CLAIMS

1. A process for the preparation of diene polymers or random vinyl arene-diene copolymers which comprises (co)polymerizing, anionically, in the presence of at least one hydrocarbon solvent, at least one conjugated diene monomer and, optionally, at least one vinyl arene, in the presence of at least one lithium-based initiator, at least one aprotic polar compound, and at least one compound containing one or more functional groups of the acetylenic type selected from compounds having general formula (II):

$$R_2-(C\equiv C-H)_n \quad (II)$$

wherein R_2 represents a hydrogen atom, or is selected from linear or branched C_1-C_{20} alkyl groups, C_3-C_{20} cycloalkyl groups, C_6-C_{20} aryl groups, said alkyl, cycloalkyl and aryl groups optionally containing one or more heteroatoms such as oxygen, nitrogen, silicon, and n is an integer ranging from 1 to 10.

2. The process for the preparation of diene polymers or random vinyl arene-diene copolymers according to claim 1, wherein said hydrocarbon solvent is selected from aliphatic or aromatic hydrocarbon solvents such as n-pentane, n-hexane, n-heptane, cyclohexane, or mixtures thereof.

3. The process for the preparation of diene polymers or random vinyl arene-diene copolymers according to claim 1 or 2, wherein said conjugated diene monomer is selected from conjugated diene monomers having

from 4 to 12 carbon atoms such as 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene (piperylene), 2-methyl-3-ethyl-1,3-butadiene, 1,3-octadiene.

4. The process for the preparation of diene polymers or random vinyl arene-diene copolymers according to any of the previous claims, wherein said vinyl arene is selected from: styrene, α-methylstyrene, 1-vinyl-naphthalene, 2-vinyl-naphthalene, or their alkyl derivates, or mixtures thereof.

5. The process for the preparation of diene polymers or random vinyl arene-diene copolymers according to any of the previous claims, wherein said process is carried out in the presence of:

- 60% by weight - 100% by weight, with respect to the total weight of the conjugated diene monomer and of the optional vinyl arene, of at least one conjugated diene monomer;
- 0% by weight - 40% by weight, with respect to the total weight of the conjugated diene monomer and of the optional vinyl arene, of at least one vinyl arene.

6. The process for the preparation of diene polymers or random vinyl arene-diene copolymers according to any of the previous claims, wherein said lithium-based initiator is selected from compounds having general formula (I):

$$R_1(Li)_m \quad (I)$$

wherein R_1 represents a linear or branched C_1-C_{20} alkyl group and m is an integer ranging from 1 to

6.

7. The process for the preparation of diene polymers or random vinyl arene-diene copolymers according to claim 6, wherein said lithium-based initiator is selected from: lithium-*n*-butyl, lithium-*n*-propyl, lithium-*iso*-butyl, lithium-*tert*-butyl, or mixtures thereof.

8. The process for the preparation of diene polymers or random vinyl arene-diene copolymers according to any of the previous claims, wherein said lithium-based initiator is used in a quantity ranging from 0.005% by weight to 0.08% by weight with respect to the total weight of the monomers used (i.e. conjugated diene monomer and optional vinyl arene).

9. The process for the preparation of diene polymers or random vinyl arene-diene copolymers according to any of the previous claims, wherein said aprotic polar compound is selected from: non-cyclic ethers such as ethyl ether; cyclic ethers such as tetrahydrofuran (THF); chelating ethers, such as ethylene glycol dimethyl ether (dimethylglyme), dioxane, 2-methoxyethyl-tetrahydrofuran (THFA-ethyl), 2-methoxyethyl-tetrahydropyrane (THPA-ethyl); tertiary amines such as tributylamine; chelating amines such as N,N,N',N'-tetramethylene-ethylenediamine (TMEDA).

10. The process for the preparation of diene polymers or random vinyl arene-diene copolymers according to any of the previous claims, wherein said aprotic polar compound is used in a quantity ranging from

0.10 moles to 100 moles per mole of lithium-based initiator.

11. The process for the preparation of diene polymers or random vinyl arene-diene copolymers according to any of the previous claims, wherein said compound containing one or more functional groups of the acetylenic type is used in such a quantity that the molar ratio between the lithium-based initiator active in the (co)polymerization and the compound having general formula (II), after the above metalation reaction, ranges from 20 to 0.1.

12. The process for the preparation of diene polymers or random vinyl arene-diene copolymers according to any of the previous claims, wherein said lithium-based initiator and said compound containing one or more functional groups of the acetylenic type are reacted with each other (i.e. metalation reaction) before being used in said process.

13. The process for the preparation of diene polymers or random vinyl arene-diene copolymers according to any of the previous claims, wherein said compound containing one or more functional groups of the acetylenic type is selected from: acetylene, 1-propine, 1-butine, 3-methyl-1-butine, *tert*-butylacetylene (or 3,3'-dimethyl-1-butine), 1-heptine, 1-octine, cyclopropylacetylene, cyclopentylacetylene, cyclohexylacetylene, 2-ethinyltoluene, 3-ethinyltoluene, 4-ethinyltoluene, trimethylsilylacetylene, 1,6-heptadine, 1,7-octadine, 1,8-nonadine,

propargylether (or dipropinylether), diethinylether, or mixtures thereof.

14. The process for the preparation of diene polymers or random vinyl arene-diene copolymers according to any of the previous claims, wherein said process is carried out in continuous.

15. The process for the preparation of diene polymers or random vinyl arene-diene copolymers according to claim 14, wherein said process is carried out in one or more reactors in series, under isotherm conditions, operating within a temperature range of 30°C to 120°C, with a control of ±5°C and with overall residence times ranging from 30 minutes to 130 minutes.

16. Use of diene polymers or random vinyl arene-diene copolymers obtained with the process according to any of the claims from 1 to 15, in the production of tyres, in particular in the production of tyre treads.

17. Use of diene polymers or random vinyl arene-diene copolymers obtained with the process according to any of the claims from 1 to 15, in the modification of plastic materials.

CLAIMS

1. A process for the preparation of diene polymers or random vinyl arene-diene copolymers which comprises (co)polymerizing, anionically, in the presence of at least one hydrocarbon solvent, at least one conjugated diene monomer and, optionally, at least one vinyl arene, in the presence of at least one lithium-based initiator, at least one aprotic polar compound, and at least one compound containing one or more functional groups of the acetylenic type selected from compounds having general formula (II):

$$R_2—(C\equiv C—H)_n \quad (II)$$

wherein R_2 represents a hydrogen atom, or is selected from linear or branched C_1-C_{20} alkyl groups, C_3-C_{20} cycloalkyl groups, C_6-C_{20} aryl groups, said alkyl, cycloalkyl and aryl groups optionally containing one or more heteroatoms such as oxygen, nitrogen, silicon, and n is an integer ranging from 1 to 10,

carrying out a metalation reaction between said lithium-based initiator and said compound containing one or more functional group of the acetylenic type to form lithium acetylide having general formula (III) which is present at the start of (co)polymerization:

$$R_2-(C\equiv C^-Li^+)_n \quad (III)$$

wherein R2 has the same meanings above reported.

2. The process for the preparation of diene polymers or random vinyl arene-diene copolymers according to claim 1, wherein said hydrocarbon solvent is selected from aliphatic or aromatic hydrocarbon solvents such as n-pentane, n-hexane, n-heptane, cyclohexane, or mixtures thereof.

3. The process for the preparation of diene polymers or random vinyl arene-diene copolymers according to claim 1 or 2, wherein said conjugated diene monomer is selected from conjugated diene monomers having from 4 to 12 carbon atoms such as 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene (piperylene), 2-methyl-3-ethyl-1,3-butadiene, 1,3-octadiene.

4. The process for the preparation of diene polymers or random vinyl arene-diene copolymers according to any of the previous claims, wherein said vinyl arene is selected from: styrene, α-methylstyrene, 1-vinyl-naphthalene, 2-vinyl-naphthalene, or their alkyl derivates, or mixtures thereof.

5. The process for the preparation of diene polymers or random vinyl arene-diene copolymers according to any of the previous claims, wherein said process is carried out in the presence of:

- 60% by weight - 100% by weight, with respect to the total weight of the conjugated diene monomer and of the optional vinyl arene, of at least one conjugated diene monomer;

- 0% by weight - 40% by weight, with respect to the total weight of the conjugated diene monomer and of the optional vinyl arene, of at least one vinyl arene.

6. The process for the preparation of diene polymers or random vinyl arene-diene copolymers according to any of the previous claims, wherein said lithium-based initiator is selected from compounds having general formula (I):

$$R_1(Li)_m \quad (I)$$

wherein R_1 represents a linear or branched C_1-C_{20} alkyl group and m is an integer ranging from 1 to 6.

7. The process for the preparation of diene polymers or random vinyl arene-diene copolymers according to claim 6, wherein said lithium-based initiator is selected from: lithium-*n*-butyl, lithium-*n*-propyl, lithium-*iso*-butyl, lithium-*tert*-butyl, or mixtures thereof.

8. The process for the preparation of diene polymers or random vinyl arene-diene copolymers according to any of the previous claims, wherein said lithium-based initiator is used in a quantity ranging from 0.005% by weight to 0.08% by weight with respect to the total weight of the monomers used (i.e. conjugated diene monomer and optional vinyl arene).

9. The process for the preparation of diene polymers or random vinyl arene-diene copolymers according to any of the previous claims, wherein said aprotic

polar compound is selected from: non-cyclic ethers such as ethyl ether; cyclic ethers such as tetrahydrofuran (THF); chelating ethers, such as ethylene glycol dimethyl ether (dimethylglyme), dioxane, 2-methoxyethyl-tetrahydrofuran (THFA-ethyl), 2-methoxyethyl-tetrahydropyrane (THPA-ethyl); tertiary amines such as tributylamine; chelating amines such as N,N,N',N'-tetramethylene-ethylenediamine (TMEDA).

10. The process for the preparation of diene polymers or random vinyl arene-diene copolymers according to any of the previous claims, wherein said aprotic polar compound is used in a quantity ranging from 0.10 moles to 100 moles per mole of lithium-based initiator.

11. The process for the preparation of diene polymers or random vinyl arene-diene copolymers according to any of the previous claims, wherein said compound containing one or more functional groups of the acetylenic type is used in such a quantity that the molar ratio between the lithium-based initiator active in the (co)polymerization and the compound having general formula (II), after the above metalation reaction, ranges from 20 to 0.1.

12. The process for the preparation of diene polymers or random vinyl arene-diene copolymers according to any of the previous claims, wherein said lithium-based initiator and said compound containing one or more functional groups of the acetylenic type are

reacted with each other (i.e. metalation reaction) before being used in said process.

13. The process for the preparation of diene polymers or random vinyl arene-diene copolymers according to any of the previous claims, wherein said compound containing one or more functional groups of the acetylenic type is selected from: acetylene, 1-propine, 1-butine, 3-methyl-1-butine, *tert*-butylacetylene (or 3,3'-dimethyl-1-butine), 1-heptine, 1-octine, cyclopropylacetylene, cyclopentylacetylene, cyclohexylacetylene, 2-ethinyltoluene, 3-ethinyltoluene, 4-ethinyltoluene, trimethylsilylacetylene, 1,6-heptadine, 1,7-octadine, 1,8-nonadine, propargylether (or dipropinylether), diethinylether, or mixtures thereof.

14. The process for the preparation of diene polymers or random vinyl arene-diene copolymers according to any of the previous claims, wherein said process is carried out in continuous.

15. The process for the preparation of diene polymers or random vinyl arene-diene copolymers according to claim 14, wherein said process is carried out in one or more reactors in series, under isotherm conditions, operating within a temperature range of 30°C to 120°C, with a control of $\pm$5°C and with overall residence times ranging from 30 minutes to 130 minutes.

16. Use of diene polymers or random vinyl arene-diene

copolymers obtained with the process according to any of the claims from 1 to 15, in the production of tyres, in particular in the production of tyre treads.

17. Use of diene polymers or random vinyl arene-diene copolymers obtained with the process according to any of the claims from 1 to 15, in the modification of plastic materials.