

**Method for continuous polymerization of diene elastomer
with lithium amide initiator**

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The present invention relates to a continuous synthesis process, by means of several reactors in series, making it possible to obtain a diene elastomer exhibiting a narrow molecular weight distribution and a high content of living polymer, in the case of an initiation with a lithium amide.

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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 employ them in the form of rubber compositions which can be used in the manufacture of various semi-finished products involved in the composition of tyre covers, such as, for example, underlayers, bonding rubbers between rubbers of different natures, coating rubbers for metal or textile reinforcing elements, sidewall rubbers or treads, and to obtain tyres with improved properties, in particular having a reduced rolling resistance.

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The reduction in the hysteresis of the mixtures is an ongoing objective of the tyre industry in order to limit fuel consumption and to thus protect the environment. This must, however, be carried out while keeping intact the processability of the mixtures.

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Many solutions have already been experimented with in order to achieve the objective of a fall in hysteresis. Mention may in particular be made of the modification of the structure of diene polymers and copolymers at the end of polymerization by means of functionalization agents, coupling agents or star-branching agents with the aim of obtaining a good interaction between the polymer, thus modified, and the filler, whether this is carbon black or a reinforcing inorganic filler. Mention may also be made of the use of a functional initiator having a functional group which interacts with the filler.

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Mention may be made, by way of illustration of this prior art, of the use of diene elastomers functionalized by alkoxysilane compounds and amine compounds.

Mention may be made of Patent JP4655706B2, in which provision is made to combine the functionalization of the living chain end with a compound of the alkoxy silane type bearing an amine functional group with the initiating with an amine-functional alkyl lithium with the aim of minimizing the hysteresis. In the same way, provision is made, in Patent Application US20120245275A1, to combine the functionalization of the living chain end with a compound of the alkoxy silane type bearing an amine functional group with the initiating with a lithium amide but also with a functional monomer of the vinylaminosilane type. Finally, in Patent Applications WO2015063161A1, WO2015044225A1, WO2015018772A1 and WO2015018600A1, provision is made to combine the initiating with a lithium amide with the reaction of the living chain end with compounds of the alkoxy silane type bearing different groups having an affinity for silica.

As illustrated above, the use of functional initiators having a group which interacts with silica, such as amine-functional alkyl lithiums or lithium amides, is advantageous in reducing the rolling resistance while decreasing the dissipation of energy related to the free chain ends. It thus appears advantageous to be able to use them on the industrial scale in competitive processes for the synthesis of elastomers.

It is known to a person skilled in the art that continuous synthesis processes are more competitive than batchwise synthesis processes, for which frequent shutdowns and restart-ups are necessary. However, while the use of initiator of the lithium amide type results in high conversions of monomers (greater than 85%) and high contents (greater than or equal to 90%) of living polymer chains in the CLi^+ form being jointly obtained in the batchwise process, a high conversion of monomers (greater than 85%) is associated with a low content of living polymer chains (less than 60%) and a high content of living polymer chains (greater than or equal to 90%) is associated with a low conversion of monomers (less than 70%) in the case of a conventional continuous process in a reactor.

The reduction in the distribution of the molecular weights before functionalization of the elastomer also makes it possible to improve the hysteresis/processing compromise of the material.

The synthesis of the elastomers with a process of batchwise type is preferable in this regard, since this type of process makes it possible to control the molecular distribution in order to obtain diene copolymers with a narrow molecular

weight distribution before functionalization, unlike a continuous process, which provides a wide molecular weight distribution.

5 Mention may be made, by way of example, of Patents US 6 313 232, EP 1318172 and EP 1 829 906, which assert that products exhibiting a low polydispersity are favourable to a reduced hysteresis. Linear polymers with narrow molecular distributions exhibit in addition an improved processing.

10 Patent US 5 587 420 describes a method for the polymerization of diene monomers in solution in a hydrocarbon solvent using, as initiator, an organolithium compound, batchwise. An organotin compound is added during or at the end of the batch. This type of batchwise process is less productive and less economical than a continuous process. This is described in Patent US 6 313 232, which describes a continuous process with a first stage of polymerization in the presence of a tin-derived compound, followed by a stage of functionalization with the tin at the outlet of the reactor for production of a diene polymer with improved physical properties, including the reduction in the hysteresis. However, the polydispersity values of polymers synthesized with this method are not indicated.

15 Moreover, as explained above, in order for the polymer obtained to be able to be upgraded, the synthesis process must be competitive and economical. In this sense, a process of continuous type is preferable. However, this type of process with a reactor, considered to be continuous stirred-tank reactor, does not make it possible to control the polydispersity index, like the processes of batchwise type.

20 Many patents describe the synthesis of functional elastomers in a continuous process. Mention may be made of Patent JP 1988-235305 (63-235305JP), which describes an economical continuous polymerization process where the polymer obtained has a broad molecular distribution.

25 Patent EP 1 829 906 describes a continuous process for the production of diene and vinylaromatic copolymers in the presence of a polarity-modifying agent (THFA-ethyl) in order to obtain a random incorporation of the monomers. The synthesis is carried out by means of at least two reactors in series. The copolymer obtained exhibits a polydispersity index of between 1.6 and 2.5.

30 Mention may also be made of Patent US 6 372 863 B1, which describes a continuous process for the polymerization of styrene and butadiene in two reactors in series, according to which all of the styrene is introduced into the first reactor with only a part of the butadiene, the remainder of the butadiene being introduced into the

second reactor. This process makes it possible to synthesize random elastomers having a low vinyl content with an absence of styrene blocks.

5 The aim of the invention is thus to identify a continuous synthesis process which makes it possible to jointly obtain a high conversion of monomers (greater than 70% by weight) and a high content of living polymer chains (greater than or equal to 90% by number) on conclusion of the polymerization stage in the case of an initiation with a lithium amide. A high content of living polymer on conclusion of the polymerization stage is desirable in order to be able to functionalize, couple or star-branch, as desired, the polymer chains. The synthesis process should also make it possible to synthesize diene elastomers exhibiting a low molecular weight distribution before functionalization which makes possible a gain with regard to the hysteresis/processing compromise of the material thus synthesized.

10 The inventors have now discovered, surprisingly, that the aims of the invention could be obtained by a continuous synthesis process comprising several reactors in series, monomer, solvent or a polar agent optionally being reinjected into one or more of the reactors other than the first, the intrinsic conversion by weight in the first reactor being less than 70%, the polymerization being continued in such a way that the total conversion by weight at the outlet of the final reactor is greater than 70%, the diene elastomer obtained exhibiting a polydispersity index varying from 1.1 to 1.7 and a low content of dead chains.

15 A subject-matter of the invention is thus a process for the continuous synthesis of a diene elastomer by means of n reactors r_1 to r_n , considered to be continuous stirred-tank reactors, which are equipped with an internal stirring system and which are arranged in series, n varying from 2 to 15, preferably from 2 to 9, the reactor r_1 being fed by an input solution comprising a solvent, one or more monomer(s), an anionic polymerization initiator chosen from lithium amides and a polar agent, one or more of the reactors r_2 to r_n additionally being optionally fed by reinjection of a purified solution comprising solvent and/or monomer(s) and/or polar agent, the temperature of each reactor varying from 20°C to 150°C, preferably varying from 30°C to 120°C, and being greater than or equal to the temperature of the reactor which immediately precedes it, the temperature of the reactor r_n being greater than the temperature of the reactor r_1 ,

25 the amount by weight W_1 of monomer(s) introduced into the reactor r_1 being such that:

$$0.1 < \frac{W_1}{\sum_{j=1}^n W_j} \leq 1$$

the amount by weight W_i of monomer(s) reinjected into the reactor r_i , when $W_i \neq 0$, i varying from 2 to n , being such that:

$$0 < \frac{W_i}{\sum_{j=1}^n W_j} < 0.9$$

and such that W_i represents from 5% to 100% by weight of the weight of the solution reinjected into the reactor r_i , when $W_i \neq 0$,

where W_j is the amount by weight of monomer(s) introduced into the reactor r_j , j varying from 1 to n ,

the amount by weight of all of the monomers entering the reactors r_1 to r_n representing from 5% to 25% by weight of the sum of the total inputs by weight of the reactors r_1 to r_n ,

the intrinsic conversion by weight $C_{\text{intrinsic},1}$ in the first reactor being less than 70%,

where $C_{\text{intrinsic},1} = P_1/W_1$

where P_1 is the weight of polymer formed in the reactor r_1 ,

the total conversion by weight C_{tot} at the outlet of the reactor r_n being greater than or equal to 70%,
where:

$$C_{\text{tot}} = \frac{\sum_{i=1}^n P_i}{\sum_{j=1}^n W_j}$$

where P_i is the weight of polymer formed in the reactor r_i ,

the overall conversion by weight $C_{\text{overall } i}$ in each reactor r_i , i varying from 1 to n , being such that:

$$\frac{C_{\text{tot}}}{n} - 0.2 \times C_{\text{tot}} < C_{\text{overall } i} < \frac{C_{\text{tot}}}{n} + 0.2 \times C_{\text{tot}}$$

and $C_{\text{overall } i} > 0$

where:

$$C_{overall\ i} = \frac{P_i}{\sum_{j=1}^n W_j}$$

5 where P_i is the weight of polymer formed in the reactor r_i , i varying from 1 to n ,

the diene elastomer obtained exhibiting a polydispersity index varying from 1.1 to 1.7, preferably varying from 1.2 to 1.6.

10 In the context of the present patent application, the term "reinjection" refers to the repeating of the action of injection into a reactor r_i , other than the reactor r_1 , already fed by the stream from r_{i-1} . The reinjection, when it takes place, can be carried out directly into one or more of the reactors or, advantageously, by mixing with the stream resulting from r_{i-1} . The reinjection can be carried out with streams having a composition identical to or different from the r_1 feed stream. When the reinjection takes place in at least two reactors, the natures of these reinjections can be
15 identical or different. The term "reinjected monomer" refers to the monomer injected into r_i not resulting from the stream originating from r_{i-1} .

20 Thus, the term "amount by weight W_i of monomer(s) introduced into the reactor r_i " is understood to mean, when $i = 1$, the amount of monomer(s) present in the input solution and introduced as such into the reactor 1 and, when $i = 2$ to n , the amount of monomer(s) optionally reinjected into the reactor i .

25 By control of the conversion in each reactor and by the number of reactors, the continuous process according to the invention makes it possible to obtain, at the outlet of the final reactor, a content of living chains of greater than or equal to 90% by number, with respect to the total number of living chains initiated by a lithium amide in the reactor r_1 . However, the reinjected solution or solutions have to be purified in order not to degrade the living polymer.

30 In the case of an anionic polymerization, the living chain is a carbanion. The carbanion is a very reactive entity. It reacts with protic entities or electrophilic entities.

Thus, if the feedstock of the first reactor contains protic impurities (alcohols, water, acids, and the like) or electrophilic impurities (carbonyls, and the like), the initiator will react first with these impurities to lead to inactive entities (alkoxides)

incapable of initiating the polymerization of the monomers. The difference between the amount of initiator introduced at the inlet of the reactor r1 and the amount of initiator which has reacted with the impurities in the reactor r1 constitutes the amount of active initiator. The number of living chains initiated in the reactor r1 is equivalent to this amount of active initiator in the reactor r1.

On the other hand, for the subsequent optional reinjection(s) between the reactors, the neutralization of the impurities introduced by the reinjection will be carried out by the polymer carbanion. This neutralization prevents the polymer chain from propagating and the chain thus becomes dead, that is to say inactive, towards the polymerization but also the functionalization. This entity is no longer reactive with the optional stopping, functionalization, coupling or star-branching agents.

This is why, apart from the feedstock of the first reactor, it is necessary to control the purity of each reinjected solution in order to guarantee the lowest possible dead-polymer content at the outlet of the reactor rn, i.e. less than 10% by number, with respect to the total number of chains initiated in the reactor r1.

The term "amount by weight of all of the monomer(s) entering the reactors r1 to rn" is understood to mean the sum of the amount by weight of monomer(s) introduced into the reactor r1 by the input solution and of the amounts by weight of the monomer(s) optionally reinjected into one or more of the reactors r2 to rn.

The term "sum of the total inputs by weight of the reactors r1 to rn" is understood to mean the sum of the amount by weight of the input solution and of the amounts by weight of the solutions optionally reinjected.

The term "polydispersity index" is understood to mean the ratio of the weight-average molecular weight to the number-average molecular weight. The weight-average and number-average molecular weights are measured by size exclusion chromatography.

The process according to the invention also makes it possible to control the polydispersity index of the polymer synthesized by the control of the conversion, by the balancing of the temperatures in each reactor and by the number of reactors.

The control of the conversion in all the reactors, in particular in the first and the final reactor, is provided by the temperature, the residence time, the amount of polar agent and the amount of monomer entering these reactors, the concentration of living polymer. A person skilled in the art knows how to vary these different parameters in order to control the conversions in the different reactors.

By operating at increasing temperature, the propagation in the reactors is accelerated. This is why, preferably, the temperature in at least one reactor r_i is greater than the temperature of the reactor r_{i-1} ; preferably, the temperature of each reactor r_i is greater than the temperature of the reactor r_{i-1} , i varying from 2 to n .

5 The optional reinjection of a portion of the monomers into one or more of the reactors starting from the second has an impact on the amount of monomers present in the reactor and the residence time within the said reactor. Thus, these reinjections, which constitute an advantageous implementation of the process according to the invention, also contribute to the balancing of the conversions and, as
10 explained above, to the control of the polydispersity index.

Advantageously, the very high purity of the monomers reinjected makes it possible to reduce the impact of the side reactions which have a tendency to widen the molecular distribution of the polymer formed.

15 The residence times and the temperatures are also chosen in order not to promote these side reactions.

Preferably, the reactors are equipped with an internal stirring mechanism.

Preferably, the intrinsic conversion by weight $C_{\text{intrinsic } 1}$ in the reactor r_1 is less than 65%, preferably less than 60%. Preferably, the total conversion by weight C_{tot} at the outlet of the reactor r_n is greater than or equal to 80%, preferably greater
20 than or equal to 85%.

Preferably, the number of reactors is equal to 2 or 3, preferably 2.

When the number of reactors is equal to 2, the process according to the invention preferably exhibits at least one of the following characteristics and more preferably all of the following characteristics:

- 25 -
- a reinjection of a solution comprising monomer(s) is carried out in the reactor r_2 ,
 - the purity of the solution optionally reinjected into the reactor r_2 is such that the content of impurities in the reinjected solution is minimized at a value of less than or equal to 5% of the number of living chains initiated
30 in the reactor r_1 ,
 - the temperature of the reactors r_1 and r_2 varies from 20°C to 150°C, preferably from 30°C to 120°C, the temperature of the reactor r_2 being greater than the temperature of the reactor r_1 ,

- the amount by weight of monomer(s) introduced into the reactor r1 is greater than 10% and less than 100% of the total amount by weight of the monomers introduced into the reactors r1 and r2, when a reinjection is carried out in r2,
- 5 - the amount by weight of monomer(s) reinjected into the reactor r2 is less than 90% by weight of the total weight of monomer(s) injected into the reactor r1 and reinjected into the reactor r2, when a reinjection is carried out in r2,
- 10 - the amount by weight of all of the monomers entering the reactors r1 and r2 represents from 5% to 25% by weight of the sum of the inputs by weight of the reactors r1 and r2, when a reinjection is carried out in r2,
- the intrinsic conversion by weight in the reactor 1 is preferably less than 65%, more preferably less than 60%.

15 Preferably, the residence time in the reactor r_i is between 1 and 60 minutes, preferably between 5 and 60 minutes, more preferably between 10 and 50 minutes. It is calculated in the following way:

$$\tau_i = \frac{V_i}{Q_{vi}}$$

with:

- V_i , volume of the reactor R_i , i varying from 1 to n
- 20 - Q_{vi} = flow rate by volume exiting the reactor i .

As explained above, a solution comprising solvent and/or monomer(s) and/or polar agent is optionally reinjected into one or more of the reactors r_2 to r_n .

25 As explained above, the purity of each reinjected solution has to be controlled.

The term "purity of a reinjected solution" is understood to mean the proportion by weight of optional monomer(s), and of optional solvent and of optional polar agent, with respect to the total weight of the reinjected solution.

30 The purification stage consists in removing, from the reinjected solution, the protic compounds (water, alcohol, acids, and the like) and electrophilic compounds (carbonyl, and the like) which can deactivate the living chain end, so as to reduce their amount in this reinjected solution to a content of less than or equal to 5 mol% of

the active initiator, preferably of less than or equal to 2 mol% of the active initiator. Each reinjected solution contains purified solvent and/or purified monomers and/or purified polar agent.

5 The constituent or each constituent of the reinjected solution(s) can be, before reinjection, purified independently by any purification means normally used to purify the constituents, for example by adsorption, liquid/liquid extraction, gas/liquid extraction or distillation.

10 In particular, the solvent and/or the monomer(s) and/or the polar agent can be independently purified by adsorption, liquid/liquid extraction, gas/liquid extraction or distillation.

 Alternatively, the solution(s) to be reinjected, comprising all or part of the combination of its constituents, can, before reinjection, be purified by any purification means normally used to purify the constituents, for example by adsorption, liquid/liquid extraction, gas/liquid extraction or distillation.

15 The adsorption can be carried out on zeolite or on alumina.

 The liquid/liquid extraction can be carried out by means of sodium hydroxide.

 The gas/liquid extraction can be carried out by means of a stream of air or nitrogen.

20 The distillation can be a single-stage distillation without reflux (or flash distillation) or a column distillation, optionally under vacuum.

 The flash distillation is carried out by means of an evaporation compartment. The column distillation is carried out by means of a distillation column.

25 Whatever the purification process chosen for each constituent or for the solution to be reinjected, the purified phase is used to constitute the stream to be reinjected.

30 According to one embodiment, the residues from the process(es) for the purification of the or each constituent or of the solution(s) to be reinjected are reinjected into the input solution feeding the first reactor. These residues consist of the monomers and/or of the solvent with a high concentration of impurities. The residues can then either constitute an extra contribution of monomer and/or of solvent and/or of polar agent to the input solution, or can constitute the sole source of

monomer and/or of solvent and/or of polar agent of the input solution. This embodiment makes it possible to limit the loss of material in the case of reinjection.

5 The term "diene elastomer" should be understood, in a known way, as meaning an (one or more is understood) elastomer resulting at least in part (i.e., a homopolymer or a copolymer) from diene monomers (monomers bearing two conjugated or non-conjugated carbon-carbon double bonds). More particularly, the term "diene elastomer" is understood to mean any homopolymer obtained by polymerization of a conjugated diene monomer having from 4 to 12 carbon atoms or any copolymer obtained by copolymerization of one or more conjugated dienes with one another or with one or more vinylaromatic monomers having from 8 to 20 carbon atoms. In the case of copolymers, the latter contain from 20% to 99% by weight of diene units and from 1% to 80% by weight of vinylaromatic units.

10 The following in particular are suitable as conjugated dienes which can be used in the process in accordance with the invention: 1,3-butadiene, 2-methyl-1,3-butadiene, 2,3-di(C₁ to C₅ alkyl)-1,3-butenes, such as, for example, 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, phenyl-1,3-butadiene, 1,3-pentadiene and 2,4-hexadiene, and the like.

15 The following in particular are suitable as vinylaromatic monomers: styrene, ortho-, meta- or para-methylstyrene, the "vinyltoluene" commercial mixture, para-(tert-butyl)styrene, methoxystyrenes, vinylmesitylene, divinylbenzene and vinylnaphthalene, and the like.

20 The diene elastomer is preferably selected from the group of highly unsaturated diene elastomers consisting of polybutadienes (BRs), synthetic polyisoprenes (IRs), butadiene copolymers, in particular copolymers of butadiene and of a vinylaromatic monomer, isoprene copolymers and the 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.

25 30 The diene elastomer is prepared by anionic polymerization in the presence of a lithium amide polymerization initiator included in the input solution.

The lithium amides are the products of the reaction of an organolithium compound, preferably an alkyllithium compound, and of a non-cyclic or cyclic, preferably cyclic, secondary amine.

Mention may be made, as secondary amine which can be used to prepare the
 5 initiators, of dimethylamine, diethylamine, dipropylamine, di(n-butyl)amine, di(sec-butyl)amine, dipentylamine, dihexylamine, di(n-octyl)amine, di(2-ethylhexyl)amine, dicyclohexylamine, N-methylbenzylamine, diallylamine, morpholine, piperazine, 2,6-dimethylmorpholine, 2,6-dimethylpiperazine, 1-ethylpiperazine, 2-methylpiperazine, 1-benzylpiperazine, piperidine, 3,3-dimethylpiperidine, 2,6-
 10 dimethylpiperidine, 1-methyl-4-(methylamino)piperidine, 2,2,6,6-tetramethylpiperidine, pyrrolidine, 2,5-dimethylpyrrolidine, azetidine, hexamethyleneimine, heptamethyleneimine, 5-benzyloxyindole, 3-azaspiro[5.5]undecane, 3-azabicyclo[3.2.2]nonane, carbazole, bistrimethylsilylamine, pyrrolidine and hexamethyleneamine.

15 The secondary amine, when it is cyclic, is preferably chosen from pyrrolidine and hexamethyleneamine.

The alkyllithium compound is preferably ethyllithium, n-butyllithium (n-BuLi), isobutyllithium, and the like.

20 The polymerization is carried out in the presence of a solvent included in the input solution.

The solvent used in the process according to the invention is preferably an inert hydrocarbon 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.

25 As explained above, the input solution, and also optionally one or more of the reinjected solutions, used in the process according to the invention comprise(s) a polar agent.

Suitable in particular as chelating polar agents which can be used in the process in accordance with the invention are the agents comprising at least one
 30 tertiary amine functional group or at least one ether functional group and preferably agents of tetrahydrofurfuryl ethyl ether or tetramethylethylenediamine type.

According to a first specific embodiment, the output stream from the reactor n containing the living chains is brought into contact with one or more agents for

stopping the polymerization as known per se, which is/are injected continuously into the process.

5 In this first embodiment, the living diene elastomer included in the output stream from the reactor n can, prior to the stopping, be reacted with one or more functionalization, coupling or star-branching agents. The distinguishing feature of these functionalization, coupling or star-branching agents is that they can either modify the elastomer so as to improve the interaction with a reinforcing filler (this is the case for functionalization, coupling and certain star-branching agents) or confer a given structure to the polymer (this is the case for certain star-branching and coupling agents).

10 According to a second specific embodiment, the living diene elastomer included in the output stream from the reactor n is reacted with one or more functionalization, coupling or star-branching agents also acting as agent for stopping the polymerization. It is then not necessary to add a conventional stopping agent known per se in order to bring the polymerization to an end.

15 Whatever the embodiment, any agent known per se can be envisaged as functionalization, coupling or star-branching agent.

20 The abovementioned characteristics of the present invention, and also others, will be better understood on reading the following description of several implementational examples of the invention, given by way of illustration and without limitation.

Measurements and tests used

25 Conversion

The conversions are measured by weighing the solids content of the solution containing the polymer. In this method, solution containing the polymer is withdrawn at the outlet of the reactor. This solution is introduced into a pre-tared tray. The mass of solution is thus weighed.

30 The sample is dried under a reduced pressure of 200 mmHg at 140°C for 15 minutes. The tray is subsequently placed in a desiccator containing silica gel for 2 minutes. Weighing the tray then makes it possible to determine the weight of polymer of the withdrawn sample.

The different conversions are then worked back to in the following way:

$$C_{\text{intrinsic } 1} = \frac{w(\text{solids content})_1}{w(\text{sample})_1} \times \frac{Q_1}{W_1}$$

with:

5 W_1 the flow rate by weight of monomers introduced into the reactor 1,
 Q_1 the sum of all the flow rates by weight of the entities entering the reactor
 1,

$$C_{\text{solids content } i} = \frac{w(\text{solids content})_i}{w(\text{sample})_i} \times \frac{Q_i}{\sum_{j=1}^i W_j}$$

10 with:

Q_i the sum of all the flow rates by weight of the entities entering the reactor
 i,

$$C_{\text{overall } i} = C_{\text{solids content } i} \times \frac{\sum_{j=1}^i W_j}{\sum_{k=1}^n W_k} - C_{\text{overall } i-1}$$

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$$C_{\text{total}} = \sum_{i=1}^n C_{\text{overall } i}$$

Glass transition temperature

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In these examples, the glass transition temperatures (T_g) of the elastomers are determined using a differential scanning calorimeter, according to standard ASTM E1356-08 (2014).

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Microstructure of the elastomers

The microstructure of the elastomers is characterized by the near-infrared (NIR) spectroscopy technique.

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Near-infrared spectroscopy (NIR) is used to quantitatively determine the content by weight of styrene in the elastomer and also its microstructure (relative distribution of the 1,2-, trans-1,4- and cis-1,4- butadiene units). The principle of the method is based on the Beer-Lambert law generalized for a multicomponent system.

As the method is indirect, it involves a multivariate calibration [Vilmin, F., Dussap, C. and Coste, N., Applied Spectroscopy, 2006, 60, 619-29] carried out using standard elastomers having a composition determined by ^{13}C NMR. The styrene content and the microstructure are then calculated from the NIR spectrum of an elastomer film having a thickness of approximately 730 μm . The spectrum is acquired in transmission mode between 4000 and 6200 cm^{-1} with a resolution of 2 cm^{-1} using a Bruker Tensor 37 Fourier-transform near-infrared spectrometer equipped with an InGaAs detector cooled by the Peltier effect.

Number-average molar mass and polydispersity index

The number-average molar mass and the polydispersity index of the polymer are determined using SEC (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.

SEC makes it possible to comprehend the average molar masses and the distributions of the molar masses of a polymer. The various number-average molar masses (M_n) and weight-average molar masses (M_w) can be determined from commercial standards and the polydispersity index ($PI = M_w/M_n$) can 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 μm before injection.

The apparatus used is a Waters Alliance chromatographic line. The elution solvent is either tetrahydrofuran or tetrahydrofuran + 1 vol% of diisopropylamine + 1 vol% of triethylamine, 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 Styragel HT6E trade name is used. The volume of the solution of the polymer sample injected is 100 μl . 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: 28% by weight of units of styrene type, 18% by weight of units of 1,2- type, 31% by weight of units of trans-1,4- type and 23% by weight of units of cis-1,4- type.

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Content of living chains in the elastomer at the outlet of the reactors

In the examples, the living polymer solution at the outlet of the polymerization reactors is brought continuously into contact with the DEAB (diethylaminobenzophenone) functionalization agent in excess with a contact time sufficient for the complete reaction of all the living chains with the functionalization agent. The content of grafted DEAB (content of functional group in the examples) is determined by an NMR analysis. This determination is carried out with respect to the amount of elastomer. In this way, the results obtained can be expressed as molar %, in mmol/kg of elastomer or as phr (per hundred grams of elastomer).

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The samples (approximately 25 mg of elastomer) are dissolved in carbon disulfide (CS₂) in approximately 1 ml. 100 μ l of deuterated cyclohexane are added for the lock signal.

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The spectra are acquired on a Bruker Avance 500 MHz spectrometer equipped with a 5 mm BBI Z-grad "broad band" probe.

The quantitative ¹H NMR experiment uses a simple 30° pulse sequence and a repetition time of 5 seconds between each acquisition. 256 accumulations are carried out at ambient temperature.

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The ¹H NMR signals of the 8 quantified protons (protons bonded to the carbons identified 1 to 4 in Figure 1) of the grafted DEAB correspond to a broad unresolved peak with a chemical shift of 3.2 ppm.

The edited 2D ¹H/¹³C ¹J HSQC NMR correlation spectrum makes it possible to confirm the nature of the grafted unit by virtue of the chemical shifts of the carbon and proton atoms. The signal of the carbons 1 to 4 has a chemical shift at 44.4 ppm.

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The ¹H NMR spectrum makes it possible to quantify the grafted DEAB units by integration of the broad unresolved peaks of signals described above: H1, H2 for the dehydrated DEAB form and H3, H4 for the carbinol DEAB form.

The grafted diethylaminobenzophenone, dehydrated and carbinol forms, has the following formula:

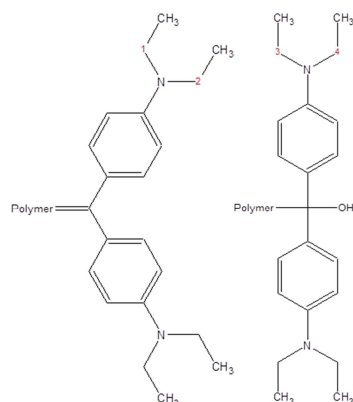


Figure 1

The chemical shifts are calibrated with respect to the protonated impurity of carbon disulfide δ ppm ^1H at 7.18 ppm, reference with regard to TMS (δ ppm ^1H at 0 ppm) and δ ppm ^{13}C at 192 ppm reference with regard to TMS (δ ppm ^{13}C at 0 ppm).

The simple pulse 1D ^1H NMR spectrum makes it possible to quantify the units of the polymer by integration of the broad unresolved peaks of characteristic signals. For example, for an SBR (styrene/butadiene rubber), the broad unresolved peaks considered for the calculation are styrene 5H (protons) between 7.4 ppm and 6.0 ppm, 1,4-PB(polybutadiene)2H + 1,2-PB 1H between 5.8 ppm and 4.9 ppm and 1,2-PB 2H between 4.9 ppm and 4.3 ppm.

Thus, knowing the total amount of chains by the M_n value obtained by SEC analysis, it is possible to determine the content of living chains corresponding to the content of DEAB-functionalized chains.

Content of HMN-initiated chains

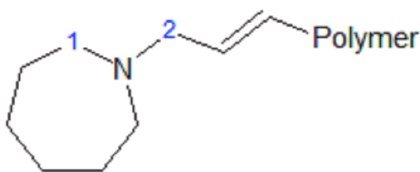
The content of HMN-initiated chains is determined by NMR analysis.

The samples (approximately 200 mg) are dissolved in approximately 1 ml of carbon disulfide (CS_2). 100 μl of deuterated cyclohexane are added to the solution for the lock of the spectrometer.

The spectra are acquired on a Bruker Avance 500 MHz spectrometer equipped with a BBI Z-grad "broad band" 5 mm cryoprobe.

The quantitative ^1H NMR experiment uses a simple 30° pulse sequence and a repetition time of 5 seconds between each acquisition. 64 to 1024 accumulations are carried out. Two-dimensional $^1\text{H}/^{13}\text{C}$ experiments were carried out in order to determine the structure of the functional polymers. The proton chemical shifts are calibrated with respect to the protonated impurity of the CS_2 at 7.18 ppm.

In the case of a butadiene homopolymer, or a polybutadiene, the quantitative simple pulse 1D ^1H NMR measurement makes it possible to observe two broad unresolved peaks (2.8 ppm to 3.0 ppm and 2.3 ppm to 2.5 ppm) respectively corresponding to the protons 1 and 2.



The integration of the protons 2 makes it possible to estimate the amount of HMN units grafted to a 1,4-butadiene and the integration of the protons 1 makes it possible to estimate the total amount of HMN units grafted to the polybutadiene chains.

In the case of a copolymer of butadiene and of styrene, the quantitative simple pulse 1D ^1H NMR measurement makes it possible to observe a single broad unresolved peak (2.8 ppm to 3.0 ppm) corresponding to the protons 2. The integration of the protons 2 makes it possible to estimate the amount of HMN units grafted to a 1,4-butadiene only. The signal of the protons 1 is masked by the aliphatic signal of the SBR matrix. In the case of an SBR, only the amount of HMN units grafted to a 1,4-butadiene can thus be estimated.

Thus, knowing the total amount of chains by the M_n value obtained by SEC analysis, it is possible to determine the content of HMN-initiated chains (only the HMN units bonded to a 1,4-butadiene unit are quantifiable in the case of copolymers of butadiene and of styrene).

Examples of preparation of elastomers

Methylcyclohexane, butadiene, styrene and tetrahydrofurfuryl ethyl ether are continuously introduced, according to the proportions described in each example, into a pilot-scale continuous polymerization plant containing one or more stirred continuous reactors, considered to be continuous stirred-tank reactors according to a person skilled in the art. n-Butyllithium is introduced in a sufficient amount in order to neutralize the protic impurities introduced by the different constituents present in the line input and then lithiated hexamethyleneimine is introduced in order to initiate the polymer chains. Lithiated hexamethyleneimine is synthesized in situ continuously by reaction of one equivalent of hexamethyleneimine and 1.02 equivalents of butyllithium in a reactor considered to be continuous stirred-tank reactor.

For Example D, a purification of the reinjected butadiene solution is carried out continuously by means of a column of aluminas. This column is packed with a fixed bed of aluminas of Axsorb 920 type.

The minimum L/D ratio of the fixed bed is 4.

The minimum column diameter/mean alumina particle diameter ratio is 10.

The empty-tank Reynolds number is greater than 2.

The minimum residence time of the fluid in the full column is 5 minutes.

The column is maintained under the following conditions:

- Temperature = 10°C

- Pressure = 5 bar.

The residence times and the concentrations indicated in the examples are calculated from the flow rates of the different constituents entering the polymerization process.

Example A – Comparative - Continuous process with 1 reactor

A synthesis of butadiene/styrene polymer is carried out according to a comparative process using 1 single stirred reactor considered to be continuous stirred-tank reactor.

The operating conditions are specified in Table 1.

Table 1

Operating conditions	Value	Unit	Reactor
Number of reactors	1	-	-
Volume of the reactors	14	l	1
% Styrene (1)	33	%	1
% Monomers by weight (2)	12	%	1
Polar agent (tetrahydro-furfuryl ethyl ether)	3.51×10^{-4}	mol/l	1
Active initiator (lithiated hexamethylene-imine)	6.45×10^{-4}	mol/l	1
Residence time	30	min	1
Temperature	90	°C	1
Conversion by weight (3)	87	%	1

(1) by weight, with respect to the sum of all the inputs by weight of monomers of the process

5 (2) by weight, with respect to the sum of all the inputs by weight of the process

(3) conversion by weight of monomers in the reactor

The characteristics of the polymer obtained at the outlet of the reactor are given in Table 2.

10

Table 2

Vinyl content (4)	25.5	%
Styrene content (5)	28	%
Tg	-45	°C
PI	2.0	-
M _n	123.2	kg/mol

Amount of HMN functional groups	6.1	mmol/kg
Content of HMN-initiated chains (6)	76	%
Amount of DEAB functional groups	4.2	mmol/kg
Content of living polymer (7)	51	%

(4) by weight, with respect to the butadiene units present in the polymer chains

(5) by weight, with respect to the butadiene and styrene units

5 (6) molar ratio of the amount of HMN functional groups, determined by NMR, to the number of chain ends, calculated from the M_n value measured on the elastomer recovered on conclusion of the stage of functionalization with DEAB.

10 (7) molar ratio of the amount of DEAB functional groups, determined by NMR, to the number of chain ends, calculated from the M_n value measured on the elastomer recovered on conclusion of the stage of functionalization with DEAB.

15 Thus, this comparative example shows that a low content of living polymer and a distribution of the molar masses which is broader than that targeted are obtained.

20 **Example B** – According to the invention - 2 reactors in series without reinjection

A synthesis of styrene/butadiene polymer is carried out according to a process according to the invention using 2 stirred reactors, considered to be continuous stirred-tank reactors, in series.

25 The operating conditions are specified in Table 3.

Table 3

Operating conditions	Value	Unit	Reactor
Number of reactors	2	-	-

Volume of the reactors	14	L	1
	14		2
% Styrene (1)	35	%	1
% Monomers by weight (2)	12	%	1
Polar agent (tetrahydrofurfuryl ethyl ether)	1.1×10^{-4}	mol/l	-
Active initiator (lithiated hexamethyleneimine)	5.54×10^{-4}	mol/l	1
Residence time	30	Min	1
	30	Min	2
Temperature	62	°C	1
	80	°C	2
Overall conversion by weight	60	%	1
	33	%	2
Intrinsic conversion by weight	60	%	1
Total conversion by weight	93	%	2

(1) by weight, with respect to the sum of all the inputs by weight of monomers of the process

(2) by weight, with respect to the sum of all the inputs by weight of the process

5 The characteristics of the polymer obtained at the outlet of the reactor 2 are given in Table 4.

Table 4

Vinyl content (3)	25	%
Styrene content (4)	29	%
T _g	-45	°C
M _n	153.4	kg/mol
PI	1.7	-
Amount of HMN functional groups	4.9	mmol/kg
Content of HMN-initiated chains (5)	75	%
Amount of DEAB functional groups	5.9	mmol/kg
Content of living polymer (6)	91	%

10 (3) by weight, with respect to the butadiene units present in the polymer chains

(4) by weight, with respect to the butadiene and styrene units

(5) molar ratio of the amount of HMN functional groups, determined by NMR, to the number of chain ends, calculated from the M_n value measured on the elastomer recovered on conclusion of the stage of functionalization with DEAB.

5 (6) molar ratio of the amount of DEAB functional groups, determined by NMR, to the number of chain ends, calculated from the M_n value measured on the elastomer recovered on conclusion of the stage of functionalization with DEAB.

10 Thus, this example shows that it is possible to concomitantly obtain, with the continuous process according to the invention, a high conversion, a high content of living polymer and a narrow distribution of the molar masses.

15

Example C – Comparative - 2 reactors in series with unpurified reinjection of butadiene

20 A synthesis of styrene/butadiene polymer is carried out according to a process according to the invention using 2 stirred reactors, considered to be continuous stirred-tank reactors, in series.

The reinjected butadiene is not purified. The operating conditions are specified in Table 5.

25

Table 5

Operating conditions	Value	Unit	Reactor
Number of reactors	2	-	-
Volume of the reactors	14	L	1
	14		2
% Styrene (1)	35	%	1
% Monomers by weight (2)	12	%	1
Polar agent (tetrahydrofurfuryl ethyl ether)	1.2×10^{-4}	mol/l	-
Active initiator (lithiated hexamethyleneimine)	5.76×10^{-4}	mol/l	1

Residence time	30	Min	1
	30	Min	2
Temperature	62	°C	1
	80	°C	2
Butadiene reinjection (3)	30	%	2
Overall conversion by weight	50	%	1
	42	%	2
Intrinsic conversion by weight	62	%	1
Total conversion by weight	92	%	2

- (1) by weight, with respect to the sum of all the inputs by weight of monomers of the process
- (2) by weight, with respect to the sum of all the inputs by weight of the process
- (3) by weight, with respect to the total weight of the monomers injected into all of the reactors

5

The characteristics of the polymer obtained at the outlet of the reactor 2 are given in Table 6.

10

Table 6

Vinyl content (4)	25	%
Styrene content (5)	28.5	%
T _g	-45.5	°C
M _n	146.0	kg/mol
PI	1.60	-
Amount of HMN functional groups	5.1	mmol/kg
Content of HMN-initiated chains (6)	75	%
Amount of DEAB functional groups	5.8	mmol/kg
Content of living polymer (7)	85	%

- (4) by weight, with respect to the butadiene units present in the polymer chains
- (5) by weight, with respect to the butadiene and styrene units
- (6) molar ratio of the amount of HMN functional groups, determined by NMR, to the number of chain ends, calculated from the M_n value measured

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on the elastomer recovered on conclusion of the stage of functionalization with DEAB.

5 (7) molar ratio of the amount of DEAB functional groups, determined by NMR, to the number of chain ends, calculated from the M_n value measured on the elastomer recovered on conclusion of the stage of functionalization with DEAB.

10 Thus, this example shows that, if the reinjection solution is not purified, then it is not possible to obtain the targeted content of living polymer and thus a high content of functionalized chains.

15 **Example D** – According to the invention - 2 reactors in series with purified reinjection of butadiene

A synthesis of styrene/butadiene polymer is carried out according to a process according to the invention using 2 stirred reactors, considered to be continuous stirred-tank reactors, in series.

20 The reinjected butadiene is purified by an alumina column. The operating conditions are specified in Table 7.

Table 7

Operating conditions	Value	Unit	Reactor
Number of reactors	2	-	-
Volume of the reactors	14	L	1
	14		2
% Styrene (1)	35	%	1
% Monomers by weight (2)	12	%	1
Polar agent (tetrahydrofurfuryl ethyl ether)	1.2×10^{-4}	mol/l	-
Active initiator (lithiated hexamethyleneimine)	5.76×10^{-4}	mol/l	1
Residence time	30	Min	1
	30	Min	2
Temperature	62	°C	1
	80	°C	2

Butadiene reinjection (3)	30	%	2
Overall conversion by weight	50	%	1
	42	%	2
Intrinsic conversion by weight	62	%	1
Total conversion by weight	92	%	2

(1) by weight, with respect to the sum of all the inputs by weight of monomers of the process

(2) by weight, with respect to the sum of all the inputs by weight of the process

(3) by weight, with respect to the total weight of the monomers injected into all of the reactors

5

The characteristics of the polymer obtained at the outlet of the reactor 2 are given in Table 8.

10

Table 8

Vinyl content (4)	25	%
Styrene content (5)	28.5	%
Tg	-45.5	°C
M _n	146.0	kg/mol
PI	1.6	-
Amount of HMN functional groups	5.1	mmol/kg
Content of HMN-initiated chains (6)	75	%
Amount of DEAB functional groups	6.4	mmol/kg
Content of living polymer (7)	93	%

(4) by weight, with respect to the butadiene units present in the polymer chains

(5) by weight, with respect to the butadiene and styrene units

15

(6) molar ratio of the amount of HMN functional groups, determined by NMR, to the number of chain ends, calculated from the M_n value measured on the elastomer recovered on conclusion of the stage of functionalization with DEAB.

(7) molar ratio of the amount of DEAB functional groups, determined by NMR, to the number of chain ends, calculated from the M_n value measured

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on the elastomer recovered on conclusion of the stage of functionalization with DEAB.

Thus, this example shows that it is possible to concomitantly obtain, with the continuous process according to the invention, a high conversion, a high content of living polymer and a narrow distribution of the molar masses.

Example E – According to the invention - 3 reactors in series with a temperature gradient and without reinjection of butadiene

A synthesis of butadiene/styrene polymer is carried out according to a process according to the invention using 3 stirred reactors, considered to be continuous stirred-tank reactors, in series.

The operating conditions are specified in Table 11.

Table 11

Operating conditions	Value	Unit	Reactor
Number of reactors	3	-	-
Volume of the reactors	14	l	1
	14		2
	14		3
% Styrene (1)	28	%	1
% Monomers by weight (2)	12	%	1
Polar agent (tetrahydrofurfuryl ethyl ether)	8.8×10^{-5}	mol/l	-
Active initiator (lithiated hexamethyleneimine)	5.86×10^{-4}	mol/l	1
Residence time	30	min	1
	30	min	2
	30	min	3
Temperature	50	°C	1
	70	°C	2
	80	°C	3
Overall conversion by	40	%	1

weight	30	%	2
	23	%	3
Total conversion by weight	93	%	3
Intrinsic conversion by weight	40	%	1

(1) by weight, with respect to the sum of all the inputs by weight of monomers of the process

(2) by weight, with respect to the sum of all the inputs by weight of the process

5 The characteristics of the polymer obtained at the outlet of the reactor 3 are given in Table 12.

Table 12

10

Vinyl content (3)	25.5	%
Styrene content (4)	27.5	%
Tg	-46	°C
PI	1.45	-
M _n	146.2	kg/mol
Amount of HMN functional groups	5.3	mmol/kg
Content of HMN-initiated chains (5)	77	%
Amount of DEAB functional groups	6.5	mmol/kg
Content of living polymer (6)	95	%

(3) by weight, with respect to the butadiene units present in the polymer chains

(4) by weight, with respect to the butadiene and styrene units

15 (5) molar ratio of the amount of HMN functional groups, determined by NMR, to the number of chain ends, calculated from the M_n value measured on the elastomer recovered on conclusion of the stage of functionalization with DEAB.

(6) molar ratio of the amount of DEAB functional groups, determined by NMR, to the number of chain ends, calculated from the M_n value measured

on the elastomer recovered on conclusion of the stage of functionalization with DEAB.

5 Thus, this example shows that it is possible to concomitantly obtain, with the continuous process according to the invention, a high conversion, a high content of living polymer and a narrow distribution of the molar masses.

CLAIMS

1. Process for the continuous synthesis of a diene elastomer by means of n reactors r1 to rn, considered to be continuous stirred-tank reactors, which are equipped with an internal stirring system and which are arranged in series, n varying from 2 to 15, preferably from 2 to 9, the reactor r1 being fed by an input solution comprising a solvent, one or more monomer(s), an anionic polymerization initiator chosen from lithium amides and a polar agent, one or more of the reactors r2 to rn additionally being optionally fed by reinjection of a purified solution comprising solvent and/or monomer(s) and/or polar agent, the temperature of each reactor varying from 20°C to 150°C, preferably varying from 30°C to 120°C, and being greater than or equal to the temperature of the reactor which immediately precedes it, the temperature of the reactor rn being greater than the temperature of the reactor r1, the amount by weight W_1 of monomer(s) introduced into the reactor r1 being such that:

$$0.1 < \frac{W_1}{\sum_{j=1}^n W_j} \leq 1$$

the amount by weight W_i of monomer(s) reinjected into the reactor ri, when $W_i \neq 0$, i varying from 2 to n, being such that:

$$0 < \frac{W_i}{\sum_{j=1}^n W_j} < 0.9$$

and such that W_i represents from 5% to 100% by weight of the weight of the solution reinjected into the reactor ri, when $W_i \neq 0$,

where W_j is the amount by weight of monomer(s) introduced into the reactor rj, j varying from 1 to n,

the amount by weight of all of the monomers entering the reactors r1 to rn representing from 5% to 25% by weight of the sum of the total inputs by weight of the reactors r1 to n,

the intrinsic conversion by weight $C_{\text{intrinsic},1}$ in the first reactor being less than 70%,

where $C_{intrinsic,1} = P_1/W_1$
 where P_1 is the weight of polymer formed in the reactor r1,
 the total conversion by weight C_{tot} at the outlet of the reactor rn being
 greater than or equal to 70%,

5

where:

$$C_{tot} = \frac{\sum_{i=1}^n P_i}{\sum_{j=1}^n W_j}$$

where P_i is the weight of polymer formed in the reactor ri,

10

the overall conversion by weight $C_{overall\ i}$ in each reactor ri, with i varying
 from 1 to n, being such that:

$$\frac{C_{tot}}{n} - 0.2 \times C_{tot} < C_{overall\ i} < \frac{C_{tot}}{n} + 0.2 \times C_{tot}$$

and $C_{overall\ i} > 0$

15

where:

$$C_{overall\ i} = \frac{P_i}{\sum_{j=1}^n W_j}$$

20

where P_i is the weight of polymer formed in the reactor ri, i varying from 1
 to n,

the diene elastomer obtained exhibiting a polydispersity index varying from
 1.1 to 1.7, preferably varying from 1.2 to 1.6.

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2. Process according to Claim 1, characterized in that the temperature in at
 least one reactor ri is greater than the temperature of the reactor ri-1; preferably, the
 temperature of each reactor ri is greater than the temperature of the reactor ri-1, i
 varying from 2 to n.

3. Process according to Claim 1 or 2, characterized in that n varies from 2 to 3, preferably $n = 2$.

5 4. Process according to any one of the preceding claims, characterized in that the intrinsic conversion by weight $C_{\text{intrinsic},1}$ in the reactor $r1$ is less than 65%, preferably less than 60%.

10 5. Process according to any one of the preceding claims, characterized in that the total conversion by weight C_{tot} at the outlet of the reactor rn is greater than or equal to 80%, preferably greater than or equal to 85%.

15 6. Process according to any one of the preceding claims, characterized in that one or more of the reactor(s) $r2$ to rn is additionally fed by reinjection of a purified solution comprising solvent and/or monomer(s) and/or polar agent.

20 7. Process according to any one of the preceding claims, characterized in that the solution(s) to be reinjected or independently the or each constituent of the reinjected solution(s) is/are, before reinjection, purified by adsorption, liquid/liquid extraction, gas/liquid extraction, or distillation.

25 8. Process according to Claim 7, characterized in that the residues from the process(es) for the purification of the or each constituent or of the solution(s) to be reinjected are reinjected into the input solution feeding the first reactor.

30 9. Process according to Claim 8, characterized in that the residues from the process(es) for the purification of the or each constituent or of the solution(s) to be reinjected constitute an extra contribution of monomer and/or of solvent and/or of polar agent to the input solution.

35 10. Process according to Claim 8, characterized in that the residues from the process(es) for the purification of the or each constituent or of the solution(s) to be reinjected constitute the sole source of monomer and/or of solvent and/or of polar agent of the input solution.

11. Process according to any one of the preceding claims, characterized in that the residence time in the reactor r_i , i varying from 1 to n , is between 1 and 60 minutes, preferably between 5 and 60 minutes, more preferably between 10 and 50 minutes.

5

12. Process according to any one of the preceding claims, characterized in that the output stream from the reactor r_n containing the living chains is brought into contact with one or more agents for stopping polymerization injected continuously into the process.

10

13. Process according to Claim 12, characterized in that the living diene elastomer included in the output stream from the reactor n , before reaction with the stopping agent, is reacted with one or more functionalization, coupling or star-branching agents.

15

14. Process according to any one of Claims 1 to 11, characterized in that the living diene elastomer included in the output stream from the reactor n is reacted with one or more functionalization, coupling or star-branching agents.