The Applicant has also found that said process, by varying the type of monodentate aromatic phosphine, allows the crystallinity of the block having a syndiotactic 1,2 structure [namely, the content of syndiotactic triads [(rr)%]] to be modulated and, consequently, the melting point (T_m), in the stereoregular diblock polybutadiene obtained, depending on the characteristics of the end-product to be obtained.

An object of the present invention therefore relates to a stereoregular diblock polybutadiene composed of a polybutadiene block with a 1,4-*cis* structure and a polybutadiene block with a syndiotactic 1,2 structure, having the following formula (I):

$$PB_1\text{-}PB_2 \quad (I)$$

wherein:

- PB_1 corresponds to the polybutadiene block having a 1,4-*cis* structure;
- PB_2 corresponds to the polybutadiene block having a syndiotactic 1,2 structure;

essentially free of 1,4-*trans* units.

A further object of the present invention relates to stereoregular diblock polybutadiene composed of a polybutadiene block having a 1,4-*cis* structure and a polybutadiene block having a 1,2 syndiotactic structure, having the following formula (I):

$$PB_1\text{-}PB_2 \quad (I)$$

wherein:

- PB_1 corresponds to the polybutadiene block having a

1,4-*cis* structure;

- PB_2 corresponds to the polybutadiene block having a 1,2 syndiotactic structure;

having a content of 1,4-*trans* units lower than 3% molar.

For the aim of the present description and of the following claims, the term "stereoregular diblock polybutadiene" means a polybutadiene in which only two polybutadiene blocks are present, having a different structure, i.e. a 1,4-*cis* structure and a syndiotactic 1,2 structure, joined to each other through a single junction and not interpenetrated.

For the aim of the present description and of the

stereoregular diblock polybutadiene composed of a polybutadiene block having a 1,4-*cis* structure and a polybutadiene block having a syndiotactic 1,2 structure.

A further object of the present invention therefore relates to a process for the preparation of a stereoregular diblock polybutadiene composed of a polybutadiene block having a 1,4-*cis* structure and a polybutadiene block having a syndiotactic 1,2 structure, which comprises:

- subjecting 1,3-butadiene to total or partial stereospecific polymerization in the presence of a catalytic system comprising at least one complex of cobalt with at least one phosphine ligand selected from hindered aliphatic phosphines or bidentate phosphines, in order to obtain polybutadiene with a living 1,4-*cis* structure;
- adding at least one monodentate aromatic phosphine and optionally 1,3-butadiene, and continuing said stereospecific polymerization, in order to obtain said stereoregular diblock polybutadiene composed of a polybutadiene block having a 1,4-*cis* structure and a polybutadiene block having a 1,2 syndiotactic structure.

Yet another object of the present invention relates to a process for the preparation of a stereoregular diblock polybutadiene as disclosed herein, comprising:

- subjecting 1,3-butadiene to total or partial stereospecific polymerization in the presence of a catalytic system comprising at least one complex of cobalt with at least one phosphine ligand selected from hindered aliphatic phosphines or bidentate phosphines, in order to obtain polybutadiene with a 1,4-*cis* living structure;

- adding at least one monodentate aromatic phosphine and optionally 1,3-butadiene, and continuing said stereospecific polymerization, in order to obtain said stereoregular diblock polybutadiene composed of a polybutadiene block having a 1,4-*cis* structure and a polybutadiene block having a 1,2 syndiotactic structure.

According to a preferred embodiment of the present invention, said complex of cobalt with at least one phosphine ligand selected from hindered aliphatic phosphines or bidentate phosphines can be selected from complexes of cobalt having general formula (I) or (II):

CLAIMS

1. Stereoregular diblock polybutadiene composed of a polybutadiene block having a 1,4-*cis* structure and a polybutadiene block having a 1,2 syndiotactic structure, having the following formula (I):

PB_1-PB_2 (I)

wherein:

- PB_1 corresponds to the polybutadiene block having a 1,4-*cis* structure;
- PB_2 corresponds to the polybutadiene block having a 1,2 syndiotactic structure;

having a content of 1,4-*trans* units lower than 3% molar.

2. The stereoregular diblock polybutadiene according to claim 1, wherein said stereoregular diblock polybutadiene has the following characteristics:

- upon infrared analysis (FT-IR), bands typical of the 1,4-*cis* and 1,2 sequences centered at 737 cm^{-1} and at 911 cm^{-1}, respectively;
- upon ^{13}C-NMR analysis, signals characteristic of the junctions between the polybutadiene block having a 1,4-*cis* structure and the polybutadiene block having a 1,2 structure at 30.7 ppm, at 25.5 ppm and at 41.6 ppm.

3. The stereoregular diblock polybutadiene according to claim 1 or 2, wherein, in said stereoregular diblock polybutadiene:

- the block having a 1,4-*cis* structure has a glass transition temperature (T_g) lower than or equal to

-100°C, a melting point (T_m) lower than or equal to -2°C and a crystallization temperature (T_c) lower than or equal to -25°C;

- the block having a 1,2 syndiotactic structure has a glass transition temperature (T_g) lower than or equal to -10°C, a melting point (T_m) higher than or equal to 70°C and a crystallization temperature (T_c) higher than or equal to 55°C.

4. The stereoregular diblock polybutadiene according to any of the previous claims, wherein said stereoregular diblock polybutadiene has a polydispersion index (PDI) corresponding to a M_w/M_n ratio (M_w = weight average molecular weight; M_n = number average molecular weight) ranging from 1.9 to 2.2.

5. The stereoregular diblock polybutadiene according to any of the previous claims, wherein in said stereoregular diblock polybutadiene, the polybutadiene block having a 1,4-*cis* structure is amorphous, at room temperature under quiescent conditions not subjected to stress and has a 1,4-*cis* content higher than or equal to 96% molar,

with respect to the total molar quantity of butadiene units present in said polybutadiene block having a 1,4-*cis* structure.

6. The stereoregular diblock polybutadiene according to any of the previous claims, wherein in said stereoregular diblock polybutadiene, the polybutadiene block having a 1,2 syndiotactic structure has a content of syndiotactic triads [(rr) %] higher than or equal to 15%.

7. The stereoregular diblock polybutadiene according to any of the previous claims, wherein in said stereoregular diblock polybutadiene, the 1,4-*cis*/1,2 molar ratio ranges from 15:85 to 80:20.

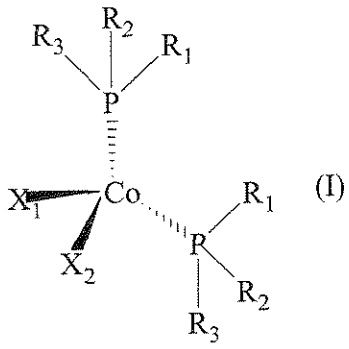
8. The stereoregular diblock polybutadiene according to any of the previous claims, wherein said stereoregular diblock polybutadiene has a weight average molecular weight (M_w) ranging from 100,000 g/mol to 800,000 g/mol.

9. A process for the preparation of a stereoregular diblock polybutadiene according to any of the previous claims, comprising:

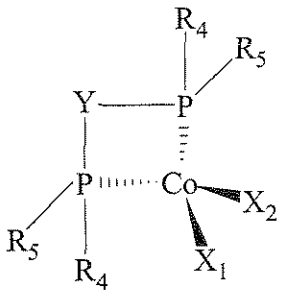
- subjecting 1,3-butadiene to total or partial stereospecific polymerization in the presence of a catalytic system comprising at least one complex of cobalt with at least one phosphine ligand selected from hindered aliphatic phosphines or bidentate phosphines, in order to obtain polybutadiene with a 1,4-*cis* living structure;

- adding at least one monodentate aromatic phosphine and optionally 1,3-butadiene, and continuing said stereospecific polymerization, in order to obtain said stereoregular diblock polybutadiene composed of a polybutadiene block having a 1,4-*cis* structure and a polybutadiene block having a 1,2 syndiotactic structure.

10. The process according to claim 9, wherein said complex of cobalt with at least one phosphine ligand selected from hindered aliphatic phosphines or bidentate phosphines, is selected from cobalt complexes having general formulae (I) or (II):



(I)



(II)

wherein:

- R_1 and R_2, the same or different, are selected from linear or branched C_1-C_{20}alkyl groups, C_3-C_{30} cycloalkyl groups;

- R_3 is selected from linear or branched C_1-C_{20}—alkyl groups, C_3-C_{30} cycloalkyl groups;
- R_4 and R_5, the same or different, are selected from linear or branched C_1-C_{20} alkyl groups, C_3-C_{30} cycloalkyl groups, C_6-C_{30} aryl groups, more preferably are selected from methyl, ethyl, *n*-propyl, *iso*-propyl, *tert*-butyl, cyclopentyl, cyclohexyl, phenyl;
- Y represents a divalent group $-(CH_2)_n-$, wherein n is an integer ranging from 1 to 5; or a divalent group $-NR_6-$ wherein R_6 represents a hydrogen atom, or a linear or branched C_1-C_{20} alkyl group, more preferably is a hydrogen atom; or a divalent group $-(CH_2)_m-R'-(CH_2)_m-$ wherein R' represents an aryl group optionally substituted;

- X_1 and X_2, the same or different, represent a halogen atom; or they are selected from linear or branched C_1-C_{20} alkyl groups, $-OCOR_7$ groups or $-OR_7$ groups wherein R_7 is selected from linear or branched C_1-C_{20} alkyl groups.

11. The process according to claim 9 or 10, wherein said catalytic system comprises at least one co-catalyst selected from organic compounds of an element M' different from carbon, said element M' being selected from elements belonging to groups 2, 12, 13 or 14 of the Periodic Table of the Elements.

12. The process according to claim 11, wherein said co-catalyst is selected from aluminium alkyls having

general formula (III):

$$Al(X')_n(R_8)_{3-n} \quad (III)$$

wherein X' represents a halogen atom such as chlorine, bromine, iodine, fluorine; R_8 is selected from linear or branched C_1-C_{20} alkyl groups, cycloalkyl groups, aryl groups, said groups being optionally substituted with one or more silicon or germanium atoms; and n is an integer ranging from 0 to 2.

13. The process according to claim 11, wherein said co-catalyst is selected from organo-oxygenated compounds of an element M' different from carbon belonging to groups 13 or 14 of the Periodic Table of the Elements, such as from aluminoxanes having general formula (IV):

$$(R_9)_2\text{-}Al\text{-}O\text{-}[\text{-}Al(R_{10})\text{-}O\text{-}]_p\text{-}Al\text{-}(R_{11})_2 \quad (IV)$$

wherein R_9, R_{10} and R_{11}, the same or different, represent a hydrogen atom, a halogen atom such as chlorine, bromine, iodine, fluorine; or they are selected from linear or branched C_1-C_{20} alkyl groups, cycloalkyl groups, aryl groups, said groups being optionally substituted with one or more silicon or germanium atoms; and p is an integer ranging from 0 to 1,000.

14. The process according to claim 11, wherein said co-catalyst is selected from organometallic compounds or mixtures of organometallic compounds of an element M' different from carbon, capable of

reacting with the cobalt complex with at least one phosphine ligand selected from selected from hindered aliphatic phosphines or bidentate phosphines, according to claim 10, extracting therefrom a mono or polyvalent anion, to form on the one hand, at least one neutral compound, and on the other, an ionic compound consisting of a cation containing the metal (Co) coordinated by the ligand, and a non-coordinating organic anion containing the metal M', wherein the negative charge is delocalized on a multicentric structure, such as organic compounds of aluminium and especially boron, such as those represented by the following general formulae (V), (VI) or (VII):

$$[(R_C)_WH_{4-W}]^+[B(R_D)_4]^-;\ B(R_D)_3;\ Al(R_D)_3;\ B(R_D)_3P;\ [Ph_3C]^+[B(R_D)_4]^- \text{ (V)}$$

$$[(R_C)_3PH]^+[B(R_D)_4]^- \text{ (VI)}$$

$$[Li]^+[B(R_D)_4]^-;\ [Li]^+[Al(R_D)_4]^- \text{ (VII)}$$

wherein w is an integer ranging from 0 to 3, each group R_C independently represents an alkyl group or an aryl group having from 1 to 10 carbon atoms and each group R_D independently represents an aryl group partially or totally, preferably totally, fluorinated, having from 6 to 20 carbon atoms, P represents a pyrrole radical optionally substituted.

15. The process according to any of the claims from 9 to 14, wherein said monodentate aromatic phosphine is selected from aromatic phosphines having general formula (VIII):

$$P\ (R)_m(Ph)_n \text{ (VIII)}$$

wherein:

- R is selected from linear or branched C_1-C_{16}—alkyl groups, C_3-C_{16} cycloalkyl groups, optionally substituted, allyl groups, phenyl optionally substituted;
- Ph is phenyl optionally substituted;
- m and n, different from each other, are 1 or 2, m+n being = 3.

16. The process according to any of the claims from 9 to 15, wherein said process is carried out in the presence of an inert organic solvent selected from: saturated aliphatic hydrocarbons such as butane, pentane, hexane, heptane, or mixtures thereof; saturated cycloaliphatic hydrocarbons such as cyclopentane, cyclohexane, or mixtures thereof; mono-olefins such as 1-butene, 2-butene, or mixtures thereof; aromatic hydrocarbons such as benzene, toluene, xylene, or mixtures thereof; halogenated hydrocarbons such as methylene chloride, chloroform, carbon tetrachloride, trichloroethylene, perchloroethylene, 1,2-dichloroethane, chlorobenzene, bromobenzene, chlorotoluene, or mixtures thereof.

17. The process according to claim 16, wherein the concentration of 1,3-butadiene to be polymerized in said inert organic solvent ranges from 5% by weight to 50% with respect to the total weight of the mixture of 1,3-butadiene and inert organic solvent.

18. The process according to any of the claims from 9 to

17, wherein said process is carried out at a temperature ranging from -70°C to +120°C.