, the polymerization inhibitor used was commercially available 4-hydroxy-TEMPO from Degussa without further workup.

Example 3:

In Example 3, the polymerization inhibitor was prepared by a process which is described by Paleos et al. in "Ready Reduction of Some Nitroxide Free Radicals Using Ascorbic Acid" (J. Chem. Soc., Chem. Comm., 1997, 345-
5 346).

Examples 4 and 5:

In Examples 4 and 5, the polymerization inhibitors were prepared by a process which is described by Merbouh et
10 al. in the experimental part on pages 24 to 26 in "Preparation of tetramethylpiperidine-1-oxoammonium salts and their use as oxidants in organic chemistry. A review" (Organic Preparations and Procedures International, 2004, 36(1), 3-31) or Golubev et al. in
15 "Some Reactions Of Free Iminoxyl Radicals With The Participation Of The Unpaired Electron" (Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, 1965, 1927-1936). The reactant used was the 4-hydroxy-TEMPO from Degussa. It was demonstrated analytically that the
20 polymerization inhibitor of Example 5 was the mono-bromide.

Example 6:

The polymerization inhibitor used in Example 6 was
25 prepared by dissolving 1 g of 1,4-dihydroxy-2,2,6,6-tetramethylpiperidine in 200 ml of degassed dichloroethane and then passing HCl gas into the solution at room temperature slowly for one hour. After postreaction for one hour, the precipitated yellow
30 solid was filtered off, washed with tert-butyl methyl ether and dried.

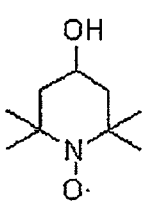
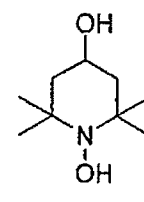
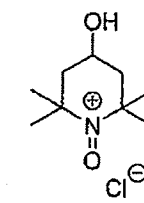
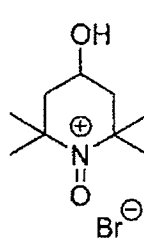
Examples 7 and 8:

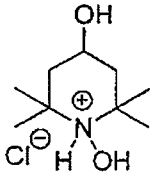
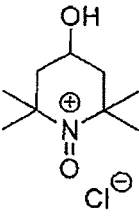
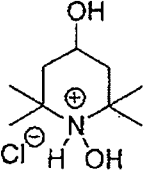
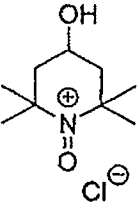
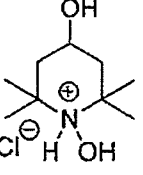
The polymerization inhibitor used in Examples 7 and 8
35 was prepared by dissolving 0.05 mol of 4-hydroxy-TEMPO from Degussa in 200 g of dichloroethane and then introducing 0.1 mol of HCl gas into the solution slowly with gentle cooling at room temperature for one hour.

After one hour of postreaction, the precipitated yellow solid was filtered off, washed with dichloromethane and dried.

- 5 **Experiments on the stability of the monomer mixture:**
Commercially available styrene (from Fluka, purum, monomer, $\geq 99.0\%$ (GC)) is freed of the tert-butyl-1,2-hydroxybenzene stabilizer at a reduced pressure of 95 hPa, a bottom temperature of 75°C and a nitrogen
- 10 blanket. A three-neck flask with a thermometer, condenser, septum and a magnetic stirrer is purged thoroughly with nitrogen in order to obtain an oxygen-free atmosphere in the flask. This nitrogen atmosphere is retained over the entire experimental duration. The
- 15 three-neck flask is charged with precisely 300 g of the distilled styrene and the particular amount of polymerization inhibitor. In order to start the experiment, the three-neck flask is immersed into an oil bath preheated to 110°C , in the course of which the
- 20 stabilized monomer composition present in the three-neck flask is stirred. The amount and the type of the polymerization inhibitor can be taken from Table 1. After the immersion of the three-neck flask into the heated oil bath, 2 g of the monomer composition are
- 25 taken as a sample at regular intervals, weighed accurately and introduced into 10 ml of methanol. After 30 minutes, the polystyrene precipitated from methanol is removed by means of a glass filter crucible, dried at 110°C for 5 hours and weighed accurately. The amount
- 30 of polystyrene present in the sample of the monomer composition is plotted against the reaction time in a diagram. As a comparative value between the examples, the time at which the sample of the monomer composition has attained a polymer content of 3% by weight
- 35 according to the measurement is determined or interpolated if necessary for each polymerization inhibitor.

Table 1:

Example	Polymerization inhibitor	Active amount of polymerization inhibitor [in ppm (m/m)]	Time after which the sample of the monomer composition had attained a polymer content of 3% by weight [in minutes]
1	-	-	50
2		100	120
3		100	90
4		100 *)	145
5		100 *)	210

6		100 ^{*)}	255
7	 	50 each (100 in total) ^{*)}	210
8	 	50 each (100 in total) ^{**)}	205

^{*)} In the calculation of the amount of polymerization inhibitors, only the molecular weight of the cation and not of the anion was taken into account for the ionic compounds.

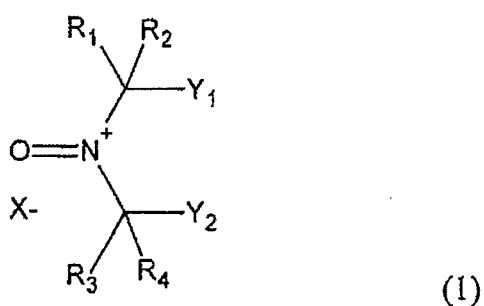
^{**)} In Example 8, in contrast to Example 7, the molecular weight of the anion was also taken into account.

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Examples 4-8 are inventive examples.

Claims:

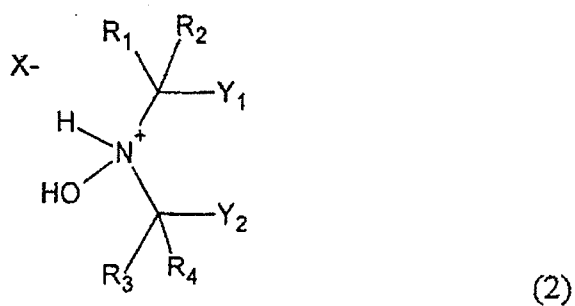
1. The use of a polymerization inhibitor for stabilizing olefinically unsaturated monomers,
 5 characterized in that
 the polymerization inhibitor comprises
 from 0 to 100% by weight of a compound of the
 formula (1)



10

and
 from 100 to 0% by weight of a compound of the
 formula (2)

15



where:

- 20 R_1, R_2, R_3 and R_4 = alkyl group having from 1 to 4 carbon atoms and
 Y_1, Y_2 = alkyl group having from 1 to 4 carbon atoms, or Y_1

and Y₂ together form a ring system,

X⁻ = inorganic or organic anion,

5 where the substituents of the R₁, R₂, R₃, R₄, Y₁ and Y₂ type are the same or different, either the substituents of the Y₁ and Y₂ type or the ring system based on the substituents of the Y₁ and Y₂ type may be unsubstituted or substituted, and the
10 sum of the percentages by weight of the compounds of the formula (1) and (2) adds up to 100% by weight,
and is mixed with an olefinically unsaturated monomer or monomer mixture which comprises at
15 least one olefinically unsaturated monomer.

2. The use according to claim 1,
characterized in that
the substituents of the Y₁ and Y₂ type are substituted, the substituent or these substituents of
20 the substituents of the Y₁ and Y₂ type being selected from alkyl, ester, ether, hydroxyl, oxo, cyano, cyanohydrin, amino, amide, carboxyl, halogen, hydantoin, ketal, acetal or urethane group.

25 3. The use according to either of claims 1 and 2, characterized in that
at least one olefinically unsaturated monomer selected from ethene, propene,
30 butadiene, vinyl acetate, (meth)acrylic acid, (meth)acrylate, acrylonitrile, acrolein, N-vinylformamide, chloroprene, isoprene, divinylbenzene or styrene is used.

35 4. The use according to at least one of claims 1 to 3,
characterized in that

from 100 ppb (m/m) to 10 000 ppm (m/m) of polymerization inhibitor is added to the monomer or to the monomer mixture, based on the olefinically unsaturated monomer.

5

5. The use according to at least one of claims 1 to 4,

characterized in that

10

from 1 ppm (m/m) to 1000 ppm (m/m) of polymerization inhibitor is added to the monomer or to the monomer mixture, based on the olefinically unsaturated monomer.

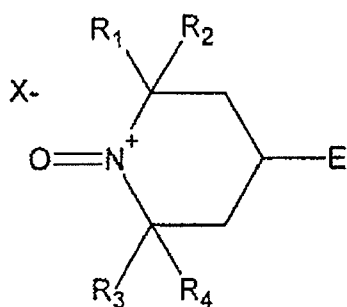
15

6. The use according to at least one of claims 1 to 5,

characterized in that

a polymerization inhibitor is used which comprises from 0 to 100% by weight of a compound of the formula (3)

20

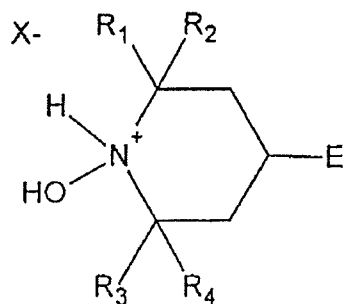


(3)

and

25

from 100 to 0% by weight of a compound of the formula (4)



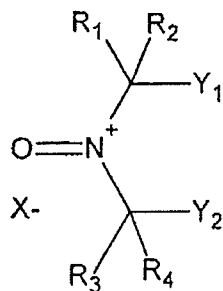
(4)

where:

- 5 R_1, R_2, R_3 and R_4 = alkyl group having from 1 to 4 carbon atoms and
- E = alkyl, ester, ether, hydroxyl, oxo, cyano, cyanohydrin, amino, amide, carboxyl, halogen, hydantoin, ketal, acetal or urethane group and
- 10 X^- = inorganic or organic anion,

15 where the substituents of the R_1, R_2, R_3 and R_4 type are the same or different.

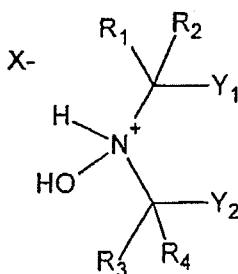
7. A monomer composition, characterized in that the monomer composition comprises a polymerization inhibitor which comprises
- 20 from 40 to 60% by weight of a compound of the formula (1)



(1)

and

from 60 to 40% by weight of a compound of the
formula (2)



(2)

where:

- 10 R_1, R_2, R_3 and R_4 = alkyl group having from 1 to 4 carbon atoms and
- Y_1, Y_2 = alkyl group having from 1 to 4 carbon atoms, or Y_1 and Y_2 together form a ring system,
- 15 X^- = inorganic or organic anion,

where the substituents of the R_1, R_2, R_3, R_4, Y_1 and Y_2 type are the same or different, either the substituents of the Y_1 and Y_2 type or the ring system based on the substituents of the Y_1 and Y_2 type may be unsubstituted or substituted, and the sum of the percentages by weight of the compounds

of the formula (1) and (2) adds up to 100% by weight, and at least one olefinically unsaturated monomer selected from alk-1-enes or alka-1, 3-dienes which may be either substituted or unsubstituted.