

Description

Title: Diene block copolymer comprising a polyether block, and rubber composition containing same

Technical field

The present invention relates to a diene block copolymer comprising at least one polyether block, and also to the process for the preparation thereof. The present invention also relates to a rubber composition containing said elastomer, which composition can be used in particular in the manufacture of tyres.

Prior art

Now that savings in fuel and the need to protect the environment have become a priority, it is desirable to produce polymers having good mechanical properties and a hysteresis which is as low as possible in order to be able to process them in the form of rubber compositions which can be used in the manufacture of various semi-finished products participating in the forming of tyres. Numerous solutions have already been experimented with in order to achieve the objective of a fall in hysteresis.

In particular, mention may be made of the modification of the structure of diene polymers by introducing polar groups, for example in the form of functions or in the form of oligomeric or polymeric polar blocks, within the polymer chain or pendent along the polymer chain,

In particular, mention may be made of the use of diene polymers containing a polyether block as described in EP 1 127 909 A1 with the aim of obtaining a good interaction between the block polymer and the inorganic filler so as to reduce the hysteresis of the mixture. . It has also been proposed, in WO 2009/000750 A1, to use other diene block polymers containing at least one polyether block. These particular copolymers make it possible to optimize the suitability for raw processing of the rubber compositions containing them and to reduce the level of hysteresis thereof in the crosslinked state.

It is an ongoing concern of designers of materials intended for the manufacture of tyres to constantly further improve the compromise in mechanical and dynamic properties of rubber compositions for the purpose of improving the performance of the tyre in which they are present, without, however, penalizing the properties of the elastomer, or even while improving them. Thus, for example, the improvement in the compromise in properties must not take place to the detriment of the flow of the elastomer, which causes major disadvantages during the transportation and storage of elastomers.

The technical problem which the invention intends to solve is that of further improving the compromise in hysteresis and processing properties of a rubber composition for the purpose of a tyre application, without penalizing the properties of the elastomer present in this composition.

This aim is achieved in that the inventors have now demonstrated that the modification of a diene elastomer by reaction of the living elastomer chains resulting from the polymerization with a linear or branched polyether comprising, at each end of the main chain, a trialkoxysilyl group, make it possible to obtain a diene block copolymer comprising a polar block giving the rubber compositions containing it, at equal molar mass of the modified elastomer, a noteworthy and unexpected improvement in the compromise between raw processing/hysteresis.

Disclosure of the invention

A subject of the invention is therefore a diene block copolymer characterized in that it comprises a linear or branched polyether block comprising, at each of the two ends of the block, a branch point to which up to three diene elastomer blocks are bonded, a - the copolymer having a Mooney viscosity of at least 10 and at most 100,

b- the compound being composed

of at least 30%, preferably 35%, of branched macromolecules comprising the polyether block to which at least three diene elastomer blocks are bonded,

of at most 70%, preferably 65%, of linear macromolecules,

c - the polyether block having a number-average molar mass ranging from 150 g/mol to 5000 g/mol, and

d - each of the two branch points consisting of a silicon atom.

Advantageously, the diene elastomer blocks of the diene block copolymer according to the invention are butadiene-styrene copolymers.

The diene block copolymer according to the invention advantageously has a Mooney viscosity of at least 30, preferably at least 40 and at most 80, preferably at most 70.

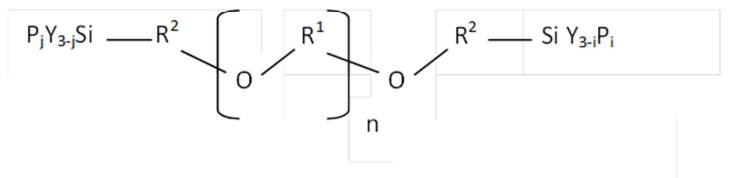
Advantageously, the polyether block is a polyoxymethylene, poly(ethylene oxide), poly(propylene oxide), or polytetrahydrofuran block, preferably the polyether block is a poly(ethylene oxide) or poly(propylene oxide) block .

Advantageously, at least 70 mol% of the elastomer branches relative to the number of moles of elastomer branches bears a function comprising a nitrogen atom, preferably a cyclic or acyclic amine function, at the end not bonded to a silicon atom.

In particular, the macromolecules composing the diene block copolymer according to the invention can be represented

_ for the branched macromolecules, by general formula I:

Formula I



in which:

- R¹ represents a linear or branched, divalent hydrocarbon-based group, preferably aliphatic group, having 1 to 10 carbon atoms, in particular a -CH(R')-CH(R'')-

group, in which R' and R'' are, independently of one another, a hydrogen atom or a C₁-C₄ alkyl substituent, preferably R1 is a C₁-C₄ alkanediyl group, more preferentially an ethanediyl or propanediyl group,

- the R₂ represent, independently of one another, a linear or branched or cyclic, saturated or unsaturated, divalent hydrocarbon-based group, preferably aliphatic group, having 1 to 50 carbon atoms, preferably a linear aliphatic group, which is preferably saturated, preferentially having 1 to 15 carbon atoms, preferably 2 to 10,

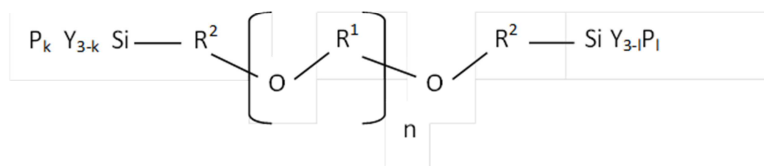
- the Y represent, in an identical or different manner, a group of formula -OR₄ in which the R₄ represent, independently of one another, a hydrogen atom, a C₁-C₁₈ alkyl, C₅-C₁₈ cycloalkoxyl or C₆-C₁₈ aryl substituent, preferably the R₄ represent a hydrogen atom or a C₁-C₄ alkyl substituent, preferably methyl or ethyl,

- i and j are numbers which are each, independently of one another, equal to 1, 2 or 3, with the proviso that (i+j) ranges from 3 to 6, and

- P represents a diene elastomer block;

_ and for the linear block macromolecules, correspond to general formula II:

Formula II



in which,

- R₁ represents a linear or branched, divalent hydrocarbon-based group, preferably aliphatic group, having 1 to 10 carbon atoms, in particular a -CH(R')-CH(R'')-group, in which R' and R'' are, independently of one another, a hydrogen atom or a C₁-C₄ alkyl substituent, preferably R₁ is a C₁-C₄ alkanediyl group, more preferentially an ethanediyl or propanediyl group,

- the R₂ represent, independently of one another, a linear or branched or cyclic, saturated or unsaturated, divalent hydrocarbon-based group, preferably aliphatic group, having 1 to 50 carbon atoms, preferably a linear aliphatic group, which is preferably saturated, preferentially having 1 to 15 carbon atoms, preferably 2 to 10,

- the Y represent, in an identical or different manner, a group of formula -OR₄ in which the R₄ represent, independently of one another, a hydrogen atom, a C₁-C₁₈ alkyl, C₅-C₁₈ cycloalkoxyl or C₆-C₁₈ aryl substituent, preferably the R₄ represent a hydrogen atom or a C₁-C₄ alkyl substituent, preferably methyl or ethyl,

- k and l are numbers which are each, independently of one another, equal to 0 or 1, with the proviso that (k+l) is equal to 1 or 2, and

- P represents a diene elastomer block.

Advantageously, the copolymer comprises at least 50% by weight of branched macromolecules consisting of a polyether block to which at least three diene elastomer branches are bonded.

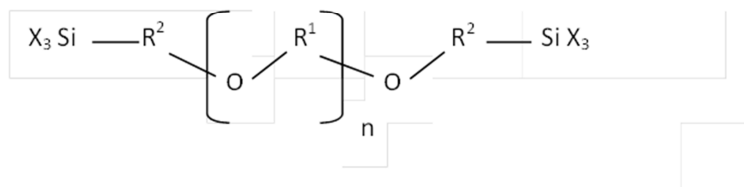
Advantageously, the copolymer comprises at most 25% by weight of branched macromolecules with four and more branches consisting of a polyether block to which four or more diene elastomer branches are bonded.

Advantageously, the copolymer comprises at least 20% by weight of branched macromolecules with three branches consisting of a polyether block to which three diene elastomer branches are bonded, preferably at least 35% by weight.

A subject of the invention is also a process for the synthesis of such a diene block copolymer, comprising the reaction of the product of the anionic polymerization, in the presence of a polymerization initiator, of at least one diene monomer, with a linear or branched functional polyether having a number-average molar mass ranging from 150 to 5000 g/mol comprising, at each end of the main chain, a trifunctional group selected from trialkoxysilyl groups or trihalosilyl groups, with a molar ratio of the functional polyether to the metal of the polymerization initiator of at least 0.1, preferably at least 0.15, more preferentially at least 0.25, and at most 0.45, preferentially at most 0.40, or even at most 0.35.

Advantageously, the functional polyether corresponds to general formula III:

Formula III



in which,

- R1 represents a linear or branched, C₁-C₁₀ divalent hydrocarbon-based group, preferably aliphatic group, in particular a -CH(R')-CH(R'')- group, in which R' and R'' are, independently of one another, a hydrogen atom or a C₁-C₄ alkyl substituent, preferably R1 is a C₁-C₄ alkanediyl group, more preferentially an ethanediyl or propanediyl group,

- the R2 represent, independently of one another, a linear or branched or cyclic, saturated or unsaturated, divalent hydrocarbon-based group, preferably aliphatic group, having 1 to 50 carbon atoms, preferably a linear aliphatic group, which is preferably saturated, preferentially having 1 to 15 carbon atoms, preferably 2 to 10,

- the X represent, in an identical or different manner, a halogen atom, preferably a chlorine atom, or a group of formula -OR3 in which the R3 represent, independently of one another, a C₁-C₁₈ alkyl, C₅-C₁₈ cycloalkoxyl or C₆-C₁₈ aryl substituent, preferably the R3 represent a C₁-C₄ alkyl substituent, preferably methyl or ethyl,

- n is a number greater than 1, so that the polyether block has a number-average molar mass of approximately from 150 to 5000 g/mol.

The process according to the invention can comprise a hydrolysis reaction at the end of the reaction of the product resulting from the polymerization of at least one diene monomer, with the functional polyether.

A further subject of the invention is a diene block copolymer directly obtained by this synthesis process.

Another subject of the invention is a rubber composition based on at least one diene block copolymer in accordance with the invention.

A subject of the invention is also a tyre which comprises, in at least one of its constituent elements, a rubber composition in accordance with the invention.

Detailed description

In the present description, unless expressly indicated otherwise, all the percentages (%) shown are % by weight. The abbreviation "phr" means parts by weight per hundred parts of elastomers present in the elastomer matrix, the elastomer matrix denoting all of the elastomers present in the rubber composition.

Furthermore, any interval of values denoted by the expression "between a and b" represents the range of values greater than "a" and less than "b" (that is to say, limits a and b excluded), whereas any interval of values denoted by the expression "from a to b" means the range of values extending from "a" up to "b" (that is to say, including the strict limits a and b). In the present document, when an interval of values is denoted by the expression "from a to b", the interval represented by the expression "between a and b" is also denoted.

In the present patent application, "predominantly" or "predominant", in connection with a compound, is understood to mean that this compound is predominant among the compounds of the same type in the composition, that is to say that it is that which represents the biggest fraction by weight among the compounds of the same type. Thus, for example, a predominant elastomer is the elastomer representing the greatest fraction by weight, with respect to the total weight of the elastomers in the composition. In the same way, a "predominant" filler is that representing the greatest fraction by weight, with respect to the total weight of the combined fillers of the composition. In a system comprising just one compound of a certain type, the latter is predominant for the purposes of the present invention.

The expression "composition based on" should be understood as meaning, in the present description, a composition comprising the mixture and/or the *in situ* reaction product of the

various constituents used, some of these base constituents (for example the elastomer, the filler or other additive conventionally used in a rubber composition intended for the manufacture of tyres) being capable of reacting or intended to react with one another, at least in part, during the various phases of manufacture of the composition intended for the manufacture of tyres.

In the present description, the term “functional polyether” is understood to mean a difunctional polyether. The functional polyether can be linear or branched and has a main chain comprising at each of the two ends a silicon atom, each substituted by three alkoxy functions or by three halogen atoms. A linear polyether comprises at both ends of the polymer chain a silicon atom, each substituted by three alkoxy functions or by three halogen atoms. A branched polyether comprises a linear main chain, all or a part of the repeating units of which are branched. A branched polyether comprises at each of the two ends of the main chain a silicon atom, each substituted by three alkoxy functions or by three halogen atoms. The branches are hydrocarbon-based, preferably aliphatic, and do not comprise a silicon atom.

In the present description, the term “diene block copolymer” is understood to mean a mixture of macromolecules resulting from the reaction of reactive living elastomer chains resulting from the polymerization of at least one diene monomer with a linear or branched functional polyether comprising at least six trialkoxysilyl or trihalosilyl reactive functions.

Those skilled in the art will understand that a reaction with a compound comprising more than one function that is reactive with respect to living elastomer chains, in this case alkoxy or halogen functions borne by the two silicon atoms, results in a mixture of linear macromolecules and branched macromolecules with at least three branches and at most as many branches as reactive functions of the functional polyether, that is to say six branches. Depending on the operating conditions, mainly the molar ratio of the number of reactive functions of the functional polyether to the living chains, certain macromolecules are present to a lesser or greater extent in the mixture.

In the present description, the expression “monomer unit”, whether it is diene or other, is understood as a unit of the polymer resulting from the monomer in question.

It should be noted that, in the context of the invention, the monomers used can be of fossil or biosourced origin. In the latter case, they may partially or completely result from biomass or be obtained from renewable starting materials resulting from biomass.

A subject of the invention is therefore a diene block copolymer characterized in that it comprises a linear or branched polyether block comprising, at each end of the block, a branch point to which up to three diene elastomer blocks are bonded,

a - the copolymer having a Mooney viscosity of at least 10, preferably at least 30 and at most 100,

b- the compound being composed

of at least 30%, preferably 35%, of branched macromolecules comprising a polyether block to which at least three diene elastomer blocks are bonded,

of at most 70%, preferably 65%, of linear macromolecules,

c - the polyether block having a number-average molar mass ranging from 150 to 5000 g/mol, and

d - each of the branch points consisting of a silicon atom.

The diene elastomer blocks consist of diene elastomers preferentially selected from the group consisting of polybutadienes (BRs), synthetic polyisoprenes (IRs), butadiene copolymers, isoprene copolymers and mixtures of these elastomers. Such copolymers are more particularly butadiene-styrene copolymers (SBRs), isoprene/butadiene copolymers (BIRs), isoprene/styrene copolymers (SIRs) and isoprene/butadiene-styrene copolymers (SBIRs). Among these copolymers, butadiene-styrene copolymers (SBRs) are particularly preferred.

The diene elastomer of the blocks of the copolymer according to the invention may itself be block, random, sequenced, microsequenced, etc. It can have any microstructure.

According to one embodiment of the invention, the end of the elastomer branches of the elastomers of the block copolymer, which end is not bonded to a silicon atom, can bear a function comprising a nitrogen atom, preferably a cyclic or acyclic amine function.

Preferably, the ends of elastomer branches of the block copolymer are functionalized to at least 70 mol%, relative to the number of moles of elastomer branches, by a cyclic or acyclic amine function.

According to one variant of the invention, the diene block copolymer may have a Mooney viscosity of at least 30, preferably at least 40, and at most 80, preferably at most 70.

According to one variant of the invention, the polyether block is a block consisting of (O-R) units, in which R is a linear or branched, divalent hydrocarbon-based group, preferably aliphatic group, having 1 to 10 carbon atoms, in particular a -CH(R')-CH(R'')- group, in which R' and R'' are, independently of one another, a hydrogen atom or a C₁-C₄ alkyl substituent, preferably R is a C₁-C₄ alkanediyl group, more preferentially an ethanediyl or propanediyl group. Mention may thus be made, as polyether block suitable for the invention, of polyoxymethylene, poly(ethylene oxide), poly(propylene oxide) or polytetrahydrofuran, preferably the polyether block is a poly(oxide ethylene) or poly(propylene oxide) block.

According to one variant of the invention, the polyether block has a number-average molar mass of approximately from 150 to 5000 g/mol and preferentially from 200 to 3000 g/mol. The number-average molar mass is calculated by the SEC (Size Exclusion Chromatography) technique which makes it possible to separate the macromolecules in solution according to their size through columns filled with a porous gel. The method is explained later in the text.

According to the invention, the branch points of the diene block copolymer to which the diene elastomer chains are bonded are silicon atoms. The two branch points are at each end of the polyether block.

Thus, a branch point can bond up to three diene elastomer blocks to the polyether block.

According to the invention, the linear macromolecules consist of a mixture of macromolecules of which the two branch points are each bonded to a diene elastomer block (linear triblock copolymer) and macromolecules of which a single branch point is bonded to a diene elastomer block (linear diblock copolymer), and also elastomer chains not bonded to a polyether block (dead chains which have not reacted with the functional

polyether). Their mass content is at most 70%, preferably at most 65% relative to the total weight of the block copolymer.

According to the invention, the branched macromolecules consist of a mixture of macromolecules of which the branch points are bonded to at least three diene elastomer blocks. For reasons of feasibility and technical reality, these macromolecules preferably exhibit a distribution of the diene elastomer blocks on either side of the polyether block. That is to say that not all the elastomer blocks are bonded to the same branch point but are distributed over the various branch points. In other words, the three-branched macromolecules preferably comprise two elastomer branches at one end of the polyether block and one elastomer branch at the other end, the four-branched macromolecules preferably comprise two elastomer branches at one end of the polyether block and two elastomer branches at the other end or three elastomer branches at one end of the polyether block and one elastomer branch at the other end, and so on. Their mass content is at least 30%, preferably at least 35% relative to the total weight of the block copolymer.

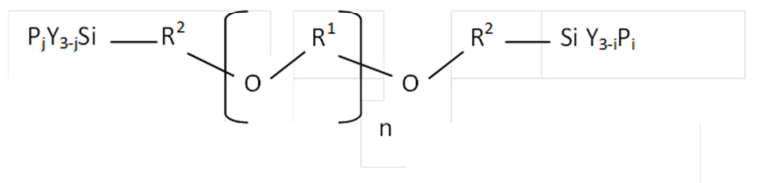
According to one embodiment of the invention, the two silicon atoms are each substituted by at most three elastomer branches and by at most three hydroxyl or C₁-C₁₈ alkoxy, C₅-C₁₈ cycloalkoxy or C₆-C₁₈ oxyaryl groups. Preferably, when the silicon atoms are substituted by alkoxy groups, these are C₁-C₄ alkoxy groups, preferably methoxy or ethoxy groups.

The alkoxy groups substituting the silicon atom can, according to some variants of the invention, be partially or completely hydrolysed to give hydroxyl groups. According to these variants, preferentially at least 50 mol% of the alkoxy functions borne by the diene block copolymer are hydrolysed to give hydroxyl groups. In particular, at least 80 mol% of the alkoxy functions borne by the diene block copolymer are hydrolysed to give hydroxyl groups, or even 100%.

The block macromolecules making up the diene block copolymer according to the invention can be represented by the following formulae I and II:

_ the branched macromolecules corresponding to general formula I:

Formula I



in which:

- R¹ represents a linear or branched, divalent hydrocarbon-based group, preferably aliphatic group, having 1 to 10 carbon atoms, in particular a -CH(R')-CH(R'')- group, in which R' and R'' are, independently of one another, a hydrogen atom or a C₁-C₄ alkyl substituent, preferably R¹ is a C₁-C₄ alkanediyl group, more preferentially a ethanediyl or a 1,2- or 1,3-propanediyl group,

- the R² represent, independently of one another, a linear or branched or cyclic, saturated or unsaturated, divalent hydrocarbon-based group, preferably aliphatic group, having 1 to 50 carbon atoms, preferably a linear aliphatic group, which is preferably saturated, preferentially having 1 to 15 carbon atoms, preferably 2 to 10,

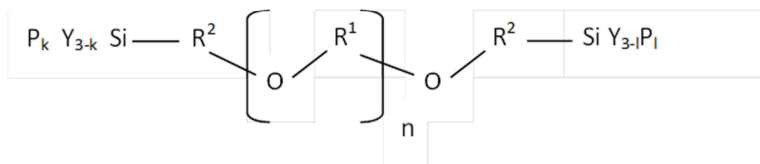
- the Y represent, in an identical or different manner, a group of formula -OR₄ in which the R₄ represent, independently of one another, a hydrogen atom, a C₁-C₁₈ alkyl, C₅-C₁₈ cycloalkyl or C₆-C₁₈ aryl substituent, preferably the R₄ represent a hydrogen atom or a C₁-C₄ alkyl substituent, preferably methyl or ethyl,

- i and j are numbers which are each, independently of one another, equal to 1, 2 or 3, with the proviso that (i+j) ranges from 3 to 6, and

- P represents a diene elastomer block;

_ the linear block macromolecules corresponding to general formula II:

Formula II



in which,

- R1 represents a linear or branched, divalent hydrocarbon-based group, preferably aliphatic group, having 1 to 10 carbon atoms, in particular a -CH(R')-CH(R'')-group, in which R' and R'' are, independently of one another, a hydrogen atom or a C₁-C₄ alkyl substituent, preferably R1 is a C₁-C₄ alkanediyl group, more preferentially a ethanediyl or 1,2- or 1,3-propanediyl group,

- the R2 represent, independently of one another, a linear or branched or cyclic, saturated or unsaturated, divalent hydrocarbon-based group, preferably aliphatic group, having 1 to 50 carbon atoms, preferably a linear aliphatic group, which is preferably saturated, preferentially having 1 to 15 carbon atoms, preferably 2 to 10,

- the Y represent, in an identical or different manner, a group of formula -OR₄ in which the R₄ represent, independently of one another, a hydrogen atom, a C₁-C₁₈ alkyl, C₅-C₁₈ cycloalkyl or C₆-C₁₈ aryl substituent, preferably the R₄ represent a hydrogen atom or a C₁-C₄ alkyl substituent, preferably methyl or ethyl,

- k and l are numbers which are each, independently of one another, equal to 0 or 1, with the proviso that (k+l) is equal to 1 or 2, and

- P represents a diene elastomer block.

According to variants of the invention which can be combined with the preceding ones, P represents a diene elastomer block bearing at the chain end a group comprising a nitrogen atom, more particularly a cyclic or acyclic amine function.

According to one variant of the invention, the diene block copolymer of the invention comprises at least 50% by weight of branched macromolecules relative to the total weight of the copolymer, preferably at least 80% by weight, the branched macromolecules being

all of the macromolecules with at least three branches of the copolymer, that is to say they consist of a polyether block to which at least three diene elastomer blocks are bonded.

The reader will understand that, when the macromolecules of the diene block copolymer correspond to formulae I and II, according to this variant, at least 50% by weight of the macromolecules relative to the total weight of the diene block copolymer, preferably at least 80% by weight, correspond to formula I.

According to one variant of the invention, which can be combined with the preceding one, at most 25% by weight of the total weight of the diene block copolymer may consist of macromolecules comprising a polyether block to which four or more diene elastomer blocks are bonded .

The reader will understand that, when the macromolecules of the diene block copolymer correspond to formulae I and II, according to this variant, at most 25% by weight of the macromolecules relative to the total weight of the diene block copolymer correspond to formula I for which $i + j$ is equal to 4 or more.

The diene block copolymer according to another preferred embodiment of the invention, which can be combined with one or the other of the two preceding variants or with the combination of the two, comprises at least 20% by weight, preferably at least 35%, more preferentially at least 40%, of the three-branched macromolecules, relative to the total weight of the copolymer, the three-branched macromolecules consisting of a polyether block to which three diene elastomer blocks are bonded.

The reader will understand that, when the macromolecules of the diene block copolymer correspond to formulae I and II, according to this variant, at least 20% by weight of the macromolecules relative to the total weight of the block copolymer, preferably at least 35%, more preferentially at least 40%, correspond to formula I for which $i + j$ is equal to 3.

The different preferential variants and aspects concerning the nature of the diene block copolymer, the functionalization of the elastomer branches, their M_n , the alkoxy function, the number of silicon atoms, the spacer group and the group comprising at least one nitrogen atom, the content of branched macromolecules, the content of three-branched macromolecules, etc., can be combined with one another, subject to their compatibility.

According to advantageous variants of the invention, the diene block copolymer comprising macromolecules comprising within their structure a linear or branched polyether block comprising at each chain end a branch point to which up to three diene elastomer blocks and up to three -OR groups are bonded, R representing, independently of one another, a C₁-C₄ alkyl substituent or a hydrogen atom, is such that at least one of the following characteristics is observed, at least two, at least three, at least four, at least five, at least six, at least seven, and preferably all:

- (i) the polyether block consists of -(OR)- units, in which R is a C₁-C₄ alkanediyl group, more preferentially a ethanediyl or 1,2- or 1,3- propanediyl group,
- (ii) the polyether block has a number-average molar mass of approximately from 150 to 5000 g/mol and preferably from 200 to 3000 g/mol;
- (iii) all or a part of the alkoxy functions substituting one or more silicon atoms are hydrolysed to give hydroxyl groups;
- (iv) the diene elastomer is a butadiene-styrene copolymer;
- (v) all or a part of the ends of elastomer branches not bonded to a silicon atom are functionalized, with respect to the number of moles of chain end, by an amine function;
- (vi) the mean Mn of the elastomer branches is less than 150 000 g/mol, preferably from 40 000 to 100 000 g/mol;
- (vii) the diene block copolymer comprises at least 50% by weight of branched macromolecules with at least three branches;
- (viii) the diene block copolymer comprises at least 20% by weight, preferably at least 35%, of branched macromolecules with three branches.

According to these advantageous variants of the invention, the modified diene elastomer can comprise, according to a preferential aspect, at most 25% by weight of branched macromolecules with four and more branches.

A subject of the invention is also a process for the synthesis of a diene block copolymer, comprising the reaction of the product of the polymerization of at least one diene

monomer, with a linear or branched functional polyether having a number-average molar mass ranging from 150 to 5000 g/mol comprising at each chain end a trifunctional group based on silicon, which is reactive with respect to the reactive end of the elastomer resulting from the polymerization step.

The polymerization step according to the invention can be carried out in a manner known per se, continuously or batchwise. The polymerization is generally carried out at temperatures of between 0°C and 110°C and preferably from 40°C to 100°C, indeed even from 50°C to 90°C. The temperature can be kept constant throughout this step or can be variable, according to the targeted characteristics of the elastomer synthesized. The polymerization process can be carried out in solution, in a more or less concentrated or dilute medium. The polymerization solvent is preferably an inert hydrocarbon-based solvent which can, for example, be an aliphatic or alicyclic hydrocarbon, such as pentane, hexane, heptane, isooctane, cyclohexane or methylcyclohexane, or an aromatic hydrocarbon, such as benzene, toluene or xylene.

Advantageously, the polymerization step according to the invention can be carried out by anionic polymerization initiated, for example, by means of an organic compound of an alkali metal or alkaline earth metal. The anionic polymerization of at least one conjugated diene monomer generates elastomer chains having a reactive site at the chain end. The term then commonly used is living elastomer or living chain.

In the context of this anionic polymerization, the polymerization initiator can be any known mono- or polyfunctional anionic initiator. However, an initiator containing an alkali metal, such as lithium, is preferentially used. Suitable organolithium initiators are in particular those comprising at least one carbon-lithium bond or at least one nitrogen-lithium bond. Representative compounds are aliphatic organolithium compounds, such as ethyllithium, n-butyllithium (n-BuLi) or isobutyllithium, or lithium amides obtained from a cyclic secondary amine, such as pyrrolidine and hexamethyleneimine. Such anionic polymerization initiators are known to those skilled in the art.

Thus, advantageously, the process which is a subject of the invention comprises a step of anionic polymerization of at least one conjugated diene monomer in the presence of an

anionic polymerization initiator, in particular those comprising a carbon-lithium bond or a nitrogen-lithium bond.

The following are especially suitable as conjugated diene monomers: 1,3-butadiene, 2-methyl-1,3-butadiene (isoprene), 2,3-di(C₁-C₅ alkyl)-1,3-butadienes, for instance 2,3-dimethyl-1,3-butadiene, 2,3-diethyl-1,3-butadiene, 2-methyl-3-ethyl-1,3-butadiene or 2-methyl-3-isopropyl-1,3-butadiene, an aryl-1,3-butadiene, 1,3-pentadiene or 2,4-hexadiene. Preferentially, the conjugated diene monomer is 1,3-butadiene or 2-methyl-1,3-butadiene.

According to some variants of the process of the invention, the conjugated diene monomer can be homopolymerized.

According to other variants of the process of the invention, the conjugated diene monomer may be copolymerized with one or more conjugated diene monomers and/or with one or more olefin monomers, preferably vinylaromatic monomers, having from 8 to 20 carbon atoms.

The following in particular are suitable as vinylaromatic monomers: styrene, ortho-, meta- or para-methylstyrene, α -methylstyrene, the "vinyltoluene" commercial mixture, para-(tert-butyl)styrene, etc., preferentially styrene.

In the context of a copolymerization of one or more conjugated diene monomers with one or more vinylaromatic monomers, the proportions of each monomer are such that the copolymers obtained contain from 10% to 99% by weight of diene units, and from 1% to 8% by weight of units derived from vinylaromatic monomers. Preferentially, the conjugated diene monomer is 1,3-butadiene and the vinylaromatic monomer is styrene.

In order to refine the microstructure of the diene elastomers, a modifying and/or randomizing agent may or may not be added in appropriate amounts. This is within the general knowledge of those skilled in the art.

The variants concerning the polymerization step can be combined with the preferential or alternative aspects and variants described below.

The polymerization of at least one conjugated diene monomer according to the invention generates elastomer chains having a reactive site at the chain end. According to one

advantageous implementation, the polymerization in the context of the invention is anionic and is carried out in the presence of a polymerization initiator. The term then commonly used is living elastomer or living chain. These living chains, or living elastomers, then react with the reactive functions of the functional polyether during the following step. The functional polyether comprises six groups which are reactive with respect to the reactive site of the living elastomer, in the case in point the alkoxy groups or the halogen atoms substituting the silicon atoms, each silicon atom being substituted by three of these groups or atoms.

The amount of functional polyether intended to react with the living diene elastomer depends essentially on the type of diene block copolymer desired.

Thus, the molar ratio of the functional polyether to the metal of the polymerization initiator is advantageously at least 0.1, preferably at least 0.15, more preferentially at least 0.25, and at most 0.45, preferentially at most 0.40, or even at most 0.35. Thus, according to a particularly advantageous variant of the modification step, the molar ratio of the functional polyether to the metal of the polymerization initiator has a value ranging from 0.25 to 0.40.

The conditions for adding the functional polyether to the elastomer and reacting it with said elastomer are conventional in terms of modifying an elastomer resulting from anionic polymerization and are known to those skilled in the art. These conditions do not comprise specific limitations.

For example, this reaction with the living diene elastomer can take place at a temperature of between -20°C and 100°C, by addition of the functional polyether to the living elastomer chains, or vice versa. This reaction can of course be carried out with one or more different functional polyethers.

The blending of the living elastomer with the functional polyether can be carried out by any suitable means, in particular using any mixer having available stirring of static type and/or any dynamic mixer of perfectly stirred type known to those skilled in the art. The latter know how to determine the reaction time between the living diene polymer and the functional polyether, which can vary from a few minutes, for example 2 minutes, to several hours, for example 2 hours.

The functional polyether can be linear or branched. According to one variant of the invention, the functional polyether is a polymer comprising $-(O-R)-$ units, in which R is a linear or branched, divalent hydrocarbon-based group, preferably aliphatic group, having 1 to 10 carbon atoms, in particular a $-CH(R')-CH(R'')$ - group, in which R' and R'' are, independently of one another, a hydrogen atom or a C_1-C_4 alkyl substituent, preferably R is a C_1-C_4 alkanediyl group, more preferentially a ethanediyl or 1,2- or 1,3- propanediyl group. Mention may thus be made of polyoxymethylene, poly(ethylene oxide), poly(propylene oxide) or polytetrahydrofuran, preferably the functional polyether is derived from a poly(oxide ethylene) or poly(propylene oxide).

The functional polyether according to the invention also comprises, at each of the chain ends, a trialkoxysilyl or trihalosilyl group.

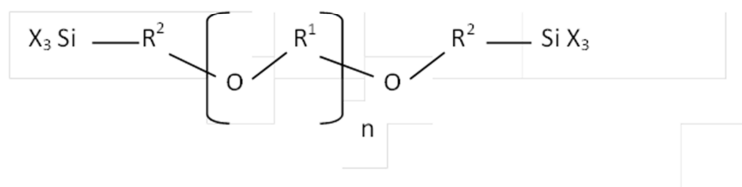
When the chain-end groups are trialkoxysilyls, the alkoxy groups are C_1-C_{18} acyclic or C_5-C_{18} cyclic, or alternatively C_6-C_{18} aryloxy, preferably C_1-C_4 acyclic alkoxy groups, preferably methoxy or ethoxy.

When the chain-end groups are trihalosilyls, the halogen atom is preferably chlorine.

Advantageously, the functional polyether has a number-average molar mass of from 150 to 5000 g/mol, preferably from 150 to 3000 g/mol and more preferentially from 200 to 3000 g/mol. The number-average molar mass is calculated by the SEC (Size Exclusion Chromatography) technique described below.

According to one variant of the invention, the functional polyether can be represented by the formula III below:

Formula III



in which,

- R1 represents a linear or branched, divalent hydrocarbon-based group, preferably aliphatic group, having 1 to 10 carbon atoms, in particular a -CH(R')-CH(R'')-group, in which R' and R'' are, independently of one another, a hydrogen atom or a C₁-C₄ alkyl substituent, preferably R1 is a C₁-C₄ alkanediyl group, more preferentially a ethanediyl or 1,2- or 1,3-propanediyl group,

- the R2 represent, independently of one another, a linear or branched or cyclic, saturated or unsaturated, divalent hydrocarbon-based group, preferably aliphatic group, having 1 to 50 carbon atoms, preferably a linear aliphatic group, which is preferably saturated, preferentially having 1 to 15 carbon atoms, preferably 2 to 10,

- the X represent, in an identical or different manner, a halogen atom, preferably Cl, or a group of formula -OR₃ in which the R₃ represent, independently of one another, a C₁-C₁₈ alkyl, C₅-C₁₈ cycloalkoxyl or C₆-C₁₈ aryl substituent, preferably the R₃ represent a C₁-C₄ alkyl substituent, preferably methyl or ethyl,

- n is a number greater than 1, so that the polyether block has a number-average molar mass of approximately from 150 to 5000 g/mol, preferably from 150 to 3000 g/mol and more preferentially from 200 to 3000 g/mol.

Among the functional polyethers corresponding to general formula III, mention may be made, for example, of poly(oxy-1,2-ethanediyl)- α -[3-(triethoxysilyl)propyl]- ω -[3-(triethoxysilyl)propoxy], poly(oxy-1,2-ethanediyl)- α -[3-(trimethoxysilyl)propyl]- ω -[3-(trimethoxysilyl)propoxy], poly[oxy(methyl-1,2-ethanediyl)]- α -[3-(trichlorosilyl)propyl]- ω -[3-(trichlorosilyl)propoxy].

The functional polyether can either be found commercially, or prepared according to methods described in the literature consisting for example in carrying out a first reaction of allylation of a polyethylene glycol in the presence of allyl bromide and of a base such as potassium hydroxide, either in aqueous solution, or in a two-phase medium or also in an organic solvent such as tetrahydrofuran, then a hydrosilylation reaction, for example using a platinum catalyst such as the platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane or hexachloroplatinic acid catalyst, in the presence of a trihalosilane such as in particular trichlorosilane or else a trialkoxysilane such as in particular trimethoxysilane or triethoxysilane, in the presence or absence of solvent.

According to variants of the invention, when the silicon atoms of the functional polyether bear halogenated reactive sites, the synthesis process can be continued with a hydrolysis or alcoholysis step known per se making it possible to generate silanol Si-OH or alkoxy silane Si-OR functions from these halogenated active sites which have not reacted with the living elastomer. This hydrolysis or alcoholysis step can be carried out by adding the polymer solution to an aqueous solution or to a solution containing an alcohol or, conversely, by adding water or the alcohol to the polymer solution. This step may or may not be carried out in the presence of a base or of a buffer. By way of example, an amine such as triethylamine may be used.

According to other variants of the invention, when the silicon atoms of the functional polyether bear alkoxy silyl reactive sites, the synthesis process can comprise a step of hydrolysis of the hydrolysable alkoxy silyl functions which have not reacted with the living elastomer, by adding an acidic, basic or neutral compound as described in document EP 2 266 819 A1. The hydrolysable alkoxy silyl functions are then converted into silanol functions.

The process for the synthesis of the diene block copolymer according to the invention can be continued in a way known per se by the steps of recovery of the copolymer.

According to variants of this process, these steps comprise a stripping step for the purpose of recovering the diene block copolymer resulting from the prior steps in dry form. This stripping step can have the effect of hydrolysing all or part of the residual hydrolysable alkoxy silyl functions of the diene block copolymer in order to convert them into silanol functions. Advantageously, at least 50 to 70 mol% of the residual hydrolysable alkoxy silyl functions can thus be hydrolysed.

The diene block copolymer according to the invention gives the rubber compositions containing it a noteworthy and unexpected improvement in the compromise between raw processing/hysteresis, compared with a diene block copolymer comprising a polyether block described in the prior art, at equal molar mass of the copolymer. The block copolymers comprising a central polyether block described in the prior art generally have a degree of branched polymers of much less than 30%, such as for example the diene block

copolymer comprising a central polyether block of Example 1 of WO 2009/000750 A1, which has less than 30% of branched macromolecules.

For this reason, a subject of the invention is also a rubber composition particularly suitable for the manufacture of tyres, based on at least one reinforcing filler and on an elastomer matrix comprising at least one diene block copolymer according to the invention.

The elastomer matrix can comprise up to 100 phr of diene block copolymer according to the invention. In the context of the reinforced rubber composition, the term “diene block copolymer according to the invention” is understood to mean not only a diene block copolymer according to the invention, but also any mixture of at least two diene block copolymers according to the invention.

According to variants of the invention, the elastomer matrix can also comprise at least one diene elastomer other than the diene block copolymer according to the invention. This or these diene elastomers can be selected from the diene elastomers conventionally used in tyres, such as natural rubber or a synthetic elastomer, whether or not it is modified, functionalized, coupled or star-branched. The synthetic diene elastomer(s) can be selected from polybutadienes (BRs), synthetic polyisoprenes (IRs), butadiene copolymers, isoprene copolymers, and mixtures of these elastomers. The butadiene copolymers are particularly butadiene-styrene (SBR) copolymers. This or these additional diene elastomers can then be present from 1 to 70 parts by weight per 100 parts of diene block copolymer according to the invention.

According to other variants, the matrix consists solely of the diene block copolymer according to the present invention.

Use may be made, as reinforcing filler, of any type of filler known for its abilities to reinforce a rubber composition which can be used in the manufacture of tyres, for example carbon black, or else a reinforcing filler other than carbon black, in particular an inorganic filler such as silica, with which is combined, in a known manner, a coupling agent, or even a mixture of these two types of filler.

According to a particularly interesting variant of the invention, the reinforcing filler is predominantly other than carbon black, that is to say that it predominantly comprises one

or more fillers other than carbon black; in particular, more than 50% by weight of the total weight of the filler is an inorganic reinforcing filler such as silica, or even the reinforcing filler consists exclusively of such a filler.

According to this variant, when carbon black is also present, it may be used at a content of less than 20 phr, more preferentially of less than 10 phr (for example between 0.5 and 20 phr, especially from 1 to 10 phr).

Preferably, the amount of reinforcing filler (carbon black and/or other reinforcing filler, such as silica) is between 10 and 200 phr, more preferably between 30 and 200 phr, the optimum being, in a known way, different according to the specific applications targeted.

All carbon blacks, used individually or in the form of mixtures, are suitable as carbon blacks, in particular the blacks conventionally employed in tyres or their treads. These carbon blacks can be used in the isolated state, as available commercially, or in any other form, for example as support for some of the rubber additives used.

Reinforcing inorganic filler should be understood here as meaning any other inorganic or mineral filler, whatever its colour and its origin (natural or synthetic), capable of reinforcing by itself alone, without means other than an intermediate coupling agent, a rubber composition intended for the manufacture of tyres; such a filler is generally characterized, in a known way, by the presence of hydroxyl groups at its surface.

Mineral fillers of the siliceous type, preferentially silica (SiO_2), are suitable in particular as reinforcing inorganic fillers. The silica used can be any reinforcing silica known to those skilled in the art, in particular any precipitated or fumed silica having a BET surface area (according to standard NF ISO 5794-1, appendix E of June 2010) and also a CTAB specific surface (according to standard NF ISO 5794-1, appendix G of June 2010) both less than $450 \text{ m}^2/\text{g}$, preferably from 30 to $400 \text{ m}^2/\text{g}$, in particular between 60 and $300 \text{ m}^2/\text{g}$.

Mention will also be made of mineral fillers of the aluminous type, in particular alumina (Al_2O_3), aluminium oxides, aluminium hydroxides, aluminosilicates, titanium oxides, silicon carbides or nitrides, all of the reinforcing type as described for example in applications WO 99/28376-A2, WO 00/73372-A1, WO 02/053634-A1, WO2004/003067-A1, WO2004/056915-A2, US6610261-B1 and US6747087-B2. Reinforcing fillers of another nature, in particular carbon black, are also suitable as reinforcing fillers, provided

that these reinforcing fillers are covered with a siliceous layer or else comprise, at their surface, functional sites, in particular hydroxyl sites, requiring the use of a coupling agent in order to form the connection between the filler and the elastomer. By way of example, mention may be made of carbon blacks partially or fully covered with silica, or carbon blacks modified with silica.

The physical state in which the reinforcing filler is provided is not important, whether it is in the form of a powder, of microbeads, of granules, or else of beads. Of course, reinforcing inorganic filler is also understood to mean mixtures of different reinforcing fillers, in particular of highly dispersible silicas as described above.

When silica is present in the composition as reinforcing filler, use may be made, as coupling agents, of organosilanes, in particular alkoxysilane polysulfides or mercaptosilanes, or else of at least bifunctional polyorganosiloxanes. Silica/elastomer bonding agents, in particular, have been described in a large number of documents, the best known being bifunctional alkoxysilanes, such as alkoxysilane polysulfides.

In the compositions in accordance with the invention, when a coupling agent is used, the content thereof is easily adjusted by those skilled in the art according to the content of the reinforcing inorganic filler, in particular of siliceous type. It is typically about 0.5% to 15% by weight relative to the weight of reinforcing inorganic filler, in particular of siliceous type.

The rubber compositions in accordance with the invention can also comprise, in addition to the coupling agents, coupling activators, agents for covering the fillers or more generally processing aids capable, in a known way, by virtue of an improvement in the dispersion of the filler in the rubber matrix and of a lowering of the viscosity of the compositions, of improving their ability to be processed in the raw state, these agents being, for example, hydrolysable silanes, such as alkylalkoxysilanes, polyols, polyethers, primary, secondary or tertiary amines, or hydroxylated or hydrolysable polyorganosiloxanes.

The rubber compositions in accordance with the invention can also comprise reinforcing organic fillers which can replace all or a portion of the carbon blacks or of the other reinforcing fillers described above. Mention may be made, as examples of reinforcing

organic fillers, of functionalized polyvinyl organic fillers, such as described in applications WO-A-2006/069792, WO-A-2006/069793, WO-A-2008/003434 and WO-A-2008/003435.

The rubber compositions in accordance with the invention can also comprise all or a portion of the usual additives generally used in the elastomer compositions intended for the manufacture of tyres, such as, for example, plasticizers or extender oils, whether the latter are aromatic or non-aromatic in nature, in particular very weakly aromatic or non-aromatic oils (e.g., paraffinic oils, hydrogenated naphthenic oils, MES oils or TDAE oils), vegetable oils, ether plasticizers, ester plasticizers (for example glycerol trioleates), fillers other than those mentioned above, for example lamellar fillers, plasticizing hydrocarbon-based resins exhibiting a high Tg, preferably of greater than 30°C, such as described, for example, in applications WO 2005/087859, WO 2006/061064 and WO 2007/017060, pigments, protective agents, such as antiozone waxes, chemical antiozonants or antioxidants, anti-fatigue agents, reinforcing resins (such as resorcinol or bismaleimide), methylene acceptors (for example phenolic novolak resin) or methylene donors (for example HMT or H3M), such as described, for example, in application WO 02/10269, a crosslinking system based either on sulfur, or on sulfur donors and/or on peroxides and/or on bismaleimides, vulcanization accelerators or retarders, vulcanization activators, and mixtures of such compositions.

Another subject of the invention is a process for the preparation of a rubber composition as described above.

The composition is manufactured in appropriate mixers, using two successive phases of preparation well known to those skilled in the art: a first phase of thermomechanical working or kneading ("non-productive" phase) at high temperature, up to a maximum temperature of between 110°C and 200°C, preferably between 130°C and 185°C, followed by a second phase of mechanical working ("productive" phase) down to a lower temperature, typically of less than 120°C, for example between 40°C and 100°C, during which finishing phase the crosslinking system is incorporated.

By way of example, the first (non-productive) phase is carried out in a single thermomechanical step during which all the necessary constituents, the optional supplementary covering agents or processing aids and various other additives, with the

exception of the vulcanization system, are introduced into an appropriate mixer, such as an ordinary internal mixer. The total duration of the kneading, in this non-productive phase, is preferably between 2 and 10 min. After cooling the mixture thus obtained during the first non-productive phase, the vulcanization system and where appropriate an adhesion promoter are then incorporated at low temperature, generally in an external mixer, such as an open mill; everything is then mixed (productive phase) for a few minutes, for example between 5 and 15 min.

According to variants of the invention, the process for the preparation of the rubber composition comprises the steps of preparation of the diene block copolymer according to the invention as described above according to its different methods of synthesis.

The final composition thus obtained may subsequently be calendered, for example in the form of a sheet or of a slab, or else extruded, for example in order to form a rubber profiled element which can be used as semi-finished product made of rubber intended for the tyre.

Due to the improvement in the hysteresis/processing compromise which characterizes a reinforced rubber composition according to the invention, it should be noted that such a composition can constitute any semi-finished product of the tyre and very particularly the tread, thus reducing its rolling resistance.

Another subject of the invention is a semi-finished product made of rubber comprising a rubber composition according to the invention, most particularly the tread.

Another subject of the invention is a tyre, at least one of the constituent elements of which is a semi-finished product made of rubber comprising a rubber composition according to the invention, most particularly the tread.

The abovementioned characteristics of the present invention, and also others, will be understood more clearly on reading the following description of several implementation examples of the invention, which are given as non-limiting illustrations.

EXAMPLES

I - MEASUREMENTS AND TESTS USED

Determination of the value of the M_n of the branch before coupling or star-branching by size exclusion chromatography

The SEC (Size Exclusion Chromatography) technique makes it possible to separate macromolecules in solution according to their size through columns filled with a porous gel. The macromolecules are separated according to their hydrodynamic volume, the bulkiest being eluted first.

Without being an absolute method, SEC makes it possible to comprehend the distribution of the molar masses of a polymer. The various number-average molar masses (M_n) and weight-average molar masses (M_w) may be determined from commercial standards and the polydispersity index ($PI = M_w/M_n$) may be calculated via a "Moore" calibration.

There is no specific treatment of the polymer sample before analysis. The latter is simply dissolved in the elution solvent at a concentration of approximately 1 g.l^{-1} . The solution is then filtered through a filter with a porosity of $0.45 \text{ }\mu\text{m}$ before injection.

The apparatus used is a Waters Alliance chromatographic line. The elution solvent is tetrahydrofuran, the flow rate is 1 ml.min^{-1} , the temperature of the system is 35°C and the analytical time is 30 min. A set of two Waters columns with the trade name "Styragel HT6E" is used. The volume of the solution of the polymer sample injected is $100 \text{ }\mu\text{l}$. The detector is a Waters 2410 differential refractometer and the software for making use of the chromatographic data is the Waters Empower system.

The calculated average molar masses are relative to a calibration curve produced for SBRs having the following microstructure: 25% by weight of units of styrene type, 23% by weight of units of 1,2- type and 50% by weight of units of trans-1,4- type.

Determination of the contents of linear macromolecules and branched macromolecules by the high-resolution size exclusion chromatography (high-resolution SEC) technique

The high-resolution SEC technique is used to determine the percentages by weight of the various populations of chains present in a polymer sample. The SEC (Size Exclusion Chromatography) technique makes it possible to separate macromolecules in solution

according to their size through columns filled with a porous gel. The macromolecules are separated according to their hydrodynamic volume, the bulkiest being eluted first.

Without being an absolute method, SEC makes it possible to comprehend the distribution of the molar masses of a polymer. The various number-average molar masses (M_n) and weight-average molar masses (M_w) may be determined from commercial standards and the polydispersity index ($PI = M_w/M_n$) may be calculated via a "Moore" calibration. A calibration curve connecting the logarithm of the molar mass ($\log M$) with the elution time (t_e) is produced beforehand with standards, and modelled.

There is no specific treatment of the polymer sample before analysis. The latter is simply dissolved in the elution solvent at a concentration of approximately 1 g.l^{-1} . The solution is then filtered through a filter with a porosity of $0.45 \text{ }\mu\text{m}$ before injection.

The apparatus used is a Waters Alliance 2695 chromatographic line. The elution solvent is tetrahydrofuran, the flow rate is 0.2 ml.min^{-1} and the temperature of the system is 35°C . A set of three identical columns in series is used (Shodex, length 300 mm, diameter 8 mm). The number of theoretical plates of the set of columns is greater than 22 000. The volume of the solution of the polymer sample injected is $50 \text{ }\mu\text{l}$. The detector is a Waters 2414 differential refractometer and the software for making use of the chromatographic data is the Waters Empower system.

The calculated molar masses are relative to a calibration curve produced for SBRs having the following microstructure: 25% by weight of units of styrene type, 23% by weight of units of 1,2- type and 50% by weight of units of trans-1,4- type.

Determination of the Mooney viscosity

For the polymers and the rubber compositions, the Mooney viscosities $ML(1+4)100^\circ\text{C}$ are measured according to Standard ASTM D-1646.

Use is made of an oscillating consistometer as described in Standard ASTM D-1646. The Mooney plasticity measurement is carried out according to the following principle: the composition in the raw state (i.e., before curing) is moulded in a cylindrical chamber heated to 100°C . After preheating for one minute, the rotor rotates within the test specimen at 2 revolutions/minute and the working torque for maintaining this movement after

rotating for 4 minutes is measured. The Mooney plasticity ML (1+4) is expressed in "Mooney unit" (MU, with 1 MU = 0.83 N.m).

Determination of the glass transition temperature of the polymers

The glass transition temperatures (T_g) of the elastomers are determined using a differential scanning calorimeter according to Standard ASTM D3418.

Dynamic properties

The dynamic properties and in particular $\tan \delta$ max are measured on a viscosity analyser (Metravib VA4000) according to Standard ASTM D 5992-96. The response of a sample of vulcanized composition (cylindrical test specimen with a thickness of 2 mm and a cross section of 79 mm²), subjected to a simple alternating sinusoidal shear stress, at a frequency of 10 Hz, under standard temperature conditions (23°C) according to Standard ASTM D 1349-99, is recorded. A strain amplitude sweep is carried out from 0.1% to 50% peak-to-peak (outward cycle) and then from 50% to 0.1% peak-to-peak (return cycle). The result more particularly made use of is the loss factor $\tan \delta$. For the return cycle, the maximum value of $\tan \delta$ observed, denoted $\tan \delta$ max, is indicated. This value is representative of the hysteresis of the material and in the present case of the rolling resistance: the smaller the value of $\tan \delta$ max, the lower the rolling resistance.

II - EXAMPLES OF PREPARATION OF THE BLOCK COPOLYMERS

Preparation of the polymer A: Diene block copolymer - control

1.74 kg of styrene and 5.84 kg of butadiene, and also 1.07 l of a 0.36 mol.l⁻¹ solution of tetrahydrofuran in methylcyclohexane, are injected into a 90-litre reactor, maintained under a nitrogen pressure of approximately 2 bar, containing 44 kg of methylcyclohexane. After neutralization of the impurities in the solution to be polymerized by addition of n-butyllithium, 716 ml of 0.06 mol.l⁻¹ n-butyllithium in methylcyclohexane are added. The polymerization is carried out at 50°C.

After 45 minutes, the degree of conversion of the monomers reaches 68%. This content is determined by weighing an extract dried at 140°C under a reduced pressure of 200 mmHg. The value of the branch M_n before coupling, determined by SEC RI, is 120 000 g.mol⁻¹.

1.19 l of a solution of poly(oxy-1,2-ethanediyl)- α -[3-(triethoxysilyl)propyl]- ω -[3-(triethoxysilyl)propoxy] (CAS 666829-33-0) at 0.018 mol.l⁻¹ in toluene are then added (npoly(oxy-1,2-ethanediyl)- α -[3-(triethoxysilyl)propyl]- ω -[3-(triethoxysilyl)propoxy])/n(n-butyllithium) = 0.5). The solution is stirred at a temperature of 50°C for 30 minutes. The solution is subsequently antioxidantized by addition of 0.8 part per hundred parts of elastomer (phr) of 4,4'-methylenebis(2,6-di(tert-butyl)phenol) and 0.2 part per hundred parts of elastomer (phr) of N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine. The copolymer thus treated is separated from its solution by a steam stripping operation and then dried on open mills at 100°C for 15 minutes.

The Mooney viscosity of the polymer is 70.

The distribution of the 1 branch, 2 branch, 3 branch, 4 branch, 5 branch and 6 branch entities (1b/2b/3b/4b/5b/6b), determined by high-resolution SEC, is as follows: 16/72/6/4/3/0.

The glass transition temperature of this copolymer is -63°C.

Preparation of the polymer B: Diene block copolymer according to the invention

1.74 kg of styrene and 5.84 kg of butadiene, and also 1.02 l of a 0.36 mol.l⁻¹ solution of tetrahydrofuran in methylcyclohexane, are injected into a 90-litre reactor, maintained under a nitrogen pressure of approximately 2 bar, containing 44 kg of methylcyclohexane. After neutralization of the impurities in the solution to be polymerized by addition of n-butyllithium, 1.1 ml of 0.06 mol.l⁻¹ n-butyllithium in methylcyclohexane are added. The polymerization is carried out at 50°C.

After 45 minutes, the degree of conversion of the monomers reaches 70%. This content is determined by weighing an extract dried at 140°C under a reduced pressure of 200 mmHg. The value of the branch Mn before coupling, determined by SEC RI, is 81 000 g.mol⁻¹.

1.37 l of a solution of poly(oxy-1,2-ethanediyl)- α -[3-(triethoxysilyl)propyl]- ω -[3-(triethoxysilyl)propoxy] (CAS 666829-33-0) at 0.018 mol.l⁻¹ in toluene are then added (npoly(oxy-1,2-ethanediyl)- α -[3-(triethoxysilyl)propyl]- ω -[3-(triethoxysilyl)propoxy])/n(n-butyllithium) = 0.35). The solution is stirred at a temperature of 50°C for 15 minutes. The solution is subsequently antioxidantized by addition of 0.8 part per hundred parts of elastomer

(phr) of 4,4'-methylenebis(2,6-di(tert-butyl)phenol) and 0.2 part per hundred parts of elastomer (phr) of N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine. The copolymer thus treated is separated from its solution by a steam stripping operation and then dried on open mills at 100°C for 15 minutes.

The Mooney viscosity of the polymer is 44.

The distribution of the 1 branch, 2 branch, 3 branch, 4 branch, 5 branch and 6 branch entities (1b/2b/3b/4b/5b/6b), determined by high-resolution SEC, is as follows: 12/29/21/38/0/0.

The glass transition temperature of this copolymer is -64°C.

Examples of preparations of the rubber compositions

The elastomers A and B have been used for the preparation of rubber compositions of tread type, each comprising silica as reinforcing filler according to two different formulations.

Each of the following compositions is produced, firstly, by thermomechanical working, then, in a second finishing step, by mechanical working, according to usual processes for preparing a rubber mixture.

The following are successively introduced into a laboratory internal mixer of Banbury type, the capacity of which is 400 cm³, which is 70% filled and which has a starting temperature of approximately 90°C: the elastomer, two thirds of the silica, the black, the coupling agent and the oil, then, approximately one minute later, the remainder of the reinforcing filler, the resin, the antioxidant, the stearic acid and the antiozone wax and then, approximately two minutes later, the zinc monoxide.

The step of thermomechanical working is carried out for 4 to 5 minutes, up to a maximum dropping temperature of approximately 160°C.

The abovementioned first step of thermomechanical working is thus carried out, it being specified that the mean speed of the blades during this first step is 50 rpm.

The mixture thus obtained is recovered and cooled and then, in an external mixer (homofinisher), the sulfur and the accelerator are added at 30°C, the combined mixture

being further mixed for a time of 3 to 4 minutes (abovementioned second step of mechanical working).

The compositions thus obtained are subsequently calendered, either in the form of plaques (with a thickness ranging from 2 to 3 mm) or thin sheets of rubber, for the measurement of their physical or mechanical properties, or in the form of profiled elements which can be used directly, after cutting and/or assembling to the desired dimensions, for example as semi-finished products for tyres, in particular for treads.

Crosslinking is carried out at 150°C for 40 min.

Each of the compositions exhibits the following formulation (expressed in phr: parts per hundred parts of elastomer):

Table 1

Ingredients	Formulation 1	Formulation 2
Polymer	100	100
Silica	110	70
Carbon black	3	3
Oil	13	0
Resin	59	46
Coupling agent	8.8	5.6
Stearic acid	3	3
Zinc oxide	1.5	1.5
DPG	2.3	1.5
Soluble sulfur	1	1
Accelerator	2.3	2.3
Antioxidant	3	3

Silica: Zeosil 1165MP from Rhodia, of HDS type.

Carbon black: ASTM N234 grade from Cabot Corporation

Oil: Sunflower oil comprising 85% by weight of oleic acid, Lubrirob Tod 1880 from Novance

Resin: Aromatic DCPD resin, Escorez 5600 or PR383, from ExxonMobil

Coupling agent: Silane TESPT Si69 from Degussa

DPG: Diphenylguanidine (Perkacit DPG from Flexsys)

Accelerator: CBS: N-cyclohexyl-2-benzothiazolesulfenamide (“Santocure CBS” from Flexsys);

Antioxidant: N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine, from Flexsys

Results:

The results presented in the tables below show:

That the elastomer according to the invention improves the hysteresis/Mooney composition compromise with respect to the reference elastomer, whether in one or the other of the two formulations.

That the elastomer according to the invention particularly improves the compromise when it is used in a composition containing a high silica content (Formulation 1).

Table 2

polymer		formulation 1		
		tan delta max 23°C	Mooney composition	Performance index
A	control	100	100	1.0
B	invention	102	65	1.5

Table 3

polymer		formulation 2		
		tan delta max 23°C	Mooney composition	Performance index
A	control	100	100	1.0
B	invention	112	64	1.4

In the table above, the tan delta or Mooney values are expressed in base 100 relative to the control.

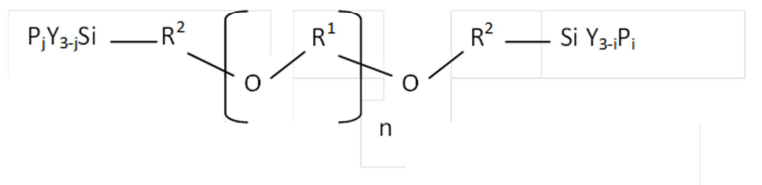
The performance index is calculated as: $10\,000 / (\text{value of tan delta} * \text{value of Mooney mixture})$. The lower the tan delta, the lower the Mooney composition, the better the rolling resistance/processing performance compromise.

Claims

1. Diene block copolymer comprising a linear or branched polyether block comprising, at each end of the block, a branch point to which up to three diene elastomer branches are bonded, characterized in that
 - a - the copolymer has a Mooney viscosity of at least 30 and at most 100,
 - b- the copolymer comprises
 - at least 30% by weight, preferably 35%, of branched macromolecules comprising a polyether block to which at least three diene elastomer blocks are bonded,
 - at most 70% by weight, preferably 65%, of linear macromolecules,
 - c - the polyether block has a number-average molar mass ranging from 150 to 5000 g/mol, and
 - d - each of the two branch points consists of a silicon atom.
2. Diene block copolymer according to Claim 1, characterized in that the two silicon atoms are each substituted by at most three elastomer branches and by at most three hydroxyl or C₁-C₁₈ alkoxy, C₅-C₁₈ cycloalkoxy or C₆-C₁₈ oxyaryl groups.
3. Diene block copolymer according to Claim 1 or 2, characterized in that the copolymer has a Mooney viscosity of at least 40 and at most 80, preferably at most 70.
4. Diene block copolymer according to any one of Claims 1 to 3, characterized in that the polyether block is a polyoxymethylene, poly(ethylene oxide), poly(propylene oxide) or polytetrahydrofuran block, preferably the polyether block is a poly(ethylene oxide) or poly(propylene oxide) block.
5. Diene block copolymer according to any one of Claims 1 to 4, characterized in that the end of the elastomer branches not bonded to a silicon atom bears a function comprising a nitrogen atom, preferably a cyclic or acyclic amine function, at the end not bonded to a silicon atom.

6. Diene block copolymer according to any one of Claims 1 to 5, characterized in that
 _ the branched macromolecules correspond to general formula I:

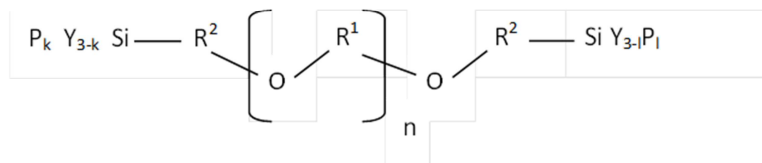
Formula I



in which,

- R1 represents a linear or branched, C₁-C₁₀ divalent hydrocarbon-based group, in particular a -CH(R')-CH(R'')- group, in which R' and R'' are, independently of one another, a hydrogen atom or a C₁-C₄ alkyl substituent, preferably R1 is a C₁-C₄ alkanediyl group, more preferentially a ethanediyl or 1,2- or 1,3- propanediyl group,
- the R2 represent, independently of one another, a linear or branched or cyclic, saturated or unsaturated, divalent hydrocarbon-based group, preferably aliphatic group, having 1 to 50 carbon atoms, preferably a linear aliphatic group, which is preferably saturated, preferentially having 1 to 15 carbon atoms, preferably 2 to 10,
- the Y represent, in an identical or different manner, a group of formula -OR4 in which the R4 represent, independently of one another, a hydrogen atom, a C₁-C₁₈ alkyl, C₅-C₁₈ cycloalkoxyl or C₆-C₁₈ aryl substituent, preferably the R4 represent a hydrogen atom or a C₁-C₄ alkyl substituent, preferably methyl or ethyl,
- i and j are numbers which are each, independently of one another, equal to 1, 2 or 3, with the proviso that (i+j) ranges from 3 to 6, and
- P represents a diene elastomer block;

_ and the linear block macromolecules correspond to general formula II:

Formula II

in which,

- R1 represents a linear or branched, C₁-C₁₀ divalent hydrocarbon-based group, in particular a -CH(R')-CH(R'')- group, in which R' and R'' are, independently of one another, a hydrogen atom or a C₁-C₄ alkyl substituent, preferably R1 is a C₁-C₄ alkanediyl group, more preferentially a ethanediyl or a 1,2- or 1,3- propanediyl group,

- the R2 represent, independently of one another, a linear or branched or cyclic, saturated or unsaturated, divalent hydrocarbon-based group, preferably aliphatic group, having 1 to 50 carbon atoms, preferably a linear aliphatic group, which is preferably saturated, preferentially having 1 to 15 carbon atoms, preferably 2 to 10,

- the Y represent, in an identical or different manner, a group of formula -OR4 in which the R4 represent, independently of one another, a hydrogen atom, a C₁-C₁₈ alkyl, C₅-C₁₈ cycloalkoxyl or C₆-C₁₈ aryl substituent, preferably the R4 represent a hydrogen atom or a C₁-C₄ alkyl substituent, preferably methyl or ethyl,

- k and l are numbers which are each, independently of one another, equal to 0 or 1, with the proviso that (k+l) is equal to 1 or 2, and

- P represents a diene elastomer block.

7. Diene block copolymer according to any one of Claims 1 to 6, characterized in that the copolymer comprises at least 50% by weight of branched macromolecules consisting of a polyether block to which at least three diene elastomer blocks are bonded.

8. Diene block copolymer according to any one of Claims 1 to 7, characterized in that the copolymer comprises at least 20% by weight, preferably at least 35%, of branched

macromolecules consisting of a polyether block to which at least three diene elastomer blocks are bonded.

9. Diene block copolymer according to any one of Claims 1 to 8, characterized in that the copolymer comprises at most 25% of branched macromolecules consisting of a polyether block to which four or more diene elastomer blocks are bonded.

10. Diene block copolymer according to any one of Claims 1 to 9, characterized in that, at each branch point, up to three diene elastomer blocks and up to three -OR groups are bonded, R representing, independently of one another, a C₁-C₄ alkyl substituent or a hydrogen atom, and in that at least one of the following characteristics is observed, at least two, at least three, at least four, at least five, at least six, at least seven, and preferably all:

(i) the polyether block is linear consisting of -(OR)- units, in which R is a C₁-C₄ alkanediyl group, more preferentially an ethanediyl or propanediyl group;

(ii) the polyether block has a number-average molar mass of approximately from 150 to 5000 g/mol and preferably from 200 to 3000 g/mol;

(iii) all or a part, preferably at least 50 mol%, of the alkoxy functions substituting one or more silicon atoms are hydrolysed to give hydroxyl groups;

(iv) the diene elastomer is a butadiene-styrene copolymer;

(v) all or a part, preferably at least 70 mol%, of the ends of elastomer branches not bonded to a silicon atom are functionalized, with respect to the number of moles of chain end, by an amine function;

(vi) the mean Mn of the elastomer branches is less than 150 000 g/mol, preferably from 40 000 to 100 000 g/mol;

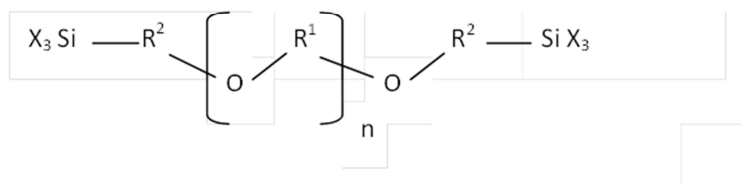
(vii) the copolymer comprises at least 50% by weight of branched macromolecules with at least three branches;

(viii) the copolymer comprises at least 20% by weight of branched macromolecules with three branches, preferably at least 35%.

11. Process for the synthesis of such a diene block copolymer, characterized in that it comprises the reaction of the product of the anionic polymerization, in the presence of a polymerization initiator, of at least one diene monomer, with a linear or branched functionalized polyether having a number-average molar mass ranging from 150 to 5000 g/mol comprising, at each end of the main chain, a trifunctional group selected from trialkoxysilyl groups or trihalosilyl groups, with a molar ratio of the functional polyether to the metal of the polymerization initiator of at least 0.1, preferably at least 0.15, more preferentially at least 0.25, and at most 0.45, preferentially at most 0.40, or even at most 0.35.

12. Process according to Claim 11, characterized in that the functionalized polyether corresponds to general formula III:

Formula III



in which:

- R1 represents a linear or branched, C₁-C₁₀ divalent hydrocarbon-based group, in particular a -CH(R')-CH(R'')- group, in which R' and R'' are, independently of one another, a hydrogen atom or a C₁-C₄ alkyl substituent, preferably R1 is a C₁-C₄ alkanediyl group, more preferentially an ethanediyl or propanediyl group,

- the R2 represent, independently of one another, a linear or branched or cyclic, saturated or unsaturated, divalent hydrocarbon-based group, preferably aliphatic group, having 1 to 50 carbon atoms, preferably a linear aliphatic group, which is preferably saturated, preferentially having 1 to 15 carbon atoms, preferably 2 to 10,

- the X represent a halogen atom, preferably a chlorine atom, or a group of formula -OR₃ in which the R₃ represent, independently of one another, a C₁-C₁₈ alkyl, C₅-

C₁₈ cycloalkoxyl or C₆-C₁₈ aryl substituent, preferably the R₃ represent a C₁-C₄ alkyl substituent, preferably methyl or ethyl,

- n is a number greater than 1, so that the polyether block has a number-average molar mass of approximately from 150 to 5000 g/mol.

13. Process according to Claim 11 or 12, characterized in that it comprises a hydrolysis reaction at the end of the reaction of the product resulting from the polymerization of at least one diene monomer with the functional polyether.

14. Rubber composition based on at least one reinforcing filler and a diene block copolymer as defined in Claims 1 to 10 or synthesized according to the process described in Claims 11 to 13.

15. Tyre characterized in that it comprises, in at least one of its constituent elements, a rubber composition according to Claim 14.