

Additive and Method for Terminating Polymerization and/or Reducing Viscosity of Polymer Solution

Technical Field

5 The present invention generally relates to the field of polymer, particularly relates to an additive and a method for terminating polymerization and/or reducing viscosity of polymer solution.

Backgrounds

10 During the solution polymerization or bulk polymerization of a monomer initiated by an initiator or a catalyst, remaining monomers in the system may continue to propagate on a living chain end if the living center has a long life and is not terminated in time and completely, resulting in an increasing molecular weight, an increasing Mooney viscosity or polymer
15 molecular weight during the storage of polymer solutions, even gelling, and accordingly the quality stability of polymer products is affected.

 Viscosity of a polymer solution generally is dependent on the concentration of the polymer solution and the chain structure of the polymer. Viscosity of the polymer solution is high if the solution has a
20 high concentration and viscosity of the polymer solution is high if the macromolecular chain has a high structural regularity. The high viscosity of polymer solution leads to difficult transporting, spraying, agglomerating, post processing and so on and results in a high energy cost.

 In order to control molecular weight and product quality efficiently
25 and to avoid continued chain propagation after discharging of polymerization, it is necessary to terminate growing polymer chain end and stop polymerization reaction timely and efficiently. Moreover, it is necessary to reduce the viscosity of polymer solution properly while maintaining the concentration of the high molecular weight polymer
30 solution concentrated enough, such that productivity can be increased and transportation resistance and energy cost of the polymer solution with high viscosity can be reduced.

Generally a terminator is added into a polymerization system according to termination techniques of growing polymer chain in prior art, wherein the terminator usually is selected from water, methanol, ethanol, isopropanol, ethylene glycol, propylene glycol or a mixture thereof, see for
5 example US2009/0043055A1, US2009/0043046A1, CN02805285.4, EP1431318, GB2225586A, EP0957115A1, US4906706, US5064910, EP0652240A1 and US5428119. Since water and small molecular alcohols are polar materials and have poor compatibilities with nonpolar polymer solutions, and since polymer solutions have high viscosities, it is difficult
10 to disperse and mix the terminator with polymer solutions quickly and thus it is hard to terminate the polymerization efficiently and completely. In order to enhance the dispersing of the terminator into the polymer solution so as to improve terminating effect, it is proposed to use higher aliphatic alcohols having 8-18 carbon atoms as the terminator, see for example
15 EP0207558A1, EP0386808A1, EP0667357A1, CN86103350 and EP0127236A1, or to use aliphatic carboxylic acids having 8-10 carbon atoms as the terminator, see for example US4663405 and US6713565. However, an additive that can terminate polymerization thoroughly and/or reducing viscosity of polymer solution efficiently are still desirable.

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Summary of the Invention

An object of present invention is to provide an additive that terminates polymerization reaction and/or decreases the viscosity of polymer solution. Another object of present invention is to provide a
25 method that terminates polymerization reaction and/or decreases the viscosity of polymer solution.

According to an aspect, the additive and method according to present invention can be used in solution polymerization or bulk polymerization systems containing living or growing polymer chains.

30 It is found surprisingly that, when the additive of present invention is mixed with a polymerization system containing living or growing polymer chains, the polymerization reaction can be terminated efficiently and the

viscosity of the polymerization system can be decreased simultaneously. It is also surprisingly found that, when the additive of present invention is mixed with a polymer solution having a high viscosity, the viscosity of the polymer solution can be decreased effectively.

5 The present invention provides an additive for terminating polymerization and/or reducing viscosity of polymer solution, comprising:

A. a carboxylic acid,

B. an alcohol,

C. an salt which is selected from the group consisting of an alkali
10 metal salt, an alkaline earth metal salt, an ammonium salt and a mixture thereof; and

E. optionally, water.

According to an embodiment of present invention, said additive further comprises component D, which is at least one selected from the
15 group consisting of an amine, a phenol, and an ester.

The present invention further provides a method for terminating polymerization and/or reducing viscosity of polymer solution, including adding the additive according to present invention into a polymer solution and then mixing the resulting mixture for about 0.5 – about 30 min at a
20 mixing temperature of about -100 °C to about 110 °C; wherein the additive is added in an amount of about 0.4wt% to about 7.5wt%, preferably about 0.7 wt% to about 6.0wt%, based on the total weight of the polymer in the polymer solution.

25 Detailed description of the invention

In one aspect, the present invention provides an additive for terminating polymerization and/or reducing viscosity of polymer solution, comprising:

A. a carboxylic acid,

30 B. an alcohol,

C. an salt which is selected from the group consisting of an alkali metal salt, an alkaline earth metal salt, an ammonium salt and a mixture

thereof; and

E. optionally, water.

According to a preferred embodiment of present invention, said additive further comprises component D, which is at least one selected
5 from the group consisting of an amine, a phenol, and an ester.

The component A carboxylic acid according to present invention can be any carboxylic acid known in the art commonly used to terminate a living or growing polymer chain. The component A carboxylic acid is preferably at least one selected from the group consisting of a saturated
10 aliphatic acid having 6-26 carbon atoms, an unsaturated aliphatic acid having 6-26 carbon atoms, and an aromatic acid having 7-26 carbon atoms.

More preferably, the component A carboxylic acid is at least one selected from the group consisting of a saturated aliphatic acid having 10-20 carbon atoms, an unsaturated aliphatic acid having 10-20 carbon
15 atoms, and an aromatic acid having 7-20 carbon atoms.

According to a preferred embodiment, said component A carboxylic acid is selected from the group consisting of decanoic acid, undecanoic acid, dodecanoic acid, tridecanoic acid, myristic acid, pentadecanoic acid, palmitic acid, heptadecanoic acid, stearic acid, hexadecenoic acid, oleic
20 acid, octadecadienoic acid, octadecatrienoic acid, eicosatetraenoic acid, ricinoleic acid, epoxy oleic acid, sebacic acid, dodecanedioic acid, tridecanedioic acid, benzoic acid, a methyl benzoic acid, an ethyl benzoic acid, a propyl benzoic acid, a butyl benzoic acid, a pentyl benzoic acid, a hexyl benzoic acid, phenylacetic acid, phenylpropionic acid,
25 2,4,6-trimethyl phenylacetic acid, a phthalic acid, and a phenylene diacetic acid; including all isomers thereof, if present.

The content of component A is generally from about 5% to about 50%, preferably from about 8% to about 48%, more preferably from about 10% to about 45%, on the basis of the total weight of the whole additive.

30 The component B alcohol according to present invention can be any alcohol known in the art commonly used to terminate a living or growing polymer chain. The component B alcohol is preferably at least one selected

from the group consisting of an aliphatic alcohol having 1-18 carbon atoms, an aromatic alcohol having 7 to 18 carbon atoms, and a polyvinyl alcohol with a weight-average molecular weight of about 1,000 ~ about 50,000. Alternatively, the component B alcohol can also be a ployol described in
5 US application 2009/0043055A1, which is incorporated herein by reference.

More preferably, the component B alcohol is at least one selected from the group consisting of methanol, ethanol, n-propanol, i-propanol, n-butanol, i-butanol, t-butanol, n-pentanol, i-pentanol, pentaerythritol,
10 n-hexanol, i-hexanol, heptanol, octanol, decanol, dodecanol, cetyl alcohol, stearyl alcohol, ethylene glycol, propylene glycol, glycerol, cyclohexanol, benzyl alcohol, 2-phenyl ethanol, a polyvinyl alcohol with a weight-average molecular weight of about 5,000 ~ about 40,000,
1,2-ethanediol, 1,2-propanediol, 1,3-propanediol,
15 2,3-dimethyl-2,3-butanediol, 2,2-dimethyl-1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 2,3-butanediol, 1,2-pentanediol, 1,3-pentanediol, 1,4-pentanediol, 1,5-pentanediol, 2,3-pentanediol, 2,4-pentanediol, 1,2-hexanediol, 1,5-hexanediol, 1,6-hexanediol, 2,5-hexanediol, diethylene glycol, triethylene glycol, dipropylene glycol,
20 diethanolamine, N-n-butyldiethanolamine, N-t-butyldiethanolamine, 3-diisopropylamino-1,2-propanediol, 1,2-cyclopentanediol, 1,3-cyclopentanediol, 1,2-cyclohexanediol, 1,3-cyclohexanediol, 1,4-cyclohexanediol, 3-methoxy-1,2-propanediol, catechol, 2-hydroxymethyl-1,3-propanediol, 1,2,4-butanetriol, 1,1,1-tris
25 (hydroxymethyl)ethane, 1,2,6-hexanetriol, 1,1,1-tris(hydroxymethyl)propane, 1,2,3-heptanetriol, 1,3,5-cyclohexanetriol, pyrogallol, triethanolamine, triisopropanolamine, 1-[N,N-bis(2-hydroxyethyl)amino]-2-propanol, 2-deoxyribose, erythritol, threitol, 1,3-dihydroxyacetone dimer, glyceraldehyde dimer, fucose,
30 2-deoxy-galactose, 2-deoxy-glucose, glucose, allose, arabinose, lyxose, ribose, xylose, xylulose, galactose, mannose, tagatose, fructose, melibiose, arabitol, hexahydroxycyclohexane, xylitol, mannitol, and sorbitol.

The content of component B is generally from about 5% to about 45%, preferably from about 8% to about 43%, more preferably from about 10% to about 40%, on the basis of the total weight of the whole additive.

The alkali metal salt or alkaline earth metal salt of component C salt according to present invention is preferably a carboxylate, a sulfonate, a sulfate, or a phosphate; and wherein the ammonium salt of component C is preferably a primary ammonium salt, a secondary ammonium salt, a tertiary ammonium salt or a quaternary ammonium salt, more preferably an alkyl-substituted primary ammonium salt, an alkyl-substituted secondary ammonium salt, an alkyl-substituted tertiary ammonium salt or an alkyl-substituted quaternary ammonium salt.

More preferably, the component C is at least one selected from the group consisting of sodium stearate, calcium stearate, sodium oleate, calcium oleate, potassium stearate, sodium laurate, calcium laurate, potassium laurate, sodium dodecyl benzene sulfonate, sodium tetradecyl sulfonate, sodium hexadecyl sulfonate, bis(2-ethylhexyl) sulfosuccinate sodium salt, sodium dibutyl naphthalene sulfonate, sodium lauryl sulfate, sodium polycarboxylate (such as, for example, 2-hydroxy-1,2,3-propanetricarboxylic acid trisodium salt, butanetetracarboxylic acid tetrasodium salt, diethylenetriamine-pentaacetic acid pentasodium salt), octadecyl ammonium chloride, dioctadecyl ammonium chloride, N,N-dimethyl octadecyl ammonium chloride, octadecyl dimethyl benzyl ammonium chloride, polycarboxylic acid sodium salt with a weight-average molecular weight of about 1,000 ~ about 20,000 (such as, for example, sodium polyacrylate, sodium polymaleate, partial esterified styrene-maleic anhydride copolymer sodium salt, partial esterified maleic anhydride-methyl methacrylate copolymer sodium salt), and polycarboxylic acid ammonium salt with a weight-average molecular weight of about 1,000 ~ about 20,000 (such as, for example, ammonium polyacrylate or ammonium polymaleate).

The content of component C is generally from about 2% to about 40%, preferably from about 4% to about 38%, more preferably from about 5% to

about 35%, on the basis of the total weight of the whole additive.

The amine of component D of present invention is preferably selected from aromatic amines. More preferably, the amine is selected from the group consisting of diphenyl amines, p-phenylene diamines, 5 dihydroquinolines and derivatives of dihydroquinoline, most preferably is selected from N-isopropyl-N'-phenyl-p-phenylene diamine, N-(1,3-dimethylbutyl)- N'-phenyl- p-phenylene diamine, N,N'-diphenyl-p-phenylene diamine, octylated diphenylamine, 4,4'-(a,a-dimethylbenzyl)diphenylamine, 10 2,2,4-trimethyl-1,2-dihydroquinoline and 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline.

The phenol of component D of present invention is preferably selected from hindered phenols. More preferably, the phenol is selected from the group consisting of 2,6-di-tert-butyl -4-methyl phenol, 15 2,2'-methylene-bis(4-methyl-6-tert-butyl-phenol), 2,2'-methylene-bis(4-ethyl-6-t-butyl-phenol), 4,4'-butylidenebis(3-methyl-6-tert-butyl-phenol), 4,4'-thio-bis(3-methyl-6-t-butyl-phenol) and 2,4-bis(n-octylthiomethyl)-6-methylphenol.

20 The ester of component D of present invention is preferably selected from carboxylate ester and phosphite. More preferably, the ester is selected from the group consisting of stearyl β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, dilauryl thiodipropionate, dimyristyl thiodipropionate, distearyl thiodipropionate, trioctyl phosphite, 25 tri(decyl) phosphite, trilauryl phosphite and tri(hexadecyl) phosphite.

The content of component D (when component D is present) is generally from about 2% to about 25%, preferably from about 4% to about 20%, more preferably from about 5% to about 19%, on the basis of the total weight of the whole additive.

30 The component E water of the additive of present invention is an optional component; that is, the additive of present invention may comprise water or may comprise no water. The content of component E

generally is from about 0 to about 60%, preferably from about 0 to about 55%, more preferably from about 0 to about 52%, on the basis of the total weight of the whole additive. Generally, there are no particular limits to the water, provided the technical effects of present invention are not impaired. For example, tap water, deionized water, pure water, purified water, distilled water and the like can be used. According to an advantageous embodiment, the conductivity of the water is usually less than 500 $\mu\text{S}/\text{cm}$, preferably less than 100 $\mu\text{S}/\text{cm}$, more preferably less than 10 $\mu\text{S}/\text{cm}$.

According to a preferred embodiment of present invention, the additive of present invention comprises:

A. from about 5% to about 50%, preferably from about 8% to about 48%, more preferably from about 10% to about 45%, of carboxylic acid, on the basis of the total weight of the whole additive;

B. from about 5% to about 45%, preferably from about 8% to about 43%, more preferably from about 10% to about 40%, of alcohol, on the basis of the total weight of the whole additive;

C. from about 2% to about 40%, preferably from about 4% to about 38%, more preferably from about 5% to about 35%, of salt, on the basis of the total weight of the whole additive, which is selected from the group consisting of an alkali metal salt, an alkaline earth metal salt, an ammonium salt and a mixture thereof; and

E. optionally, from about 0 to about 60%, preferably from about 0 to about 55%, more preferably from about 0 to about 52%, of water, on the basis of the total weight of the whole additive.

According to a more preferred embodiment of present invention, the additive of present invention comprises:

A. from about 5% to about 50%, preferably from about 8% to about 48%, more preferably from about 10% to about 45%, of carboxylic acid, on the basis of the total weight of the whole additive;

B. from about 5% to about 45%, preferably from about 8% to about 43%, more preferably from about 10% to about 40%, of alcohol, on the

basis of the total weight of the whole additive;

C. from about 2% to about 40%, preferably from about 4% to about 38%, more preferably from about 5% to about 35%, of salt, on the basis of the total weight of the whole additive, which is selected from the group consisting of an alkali metal salt, an alkaline earth metal salt, an ammonium salt and a mixture thereof;

D. from about 2% to about 25%, preferably from about 4% to about 20%, more preferably from about 5% to about 19%, of at least one selected from the group consisting of an amine, a phenol, and an ester, on the basis of the total weight of the whole additive; and

E. optionally, from about 0 to about 60%, preferably from about 0 to about 55%, more preferably from about 0 to about 52%, of water, on the basis of the total weight of the whole additive.

A further aspect of present invention relates to a method for terminating polymerization and/or decreasing viscosity of polymer solution, including adding the additive according to present invention into a polymer solution and mixing the resulting mixture homogeneously.

The method of present invention includes adding said additive into a polymer solution containing living or growing polymer chains such as those polymer solutions obtained by solution polymerization or bulk polymerization, or adding said additive into a preformed polymer solution, and then mixing the resulting mixture homogeneously. As will be appreciated by those skilled in the art, the method of present invention has no particular limits to the solution polymerization or bulk polymerization, and the solution polymerization or bulk polymerization can be any solution polymerization or bulk polymerization. Said preformed polymer solution means a polymer solution obtained by adding a polymer into a solvent and then dissolving the polymer in solvent, wherein the polymer can be, for example, a commercial available polymer.

Surprisingly, the inventors of present invention found that the additive of present invention not only decreases the viscosity of solution but also terminates polymerization reaction in a polymer solution

containing living or growing polymer chains obtained by solution polymerization or bulk polymerization (excellent dual actions), or decreases the viscosity of a preformed polymer solution dramatically.

The mixing of the additive and the polymer solution mentioned above
5 can be conducted via various mixing modes, such as for example mixing by mechanical agitation, or by using a static mixer or a dynamic mixer. When mixed homogeneously, the additive of present invention can terminate polymerization efficiently (if living or growing polymer chains exist in polymer solution) such that molecule weight of the polymer is
10 maintained unchanged. In addition, the additive of present invention can reduce the viscosity of the polymer solution. According to an embodiment of present invention, the viscosity of the polymer solution can be decreased to lower than 5000 mPa•s, or even lower than 1400 mPa•s. According to an embodiment of present invention, the viscosity of the
15 polymer solution can be decreased by from about 20% to about 90%, preferably from about 28% to about 85%, relative to the viscosity of the polymer solution before adding the additive of present invention.

Although there are no particular limits to the concentration of the polymer solution, the polymer solution in present invention generally has a
20 concentration of from about 50 to about 350 g/L.

Components A, B, C, D (if present) and E (if present) in the additive of present invention, independently with each other, can be used directly, such as used in commercial available form, or can be formulated into a solution with a solvent before use. The solvent can be a solvent identical to
25 that used in the polymer solution, can be water (i.e. component E of present invention), or can be any solvent that does not impair the effects of present invention substantially.

There are no particular limits to the addition mode of the additive in the method of present invention. Components A, B, C, D (if present) and E
30 (if present) in the additive can be added, in desired amounts, into a polymer solution through, for example, the following addition modes:

adding each component separately into the polymer solution;

adding one or more mixture(s) obtained by mixing any two, three or four components and remaining component(s) separately into the polymer solution; or

5 mixing all components together and then adding the resulting mixture into the polyme solution.

Generally, there are no particular limits to the addition sequence of said components or mixture(s) thereof.

After the additive is added into a polymer solution, mixing is conducted. There are no particular limits to mixing temperature and
10 mixing period. For example, the mixing temperature can be from about -100° to about 110°C. For example, the mixing period can be from about 0.5min to about 30min, preferably from about 2 min to about 20min.

Those skilled in the art can determine the using amount of the additive of present invention properly. Without wishing to be bound by
15 any theory, it is believed that the use level of the additive of present invention is relevant to the content and the molecule weight of the polymer in the polymer solution. Generally, the higher the content or molecule weight of the polymer, the higher the use level of the additive. The amount of the additive used generally is from about 0.4% to about 7.5%,
20 preferably from about 0.7% to about 6.0% and more preferably from about 1.3% to about 5.0%, on the basis of the weight of the polymer.

According to an embodiment of present invention, the component E water (in whole or in part) can be mixed with component B and/or C and then added into the polymer solution, or component E water can be added
25 into the solution after all other components are added into the polymer solution.

Generally there are no limits to the types of the polymer in polymer solutions of present invention. For example, said polymer can be any polymer than can be obtained through solution polymerization or bulk
30 polymerization. According to an embodiment of present invention, the polymer in the polymer solution systems in which the additive of present invention is applicable is selected from polybutadiene, polyisoprene,

polystyrene, butadiene-isoprene copolymer, styrene-butadiene copolymer, styrene-isoprene copolymer, butadiene-isoprene-styrene copolymer, ethylene-propylene copolymer, ethylene-propylene-ethylidene-2-norbornene copolymer, 5 ethylene-propylene-dicyclopentadiene copolymer, polyisobutene, isobutene-isoprene copolymer, isobutene-p-methyl styrene copolymer, and etc.

Generally there are no limits to the solvent used in the polymer solution of present invention. Those skilled in the art can select an 10 appropriate solvent according to, for example, the type of the polymer. According to an embodiment of present invention, said solvent can be the solvent used in solution polymerization or bulk polymerization. According to an embodiment of present invention, the solvent used in the polymer solution is selected from alkane, alkene, cycloalkane, aromatic 15 hydrocarbon, halohydrocarbon or any mixture thereof.

It is believed that the additive of present invention, when mixed with a polymer reaction solution containing living or growing polymer chains, can terminate living or growing polymer chain ends efficiently and can destroy the initiating or catalytic active centers, so as to terminate 20 polymerization reaction effectively. Moreover, said additive of present invention can reduce the viscosity of a polymer solution substantially. For example, the viscosity of the polymer solution can be reduced by from about 20% to about 90%, relative to the viscosity of the polymer solution before addition of the additive. The additive of present invention achieves 25 the dual effects of terminating polymerization reaction completely (terminating living or growing polymer chains and destroying the initiating or catalytic active centers) and reducing viscosity of polymer solution substantially. Thus the additive of present invention can reduce the transportation resistance and energy cost of the polymer solution and is 30 beneficial to increase concentration of the polymer solution, productivity and output.

The additive of present invention, due to reduction of viscosity of

polymer solution, is capable of reducing the transportation resistance and energy cost of high-viscosity polymer solution and thus is beneficial to increase concentration of the polymer solution, productivity and output and to maintain product quality stable. Further, it is believed that most of
5 the additive is maintained in the polymer and can further stabilize the polymer and improve processability.

Examples

The following non-limiting examples are provided to further illustrate
10 the invention.

Testing procedures:

1. Viscosity of polymer solution: determined by using Digital Rotational Viscometer NDJ-5S from Shanghai Hengping Scientific Instrument Co., Ltd according to GB/T2794-1995.

15 2. Weight average molecular weight of polymer: determined by using Mode 1515 Gel Permeation Chromatography from Waters Corp. under following conditions:

solvent: tetrahydrofuran; polymer being formulated into 1.5g/L solution; four columns HT3, HT4, HT5 and HT6 being equipped; eluting
20 solvent: tetrahydrofuran; temperature: 30°C; the calibration is performed by using polystyrene standards.

Materials used in examples

Butadiene, styrene and isoprene, from Tianjin Lilang Chemical Scientific and Tech Co.,Ltd;

25 sebacic acid, octadecenoic-9-acid (A) and stearic acid, from Jinan Hongxin Chemical Co., LTD;

Ethanol, ethylene glycol, isopropanol, butanol, cyclohexanol, glycerol and polyvinyl alcohol with different molecular weights, from Beijing Yili Fine Chemicals Co., Ltd;

30 Calcium stearate, sodium dodecyl benzene sulfonate, N,N-dimethyl octadecyl ammonium chloride, sodium polyacrylate, sodium polymaleate, ammonium polyacrylate, partial esterified styrene-maleic anhydride

copolymer sodium salt and partial esterified maleic anhydride-methyl methacrylate copolymer sodium salt with different molecular weights, from Beijing Tongguang Fine Chemicals Company;

Stearyl β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionate,
5 2,4-bis(n-octylthiomethyl)-6-methylphenol,
2,6-di-tert-butyl-4-methylphenol, tri(hexadecyl) phosphite and
N-isopropyl-N'-phenyl- p-phenylene diamine, from JiYi Chemical(Beijing)
Co., Ltd.

10 Example 1

Into a polymerization system containing living or growing polybutadiene chains and hexane produced via the solution polymerization of butadiene in hexane at 35°C, a mixed liquid of octadecenoic -9- acid (A), butanol (B), sodium polyacrylate having a Mw of 8000 (C), stearyl
15 β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (D),
2,4-bis(n-octylthiomethyl)-6-methylphenol (D) and water (E) were added, wherein the amounts of components A, B, C, D and E were respectively 0.25%, 0.28%, 0.25%, 0.2% and 1.0% by weight on the basis of polybutadiene polymer, and wherein the ratio of stearyl
20 β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (D) to
2,4-bis(n-octylthiomethyl)-6-methylphenol (D) was 3:1 by weight. It was mixed for 0.5 min and the viscosity of the polymer solution was decreased from 22000 mPa•s to 3300 mPa•s (decreasing by 85%). The molecular weight of the polymer was maintained unchanged after the polymer
25 solution was left to stand for 168 hours. The weight average molecular weights (Mw) of the polymer, after mixing for 0.5 min and after being left stand for 168 hours, were both around 1.5×10^6 .

Example 2

30 Into a polymerization system containing living or growing polyisoprene chains and isoprene produced from bulk polymerization of isoprene, at a temperature of 15°C, a mixed liquid of octadecenoic-9-acid

(A) and ethanol (B), a mixed solution of calcium stearate (C) and water (E), and 2,6-di-tert-butyl-4-methylphenol (D) were added sequentially, wherein the amounts of components A, B, C, D and E were respectively 0.8%, 0.8%, 0.8%, 0.3% and 2.0% by weight on the basis of the polyisoprene polymer. It was mixed for 10 min after all components were added in and the viscosity of the polymer solution was decreased from 12600 mPa•s to 4300 mPa•s (decreasing by 66%). The molecular weight of the polymer was maintained almost unchanged after the polymer solution was left to stand for 48 hours. The weight average molecular weights (M_w) of the polymer, after mixing for 10 min and after being left stand for 48 hours, were both 9.8×10^5 .

Example 3

Into a polymerization system containing living or growing polybutadiene chains and hexane-cyclohexane solvent mixture produced from solution polymerization of butadiene in hexane-cyclohexane solvent mixture, at a temperature of 25°C, octadecenoic-9-acid (A), ethylene glycol (B), polyvinyl alcohol having a M_w of 35000 (B), a mixed solution of partial esterified styrene-maleic anhydride copolymer sodium salt having a M_w of 5000 (C) and water (E), and stearyl β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (D) and tri(hexadecyl) phosphite (D) were added sequentially, wherein the amounts of components A, B, C, D and E were respectively 0.95%, 1%, 0.25%, 0.5% and 1.0% by weight on the basis of the polybutadiene polymer, and wherein the ratio by weight between ethylene glycol and polyvinyl alcohol was 20:1, the ratio by weight between stearyl β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (D) and tri(hexadecyl) phosphite (D) was 40:1. It was mixed for 20 min and the viscosity of the solution was decreased from 6300 mPa•s to 1400 mPa•s (decreasing by 77%). The molecular weight of the polymer was maintained unchanged after the polymer solution was left to stand for 24 hours. The weight average molecular weights (M_w) of the polymer, after mixing for 20 min

and after being left stand for 24 hours, were both 3.8×10^5 .

Example 4

At a temperature of 25°C, 2,6-di-tert-butyl-4-methylphenol (D), a mixture of sebacic acid (A) and isopropanol (B), sodium polymaleate having a Mw of 3000 (C) and partial esterified maleic anhydride-methyl methacrylate copolymer sodium salt(C) having a Mw of 2000 were added sequentially into a butadiene-styrene copolymer/cyclohexane solution, wherein the amounts of components A, B, C, and D were respectively 1.0%, 0.88%, 0.18%, and 0.22% by weight on the basis of the butadiene-styrene copolymer. The butadiene-styrene copolymer/cyclohexane solution was obtained by dissolving the butadiene-styrene copolymer into cyclohexane with a concentration of 80 g/L. It was mixed for 5 min and the viscosity of the solution was decreased from 2900 mPa•s to 1700 mPa•s (decreasing by 41%). The weight average molecular weights (Mw) of the polymer, after mixing for 5 min and after being left stand for 48 hours, were both 2.5×10^5 .

Example 5

Into a polymerization system containing living or growing isobutene-isoprene copolymer chains and hexane-chloroethane solvent mixture produced from solution polymerization of isobutene-isoprene in hexane-chloroethane mixed solvent, at a temperature of -80°C, 2,6-di-tert-butyl-4-methylphenol (D), a mixture of epoxy oleic acid (A) and ethylene glycol (B), and sodium dodecyl benzene sulfonate (C) were added sequentially, wherein the amounts of components A, B, C and D were respectively 0.5%, 0.5%, 0.4% and 0.3% by weight on the basis of the isobutene-isoprene copolymer. It was mixed for 10 min and the viscosity of the solution was decreased from 3100 mPa•s to 2100 mPa•s (decreasing by 32%). The molecular weight of the polymer was maintained unchanged after the polymer solution was left to stand for 24 hours. The weight average molecular weights (Mw) of the polymer, after mixing for

10 min and after being left stand for 24 hours, were both 4.5×10^5 .

Example 6

Into a polymerization system containing living or growing
5 polybutadiene and hexane-cyclohexane solvent mixture produced from
solution polymerization of butadiene in hexane-cyclohexane, at a
temperature of 40°C, ammonium polyacrylate having a Mw of 15000 (C),
eicosatetraenoic acid(A), isopropanol (B) and cyclohexanol (B), and
stearyl β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (D) and
10 N-isopropyl-N'-phenyl- p-phenylene diamine (D) were added sequentially,
wherein the amounts of components A, B, C and D were respectively 0.5%,
0.6%, 0.6% and 0.2% by weight on the basis of the polybutadiene polymer,
and wherein the ratio by weight between isopropanol and cyclohexanol
was 1:20, the weight ratio of stearyl
15 β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionate to
N-isopropyl-N'-phenyl- p-phenylene diamine was 1:25. It was mixed for 3
min and the viscosity of the solution was decreased from 3200 mPa•s to
2200 mPa•s (decreasing by 31%). The molecular weight of the polymer
was maintained unchanged after the polymer solution was left to stand for
20 120 hours. The weight average molecular weights (Mw) of the polymer,
after mixing for 3 min and after being left stand for 120 hours, were both
 3.1×10^5 .

Example 7

25 Into a polymerization system containing living or growing
polybutadiene and hexane-cyclohexane solvent mixture produced from
solution polymerization of butadiene in hexane-cyclohexane mixed solvent,
at a temperature of 60°C, a mixed solution of stearic acid (A) and glycerol
(B), a mixed solution of N,N-dimethyl octadecyl ammonium chloride (C)
30 and water (E), and stearyl β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionate
(D) and 2,4-bis(n-octylthiomethyl)-6-methylphenol (D) were added
sequentially, wherein the amounts of components A, B, C, D and E were

respectively 0.8%, 0.8%, 0.5% , 0.5% and 2.0% by weight on the basis of the polybutadiene polymer, and wherein the ratio by weight of stearyl β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionate to 2,4-bis(n-octylthiomethyl)-6-methylphenol was 1:1. It was mixed for 5 min and the viscosity of the solution was decreased from 3200 mPa•s to 2100 mPa•s (decreasing by 34%). The molecular weight of the polymer was maintained unchanged after the polymer solution was left to stand for 120 hours. The weight average molecular weights (Mw) of the polymer, after mixing for 5 min and after being left stand for 120 hours, were both 3.1×10^5 .

Example 8

Into a polymerization system containing living or growing polybutadiene and hexane produced from the solution polymerization of butadiene in hexane, at a temperature of 80°C, octadecenoic-9-acid (A), butanol (B), and sodium polymaleate having a Mw of 5000 (C) were added sequentially, wherein the amounts of components A, B and C were respectively 0.5%, 0.3% and 0.25% on the basis of the polybutadiene polymer. It was mixed for 5 min and the viscosity of the polymer solution was decreased from 9300 mPa•s to 6400 mPa•s. The molecular weight of the polymer was maintained unchanged after the polymer solution was left to stand for 48 hours. The weight average molecular weights (Mw) of the polymer, after mixing for 5 min and after being left stand for 48 hours, were both 4.2×10^5 .

Example 9

Into a polymerization system containing living or growing polybutadiene and hexane produced from the solution polymerization of butadiene in hexane, at a temperature of 50°C, octadecenoic-9-acid (A), butanol (B), ammonium polyacrylate having a Mw of 15000 (C) and water (E) were added sequentially, wherein the amounts of components A, B, C and E were respectively 1.0%, 0.25%, 0.25% and 2% by weight on the

basis of the polybutadiene polymer. It was mixed for 5 min and the viscosity of the polymer solution was decreased from 9600 mPa•s to 6700 mPa•s. The molecular weight of the polymer was maintained unchanged after the polymer solution was left to stand for 48 hours. The weight
5 average molecular weights (M_w) of the polymer, after mixing for 10 min and after being left stand for 48 hours, were both 4.0×10^5 .

Comparative example 1

Into a polymerization system containing living or growing
10 polybutadiene and hexane produced from the solution polymerization of butadiene in hexane, at a temperature of 60°C, octadecenoic-9-acid in amount of 0.8% by weight on the basis of the polybutadiene polymer was added. The weight average molecular weight (M_w) of the polymer, after mixing for 5 min and after being left stand for 24 hours, were determined
15 to be 1.1×10^6 and 1.4×10^6 , respectively. It was clear that the polymerization was not terminated effectively, leading to an increasing of molecular weight during standing and consequently resulting in an increased viscosity (from 13000 mPa•s to 37000 mPa•s).

20 Comparative example 2

Into a polymerization system containing living or growing
polybutadiene and hexane produced from the solution polymerization of butadiene in hexane, at a temperature of 50°C, ethanol in amount of 0.5% by weight and water in amount of 0.8% by weight, both on the basis of the
25 polybutadiene polymer, were added. The weight average molecular weight (M_w) of the polymer, after mixing for 5 min and after being left stand for 48 hours, were determined to be 3.5×10^5 and 5.8×10^5 , respectively. It was clear that the polymerization was not terminated effectively, leading to an increasing of molecular weight during standing and consequently resulting
30 in an increased viscosity (from 4000 mPa•s to 10000 mPa•s).

CLAIMS

1. An additive for terminating polymerization and/or reducing viscosity of polymer solution, comprising:

5 A. a carboxylic acid,

 B. an alcohol,

 C. an salt which is selected from the group consisting of an alkali metal salt, an alkaline earth metal salt, an ammonium salt and a mixture thereof; and

10 E. optionally, water.

 2. The additive according to claim 1, further comprising

 D. at least one selected from the group consisting of an amine, a phenol, and an ester.

 3. The additive according to claim 2, wherein the contents of the
15 components A, B, C, D, and E in the additive are respectively about 5%~about 50%, about 5%~about 45%, about 2%~about 40%, about 2%~about 25% and 0~about 60%, on the basis of the total weight of the additive; and preferably the contents of the components A, B, C, D, and E in the additive are respectively about 8%~about 48%, about 8%~about
20 43%, about 4%~about 38%, about 4%~about 20% and about 0~about 55%, on the basis of the total weight of the additive.

 4. The additive according to any of claims 1-3, wherein the component A carboxylic acid is at least one selected from the group consisting of a saturated aliphatic acid having 6-26 carbon atoms, an
25 unsaturated aliphatic acid having 6-26 carbon atoms, and an aromatic acid having 7-26 carbon atoms.

 5. The additive according to claim 4, wherein the component A carboxylic acid is at least one selected from the group consisting of a saturated aliphatic acid having 10-20 carbon atoms, an unsaturated
30 aliphatic acid having 10-20 carbon atoms, and an aromatic acid having 7-20 carbon atoms; preferably the component A carboxylic acid is at least one selected from the group consisting of decanoic acid, undecanoic acid,

dodecoic acid, tridecanoic acid, myristic acid, pentadecanoic acid, palmitic acid, heptadecanoic acid, stearic acid, hexadecenoic acid, octadecenoic acid, octadecadienoic acid, octadecatrienoic acid, eicosatetraenoic acid, ricinoleic acid, epoxy oleic acid, sebacic acid, dodecanedioic acid, 5 tridecanedioic acid, benzoic acid, methyl benzoic acid, ethyl benzoic acid, propyl benzoic acid, butyl benzoic acid, pentyl benzoic acid, hexyl benzoic acid, phenylacetic acid, phenylpropionic acid, 2,4,6-trimethyl phenylacetic acid, phthalic acid, and phenylene diacetic acid.

6. The additive according to any of claims 1-3, wherein the 10 component B alcohol is at least one selected from the group consisting of an aliphatic alcohol having 1-18 carbon atoms, an aromatic alcohol having 7 to 18 carbon atoms, and a polyvinyl alcohol with a weight-average molecular weight of about 1,000 ~ about 50,000.

7. The additive according to claim 6, wherein the component B is at 15 least one selected from the group consisting of methanol, ethanol, n-propanol, i-propanol, n-butanol, i-butanol, t-butanol, n-pentanol, i-pentanol, pentaerythritol, n-hexanol, i-hexanol, heptanol, octanol, decanol, dodecanol, cetyl alcohol, stearyl alcohol, ethylene glycol, propylene glycol, glycerol, cyclohexanol, benzyl alcohol, 2-phenyl ethanol, 20 a polyvinyl alcohol with a weight-average molecular weight of about 5,000 ~ about 40,000, 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, 2,3-dimethyl-2,3-butanediol, 2,2-dimethyl-1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 2,3-butanediol, 1,2-pentanediol, 1,3-pentanediol, 1,4-pentanediol, 1,5-pentanediol, 2,3-pentanediol, 25 2,4-pentanediol, 1,2-hexanediol, 1,5-hexanediol, 1,6-hexanediol, 2,5-hexanediol, diethylene glycol, triethylene glycol, dipropylene glycol, diethanolamine, N-n-butyldiethanolamine, N-t-butyldiethanolamine, 3-diisopropylamino-1,2-propanediol, 1,2-cyclopentanediol, 1,3-cyclopentanediol, 1,2-cyclohexanediol, 1,3-cyclohexanediol, 30 1,4-cyclohexanediol, 3-methoxy-1,2-propanediol, catechol, 2-hydroxymethyl-1,3-propanediol, 1,2,4-butanetriol, 1,1,1-tris (hydroxymethyl)ethane, 1,2,6-hexanetriol,

1,1,1-tris(hydroxymethyl)propane, 1,2,3-heptanetriol,
1,3,5-cyclohexanetriol, pyrogallol, triethanolamine, triisopropanolamine,
1-[N,N-bis(2-hydroxyethyl)amino]-2-propanol, 2-deoxyribose, erythritol,
threitol, 1,3-dihydroxyacetone dimer, glyceraldehyde dimer, fucose,
5 2-deoxy-galactose, 2-deoxy-glucose, glucose, allose, arabinose, lyxose,
ribose, xylose, xylulose, galactose, mannose, tagatose, fructose, melibiose,
arabitol, hexahydroxycyclohexane, xylitol, mannitol, and sorbitol.

8. The additive according to any of claims 1-3, wherein the alkali
metal salt and alkaline earth metal salt of component C salt are
10 respectively a carboxylate, a sulfonate, a sulfate, or a phosphate; and
wherein the ammonium salt is a primary ammonium salt, a secondary
ammonium salt, a tertiary ammonium salt or a quaternary ammonium salt,
preferably an alkyl-substituted primary ammonium salt, an
alkyl-substituted secondary ammonium salt, an alkyl-substituted tertiary
15 ammonium salt or an alkyl-substituted quaternary ammonium salt.

9. The additive according to claim 8, wherein the component C is at
least one selected from the group consisting of sodium stearate, calcium
stearate, sodium oleate, calcium oleate, potassium stearate, sodium laurate,
calcium laurate, potassium laurate, sodium dodecyl benzene sulfonate,
20 sodium tetradecyl sulfonate, sodium hexadecyl sulfonate,
bis(2-ethylhexyl) sulfosuccinate sodium salt, sodium dibutyl naphthalene
sulfonate, sodium lauryl sulfate, sodium polycarboxylate, octadecyl
ammonium chloride, dioctadecyl ammonium chloride, octadecyl dimethyl
ammonium chloride, octadecyl dimethyl benzyl ammonium chloride,
25 polycarboxylic acid sodium salt with a weight-average molecular weight
of about 1,000 ~ about 20,000, and polycarboxylic acid ammonium salt
with a weight-average molecular weight of about 1,000 ~ about 20,000.

10. The additive according to claim 2 or 3, wherein the amine of
component D is selected from aromatic amine, the phenol of component D
30 is selected from hindered phenol, and the ester of component D is selected
from carboxylate ester and phosphite.

11. The additive according to claim 10, wherein

the aromatic amine is at least one selected from the group consisting of diphenyl amines, p-phenylene diamines, dihydroquinolines and derivatives of dihydroquinoline, preferably is at least one selected from N-isopropyl-N'-phenyl- p-phenylene diamine, N-(1,3-dimethylbutyl)-
5 N'-phenyl- p-phenylene diamine, N,N'-diphenyl- p-phenylene diamine, octylated diphenylamine, 4,4'- (a,a-dimethylbenzyl) diphenylamine, 2,2,4-trimethyl-1,2-dihydroquinoline and 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline;

the hindered phenol is at least one selected from the group consisting
10 of 2,6-di-tert-butyl -4-methyl phenol, 2,2'-methylene-bis(4-methyl-6-tert-butyl-phenol), 2,2'-methylene-bis(4-ethyl-6- tert-butyl-phenol), 4,4'-butylidenebis(3-methyl-6-tert-butyl-phenol), 4,4'-thio-bis(3-methyl-6-t-butyl-phenol) and
15 2,4-bis(n-octylthiomethyl)-6-methylphenol; and

the ester is at least one selected from the group consisting of stearyl β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, dilauryl thiodipropionate, dimyristyl thiodipropionate, distearyl thiodipropionate, trioctyl phosphite, tri(decyl) phosphite, trilauryl phosphite and
20 tri(hexadecyl) phosphite.

12. A method for terminating polymerization and/or reducing viscosity of polymer solution, including adding the additive according to any one of claims 1-11 into a polymer solution and then mixing the resulting mixture for about 0.5 – about 30 min at a mixing temperature of
25 about -100 °C to about 110 °C; wherein the additive is added in an amount of about 0.4 wt% to about 7.5wt%, preferably about 0.7 wt% to about 6.0wt%, based on the total weight of the polymer in the polymer solution.

13. The method according to claim 12, wherein the polymer solution contains living polymer chains.

30 14. The method according to claim 12 or 13, wherein the polymer solution is obtained from a solution polymerization or a bulk

polymerization, or the polymer solution is obtained by dissolving a polymer in a solvent.

15. Use of the additive according to any one of claims 1-11 for terminating polymerization and/or reducing viscosity of polymer solution.

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