

CLAIMS

1. Method for the continuous synthesis of a modified diene elastomer, characterized in that it comprises the steps:

- 5 - of anionic polymerization of at least one conjugated diene monomer in the presence of a polymerization initiator,
- of modifying the diene elastomer in a functionalizing device, by bringing the living diene elastomer bearing an active site obtained in the previous step into contact, in a single step, with a non-polymerizable functionalizing agent
- 10 comprising (a) where appropriate, a function capable of interacting with a reinforcing filler and (b) a trialkoxysilane group, the optionally hydrolysable alkoxy radical having 1 to 10 carbon atoms,

➤ the modification comprising three reactions in series

Reaction	Mechanism
R1	$PLi + A \xrightarrow{k_1} PA$
R2	$PLi + PA \xrightarrow{k_2} P_2A$
R3	$PLi + P_2A \xrightarrow{k_3} P_3A$

where

- 15 - A represents the functionalizing agent,
- PLi represents a living elastomer chain,
- PA represents the chain-end functionalized elastomer,
- P₂A represents the coupled elastomer,
- P₃A represents the three-arm star-shaped elastomer, and
- 20 - k_i represents the rate constant of the reaction R_i,

that are carried out according to the following rate law:

Reactions	Rate of reaction
R1	$V_1 = k_1[PLi][A]$
R2	$V_2 = k_2[PLi][PA]$
R3	$V_3 = k_3[PLi][P_2A]$

where

- k_1 , k_2 and k_3 are the rate constants respectively of the reactions R1, R2 and R3 (expressed in $(\text{m}^3/\text{mol})\cdot\text{s}^{-1}$),
- $[PLi]$ is the concentration of living chains (expressed in mol/m^3),
- $[A]$ is the concentration of modifying agent A (expressed in mol/m^3),
- $[PA]$ is the concentration of chain-end functionalized elastomer (expressed in mol/m^3),
- $[P_2A]$ is the concentration of coupled elastomer (expressed in mol/m^3),
- $[P_3A]$ is the concentration of the three-arm star-shaped elastomer (expressed in mol/m^3),

with a ratio of the rate constants, defined as: $K = \frac{k_1}{k_2} = \frac{k_2}{k_3}$, of greater than 1,

and

- the residence time distribution in a functionalizing device (i) or (ii) is expressed respectively according to equations 1 or 3 below:

(i) in a functionalizing device having at least one tubular continuous reactor or having at least one cascade of at least two stirred reactors,

$$E_1(t) = \frac{1}{2} \left(\frac{P}{\pi \theta_1 t} \right)^{\frac{1}{2}} e^{-\frac{P(\theta_1 - t)^2}{4 \theta_1 t}} \quad \text{Eq 1}$$

in which:

- P is the dimensionless parameter of resistance to dispersion,
- θ_1 is the residence time defined as the reactor volume/total volume flow rate ratio, preferably equal to at least 0.1 minute and at most to 10 minutes, more preferably at most to 5 minutes,

- t is the variable time of the residence time distribution,

(ii) in a functionalizing device that is a combination of the device (i) and of a device having at least one continuous stirred reactor, having a residence time distribution characterized by the following equation:

$$E_2(t) = \frac{e\left(-\frac{t}{\theta_2}\right)}{\theta_2} \quad \text{Eq 2}$$

5 in which:

- θ_2 is the residence time defined as the reactor volume/total volume flow rate ratio, preferably between 0 and 60 minutes, more preferably between 5 and 50 minutes,
- t is the variable time of the residence time distribution,

10 the device (ii) having a residence time distribution characterized by the equation 3 below, which is the result of the convolution of equations 1 and 2:

$$E_{12}(t) = \int_0^t E_1(t-T) E_2(T) dT \quad \text{Eq 3}$$

$$E_{12}(t) = \int_0^t \frac{1}{2} \left(\frac{P}{\pi \theta_1 (t-T)} \right)^{\frac{1}{2}} e^{-\frac{P(\theta_1 - (t-T))^2}{4 \theta_1 (t-T)}} \frac{e\left(-\frac{T}{\theta_2}\right)}{\theta_2} dT$$

in which:

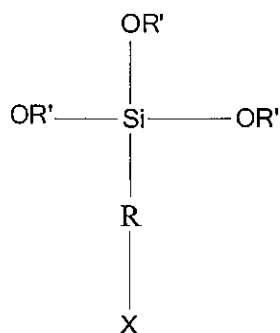
- θ_1 and θ_2 are the residence times as defined above,
- P is the dimensionless parameter of resistance to dispersion,
- 15 • t is the variable time of the residence time distribution,
- T is the integration variable.

2. Method for the continuous synthesis of a modified diene elastomer according to Claim 1, characterized in that K is greater than or equal to 10.

3. Method for the continuous synthesis of a modified diene elastomer according to Claim 1 or 2, characterized in that P is greater than 6.9, more preferably greater than or equal to 9.6.

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4. Method for the continuous synthesis of a modified diene elastomer according to any one of Claims 1 to 3, characterized in that the functionalizing agent is represented by formula 1:



Formula 1

5 in which,

- R is a C₁-C₁₈ cyclic or non-cyclic, saturated or unsaturated, aliphatic or C₆-C₁₈ aromatic divalent hydrocarbon radical, preferably a C₁-C₁₀ aliphatic, linear or branched, divalent hydrocarbon radical, more preferably a C₁-C₆ aliphatic, linear, divalent hydrocarbon radical, more preferably still the C₃ linear hydrocarbon radical,
- X is a hydrogen atom or a function capable of interacting with a reinforcing filler,
- the R' radicals, which are substituted or unsubstituted, identical or different, represent a C₁-C₁₀, or even C₁-C₈, alkyl group, preferably a C₁-C₄ alkyl group, more preferably methyl and ethyl.

5. Method for the continuous synthesis of a modified diene elastomer according to Claim 4, characterized in that X is a function capable of interacting with a reinforcing filler selected from cyclic or non-cyclic, primary, secondary or tertiary amines, isocyanates, imines, cyano compounds, thiols, carboxylates, epoxides and primary, secondary or tertiary phosphines.

6. Method for the continuous synthesis of a modified diene elastomer according to Claim 5, characterized in that the function capable of interacting with a reinforcing filler is a secondary amine optionally protected by a trialkylsilyl group

or a tertiary amine, the nitrogen atom being substituted by C₁-C₁₀ alkyl radicals, preferably C₁-C₄ alkyl radicals, more preferably a methyl or ethyl radical, or else a cyclic amine that forms a heterocycle containing a nitrogen atom and at least one carbon atom, preferably 2 to 6 carbon atoms.

- 5 7. Method for the continuous synthesis of a modified diene elastomer according to Claim 6, characterized in that the functionalizing agent is selected from 3-(N,N-dimethylaminopropyl)trimethoxysilane, 3-(N,N-dimethylaminopropyl)triethoxysilane, 3-(N,N-diethylaminopropyl)trimethoxysilane, 3-(N,N-diethylaminopropyl)-triethoxysilane, 3-(N,N-dipropylaminopropyl)trimethoxysilane, 3-(N,N-dipropyl-aminopropyl)triethoxysilane, 3-(N,N-dibutylaminopropyl)trimethoxysilane, 3-(N,N-dibutylaminopropyl)triethoxysilane, 3-(N,N-dipentylaminopropyl)trimethoxysilane, 3-(N,N-dipentylaminopropyl)triethoxysilane, 3-(N,N-dihexylaminopropyl)-trimethoxysilane, 3-(N,N-dihexylaminopropyl)triethoxysilane, 3-(hexamethylene-aminopropyl)trimethoxysilane and 3-(hexamethyleneaminopropyl)triethoxysilane.
- 10 8. Method for the continuous synthesis of a modified diene elastomer according to any one of Claims 1 to 6, characterized in that it comprises, subsequent to the modification step, a step of deprotection when the function capable of interacting with the reinforcing filler is a protected primary or secondary amine, protected thiol or protected primary or secondary phosphine function.
- 15 9. Method for the continuous synthesis of a modified diene elastomer according to any one of the preceding claims, characterized in that it comprises, subsequent to the modification step, a step of hydrolysis of the modified elastomer obtained in the preceding step.
- 20 10. Method for the continuous synthesis of a modified diene elastomer according to any one of the preceding claims, characterized in that the molar ratio of the functionalizing agent to the polymerization initiator has a value ranging from 0.40 to 0.75.
- 25 11. Method for the continuous synthesis of a modified diene elastomer according to any one of Claims 1 to 9, characterized in that the molar ratio of the functionalizing agent to the polymerization initiator has a value ranging from 0.15 to 0.40.
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12. Method for the continuous synthesis of a modified diene elastomer according to any one of Claims 1 to 9, characterized in that the molar ratio of the functionalizing agent to the polymerization initiator has a value greater than or equal to 0.75.
- 5 13. Modified diene elastomer, characterized in that it is obtained according to the continuous synthesis method as described in any one of the preceding claims.
14. System for the continuous synthesis of a modified diene elastomer, characterized in that it comprises a device for modifying the living diene elastomer resulting from the anionic polymerization step, modelled on one of the
- 10 following models:
1. a tubular reactor with axial dispersion,
 2. a tubular reactor with axial dispersion, in series with at least one continuous stirred reactor, presumed to be perfectly stirred,
 3. at least one tubular reactor with axial dispersion, in series with a
 - 15 continuous stirred reactor, presumed to be perfectly stirred,
 4. several tubular reactors with axial dispersion, in series with several continuous stirred reactors, presumed to be perfectly stirred,
 5. at least two continuous stirred reactors, presumed to be perfectly stirred, in series.
- 20 15. Use of a system according to Claim 14 for the implementation of the method according to Claims 1 to 12.
16. Unit for the continuous preparation of a modified diene elastomer, characterized in that it incorporates the system according to Claim 14 and in that the modifying device is in contact downstream with a device for recovering the
- 25 diene elastomer.

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- of modifying the diene elastomer in a functionalizing device, by bringing the living diene elastomer bearing an active site obtained in the previous step into contact, in a single step, with a non-polymerizable functionalizing agent comprising (a) where appropriate, a function capable of interacting with a reinforcing filler and (b) a trialkoxysilane group, the optionally hydrolysable alkoxy radical having 1 to 10 carbon atoms,

➤ the modification comprising three reactions in series

Reaction	Mechanism
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with a ratio of the rate constants, defined as: $K = \frac{k_1}{k_2} = \frac{k_2}{k_3}$, of greater than 1, and

- the residence time distribution in a functionalizing device (i) or (ii) is expressed respectively according to equations 1 or 3 below:

(i) in a functionalizing device having at least one tubular continuous reactor or having at least one cascade of at least two stirred reactors,

$$E_1(t) = \frac{1}{2} \left(\frac{P}{\pi \theta_1 t} \right)^{\frac{1}{2}} e^{-\frac{P(\theta_1 - t)^2}{4 \theta_1 t}} \quad \text{Eq 1}$$

in which:

- P is the dimensionless parameter of resistance to dispersion,
- θ_1 is the residence time defined as the reactor volume/total volume flow rate ratio, preferably equal to at least 0.1 minute and at most to 10 minutes, more preferably at most to 5 minutes,
- t is the variable time of the residence time distribution,

- 5 (ii) in a functionalizing device that is a combination of the device (i) and of a device having at least one continuous stirred reactor, having a residence time distribution characterized by the following equation:

$$E_2(t) = \frac{e^{\left(\frac{-t}{\theta_2}\right)}}{\theta_2} \quad \text{Eq 2}$$

in which:

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- θ_2 is the residence time defined as the reactor volume/total volume flow rate ratio, preferably between 0 and 60 minutes, more preferably between 5 and 50 minutes,
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the device (ii) having a residence time distribution characterized by the equation 3 below, which is the result of the convolution of equations 1 and 2:

$$E_{12}(t) = \int_0^t E_1(t-T) E_2(T) dT \quad \text{Eq 3}$$

$$E_{12}(t) = \int_0^t \frac{1}{2} \left(\frac{P}{\pi \theta_1 (t-T)} \right)^{\frac{1}{2}} e^{-\frac{P(\theta_1 - (t-T))^2}{4 \theta_1 (t-T)}} \frac{e^{\left(\frac{-T}{\theta_2}\right)}}{\theta_2} dT$$

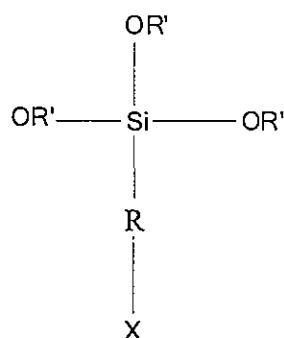
in which:

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4. Method for the continuous synthesis of a modified diene elastomer according to any one of Claims 1 to 3, characterized in that the functionalizing agent is represented by formula 1:



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Formula 1

in which,

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- R is a C₁-C₁₈ cyclic or non-cyclic, saturated or unsaturated, aliphatic or C₆-C₁₈ aromatic divalent hydrocarbon radical, preferably a C₁-C₁₀ aliphatic, linear or branched, divalent hydrocarbon radical, more preferably a C₁-C₆ aliphatic, linear, divalent hydrocarbon radical, more preferably still the C₃ linear hydrocarbon radical,
- X is a hydrogen atom or a function capable of interacting with a reinforcing filler,
- the R' radicals, which are substituted or unsubstituted, identical or different, represent a C₁-C₁₀, or even C₁-C₈, alkyl group, preferably a C₁-C₄ alkyl group,

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5. Method for the continuous synthesis of a modified diene elastomer according to Claim 4, characterized in that X is a function capable of interacting with a reinforcing filler selected from cyclic or non-cyclic, primary, secondary or tertiary amines, isocyanates, imines, cyano compounds, thiols, carboxylates, epoxides and primary, secondary or tertiary phosphines.

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6. Method for the continuous synthesis of a modified diene elastomer according to Claim 5, characterized in that the function capable of interacting with a reinforcing filler is a secondary amine optionally protected by a trialkylsilyl group or a tertiary amine, the nitrogen atom being substituted by C₁-C₁₀ alkyl radicals, preferably C₁-C₄ alkyl radicals, more preferably a methyl or ethyl radical, or else a cyclic amine that forms a heterocycle containing a nitrogen atom and at least one carbon atom, preferably 2 to 6 carbon atoms.

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7. Method for the continuous synthesis of a modified diene elastomer according to Claim 6, characterized in that the functionalizing agent is selected from 3-(N,N-

5 dimethylaminopropyl)trimethoxysilane, 3-(N,N-dimethylaminopropyl)triethoxysilane, 3-(N,N-diethylaminopropyl)trimethoxysilane, 3-(N,N-diethylaminopropyl)triethoxysilane, 3-(N,N-dipropylaminopropyl)trimethoxysilane, 3-(N,N-dipropylaminopropyl)triethoxysilane, 3-(N,N-dibutylaminopropyl)trimethoxysilane, 3-(N,N-dibutylaminopropyl)triethoxysilane, 3-(N,N-dipentylaminopropyl)trimethoxysilane, 3-(N,N-dipentylaminopropyl)triethoxysilane, 3-(N,N-dihexylaminopropyl)trimethoxysilane, 3-(N,N-dihexylaminopropyl)triethoxysilane, 3-(hexamethyleneaminopropyl)trimethoxysilane and 3-(hexamethyleneaminopropyl)triethoxysilane.

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8. Method for the continuous synthesis of a modified diene elastomer according to any one of Claims 1 to 6, characterized in that it comprises, subsequent to the modification step, a step of deprotection when the function capable of interacting with the reinforcing filler is a protected primary or secondary amine, protected thiol or protected primary or secondary phosphine function.

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9. Method for the continuous synthesis of a modified diene elastomer according to any one of the preceding claims, characterized in that it comprises, subsequent to the modification step, a step of hydrolysis of the modified elastomer obtained in the preceding step.

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10. Method for the continuous synthesis of a modified diene elastomer according to any one of the preceding claims, characterized in that the molar ratio of the functionalizing agent to the polymerization initiator has a value ranging from 0.40 to 0.75.

11. Method for the continuous synthesis of a modified diene elastomer according to any one of Claims 1 to 9, characterized in that the molar ratio of the functionalizing agent to the polymerization initiator has a value ranging from 0.15 to 0.40.

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12. Method for the continuous synthesis of a modified diene elastomer according to any one of Claims 1 to 9, characterized in that the molar ratio of the functionalizing agent to the polymerization initiator has a value greater than or equal to 0.75.

13. System for the continuous synthesis of a modified diene elastomer, characterized in that it comprises a device for modifying the living diene elastomer resulting from an anionic polymerization step, modelled on one of the following models:

30

1. a tubular reactor with axial dispersion,

- 5 2. a tubular reactor with axial dispersion, in series with at least one continuous stirred reactor, presumed to be perfectly stirred,
3. at least one tubular reactor with axial dispersion, in series with a continuous stirred reactor, presumed to be perfectly stirred,
4. several tubular reactors with axial dispersion, in series with several continuous stirred reactors, presumed to be perfectly stirred,
- 10 5. at least two continuous stirred reactors, presumed to be perfectly stirred, in series.
14. Use of a system according to Claim 13 for the implementation of the method according to Claims 1 to 12.
- 15 15. Unit for the continuous preparation of a modified diene elastomer, characterized in that it incorporates the system according to Claim 13 and in that the modifying device is in contact downstream with a device for recovering the diene elastomer.