CLAIMS

1. A process for the preparation a random butadiene-isoprene copolymer having a high content of *cis*-1,4 units comprising copolymerizing butadiene and isoprene in the presence of at least one organic solvent and of a catalytic system prepared *in situ* comprising:

   (a_1) at least one neodymium carboxylate which is soluble in said organic solvent, containing a variable amount of water, the H_2O/Nd molar ratio being between 0.001/1 and 0.50/1;

   (a_2) at least one aluminum alkyl compound; and

   (a_3) at least one aluminum alkyl compound containing at least one halogen atom;

   in which the molar ratio between the halogen present in the aluminum alkyl compound containing at least one halogen atom (a_3) and the neodymium carboxylate (a_1) is between 2.5/1 and 5.5/1.

2. The process for the preparation of a random butadiene-isoprene copolymer having a high content of *cis*-1,4 units according to claim 1, in which said butadiene and said isoprene are present in a total amount (i.e. butadiene amount + isoprene amount) between 5% by weight and 40% by weight, preferably between 10% by weight and 25% by weight, with respect to the total weight of the organic solvent.

3. The process for the preparation of a random butadiene-isoprene copolymer having a high content of *cis*-1,4 units according to claim 1 or 2, in which said organic solvent is selected from: saturated aliphatic hydrocarbons such as butane, *n*-pentane, *n*-hexane, *n*-heptane, or mixtures thereof; saturated cycloaliphatic hydrocarbons such as cyclohexane, cyclopentane, or mixtures thereof; monoolefins such as 1-butene, 2-butene, or mixtures thereof; halogenated hydrocarbons such as methylene chloride, chloroform, carbon tetrachloride, trichlorethylene,

perchlorethylene, 1,2-dichloroethane, chlorobenzene, bromobenzene, chlorotoluene, or mixtures thereof; preferably, said organic solvent is selected from saturated aliphatic hydrocarbons, more preferably from: *n*-hexane; a mixture comprising 35% by weight with respect to the total weight of the mixture of *n*-hexane and 65% by weight with respect to the total weight of the mixture of a mixture comprising *n*-hexane isomers, aliphatic compounds and cycloaliphatic compounds.

4. The process for the preparation of a random butadiene-isoprene copolymer having a high content of *cis*-1,4 units according to any one of the previous claims, in which said neodymium carboxylate (a_1) is neodymium versatate [Nd (versatate)$_3$]; preferably said neodymium versatate [Nd(versatate)$_3$] has a free versatic acid/Nd molar ratio of less than 2, more preferably less than 0.5.

5. The process for the preparation of a random butadiene-isoprene copolymer having a high content of *cis*-1,4 units according to any one of the previous claims, in which said neodymium carboxylate is used in an amount of between 0.1 mmoles to 10 mmoles, preferably between 0.5 mmol and 5 mmol, per 1000 g of monomers (butadiene + isoprene) being polymerized.

6. The process for the preparation of a random butadiene-isoprene copolymer having a high content of *cis*-1,4 units according to any one of the previous claims, in which said aluminum alkyl compound (a_2) is selected from compounds having general formula (I) or (II):

$$Al(R^1)_3 \text{ (I)}$$

$$AlH(R^1)_2 \text{ (II)}$$

in which R^1 represents a linear or branched C_1-C_{10} alkyl group, preferably from triethyl aluminum (TEA), tri-isobutyl aluminum, diethyl aluminum hydride, di-isobutyl

aluminum hydride (DIBAH); more preferably it is di-isobutyl aluminum hydride (DIBAH).

7. The process for the preparation of a random butadiene-isoprene copolymer having a high content of *cis*-1,4 units according to any one of the previous claims, in which said alkyl aluminum compound containing at least one halogen atom (a_3) is selected from compounds having general formula (III):

$$AlXnR^2_{3-n} \text{ (III)}$$

in which R^2 represents a linear or branched C_1-C_{10} alkyl group, X represents a halogen atom such as chlorine, bromine, fluorine, iodine, preferably chlorine, n is 1 or 2; preferably from diethyl aluminum chloride (DEAC), ethyl aluminum sesquichloride (EASC); more preferably it is diethyl aluminum chloride (DEAC).

8. The process for the preparation of a random butadiene-isoprene copolymer having a high content of *cis*-1,4 units according to any one of the previous claims, in which the molar ratio between the aluminum alkyl compound (a_2) and the neodymium carboxylate (a_1) is between 1/1 and 30/1, preferably between 1/1 and 10/1.

9. The process for the preparation of a random butadiene-isoprene copolymer having a high content of *cis*-1,4 units according to any one of the previous claims, in which the molar ratio between the halogen present in the aluminum alkyl compound containing at least one halogen atom (a_3) and the neodymium carboxylate (a_1) is between 2.8/1 and 5.2/1.

10. The process for the preparation of a random butadiene-isoprene copolymer having a high content of *cis*-1,4 units according to any one of the previous claims, in which the aluminum compound containing at least one halogen atom (a_3) is used in such an amount that the ratio between the halogen present in said compound (a_3) and the aluminum alkyl compound (a_2) is between 0.4 and 5, more preferably between

0.5 and 2.0.

11. The process for the preparation of a random butadiene-isoprene copolymer having a high content of *cis*-1,4 units according to any one of the previous claims, in which said method is carried out:
    - at a temperature of between 20°C and 150°C, preferably between 40°C and 120°C; and/or
    - at a pressure of between 1 bar and 10 bar, preferably between 3 bar and 7 bar.

12. The random butadiene-isoprene copolymer having a high content of *cis*-1,4 units having the following characteristics:
    - *cis*-1,4-butadiene units content greater than or equal to 92%;
    - *cis*-1,4-isoprene units content greater than or equal to 92%;
    - isoprene randomization index (R.I.) calculated according to the following equation:

      R.I. = [(BI + IB)/2]/total moles of bound isoprene

      in which BI and IB are the amounts of butadiene-isoprene and isoprene-butadiene dyad, respectively, present in the random butadiene-isoprene copolymer having a high content of *cis*-1,4 units, of between 0.5 and 1;
    - a weight ratio (% by weight) between bound butadiene and bound isoprene of between 99:1 and 40:60;
    - a single glass transition temperature value (Tg), an indicator of the actual randomization of both comonomers, of between -107 °C to -65 °C;
    - a Mooney viscosity (ML1+ 4@100 °C) of between 30 and 70;
    - a molecular weight distribution, indicated as a polydispersion index corresponding to the ratio between the weight average molecular weight (M_w)

and the number average molecular weight (M_n) (i.e. the ratio M_w/M_n) of between 2.0 and 3.2.

13. The random butadiene-isoprene copolymer having a high content of *cis*-1,4 units according to claim 12, having the following characteristics:

- *cis*-1,4-butadiene units content between 95% and 99%;
- *cis*-1,4-isoprene units content between 95% and 99.95%;
- isoprene randomization index (R.I.) calculated according to the following equation:

$$R.I. = [(BI + IB)/2]/\text{total moles of bound isoprene}$$

in which BI and IB are the amounts of butadiene-isoprene and isoprene-butadiene dyad, respectively, present in the random butadiene-isoprene copolymer having a high content of *cis*-1,4 units, of between 0.6 and 0.9;

- a weight ratio (% by weight) between bound butadiene and bound isoprene of between 90:10 and 45:55;
- a single glass transition temperature value (Tg), an indicator of the actual randomization of both comonomers, of between -105 °C and -85 °C;
- a Mooney viscosity (ML1+ 4@100 °C) of between 35 and 65;
- a molecular weight distribution, indicated as a polydispersion index corresponding to the ratio between the weight average molecular weight (M_w) and the number average molecular weight (M_n) (i.e. the ratio M_w/M_n) of between 2.0 and 3.2.

14. A vulcanizable elastomer composition comprising at least one random butadiene-isoprene copolymer having a high content of *cis*-1,4 units according to claim 12 or 13, at least one filler selected from silica, carbon black, or mixtures thereof, and at least one vulcanizing agent.

15. A vulcanized product obtained from vulcanization of the vulcanizable elastomer composition according to claim 14.