Title: STEREOREGULAR DIBLOCK POLYBUTADIENES HAVING A 1,4-CIS/SYNDIOTACTIC 1,2 STRUCTURE FROM STEREOSELECTIVE POLYMERIZATION

Abstract: Stereoregular diblock polybutadiene composed of a polybutadiene block having a 1,4-cis structure and a polybutadiene block having a syndiotactic 1,2 structure. Said stereoregular diblock polybutadiene can be advantageously used in both the footwear industry (for example, in the production of soles for shoes) and in the production of tires for motor vehicles and/or trucks.

Figure 1

FT-IR spectra of the polybutadiene obtained: (a) M M46 (Example 6); (b) M M48 (Example 7); (c) MM49 (Example 8); (d) MM47 (Example 9).

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STEREOREGULAR DIBLOCK POLYBUTADIENES HAVING A 1,4-CIS/SYNDIOTACTIC 1,2 STRUCTURE FROM STEREOSPECIFIC POLYMERIZATION

5 The present invention relates to a stereoregular diblock polybutadiene having a 1,4-cis/syndiotactic 1,2 structure.

More specifically, the present invention relates to 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.

The present invention also 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 cobalt complex with at least one phosphine ligand selected from hindered aliphatic phosphines or bidentate phosphines, and subsequently adding at least one monodentate aromatic phosphine and optionally 1,3-butadiene, and continuing said stereospecific polymerization.

Said stereoregular diblock polybutadiene can be advantageously used in both the footwear industry (for example, in the production of soles for shoes) and in the
production of tires for motor vehicles and/or trucks.

It is known that the stereospecific polymerization of conjugated dienes is an extremely important process in the chemical industry for obtaining products which are among the most widely-used rubbers.

It is also known that among the various polymers that can be obtained from the stereospecific polymerization of 1,3-butadiene (i.e. 1,4-cis; 1,4-trans; syndiotactic 1,2; isotactic 1,2; atactic 1,2; a mixed 1,4-cis/1,2 structure having a variable content of 1,2 units), only 1,4-cis polybutadiene and syndiotactic 1,2 polybutadiene are industrially produced and commercialized. Further details relating to said polymers can be found, for example, in: Takeuchi Y. et al., "New Industrial Polymers", "American Chemical Society Symposium Series" (1974), Vol. 4, pages 15-25; Halasa A. F. et al., "Kirk-Othmer Encyclopedia of Chemical Technology" (1989), 4th Ed., Kroschwitz J. I. Ed., John Wiley and Sons, New York, Vol. 8, pages 1031-1045; Tate D. et al., "Encyclopedia of Polymer Science and Engineering" (1989), 2nd Ed., Mark H. F. Ed., John Wiley and Sons, New York, Vol. 2, pages 537-590; Kerns M. et al., "Butadiene Polymers", in "Encyclopedia of Polymer Science and Technology" (2003), Mark H. F. Ed., Wiley, Vol. 5, pages 317-356.

1,4-cis polybutadiene is a synthetic elastomer generally having a content of 1,4-cis units equal to 96%-97%, a melting point \( (T_m) \) of about -2°C, a crystallization
temperature \((T_c)\) of about \(-25^\circ\) and a glass transition temperature \((T_g)\) below \(-100^\circ\)), whose properties are extremely similar to those of natural rubber and whose main use is in the production of tires for motor vehicles and/or trucks. In particular, in the production of tires, polybutadiene with a high content of 1,4-cis units, is used.

1,4-cis polybutadiene is generally prepared through polymerization processes which use various catalytic systems comprising catalysts based on titanium (Ti), cobalt (Co), nickel (Ni), neodymium (Nd). Catalytic systems comprising catalysts based on cobalt have a high catalytic activity and stereospecificity and can be considered as being the most versatile among those listed above as, by varying their formulation, they are capable of giving all the possible stereoisomers of polybutadiene indicated above, as described, for example, in Porri L. et al., "Comprehensive Polymer Science" (1989), Eastmond G.C. et al. Eds., Pergamon Press, Oxford, UK, Vol. 4, Part II, pages 53-108; Thiele S. K. H. et al., "Macromolecular Science. Part C: Polymer Reviews" (2003), C43, pages 581-628; Osakada, K. et al., "Advanced Polymer Science" (2004), Vol. 171, pages 137-194; Ricci G. et al., "Advances in Organometallic Chemistry Research" (2007), Yamamoto K. Ed., Nova Science Publisher, Inc., USA, pages 1-36; Ricci G. et al., "Coordination Chemistry Reviews" (2010), Vol. 254, pages 661-676; Ricci G. et al., "Cobalt: Characteristics of Compounds".
The catalytic system cobalt bis-acetylacetonate/diethylaluminium chloride/water \([\text{Co (acac) }_2/\text{AlEt}_2\text{Cl}/\text{H}_2\text{O}]\), for example, provides a polybutadiene having a content of 1,4-cis units equal to about 97%, and is that normally used for the industrial production of this polymer as described, for example, in Racanelli P. et al., "European Polymer Journal" (1970), Vol. 6, pages 751-761. The catalytic system cobalt tris-acetylacetonate/methylaluminoxane \([\text{Co (acac) }_3/\text{MAO}]\) also provides a polybutadiene having a content of 1,4-cis units equal to about 97%, as described, for example, in Ricci G. et al., "Polymer Communication" (1991), Vol. 32, pages 514-517.

The catalytic system cobalt tris-acetylacetonate/tri-ethylaluminium/water \([\text{Co (acac) }_3/\text{AlEt}_3/\text{H}_2\text{O}]\), on the other hand, provides a polybutadiene having a mixed 1,4-cis/1,2 equibinary structure as described, for example, in: Furukawa J. et al., "Polymer Journal" (1971), Vol. 2, pages 371-378. Said catalytic system, in the presence of carbon disulfide \((\text{CS}_2)\), however, is used in processes for the industrial production of highly crystalline syndiotactic 1,2-polybutadiene. Further details relating to these processes can be found, for example, in:

An extremely active and stereospecific catalytic system for the preparation of syndiotactic 1,2-polybutadiene can be obtained from the combination of the allyl cobalt complex \((\eta^1\text{C}_8\text{H}_8)^{\cdot}(\cdot\cdot\cdot\text{C}_8\text{H}_3)\text{Co}\) described, for example, in Natta G. et al., "Chemical Communications" (1967), Issue 24, pages 1263-1265, with carbon disulfide (CS2), as described, for example, in Ricci G. et al., "Polymer Communication" (1988), Vol. 29, pages 305-307. This allyl cobalt complex alone is capable of dimerizing 1,3-butadiene at room temperature as described, for example, in American patent US 5,879,805, but is only capable of giving syndiotactic 1,2-polybutadiene operating at a low temperature (-30°C) as described, for example, in Ricci G. et al., "Polymer Communication" (1988), Vol. 29, pages 305-307.

Polybutadienes with a syndiotactic 1,2 structure or a mixed 1,4-cis/1,2 structure, having the 1,4-cis and 1,2 units randomly distributed along the polymeric chain, can also be produced using catalytic systems obtained by the combination of cobalt dichloride (CoCl2) or of cobalt dibromide (CoBr2) with organic aluminium compounds (e.g., alkyl compounds of aluminium or aluminoxanes), in the presence of phosphines (e.g., triphenylphosphine) as described, for example, in the following American

Further details relating to the polymerization of 1,3-butadiene with catalytic systems comprising preformed complexes of cobalt with various phosphines, are provided, for example, in Italian patents IT 1,349,141, IT 1,349,142, IT 1,349,143, and in International patent application WO 2003/018649. The use of different phosphines derives from the fact that it is well-known that steric and electronic properties of phosphines greatly depend on the type of substituents on the phosphorous atom, as described, for example, in: Dierkes P. et al., "Journal of Chemical Society, Dalton Transactions" (1999), pages 1519-1530; van Leeuwen P. et al., "Chemical Reviews" (2000), Vol. 100, pages 2741-
The documents relating to the use of phosphines indicated above, show how the use of preformed phosphine complexes of cobalt combined with methylaluminoxane (MAO) can enable the microstructure of polybutadiene to be managed, thus allowing polybutadienes with various structures to be obtained, depending on the type of phosphine coordinated with the cobalt atom.

The stereospecific polymerization of 1,3-butadiene with catalytic systems comprising complexes of cobalt with hindered monodentate aliphatic phosphines (e.g., \( P\cdot Bu_3, P\cdot Pr_3, P\cdot Bu_2\cdot Pr, P\cdot Bu_2\cdot Me, P\cdot Bu_2\cdot Cy, P\cdot Bu_2\cdot Cy_2, PCy_3, PCy_2 \)) wherein \( P = \) phosphorous, \( \frac{3}{4} u = \) tert-butyl, \( ^i Pr = \) iso-propyl, \( Cy = \) cyclohexyl and \( Cyp = \) cyclopentyl), provides polybutadienes with a prevalently 1,4-cis structure, whereas polybutadienes having a mixed 1,4-cis/1,2 structure have been obtained using catalytic systems comprising complexes of cobalt with phosphines having a lesser steric hindrance (e.g., \( PCy_2H; P\cdot Bu_2\cdot H; PEt_3; P\cdot Pr_3 \)) wherein \( P = \) phosphorous, \( Cy = \) cyclohexyl, \( ' Bu = \) tert-butyl, \( Et = \) ethyl and \( " Pr = \) \( \Omega \)-propyl), as described, for example, in international patent application WO 2003/1018649.

Polybutadienes with a high content of 1,4-cis units (> 96%) have been obtained with catalytic systems comprising complexes of cobalt with bidentate phosphines.
[e.g., CoCl₂[R₂P(CH₂)ₙPR₂]/MAO, wherein Co = cobalt, Cl = chlorine, R = methyl, ethyl, phenyl, n = 1 or 2, P = phosphorous and MAO = methylaluminoxane], regardless of the type of bidentate phosphine coordinated with the cobalt atom, as described, for example, in Ricci G. et al., "Coordination Chemistry Reviews" (2010), Vol. 254, pages 661-676; Ricci G. et al., "Cobalt: Characteristics, Compounds, and Applications" (2011), Lucas J. Vidmar Ed., Nova Science Publisher, Inc., USA, pages 39-81.

Catalytic systems comprising complexes of cobalt with ligands selected from aromatic phosphines [e.g., CoCl₂(PRPh₂)₂/MAO (wherein Co = cobalt, Cl = chlorine, P = phosphorous, R = methyl, Ψ-propyl, ethyl, iso-propyl, cyclohexyl, Ph = phenyl, MAO = methylaluminoxane] have, on the other hand, proved to be extremely active for the 1,2 polymerization of 1,3-butadiene, as described, for example, in Italian patents IT 1,349,142, IT 1,349,143. Using said catalytic systems, in fact, polybutadienes having an essentially 1,2 structure (within a range of 70% to 90%) have been obtained, having a variable content of 1,2 units in relation to the type of complex and the polymerization conditions. It has also been seen that the tacticity of the polybutadienes obtained greatly depends on the type of complex, i.e. the type of phosphine bound to the cobalt atom, and that the syndiotacticity index, expressed as content (i.e. percentage) of syndiotactic triads [(rr) %], determined by the ¹³C-NMR spectra, increases with an increase in the steric requirement of
the alkyl group bound to the phosphorous atom.

The 1,2 polybutadienes obtained with systems of cobalt with less sterically hindered phosphine ligands (e.g., PMePh₂; PEtPh₂; PⁿPrPh₂ wherein P = phosphorous, Me⁵ = methyl, Et = ethyl, Ph = phenyl, ᵈPr = n-propyl) have proved to have a low crystallinity and with a content of syndiotactic triads [(rr)₂] ranging from 20% to 50%, whereas the polybutadienes obtained with catalytic systems using phosphine ligands with a higher steric hindrance (e.g., P²PrPh₂, PCyPh₂ wherein P = phosphorous, ᵃPr = iso-propyl, Ph = phenyl, Cy = cyclohexyl) have proved to be crystalline, with a melting point (Tₘ) ranging from 100°C to 140°C and with a content of syndiotactic triads [(rr)₂] ranging from 60% to 80%, depending on the polymerization conditions.

The polymerization of 1,3-butadiene with catalytic systems comprising complexes of cobalt with aromatic phosphines having formula C0Cl₂(PR₂Ph)₂/MAO (wherein Co = cobalt, Cl = chlorine, R = methyl, ethyl, cyclohexyl, Ph = phenyl, MAO = methylaluminoxane) as described, for example, in Italian patents IT 1,349,141, IT 1,349,142, has also been studied. Using said catalytic systems, essentially 1,2-polybutadienes have been obtained, but the syndiotacticity index of the polymers, under the same polymerization conditions, has proved to be generally slightly lower with respect to that of the 1,2-polybutadienes obtained with catalytic systems comprising complexes of cobalt with the aromatic phosphines having
formula C\text{OCl}_{2}\left(\text{PRPh}_{2}\right)_{2}/\text{MAO} described above: the content of syndiotactic triads \([(rr)\frac{1}{4}]\), in fact, ranges from 15% to 45%.

Symmetrical or asymmetrical, diblock or triblock polymers based on butadiene are also known in the art, which, however, differ enormously from the stereospecific diblock polybutadiene object of the present invention, from the point of view of both the composition and microstructure, and also of the production method. The diblock or triblock polymers known in the art are in fact essentially obtained by post-modification reactions (e.g., grafting) of various homopolymers, or by anionic polymerization, using lithiumalkyls as reagents, or by emulsion polymerization, using radical initiators. Said diblock or triblock polymers often consist of the joining of polybutadiene blocks having different structures (prevalently, a 1,4-trans structure, as this is the predominant structure in the anionic or radicalic polymerization of butadiene) with blocks of polyisoprene, styrene or styrene-butadiene. In particular, it should be pointed out that in a block of polybutadiene having a 1,4-trans structure, the double bonds are along the main chain, whereas in the block of polybutadiene having a syndiotactic 1,2 structure of the stereoregular diblock polybutadiene object of the present invention, the double bonds are outside the main chain.

Further details relating to the above diblock or triblock polymers can be found, for example, in: Szwark

It is also well-known that although anionic or radicalic polymerizations allow the composition of the diblock or triblock polymers obtained to be controlled (i.e. the percentage of comonomers present), they are not able to exert an adequate control on the type of stereoregularity of the blocks (e.g., in the case of butadiene, the 1,4-cis vs. 1,2 vs. 1,4-trans selectivity) contrary to what happen on the stereospecific polymerization.

Zhang X. et al., in "Polymer" (2009), Vol. 50, pages 5427-5433, for example, describe the synthesis and the characterization of triblock polybutadienes containing a block of crystallizable high 1,4-trans polybutadiene. Said synthesis was carried out by means of the sequential anionic polymerization of butadiene, in the presence of the barium salt of di(ethylene glycol) ethylether/tri-isoo-butyl-aluminium/-dilithium (BaDEGEE/TIBA/DLi), as initiator. The triblock polybutadienes thus obtained were
analyzed and showed the following composition: high 1,4-
trans-b-low 1,4-cis-b-high 1,4-trans (HTPB-b-LCPB-b-
HTPBs). Said triblock polybutadienes consisted of an
elastic block with a low content of 1,4-cis units
chemically bound to blocks with a high content of
crystallizable 1,4-trans units. The ratio between the
(HTPB:LCPB:HTPBs) blocks was the following: 25:50:25. The
triblock polybutadienes HTPB-b-LCPB-b-HPBs obtained
consisted of the LCPB block with a 1,4-trans content
equal to 52.5% and of the HTPB blocks with a 1,4-trans
content ranging from 55.9% to 85.8%. These values clearly
indicate that the stereoregularity of the blocks is not
high. The triblock polybutadienes obtained showed a glass
transition temperature (Tg) equal to about -92°C and,
only in the presence of a 1,4-trans content >70%, a
crystallization temperature (Tc) equal to about -66°C.

Analogously, Zhang X. et al., in "Polymer Bulletin"
(2010), Vol. 65, pages 201-213, describe the synthesis
and the characterization of triblock copolymers
containing a block of crystallizable high 1,4-trans
polybutadiene. Various triblock copolymers containing a
block of crystallizable high 1,4-trans polybutadiene were
synthesized by means of the sequential anionic
polymerization of 1,3-butadiene (Bd) with isoprene (Ip)
or styrene (St), in the presence of the barium salt of
di(ethyleneglycol) ethylether/tri-iso-butyl-aluminium/-
dilithium (BaDEGEE/TIBA/DLi ), as initiator. The results
obtained from the analysis of said triblock copolymers
indicated that the medium-3, 4-polyisoprene-\(\beta\)-high-1,4-
trans-polybutadiene-\(\beta\)-medium 3,4-polyisoprene copolymers
and the polystyrene-\(\beta\)-high-1,4-trans-polybutadiene-\(\beta\)-
polystyrene copolymers had a block of polybutadiene
having a high content of 1,4-\textit{trans} units (maximum content
equal to 83%), blocks of polyisoprene having a medium
content of 3,4 units (content ranging from 22% to 27%)
and a total content of 1,4 (cis + \textit{trans}) units ranging
from 72% to 80%, whereas the blocks of polystyrene proved
to be atactic. Said copolymers had a glass transition
temperature \(T_g\) equal to about -80°C and a melting point
\(T_m\) equal to about 3°C.

From what is indicated above, it can therefore be
easily deduced that the various studies carried out for
improving/controlling the stereoregularity of diblock or
triblock polymers based on butadiene, have proved to be
unsatisfactory.

Another means adopted, again with the objective of
improving/controlling the stereoregularity of diblock or
triblock polymers based on butadiene, was the use of
coordination catalysts based on transition metals.

In this respect, for example, Naga N. et al. in
"Journal of Polymer Science Part A: Polymer Chemistry"
(2003), Vol. 41 (7), pages 939-946 and the European
patent application EP 1,013,683, indicate the use of the
catalytic complex \(\text{CpTiCl}_3/\text{MAO}\) (wherein \(\text{Cp} =
cyclopentadienyl\), \(\text{Ti} =\) titanium, \(\text{Cl} =\) chlorine, \(\text{MAO} =
methylaluminoxane\)) as catalyst, in order to synthesize
block copolymers containing polybutadiene blocks having a 1,4-cis structure and blocks of polystyrene having a syndiotactic structure. Also in this case, however, block copolymers were not obtained but rather copolymers having random multi-sequences, also due to a loss in the living nature of the polymerization.

Ban H. T. et al. in "Journal of Polymer Science Part A: Polymer Chemistry" (2005), Vol. 43, pages 1188-1195, using the catalytic complex $\text{Cp}^*\text{TiMe}_3/\text{B(C}_6\text{F}_5)_3/\text{AlR}_3$ (wherein $\text{Cp}^* = \text{cyclopentadienyl}$, $\text{Ti} = \text{titanium}$, $\text{Me} = \text{methyl}$, $\text{B(C}_6\text{F}_5)_3 = \text{tris(pentafluorophenyl)borane}$, $\text{AlR}_3 = \text{trialkylaluminium}$) and Caprio M. et al. in "Macromolecules" (2002), Vol. 35, pages 9315-9322, using a similar catalytic complex, i.e. $\text{CpTiCl}_3/\text{Ti(OR}_4)/\text{MAO}$ (wherein $\text{Cp} = \text{cyclopentadienyl}$, $\text{Ti} = \text{titanium}$, $\text{Cl} = \text{chlorine}$, $\text{R} = \text{alkyl}$, $\text{MAO} = \text{methylaluminoxane}$), obtained, operating under specific polymerization conditions, multi-block copolymers containing blocks of polystyrene with a syndiotactic structure and blocks of polybutadiene with a 1,4-cis structure. Operating under drastic conditions, in particular, at low polymerization temperatures ($-20^\circ\text{C}$ for the block of syndiotactic polystyrene and $-40^\circ\text{C}$ for the block of 1,4-cis polybutadiene), in order to maintain the living nature of the polymerization, Ban H. T. et al. obtained, with low yields, a copolymer having a block of syndiotactic polystyrene (content of syndiotactic units > 95%) and a block of 1,4-cis polybutadiene (content of 1,4-cis units
which showed a melting point \( T_m \) equal to 270°C, attributed to the block of syndiotactic polystyrene. Caprio M. et al., on the other hand, operating at a polymerization temperature ranging from 25°C to 70°C, obtained, with low yields, a multi-block copolymer having sequences of syndiotactic polystyrene, amorphous polystyrene and polybutadiene with a prevalently 1,4-cis structure. Using the above catalytic complexes, however, the control of the composition of the final copolymer was poor, requiring, among other things, a fractionation of the product obtained at the end of the polymerization in order to recover the copolymer of interest.

American patent US 4,255,296 describes a composition comprising a polybutadiene rubber containing a polymer obtained through the block polymerization or graft polymerization of 1,4-cis polybutadiene with syndiotactic 1,2-polibutadiene, whose microstructure comprises a content of 1,4-cis units ranging from 78% by weight to 93% by weight and a content of syndiotactic 1,2 units ranging from 6% by weight to 20% by weight, at least 40% by weight of said syndiotactic 1,2-polibutadiene being crystallized and having a form of the short-fiber type having an average diameter ranging from 0.05 \( \mu \text{m} \) to 1\( \mu \text{m} \) and an average length ranging from 0.8 \( \mu \text{m} \) to 10 \( \mu \text{m} \). As the joining of the blocks was not carried out via synthesis but by post-modification reaction (i.e. graft polymerization) on the 1,4-cis polybutadiene and on the 1,2 polybutadiene, the polymer obtained probably has
multiple junction points: said polymer is consequently completely different from the diblock polybutadiene object of the present invention, obtained by means of stereospecific polymerization and wherein the two blocks, i.e. the block with a 1,4-cis structure and the block with a syndiotactic 1,2 structure, are joined to each other by means of a single junction and not interpenetrated.

American patent US 3,817,968 describes a method for the preparation of equibinary 1,4-cis/1,2 polybutadiene, which comprises polymerizing butadiene at a temperature ranging from -80°C to 100°C, in an inert atmosphere, in a non-aqueous medium, in the presence of a catalyst obtained from the reaction of:

15 (a) trialkylaluminium having general formula:

$$\text{Al} (\text{R})_3$$

wherein R represents a linear hydrocarbon radical having from 1 to 6 carbon atoms; and

(b) dialkoxy molybdenum trichloride having formula:

$$\text{MoCl}_3 (\text{OR'})_2$$

wherein R' represents a hydrocarbon radical having from 1 to 6 carbon atoms;

the molar ratio (a) / (b) being not lower than 6. The polybutadiene thus obtained has polybutadiene blocks with a 1,4-cis structure and polybutadiene blocks with a syndiotactic 1,2 structure randomly distributed along the polymeric chain, which means that neither amorphous
polybutadiene blocks with a 1,4-cis structure, nor crystalline polybutadiene blocks with a 1,2 structure, are present. Also in this case, therefore, these polymers are completely different from the diblock polybutadiene object of the present invention, obtained by means of stereospecific polymerization and wherein the two blocks, i.e. the block with a 1,4-cis structure and the block with a syndiotactic 1,2 structure, are joined to each other by means of a single junction and not interpenetrated.

As specified above, as polybutadiene is among the polymers which are most widely-used industrially, in particular for the production of tires, the study of new polybutadienes is still of great interest. In particular, the study of a stereoregular diblock polybutadiene with a 1,4-cis/syndiotactic 1,2 structure which could be advantageously used in both the footwear industry (for example, in the production of shoe soles) and in the production of tires for motor vehicles and/or trucks, is of great interest.

The Applicant has therefore considered the problem of finding a stereoregular diblock polybutadiene having a 1,4-cis/syndiotactic 1,2 structure. More specifically, the Applicant has considered the problem of finding 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.

The Applicant has also found that the preparation of
stereoregular diblock polybutadiene composed of a polybutadiene block having a 1,4-cis structure and a polybutadiene block having a syndiotactic 1,2 structure, can be advantageously carried out by means of a process 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, and subsequently adding at least one monodentate aromatic phosphine and optionally 1,3-butadiene, and continuing said stereospecific polymerization. In particular, the Applicant has found that the use of said complex of cobalt with at least one phosphine ligand selected from hindered aliphatic phosphines or bidentate phosphines, allows a polybutadiene with a living 1,4-cis structure to be obtained and that the subsequent stereospecific polymerization of the residual, or optionally added, 1,3-butadiene, in the presence of said monodentate aromatic phosphine, is capable of giving the above stereoregular diblock polybutadiene. Furthermore, the Applicant has found that said process, by varying the addition time of said monodentate aromatic phosphine or the quantity of 1,3-butadiene, allows the length of the two blocks (i.e. the block with a 1,4-cis structure and the block with a syndiotactic 1,2 structure) to be modulated in the stereoregular diblock polybutadiene obtained, depending on the characteristics of the end-product to be obtained.
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 \([\langle rr \rangle_4]\)] 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):

\[
P_{Bi}-P_{B_2} \quad (I)
\]

wherein:

- \(P_{Bi}\) corresponds to the polybutadiene block having a 1,4-cis structure;
- \(P_{B_2}\) corresponds to the polybutadiene block having a syndiotactic 1,2 structure;

essentially free of 1,4-trans units.

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
following claims, the term "essentially free of 1,4-trans units" means that, when present, said 1,4-trans units are present in a quantity lower than 3% molar, preferably lower than 1% molar, with respect to the total molar quantity of the butadiene units present in said stereoregular diblock polybutadiene.

For the aim of the present description and of the following claims, the definitions of the numerical ranges always comprise the extremes unless otherwise specified.

For the aim of the present description and of the following claims, the term "comprising" also includes the terms "which essentially consists of" or "which consists of".

According to a preferred embodiment of the present invention, said stereoregular diblock polybutadiene has the following characteristics:
- upon infrared analysis (FT-IR), bands typical of the 1,4-cis and 1,2 units 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.

The infrared analysis (FT-IR) and the \(^{13}\)C-NMR analysis were carried out as indicated hereunder in the paragraph "Analysis and characterization methods".

According to a further preferred embodiment of the present invention, in said stereoregular diblock
- the block having a 1,4-cis structure can have a glass transition temperature \((T_g)\) lower than or equal to \(-100^\circ C\), preferably ranging from \(-104^\circ C\) to \(-113^\circ C\), a melting point \((T_m)\) lower than or equal to \(-2^\circ C\), preferably ranging from \(-5^\circ C\) to \(-20^\circ C\), and a crystallization temperature \((T_c)\) lower than or equal to \(-25^\circ C\), preferably ranging from \(-30^\circ C\) to \(-54^\circ C\);
- the block having a syndiotactic 1,2 structure can have a glass transition temperature \((T_g)\) lower than or equal to \(-10^\circ C\), preferably ranging from \(-14^\circ C\) to \(-24^\circ C\), a melting point \((T_m)\) higher than or equal to \(70^\circ C\), preferably ranging from \(95^\circ C\) to \(140^\circ C\), and a crystallization temperature \((T_c)\) higher than or equal to \(55^\circ C\), preferably ranging from \(60^\circ C\) to \(130^\circ C\).

It should be pointed out that the wide range within which the melting point \((T_m)\) and the crystallization temperature \((T_c)\) of the block having a 1,2 structure vary, can be attributed to the different content of syndiotactic triads \([(rr) \%]\) which depends on the type of phosphine used in the polymerization [i.e. the degree of stereoregularity, namely the content of syndiotactic triads \([(rr) \%]\) increases with an increase in the steric hindrance of the aromatic phosphine used].

Said glass transition temperature \((T_g)\), said melting point \((T_m)\) and said crystallization temperature \((T_c)\), were determined by means of DSC thermal analysis ("Differential Scanning Calorimetry") which was carried...
out as indicated hereunder in the paragraph "Analysis and characterization methods".

According to a further preferred embodiment of the present invention, said stereoregular diblock polybutadiene can have 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.

Said polydispersion index (PDI) was determined by means of GPC ("Gel Permeation Chromatography") which was carried out as indicated hereunder in the paragraph "Analysis and characterization methods".

It should be pointed out that the presence of a narrow and monomodal peak, i.e. of a polydispersion index (PDI) ranging from 1.9 to 2.2, indicates the presence of a homogeneous polymeric species, at the same time excluding the presence of two different homopolymers (i.e. homopolymers with a 1,4-cis and 1,2 structure).

It should also be pointed out that the isolated fractions (i.e. extract soluble in ether and residue insoluble in ether) obtained by subjecting the stereoregular diblock polybutadiene object of the present invention, to extraction in continuous with diethylether at boiling point, for 4 hours, always have a composition/structure completely analogous to that of the "nascent" starting polymer.

The stereoregular diblock polybutadiene, object of the present invention, when subjected to Atomic Force
Microscopy (AFM), shows two clearly distinct domains relating to the block with a 1,4-cis structure and to the block with a syndiotactic 1,2 structure and, in particular, a homogeneous distribution of said domains as shown in Figures 19 and 20 provided hereunder.

Said Atomic Force Microscopy (AFM) was carried out as indicated hereunder in the paragraph "Analysis and characterization methods".

Furthermore, the stereoregular diblock polybutadiene object of the present invention, when subjected to Dynamic Mechanical Analysis (DMA), shows a elastic modulus value \( G' \) higher than that of commercial polybutadienes (i.e. Europrene NEOCIS® BR 40 of Versalis Spa) as shown in Figure 15 provided hereunder.

Said Dynamic Mechanical Analysis (DMA) was carried out as indicated hereunder in the paragraph "Analysis and characterization methods".

According to a preferred embodiment of the present invention, in said stereoregular diblock polybutadiene, the polybutadiene block having a 1,4-cis structure is amorphous, at room temperature under quiescent conditions (i.e. not subjected to stress), and can have a 1,4-cis content higher than or equal to 96% molar, preferably ranging from 97% molar to 99% molar, with respect to the total molar quantity of butadiene units present in said polybutadiene block having a 1,4-cis structure.

It should be pointed out that in said polybutadiene block having a 1,4-cis structure, the complement to 100,
i.e. a content lower than or equal to 4% molar, preferably ranging from 1% molar to 3% molar, can be with a 1,2 structure or, if present, a 1,4-trans structure in the quantities indicated above.

In the stereoregular diblock polybutadiene, object of the present invention, the polybutadiene block having a syndiotactic 1,2 structure can have a varying degree of crystallinity depending on the content of syndiotactic triads [(rr) %], i.e. the type of monodentate aromatic phosphine used: in particular, the degree of crystallinity increases with an increase in the content of syndiotactic triads [(rr) %]. Said content of syndiotactic triads [(rr) %] is preferably higher than or equal to 15%, preferably ranging from 60% to 80%.

It should be pointed out that, in the stereoregular diblock polybutadiene object of the present invention, also when the polybutadiene block having a 1,2 structure is characterized by a low content of syndiotactic triads [(rr) %] (i.e. a content ranging from 15% to 20%) and, therefore, it proves to be at low crystallinity, tendentially amorphous, the content of 1,2 units always remains higher than or equal to 80%.

The content of syndiotactic triads [(rr) %] was determined by means of $^{13}$C-NMR spectroscopy analysis which was carried out as indicated hereunder in the paragraph "Analysis and characterization methods".

According to a preferred embodiment of the present invention, in said stereoregular diblock polybutadiene,
the 1,4-cis/1,2 molar ratio can range from 15:85 to 80:20, preferably ranging from 25:75 to 70:30.

According to a preferred embodiment of the present invention, said stereoregular diblock polybutadiene can have a weight average molecular weight ($M_w$) ranging from 100,000 g/mol to 800,000 g/mol, preferably ranging from 150,000 g/mol to 600,000 g/mol.

The analyses and the characterization to which the stereoregular diblock polybutadiene object of the present invention, was subjected, show that it can have the following characteristics:

- the polybutadiene block with a syndiotactic 1,2 structure (hard block), when present in crystalline form, under conditions in which the polybutadiene with a 1,4-cis structure is amorphous (soft block), i.e. at room temperature under quiescent conditions, can act as a hard filler (see Figure 15 which provides a comparison with the theoretical trends envisaged by the Guth-Gold and Thomas laws as described, for example, in Eggers E. et al., "Rubber Chemistry and Technology" (1996), Vol. 69, No. 2, pages 253-265 and references indicated therein);

- upon high-temperature Dynamic Mechanical Analysis (DMA), in particular at 130°C, the stereoregular diblock polybutadiene shows a behaviour typical of branched systems characterized by phase separation between the hard block and soft block; the block with a syndiotactic 1,2 structure (hard block), in
fact, in high-temperature phase separation, mainly acts as a branching point, in particular when it is present in a minority percentage, as long as the temperature remains lower than the order-disorder temperature (ODT) of the stereoregular diblock polybutadiene; furthermore, the presence of phase separation at a temperature lower than the order-disorder temperature (ODT) and, even more so, at a temperature lower than the melting point ($T_m$) of the polybutadiene block with a syndiotactic 1,2 structure (hard block), gives the stereoregular diblock polybutadiene properties typical of a thermoplastic elastomer [in this respect, reference should be made to what is described, for example, in: "Thermoplastic Elastomers" (2004), 3rd edition, Holden, G., Kricheldorf, H. R., and Quirk, R. P., Eds., Hanser Publishers, Munich; I.W. Hamley, "The Physics of Block Copolymers" (1998), Hamley I. W., Oxford University Press], particularly evident when the polybutadiene block with a 1,4-cis structure (soft block) is present in a higher percentage;

- upon low-temperature Dynamic Mechanical Analysis (DMA), i.e. at a temperature lower than the melting point ($T_m$) of the polybutadiene block with a syndiotactic 1,2 structure (hard block), the stereoregular diblock polybutadiene shows a much higher elastic modulus value ($G'$) with respect to commercial polybutadienes with a high 1,4-cis
content (see Figure 15) mainly due to the hardness of the polybutadiene block with a syndiotactic 1,2 structure (hard block), present in crystalline form.

It should also be pointed out that the stereoregular diblock polybutadiene object of the present invention, has numerous differences with respect to both commercial polybutadienes with a high 1,4-cis structure, and also the reference homopolymers obtained as described in the following examples, such as, for example:

- the response to Dynamic Mechanical Analysis (DMA) of stereoregular diblock polybutadiene becomes increasingly more complex from a thermo-rheological point of view (e.g., failure of the time-temperature superposition with an increase in the percentage of the polybutadiene block with a syndiotactic 1,2 structure (hard block) present in said stereoregular diblock polybutadiene (as shown in the Van Gurp-Palmen diagrams of various polybutadienes), due to the phase transition (transition of the first order) of said polybutadiene block with a syndiotactic 1,2 structure (hard block); said phase transition allows the dynamic-mechanical characteristics of the stereoregular diblock polybutadiene to vary considerably with a variation in the temperature, thus allowing them to be regulated in relation to the final application; furthermore, said phase transition can be regulated and consequently also
the complexity from a thermo-rheological point of view of said stereoregular diblock polybutadiene, and its mechanical performances in general, not only by regulating the stereoregularity of the polybutadiene block with a syndiotactic 1,2 structure (i.e. by varying the content of syndiotactic triads [(rr) %]), but also by regulating both the molecular weight of said polybutadiene block with a syndiotactic 1,2 structure (hard block), and also the percentage of polybutadiene block with a syndiotactic 1,2 structure (hard block) present in said stereoregular diblock polybutadiene [further details relating to these diagrams can be found, for example, in: Van Gurp M. et al., "Rheological Bulletin" (1998), Vol. 67, pages 5-8; Trinckle S. et al., "Rheological Acta" (2001), Vol. 40, pages 322-328; Trinckle S. et al., "Rheological Acta" (2002), Vol. 41, pages 103-113]; the possibility, in the stereoregular diblock polybutadiene, of selectively cross-linking (for example, in the presence of peroxides and/or sulfur and, optionally, of adjuvant agents), only one of the two blocks, in particular the polybutadiene block with a 1,4-cis structure (soft block), by mixing the cross-linking ingredients with the stereoregular diblock polybutadiene at a temperature lower than the melting point ($T_m$) of the polybutadiene block with a syndiotactic 1,2
structure (hard block), so as to reduce or even to prevent the dispersion of said ingredients in the polybutadiene block with a syndiotactic 1,2 structure (hard block);

- the possibility of increasing, with respect to a homopolymer having a 1,4-cis structure, the tendency of the polybutadiene block with a 1,4-cis structure (soft block) to crystallize, also at temperatures higher than the melting point ($T_m$) of said block under quiescent conditions, under the action of a deformation or stress imposed from the outside; thanks to the presence of the polybutadiene block with a syndiotactic 1,2 structure (hard block) that acts as a branching point and consequently increases the viscoelastic memory of the stereoregular diblock polybutadiene (with respect to the positive effect of the viscoelastic memory on the crystallization induced by the deformation, reference should be made, for example, to Coppola S. et al., "Macromolecules" (2001), Vol. 34, pages 5030-5036); this possibility can allow the stereoregular diblock polybutadiene to be used in elastomeric blends, in particular in elastomeric blends for tire sidewalls, preferably in the presence of 1,4-cis polybutadiene and/or of natural rubber (it is, in fact, known in literature, as described, for example, by Santangelo P. G. et al. in "Rubber Chemistry & Technology" (2003), Vol.76, No. 4, pages 892-898, that rubbers
that have the possibility of crystallizing due to a deformation and/or to a stress imposed from the outside, positively contribute to the fatigue resistance of elastomeric blends).

It should also be pointed out that, unlike what is the case, for example, with polystyrene-polydiene copolymers known in the art, in which the polystyrene block cannot be crosslinked in the presence of sulfur alone as crosslinking agent due to the absence of isolated residual double bonds, in the stereoregular diblock polybutadiene object of the present invention, both blocks, i.e. both the polybutadiene block with a syndiotactic 1,2 structure (hard block), and the polybutadiene block with a 1,4-cis structure (soft block), can be crosslinked (for example, in the presence of peroxides and/or sulfur and, optionally, of adjuvant agents), operating according to procedures known in literature for the crosslinking of diene polymers (in this respect, reference should be made to what is described, for example, in: "Science and Technology of Rubber" (2005), Mark J. E., Erman B., Eirich F. R., Eds., 3rd edition, Elsevier; "Rubber Technology" (1987), Morton M. Ed., 3rd edition, Van Nostrand Reinhold; "Rubber Compounding – Chemistry and Applications" (2004), Rodgers B. Ed., Marcel Dekker; ASTM D3189; ASTM D3186; ISO 2476: 2009, and subsequent updates).

As already indicated above, the present invention also 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.

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.

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):

\[
\text{(I)}
\]

\[
\text{(II)}
\]
wherein:

5 - \( R_1 \) and \( R_2 \), the same or different, are selected from linear or branched \( \text{C}_1-\text{C}_{20} \), preferably \( \text{C}_1-\text{C}_{15} \), alkyl groups, \( \text{C}_3-\text{C}_{30} \), preferably \( \text{C}_4-\text{C}_{15} \), cycloalkyl groups, more preferably are selected from iso-propyl, tert-butyl, cyclopentyl, cyclohexyl;

10 - \( R_3 \) is selected from linear or branched \( \text{C}_1-\text{C}_{20} \), preferably \( \text{C}_1-\text{C}_{15} \), alkyl groups, \( \text{C}_3-\text{C}_{30} \), preferably \( \text{C}_4-\text{C}_{15} \), cycloalkyl groups, more preferably is selected from methyl, ethyl, \( \text{n} \)-propyl, iso-propyl, tert-butyl, cyclopentyl, cyclohexyl;

15 - \( R_4 \) and \( R_5 \), the same or different, are selected from linear or branched \( \text{C}_1-\text{C}_{20} \), preferably \( \text{C}_1-\text{C}_{15} \), alkyl groups, \( \text{C}_3-\text{C}_{30} \), preferably \( \text{C}_4-\text{C}_{15} \), cycloalkyl groups, \( \text{C}_6-\text{C}_{30} \), preferably \( \text{C}_6-\text{C}_{15} \), aryl groups, more
preferably are selected from methyl, ethyl, \(n\)-propyl, iso-propyl, tert-butyl, cyclopentyl, cyclohexyl, phenyl;

- \(Y\) represents a divalent group \(-(C\%)_n\)-, 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 \(\text{C}_1\text{C}_{20}\), preferably \(\text{C}_1\text{C}_{15}\), alkyl group, more preferably is a hydrogen atom; or a divalent group \(-(\text{CH}_2)_mR'-(C\%)_m\)- wherein \(R'\) represents an aryl group optionally substituted, preferably a phenyl group optionally substituted, and \(m\) is 0, 1 or 2;

- \(X_1\) and \(X_2\), the same or different, represent a halogen atom such as, for example, chlorine, bromine, iodine, preferably chlorine; or they are selected from linear or branched \(\text{C}_1\text{C}_{20}\), preferably \(\text{C}_1\text{C}_{15}\), alkyl groups, preferably methyl, ethyl, \(-\text{OCOR}_7\) groups or \(-\text{OR}_7\) groups wherein \(R_7\) is selected from linear or branched \(\text{C}_1\text{C}_{20}\), preferably \(\text{C}_1\text{C}_{15}\), alkyl groups, preferably methyl, ethyl.

Further details relating to said complex of cobalt with at least one phosphine ligand selected from hindered aliphatic phosphines or bidentate phosphines having general formula (I) or (II), together with its preparation, can be found in the following documents, whose content is incorporated herein as reference: International patent application WO 2003/018649; Italian patents IT 1,349,143, IT 1,349,142, IT 1,349,141; Ricci

The complex of cobalt with at least one phosphine ligand selected from hindered aliphatic phosphines or bidentate phosphines having general formula (I) or (II) should be considered as being, in accordance with the present invention, in any physical form such as, for example, isolated and purified solid form, solvated form with a suitable solvent, or supported form on suitable organic or inorganic solids, preferably having a granular or powder physical form.

It should also be pointed out that, in accordance with the present invention, said complex of cobalt with at least one phosphine ligand selected from hindered aliphatic phosphines or bidentate phosphines having
general formula (I) or (II) can be prepared in situ, i.e. directly in the polymerization environment. In this respect, said complex of cobalt with at least one phosphine ligand selected from hindered aliphatic phosphines or bidentate phosphines having general formula (I) or (II) can be prepared by separately introducing the ligand (obtained as described, for example, in the following examples), the compound containing cobalt [for example, cobalt dichloride (CoCl₂)] and the preselected 1,3-butadiene to be polymerized, operating under the conditions in which the polymerization is carried out.

According to a preferred embodiment of the present invention, said catalytic system can comprise 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, preferably from: boron, aluminium, zinc, magnesium, gallium, tin, even more preferably from aluminium, boron.

The formation of the catalytic system comprising the complex of cobalt with at least one phosphine ligand selected from hindered aliphatic phosphines or bidentate phosphines having general formula (I) or (II) and the co-catalyst, is generally and preferably carried out in an inert liquid medium, more preferably in a hydrocarbon solvent. The choice of the complex of cobalt with at least one phosphine ligand selected from hindered aliphatic phosphines or bidentate phosphines having
general formula (I) or (II) and of the co-catalyst, as well as the particular method used, can vary in relation to the molecular structures and to the desired result.

According to a further preferred embodiment of the present invention, said co-catalyst can be selected from aluminium alkyls having general formula (III):

$$\text{Al} \; (X')_n \; (R_8)_{3-n}$$

wherein $X'$ represents a halogen atom such as, for example, chlorine, bromine, iodine, fluorine; $R_8$ is selected from linear or branched $C_1-C_2$ 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.

According to a further preferred embodiment of the present invention, said co-catalyst can be selected from organo-oxygenated compounds of an element $M'$ different from carbon belonging to groups 13 or 14 of the Periodic Table of Elements, preferably organo-oxygenated compounds of aluminium, gallium, tin. Said organo-oxygenated compounds can be defined as organic compounds of $M'$, wherein the latter is bound to at least one oxygen atom and to at least one organic group consisting of an alkyl group having from 1 to 6 carbon atoms, preferably methyl.

According to a further preferred embodiment of the present invention, said co-catalyst can be selected from organometallic compounds or mixtures of organometallic compounds of an element $M'$ different from carbon capable of reacting with the complex of cobalt with at least one
phosphine ligand selected from hindered aliphatic phosphines or bidentate phosphines having general formula (I) or (II), extracting therefrom a mono- or poly-valent 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.

It should be noted that, for the aim of the present invention and of the following claims, the term "Periodic Table of the Elements" refers to the IUPAC version of the "Periodic Table of the Elements" dated June 22, 2007, provided in the following Internet website

For the aim of the present description and of the following claims, the phrase "room temperature" refers to a temperature ranging from 20°C to 25°C.

Specific examples of aluminium alkyls having general formula (III) which are particularly useful for the aim of the present invention are: tri-methyl-aluminium, tri-(2, 3,3-tri-methyl-butyl )-aluminium, tri-(2, 3-di-methyl-hexyl) -aluminium, tri-(2, 3-di-methyl-butyl )-aluminium, tri-(2,3-di-methyl-pentyl )-aluminium, tri-(2,3-di-methyl-heptyl) -aluminium, tri- (2-methyl-3-ethyl-pentyl )-aluminium, tri-(2-methyl-3-ethyl-hexyl )-aluminium, tri-(2-methyl-3-ethyl-heptyl )-aluminium, tri-(2-methyl-3-ethyl-heptyl )-aluminium, tri-(2-methyl-3-ethyl-heptyl )-aluminium, tri-(2-methyl-3-ethylene...
propyl-hexyl) -aluminium, tri-ethyl-aluminium, tri- (2-ethyl-3-methyl-butyl) -aluminium, tri- (2-ethyl-3-methyl-pentyl) -aluminium, tri- (2, 3-di-ethyl-pentyl-aluminium), tri- n-propyl-aluminium, tri-iso-propyl-aluminium, tri- (2-propyl-3-methyl-butyl) -aluminium, tri- (2-iso-propyl-3-methyl-butyl) -aluminium, tri-n-butyl-aluminium, tri-iso-butyl-aluminium (TIBA), tri-tert-butyl-aluminium, tri- (2-iso-butyl-3-methyl-pentyl) -aluminium, tri- (2, 3, 3-tri-methyl-pentyl) -aluminium, tri- (2, 3, 3-tri-methyl-hexyl) -aluminium, tri- (2-ethyl-3, 3-di-methyl-butyl) -aluminium, tri- (2-ethyl-3, 3-di-methyl-pentyl) -aluminium, tri- (2-isopropyl-3, 3-dimethyl-butyl) -aluminium, tri- (2-tri-methylsilyl-propyl) -aluminium, tri-2-methyl-3-phenyl-butyl) -aluminium, tri- (2-ethyl-3-phenyl-butyl) -aluminium, tri- (2, 3-di-methyl-3-phenyl-butyl) -aluminium, tri- (2-phenyl-propyl) -aluminium, tri- [2- (4-fluoro-phenyl) -propyl] -aluminium, tri- [2- (4-chloro-phenyl) -propyl] -aluminium, tri- [2- (3-isopropyl-phenyl-tri- (2-phenyl-butyl) -aluminium, tri- (3-methyl-2-phenyl-butyl) -aluminium, tri- (2-phenyl-pentyl) -aluminium, tri- [2- (penta-fluoro-phenyl) -propyl] -aluminium, tri- (2, 2-diphenyl-ethyl) -aluminium, tri- (2-phenyl-methyl-propyl) -aluminium, tri-pentyl-aluminium, tri-hexyl-aluminium, tri-cyclohexyl-aluminium, tri-octyl-aluminium, di-ethyl-aluminium hydride, di-n-propyl-aluminium hydride, di-n-butyl-aluminium hydride, di-iso-butyl-aluminium hydride (DIBAH), di-hexyl-aluminium hydride, di-iso-hexyl-aluminium hydride, di-octyl-aluminium hydride, di-iso-
octyl-aluminium hydride, ethyl-aluminium di-hydride, n-propyl-aluminium di-hydride, iso-butyl-aluminium di-hydride, di-ethyl-aluminium chloride (DEAC), mono-ethyl-aluminium dichloride (EADC), di-methyl-aluminium chloride, di-iso-butyl-aluminium chloride, iso-butyl-aluminium dichloride, ethylaluminium sesquichloride (EASC), and also the corresponding compounds in which one of the hydrocarbon substituents is substituted by a hydrogen atom and those in which one or two of the hydrocarbon substituents are substituted with an iso-butyl group. Di-ethyl-aluminium chloride (DEAC), mono-ethyl-aluminium dichloride (EADC), ethylaluminium sesquichloride (EASC), are particularly preferred.

When used for the formation of a catalytic polymerization system according to the present invention, the aluminium alkyls having general formula (III) can be preferably put in contact with a complex of cobalt with at least one phosphine ligand selected from hindered aliphatic phosphines or bidentate phosphines having general formula (I) or (II) in such proportions that the molar ratio between the cobalt present in the complex of cobalt with at least one phosphine ligand selected from hindered aliphatic phosphines or bidentate phosphines having general formula (I) or (II) and the aluminium present in the aluminium alkyls having general formula (III) can range from 5 to 5,000, preferably ranging from 10 to 1,000. The sequence with which the complex of cobalt with at least one phosphine ligand selected from
hindered aliphatic phosphines or bidentate phosphines having general formula (I) or (II) and aluminium alkyl having general formula (III) are put in contact with each other, is not particularly critical.

Further details relating to the aluminium alkyls having general formula (III) can be found in International patent application WO 2011/061151.

According to a particularly preferred embodiment of the present invention, said organo-oxygenated compounds can be selected from aluminoxanes having general formula (IV):

\[(R_9)_{2-Al-O-\{Al (R_{i0})_0-O-\}p-Al- (R_n)_2}\ (IV)\]

wherein \(R_9\), \(R_{i0}\) and \(R_n\), the same or different, represent a hydrogen atom, a halogen atom such as, for example, chlorine, bromine, iodine, fluorine; or they are selected from linear or branched \(C_1\) to \(C_{20}\) 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.

As is known, aluminoxanes are compounds containing Al-O-Al bonds, with a variable O/Al ratio, which can be obtained by means of processes known in the art such as, for example, by reaction, under controlled conditions, of an aluminium alkyl, or an aluminium alkyl halide, with water or with other compounds containing predetermined quantities of available water, as, for example, in the case of the reaction of aluminium trimethyl with aluminium sulfate hexahydrate, copper sulfate
pentahydrate, or iron sulfate pentahydrate.

Said aluminoxanes, and in particular methyl aluminoxane (MAO), are compounds which can be obtained by means of known organometallic chemical processes such as, for example, by the addition of aluminium trimethyl to a suspension in hexane of aluminium sulfate hydrate.

When used for the formation of a catalytic polymerization system according to the present invention, the aluminoxanes having general formula (IV) can be preferably put in contact with a complex of cobalt with at least one phosphine ligand selected from hindered aliphatic phosphines or bidentate phosphines having general formula (I) or (II), in such proportions that the molar ratio between the aluminium (Al) present in the aluminoxane having general formula (IV) and the cobalt present in the complex of cobalt with at least one phosphine ligand selected from hindered aliphatic phosphines or bidentate phosphines having general formula (I) or (II) is ranging from 10 to 10,000, preferably ranging from 100 to 5,000. The sequence with which the complex of cobalt with at least one phosphine ligand selected from hindered aliphatic phosphines or bidentate phosphines having general formula (I) or (II) and the aluminoxane having general formula (IV) are put in contact with each other, is not particularly critical.

In addition to the above preferred aluminoxanes having general formula (IV), the definition of the compound according to the present invention can also
include galloxanes, wherein, in general formula (IV), gallium is present in substitution of aluminium, and stannoxanes, wherein, in general formula (IV), tin is present in substitution of aluminium, whose use as co-catalysts in the polymerization of olefins in the presence of metallocene complexes, is known. Further details relating to said galloxanes and stannoxanes can be found, for example, in American patents US 5,128,295 and US 5,258,475.

Specific examples of aluminoxanes having general formula (IV) which are particularly useful for the aim of the present invention are: methylaluminoxane (MAO), ethyl-aluminoxane, \(\eta\)-butyl-aluminoxane, tetra-iso-butyl-aluminoxane (TIBAO), tert-butyl-aluminoxane, tetra-(2,4,4-tri-methyl-pentyl)-aluminoxane (TIOAO), tetra-(2,3-di-methyl-butyl)-aluminoxane (TDMAO), tetra-(2,3,3-tri-methyl-butyl)-aluminoxane (TTMBAO). Methylaluminoxane (MAO) is particularly preferred.

Further details relating to the aluminoxanes having general formula (IV) can be found in International patent application WO 2011/061151.

According to a preferred embodiment of the present invention, said compounds or mixtures of compounds can be selected from organic compounds of aluminium and especially boron, such as, for example, those represented by the following general formulae (V), (VI) or (VII):

\[
[(R_c)_wH_{w-1}] \cdot [B(R_D)_4]^{-}; B(R_D)_3; AI(R_D)_3; B(R_D)_3P; [Ph_3C]+ [B(R_D)_4]^{-}\]  

(V)
[\((Rc)\)_3PH]^{+} - [B(RD)_4]^{-} \quad \text{(VI)}

[Li]^{+} \cdot [B(RD)_4]^{-}; \quad [Li]^{+} - [Al(RD)_4]^{-} \quad \text{(VII)}

wherein \(w\) is an integer ranging from 0 to 3, each group \(Rc\) independently represents an alkyl group or an aryl group having from 1 to 10 carbon atoms and each group \(RD\) 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.

When used for the formation of a catalytic polymerization system according to the present invention, the compounds or mixtures of compounds having general formulae (V), (VI) or (VII), can be preferably put in contact with a complex of cobalt with at least one phosphine ligand selected from hindered aliphatic phosphines or bidentate phosphines having general formula (I) or (II), in such proportions that the molar ratio between the metal (M') present in the compounds or mixtures of compounds having general formulae (V), (VI) or (VII), and the cobalt present in the complex of cobalt with at least one phosphine ligand selected from hindered aliphatic phosphines or bidentate phosphines having general formula (I) or (II), is ranging from 0.1 to 15, preferably ranging from 0.5 to 10, more preferably ranging from 1 to 6. The sequence with which the complex of cobalt with at least one phosphine ligand selected from hindered aliphatic phosphines or bidentate phosphines having general formula (I) or (II) and the
compound or mixtures of compounds having general formulae (V), (VI) or (VII), are put in contact with each other, is not particularly critical.

Said compounds or mixtures of compounds having general formulae (V), (VI) or (VII), especially when $X_1$ and $X_2$ in general formulae (I) or (II) are different from alkyl, must be used in a combination with an alumin oxide having general formula (IV) such as, for example, methylalumin oxide (MAO), or, preferably, with an aluminium alkyl having general formula (III), more preferably an aluminium trialkyl having from 1 to 8 carbon atoms in each alkyl residue such as, for example, tri-methyl-aluminium, tri-ethyl-aluminium, tri-iso-butylaluminium (TIBA).

Examples of methods generally used for the formation of a catalytic polymerization system according to the present invention, when compounds or mixtures of compounds having general formulae (V), (VI) or (VII), are used, are qualitatively schematized in the following list, which however in no way limits the overall scope of the present invention:

(m1) contact of a complex of cobalt with at least one phosphine ligand selected from hindered aliphatic phosphines or bidentate phosphines having general formula (I) or (II), wherein at least one of $X_1$ and $X_2$ is an alkyl group, with at least one compound or mixtures of compounds having general formulae (V), (VI) or (VII), whose cation is capable of reacting
with said alkyl group to form a neutral compound, and whose anion is voluminous, non-coordinating and capable of delocalizing the negative charge;

(\textsuperscript{m_2}) reaction of a complex of cobalt with at least one phosphine ligand selected from hindered aliphatic phosphines or bidentate phosphines having general formula (I) or (II), with at least one aluminium alkyl having general formula (III), preferably an aluminium trialkyl, used in a molar excess of 10/1 to 300/1, followed by reaction with a strong Lewis acid selected from compounds or mixtures of compounds having general formulae (V), (VI) or (VII), such as, for example, tris(pentafluorophenyl)boron, in an almost stoichiometric quantity or in slight excess with respect to the cobalt (Co);

(\textsuperscript{m_3}) contact and reaction of a complex of cobalt with at least one phosphine ligand selected from hindered aliphatic phosphines or bidentate phosphines having general formula (I) or (II), with a molar excess of 10/1 to 1,000/1, preferably from 100/1 to 500/1, of at least one aluminium trialkyl or of an alkyl aluminium halide represented by the formula \( \text{AlR''}^\text{m}Z_{3-m} \) wherein \( \text{R''} \) is a linear or branched \( \text{C}_1-\text{C}_8 \) alkyl group, or a mixture thereof, \( Z \) is a halogen, preferably chlorine or bromine, and \( m \) is a decimal number ranging from 1 to 3, followed by addition, to the composition thus obtained, of at
least one compound or mixture of compounds having
general formulae (V), (VI) or (VII), in such
quantities that the ratio between said compound or
mixture of compounds having general formulae (V),
(VI) or (VII), or the aluminium of said compound or
mixture of compounds having general formulae (V),
(VI) or (VII), and the cobalt of the complex of
cobalt with at least one phosphine ligand selected
from hindered aliphatic phosphines or bidentate
phosphines having general formula (I) or (II),
ranges from 0.1 to 15, preferably from 1 to 6.
Examples of compounds or mixtures of compounds
having general formulae (V), (VI) or (VII), capable of
producing an ionic catalytic system by reaction with a
complex of cobalt with at least one phosphine ligand
selected from hindered aliphatic phosphines or bidentate
phosphines having general formula (I) or (II) according
to the present invention, are described, although with
reference to the formation of ionic metalloocene
complexes, in the following publications, whose contents
are incorporated herein as reference:
- W. Beck et al., "Chemical Reviews" (1988), Vol. 88,
  pages 1405-1421;
- S. H. Stares, "Chemical Reviews" (1993), Vol. 93,
  pages 927-942;
- European patent applications EP 277 003, EP 495 375,
- published International patent applications WO
Specific examples of compounds or mixtures of compounds having general formulae (V), (VI) or (VII), particularly useful for the aim of the present invention are: tributylammonium-tetrakis-pentafluorophenyl-borate, tributylammonium-tetrakis-pentafluorophenyl-aluminate, tributylammonium-tetrakis-[(3, 5-di-( trifluorophenyl ))-borate, tributylammonium-tetrakis-(4-fluorophenyl )]-borate, N,N-dimethylbenzylammonium-tetrakis-pentafluorophenyl-borate, N,N-di-methylhexylammonium-tetrakis-pentafluorophenyl-borate, N,N-dimethylanilinium-tetrakis-pentafluorophenyl-borate, N,N-dimethylanilinium-tetrakis-(pentafluorophenyl )-aluminate, di-(propyl)-ammonium-tetrakis-(pentafluorophenyl )-borate, di-(cyclohexyl)-ammonium-tetrakis-(pentafluorophenyl )-borate, tri-phenyl-carbenium-tetrakis-(pentafluorophenyl )-borate, tri-phenylcarbenium-tetrakis-(penta-fluorophenyl )-aluminate, tris-(pentafluorophenyl )boron, tris-(penta-fluorophenyl )-aluminium, or mixtures thereof. Tetrakis-pentafluorophenyl-borates are preferred.

For the aim of the present description and of the following claims, the term "mole" and "molar ratio" are used with reference to compounds consisting of molecules and also with reference to atoms and ions, omitting, for the latter, the terms gram atom or atomic ratio, even if scientifically more correct.

Other additives or components can be optionally
added to the above catalytic system in order to adapt it so as to satisfy specific practical requirements. The catalytic systems thus obtained should therefore be considered as being included in the scope of the present invention. Additives and/or components which can be added in the preparation and/or formulation of the above catalytic system are, for example: inert solvents, such as, for example, aliphatic and/or aromatic hydrocarbons; aliphatic and/or aromatic ethers; weakly coordinating additives (e.g., Lewis bases) selected, for example, from non-polymerizable olefins; sterically hindered or electronically poor ethers; halogenating agents such as, for example, silicon halides, halogenated hydrocarbons, preferably chlorinated; or mixtures thereof.

As already specified above, said catalytic system can be prepared according to methods known in the art.

Said catalytic system, for example, can be prepared separately (preformed) and subsequently introduced into the polymerization environment. In this respect, said catalytic system can be prepared by reacting at least one complex of cobalt with at least one phosphine ligand selected from hindered aliphatic phosphines or bidentate phosphines having general formula (I) or (II) with at least one co-catalyst, optionally in the presence of other additives or components selected from those listed above, in the presence of a solvent such as, for example, toluene, heptane, at a temperature ranging from 20°C to 60°C, for a time ranging from 10 seconds to 10 hours,
preferably ranging from 30 seconds to 5 hours. Further details on the preparation of said catalytic system can be found in the examples provided hereunder.

Alternatively, said catalytic system can be prepared in situ, i.e. directly in the polymerization environment. In this respect, said catalytic system can be prepared by introducing the complex of cobalt with at least one phosphine ligand selected from hindered aliphatic phosphines or bidentate phosphines having general formula (I) or (II), the co-catalyst and the preselected 1,3-buta diene to be polymerized, separately, operating under the conditions in which the polymerization is carried out.

For the aim of the process object of the present invention, said catalytic systems can also be supported on inert solids, preferably consisting of silicon and/or aluminium oxides, such as, for example, silica, alumina or silico-aluminates. Known supporting techniques can be used for supporting said catalytic systems, generally comprising contact, in a suitable inert liquid medium, between the carrier, optionally activated by heating to temperatures higher than 200°C, and one or both of the components, i.e. the complex of cobalt with at least one phosphine ligand selected from hindered aliphatic phosphines or bidentate phosphines having general formula (I) or (II) and the co-catalyst, of the catalytic system, object of the present invention. For the aim of the present invention, it is not necessary for both
components to be supported, as either the complex of cobalt with at least one phosphine ligand selected from hindered aliphatic phosphines or bidentate phosphines having general formula (I) or (II) alone, or the co-catalyst, can be present on the surface of the carrier. In the latter case, the missing component on the surface is subsequently put in contact with the supported component, at the moment in which the catalyst active for the polymerization is to be formed.

The complex of cobalt with at least one phosphine ligand selected from hindered aliphatic phosphines or bidentate phosphines having general formula (I) or (II), and the catalytic systems based thereon, which have been supported on a solid by the functionalization of the latter and formation of a covalent bond between the solid and the complex of cobalt with at least one phosphine ligand selected from hindered aliphatic phosphines or bidentate phosphines having general formula (I) or (II), are also included in the scope of the present invention.

The quantity of complex of cobalt with at least one phosphine ligand selected from hindered aliphatic phosphines or bidentate phosphines having general formula (I) or (II) and of co-catalyst that can be used in the process object of the present invention, varies according to the polymerization process to be carried out. Said quantity is in any case such as to obtain a molar ratio between the cobalt present in the complex of cobalt with at least one phosphine ligand selected from hindered
aliphatic phosphines or bidentate phosphines having general formula (I) or (II) and the metal present in the co-catalyst, e.g., aluminium when the co-catalyst is selected from aluminium alkyls having general formula (III) or aluminoxanes having general formula (IV), boron when the co-catalyst is selected from compounds or mixtures of compounds having general formulae (V), (VI) or (VII), included within the values indicated above.

According to a preferred embodiment of the present invention, said monodentate aromatic phosphine can be selected from aromatic phosphines having general formula (VIII):

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

wherein:

- \( R \) is selected from linear or branched \( C_1-C_{16} \), preferably \( C_1-C_8 \), alkyl groups, \( C_3-C_{16} \), preferably \( C_3-C_8 \), cycloalkyl groups, optionally substituted, allyl groups, phenyl optionally substituted;
- \( \text{Ph} \) is phenyl optionally substituted;
- \( m \) and \( n \), different from each other, are 1 or 2, \( m+n \) being = 3.

According to a preferred embodiment of the present invention, said monodentate aromatic phosphine can be selected from: cyclohexyl-diphenylphosphine \( (\text{PCyPh}_2) \), iso-propyl-diphenylphosphine \( (\text{PPrPh}_2) \), methyl-diphenylphosphine \( (\text{PMePh}_2) \), ethyl-diphenylphosphine \( (\text{PETPh}_2) \), \( \Omega \)-propyl-diphenylphosphine \( (\text{P}^\omega \text{PrPh}_2) \), dimethyl-phenylphosphine \( (\text{PMe}_2\text{Ph}) \), diethyl-phenylphosphine
(PEt₂Ph), dicyclohexyl-phenylphosphine (PCy₂Ph), tri-phenylphosphine (PPh₃). Cyclohexyl-diphenylphosphine (PCyPh₂), iso-propyl-diphenylphosphine (PPrPh₂), are preferred.

It should be pointed out that when a monodentate aromatic phosphine with a high steric hindrance is used, such as, for example, cyclohexyl-diphenylphosphine (PCyPh₂) having a cone angle (Θ) equal to 153°, iso-propyl-diphenylphosphine (PPrPh₂) having a cone angle (Θ) equal to 150°, a stereoregular diblock polybutadiene is obtained, in which the polybutadiene block having a 1,2 structure has a higher crystallinity degree, i.e. it has a content of syndiotactic triads [(rr) %] higher than or equal to 50%, preferably ranging from 60% to 80%, and has a melting point (T_m) higher than or equal to 70°C, preferably ranging from 95°C to 140°C, when a monodentate aromatic phosphine with a lower steric hindrance is used, such as, for example, methyl-diphenylphosphine (PMePh₂) having a cone angle (Θ) equal to 136°, ethyl-diphenylphosphine (PEtPh₂) having a cone angle (Θ) equal to 141°, α-propyl-diphenylphosphine (PαPrPh₂) having a cone angle (Θ) equal to 142°, dimethyl-phenylphosphine (PMe₂Ph) having a cone angle (Θ) equal to 127°, diethyl-phenylphosphine (PET₂Ph) having a cone angle (Θ) equal to 136°, a stereoregular diblock polybutadiene is obtained, in which the polybutadiene block having a 1,2 structure has a lower crystallinity degree, i.e. it has a content of syndiotactic triads [(rr) %] lower than or equal to
50%, preferably ranging from 30% to 40%, and has a melting point ($T_m$) ranging from 50°C to 70°C. The cone angle ($\Theta$) is that indicated by Tolman C. A. in "Chemical Reviews" (1977), Vol. 77, pages 313-348.

According to a preferred embodiment of the present invention, said process can be carried out in the presence of an inert organic solvent selected, for example, from: saturated aliphatic hydrocarbons such as, for example, 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. Said solvent is preferably selected from saturated aliphatic hydrocarbons.

Alternatively, said process can be carried out using, as solvent, the same 1,3-butadiene to be polymerized, according to the process known as "bulk process".

According to a preferred embodiment of the present invention, the concentration of 1,3-butadiene to be polymerized in said inert organic solvent can range from 5% by weight to 50% by weight, preferably ranging from
10% by weight to 20% by weight, with respect to the total weight of the mixture of 1,3-butadiene and inert organic solvent.

According to a preferred embodiment of the present invention, said process can be carried out at a temperature ranging from -70°C to +120°C, preferably from -20°C to +100°C.

As far as the pressure is concerned, it is preferable to operate at the pressure of the components of the mixture to be polymerized, said pressure differing according to the polymerization temperature used.

Said process can be carried out either in continuous or batchwise.

Some illustrative and non-limiting examples are provided hereunder for a better understanding of the present invention and for its practical embodiment.

EXAMPLES

Reagents and materials

The reagents and materials used in the following examples of the invention are indicated in the following list, together with their optional pretreatments and their supplier:

- cobalt dichloride \((\text{CoCl}_2)\) (Strem Chemicals) : used as such;
- di-tert-butylphosphine (Strem Chemicals) : used as such;
- di-tert-butylmethylphosphine (Strem Chemicals) : used as such;
- di-tert-butylcyclohexylphosphine (Strem Chemicals) : used as such;
- di-cyclohexyl-tert-butylphosphine (Strem Chemicals) : used as such;
- 1,2-bis-(diphenylphosphine) ethane (Strem Chemicals) : used as such;
- ethanol (Carlo Erba, RPE) : used as such, or anhydridied by distillation on magnesium (Mg);
- pentane (Aldrich) : pure, ≥ 99.5%, distilled on sodium (Na) in an inert atmosphere;
- 1,3-butadiene (Air Liquide) : pure, ≥ 99.5%, evaporated from the container before each production, dried by passing it through a column packed with molecular sieves and condensed inside the reactor which has been pre-cooled to -20°C;
- toluene (Aldrich) : pure, ≥ 99.5%, distilled on sodium (Na) in an inert atmosphere;
- methylaluminoxane (MAO) (toluene solution at 10% by weight) (Aldrich) : used as such;
- hydrochloric acid in aqueous solution at 37% (Aldrich) : used as such;
- iso-propyl-diphenylphosphine (P'PrPh₂) (Strem Chemicals) : used as such;
- methyl-diphenylphosphine (PMéPh₂) (Strem Chemicals) : used as such;
- tetrahydrofuran (THF) (Carlo Erba, RPE) : maintained at reflux temperature on postassium/benzophenone and then distilled under nitrogen;
- deuterated tetrachloroethane (C₂D₂Cl₄) (Acros) : used as such;
- deuterated chloroform (CDCl₃) (Acros) : used as such.

The following analysis and characterization methods were used.

**Elemental analysis**

a) **Determination of Co**

For the determination of the weight quantity of cobalt (Co) in the complexes of cobalt used for the aim of the present invention, an aliquot weighed exactly, operating in a dry-box under a nitrogen flow, of about 30-50 mg of sample, was placed in a platinum crucible of about 30 ml, together with a mixture of 1 ml of hydrofluoric acid (HF) at 40%, 0.25 ml of sulfuric acid (H₂SO₄) at 96% and 1 ml of nitric acid (HNO₃) at 70%. The crucible was then heated on a plate, increasing the temperature until the appearance of white sulfuric fumes (about 200°C). The mixture thus obtained was cooled to room temperature (20°C-25°C), 1 ml of nitric acid (HNO₃) at 70% was added and the mixture was then heated until the re-appearance of fumes. After repeating the sequence a further two times, a limpid, almost colourless solution was obtained. 1 ml of nitric acid (HNO₃) and about 15 ml of water were then cold added and the mixture was then heated to 80°C for about 30 minutes. The sample thus prepared was diluted with water having a MilliQ purity up to a weight of about 50 g, weighed exactly, to obtain a
solution on which an analytical instrumental determination was carried out using an ICP-OES (optical detection plasma) Thermo Optek IRIS Advantage Duo spectrometer, by comparison with solutions at a known concentration. For this purpose, a calibration line was prepared for each analyte, within the range of 0 ppm - 10 ppm, measuring solutions having a known titre obtained by dilution by weight of certified solutions.

The solution of the sample prepared as described above was diluted again by weighing so as to obtain concentrations close to those used as reference, before carrying out spectrophotometric analysis. All the samples were prepared in duplicate. The results were considered acceptable if the single data of the tests in duplicate did not differ by more than 2% relative with respect to their average value.

b) Chlorine determination

For this purpose, samples of the complexes of cobalt used for the aim of the present invention, about 30 mg - 50 mg, were weighed exactly in 100 ml glasses in a dry-box under a stream of nitrogen. 2 g of sodium carbonate ($\text{Na}_2\text{CO}_3$) and, outside the dry-box, 50 ml of MillQ water, were added. The mixture was brought to boiling point on a plate under magnetic stirring for about 30 minutes. It was left to cool, diluted sulfuric acid ($\text{H}_2\text{SO}_4$) 1/5, was added until the reaction became acid and the mixture was titrated with silver nitrate ($\text{AgNO}_3$) 0.1 N with a potentiometer titrator.
c) Determination of carbon, hydrogen and phosphorous

The determination of the carbon, hydrogen, and phosphorous, in the complexes of cobalt used for the aim of the present invention, as well as in the ligands used for the aim of the present invention, was carried out using a Carlo Erba automatic analyzer Mod. 1106.

13C-HMR and 1H-HMR spectra

The 13C-HMR and 1H-HMR spectra were registered by means of a nuclear magnetic resonance spectrometer mod. Bruker Avance 400, using deuterated tetrachloroethane (C2D2Cl4) at 103°C, and hexamethyldisiloxane (HDMS) as internal standard, or using deuterated chloroform (CDCl3), at 25°C, and tetramethylsilane (TMS) as internal standard. Polymeric solutions having concentrations equal to 10% by weight with respect to the total weight of the polymeric solution, were used for the purpose.

The microstructure of the polymers, i.e. content of 1,4-cis units (%), content of 1,2 units (%) and content of syndiotactic triads [(rr) (%)], was determined by analysis of the above spectra on the basis of what is indicated in literature by Mochel, V. D., in "Journal of Polymer Science Part A-1: Polymer Chemistry" (1972), Vol. 10, Issue 4, pages 1009-1018.

Two-dimensional 13C-NMR spectra

The two-dimensional 13C-NMR spectra were registered by means of a nuclear magnetic resonance spectrometer mod. Bruker Avance 400, using deuterated tetrachloroethane (C2D2Cl4) at 103°C, and
hexamethyldisiloxane (HDMS) as internal standard. Polymeric solutions having concentrations equal to 10% by weight with respect to the total weight of the polymeric solution, were used for the purpose.

The attribution of the signals was carried out by means of two-dimensional HSQC ("Heteronuclear Single Quantum Correlation") and HMBC ("Heteronuclear Multiple Bond Correlation") NMR techniques which allow long-term proton-carbon correlations to be established ("\(^1\text{H}-\text{C}\) long term correlations") : in this way, the signals characteristic of the junctions between the polybutadiene block having a 1,4-cis structure and the polybutadiene block having a 1,2 structure, could be identified (see figure A):

![Figure A](image)

Furthermore, the two-dimensional \(^1\text{H}-\text{H}\) COSY ("Correlation Spectroscopy") NMR technique allowed the chemical shifts of the protons of the adjacent 1,4-cis and 1,2 units (i.e. the junction units indicated with ") "different" from those attributable to the 1,4-cis and 1,2 units inside the respective blocks, to be identified. By crossing the data obtained with said \(^1\text{H}-\text{H}\) COSY technique, with the data obtained with the above-mentioned HSQC and HMBC techniques, it was possible to
identify the signals relating to the junctions between different units.

**I.R. Spectra**

The I.R. spectra (FT-IR) were registered by means of Thermo Nicolet Nexus 670 and Bruker IFS 48 spectrophotometers.

The I.R. spectra (FT-IR) of the ligands used in the present invention, were obtained by dispersing the ligand to be analyzed in anhydrous potassium bromide (KBr) (disks of KBr), or in a suspension of nujol.

The I.R. spectra (FT-IR) of the complexes of cobalt used in the present invention, were obtained by dispersing the complex of cobalt to be analyzed in anhydrous potassium bromide (KBr) (disks of KBr), or in a suspension of nujol.

The I.R. (FT-IR) spectra of the polymers were obtained from polymeric films on tablets of potassium bromide (KBr), said films being obtained by deposition of a solution of the polymer to be analyzed in hot o-dichlorobenzene. The concentration of the polymeric solutions analyzed was equal to 10% by weight with respect to the total weight of the polymeric solution.

**Thermal Analysis (DSC)**

The DSC ("Differential Scanning Calorimetry") thermal analysis, for determining the melting point ($T_m$), the glass transition temperature ($T_g$) and the crystallization temperature ($T_c$) of the polymers obtained, was carried out using a differential scanning calorimeter.
DSC Q1000 of TA Instruments.

Standard DSC ("Differential Scanning Calorimetry" - DSC STD) thermal analysis envisages the use of isothermal conditions or a constant variation in the temperature over the whole measurement range. Under these conditions, the interpretation of some transformations, or the quantification of some processes and the energy involved therein, is often complex and at times impossible. In order to solve these difficulties, the Temperature Modulated Differential Scanning Calorimetry" technique (TMDSC) was introduced, in which a variation in relation to the time, called modulation, is applied to the classical temperature profile. The basic difference between DSC STD and TMDSC therefore lies in the application of a modulated temperature profile superimposed with respect to the simple linear variation of the temperature, with a consequent continuous variation of the instantaneous heating rate. This allows the contribution to the heat flow given by phenomena which relate to the variation in the heating rate (i.e. the reversing heat flow) such as the heat capacity (Cp), to be identified and deconvolved. By the difference between the total heat flow (measured at a constant rate) and the reversing heat flow, the contribution given by phenomena which do not relate to the heat capacity (i.e. the non-reversing heat flow), can be separated.

In practice, this separation consists of being able to distinguish processes of the glass
transition/melting/crystallization type which take place within the same temperature range according to the following equation:

\[ \frac{dH}{dt} = C_p \left( \frac{dT}{dt} \right) + f(T,t) \]

wherein:
- \( \frac{dH}{dt} \) is the total heat flow;
- \( C_p \) is the heat capacity;
- \( \left( \frac{dT}{dt} \right) \) is the heating rate;
- \( C_p \left( \frac{dT}{dt} \right) \) is the reversing heat flow;
- \( f(T,t) \) is the non-reversing heat flow.

For these reasons, the following thermal cycles were applied, in which the Temperature Modulated Differential Scanning Calorimetry (TMDSC) was applied during cooling cycles so as to be able to distinguish the crystallization phenomenon from the glass transition temperature (s) (\( \tau_g \)).

The cycles were repeated in order to ensure that the product does not degrade due to the temperature (\( T_{\text{max}} = 155^\circ C \)).

For this purpose, the thermal cycle applied to the samples was the following (\( \tau = \) temperature; \( v = \) scanning rate):
- conditioning of the sample: heating from \( T = 25^\circ C \) to \( T = 155^\circ C \) at \( v = 10^\circ C/\text{min} \) in standard scanning followed by a cooling profile from \( T = 155^\circ C \) to \( T = -130^\circ C \) at \( v = 3^\circ C/\text{min} \) in a modulation of +/-0.47°C every 60 seconds with TMDSC (i.e. Modulated DSC) (1st cycle);
subsequent heating from $T = -130^\circ C$ to $T = 155^\circ C$ at $v = 10^\circ C/min$ (standard scanning) (2nd cycle); 
- maintaining the sample at $T = 155^\circ C$ for 2 minutes and subsequent cooling with the same procedure as the 1st cycle (IMDSC) (3rd cycle);
- tail heating $T = -130^\circ C$ to $T = 155^\circ C$ with the same procedure as the 2nd cycle (standard scanning) (4th cycle).

**Molecular weight determination**

The determination of the molecular weight (MW) of the polymers obtained was carried out by means of GPC ("Gel Permeation Chromatography") operating under the following conditions:
- Agilent 1100 pump;
- I.R. Agilent 1100 detector;
- PL Mixed-A columns;
- solvent/eluent: tetrahydrofuran (THF);
- flow-rate: 1 ml/min;
- temperature: 25°C;

- molecular mass calculation: Universal Calibration method.

The weight average molecular weight $M_w$ and the polydispersion Index" (PDI) corresponding to the $M_w/M_n$ ratio ($M_n$ = number average molecular weight), are reported.

**Atomic Force Microscopy (AFM)**

For this purpose, a thin film of the stereoregular diblock polybutadiene to be analyzed was prepared, by
depositing a solution in chloroform or in toluene, of said stereoregular diblock polybutadiene, by means of spin-coating on a silicon substrate.

The analysis was carried out without dynamic contact (non-contact mode or tapping mode), using a NTEGRA Spectra atomic force microscope (AFM) of N-MDT. During the scanning of the surface of said thin film, the variations in the amplitude of the oscillations of the tip provide topographical information relating to the surface of the same (HEIGHT image). Furthermore, the phase variations of the oscillations of the tip can be used for distinguishing between different types of materials present on the surface of said film (different phases of the material). Figures 19 and 20 provided hereunder, for example, show the data obtained for the stereoregular diblock polybutadiene obtained in Example 27 (MM71).

Dynamic Mechanical Analysis (DMA)

The Dynamic Mechanical Analysis (DMA) was carried out using a RMS 800 rheometer of Rheometrics Scientific, equipped with 8 mm parallel plates geometry.

The samples to be analyzed were charged into the rheometer and thermostat-regulated at 130°C before being analyzed. Four consecutive frequency sweeps were carried out for each sample, at 130°C, at 100 rad/s and at 0.01 rad/s, in order to reach the complete relaxation of the stress connected with the charging and the squeezing of the sample between the plates. A further series of
frequency sweeps was carried out, on the same sample, downstream of this series of frequency sweeps, from 100 rad/s to 0.1 rad/s, at 110°C, 90°C, 70°C, 50°C and 30°C, in order to study the response of the sample in relation to both the frequency and the temperature.

As a comparison, in addition to the polybutadiene sample obtained in Example 19 (G1168) [1,4-cis polybutadiene (reference homopolymer)], a sample obtained from commercial polybutadienes with a high 1,4-cis content, i.e. Europrene NEOCIS® BR 40 (BR40) was subjected to the same analysis.

As an example, Figure 15 provided hereunder, shows the elastic modulus values (G') for the stereoregular diblock polybutadienes of Examples 20 (MM59), and 21 (MM57) and for the polybutadiene reference samples of Example 19 (G1168) and Europrene NEOCIS® BR 40 (BR40).

EXAMPLE 1

Synthesis of CoCl₂(P'Bu₃)₂

A solution of tri-tert-butylphosphine (1.14 g, 5.6 mmoles) in ethanol (20 ml) was added dropwise, under stirring, to a solution of anhydrous cobalt dichloride (CoCl₂) (0.293 g, 2.26 mmoles) in ethanol (30 ml). A light blue precipitate was formed.

The suspension obtained was kept, under stirring, at room temperature (25°C), for 20 hours, and subsequently filtered on a vacuum filter. The residue remaining on the filter was dried under vacuum, washed with pentane (2 x 15 ml) and with ethanol (2 x 10 ml), at a low temperature.
(-50°C), in order to remove traces of tri-tert-butylphosphine in excess and unreacted cobalt dichloride (CoCl₂).

The solid residue obtained was dried under vacuum, overnight, obtaining 0.75 g of a light-blue solid (yield equal to 62.1% based on the cobalt dichloride (CoCl₂) charged).

Elemental analysis [found (calculated)]: Co: 11.09% (11.03%); Cl: 13.01% (13.27%); P: 11.41% (11.59%).

FT-IR (KBr): ν (cm⁻¹) 2954 (m); 2924 (s); 2854 (m); 1465 (s); 1378 (m).

**EXAMPLE 2**

**Synthesis of CoCl₂(P^{+}Bu₂Me)₂**

A solution of di-tert-butylmethylphosphine (1.35 g, 8.4 mmoles) in ethanol (10 ml) was added to a solution of anhydrous cobalt dichloride (CoCl₂) (0.37 g, 2.8 mmoles) in ethanol (25 ml). A blue suspension was immediately formed, which was kept, under stirring, at room temperature (25°C), for 24 hours, and subsequently filtered on a vacuum filter.

The blue residue remaining on the filter was washed with small quantities of ethanol and pentane, and subsequently dried under vacuum, obtaining a blue solid which was subjected to extraction, in continuous, with pentane at boiling point, obtaining a solid in the form of crystals. Said crystals were formed directly during the extraction process on the bottom of the flask used for the purpose, further crystals were subsequently
obtained by removing the pentane solution and cooling the
same to -30°C, obtaining 0.88 g of a solid in the form of
blue-coloured crystals (yield equal to 70.3% based on the
cobalt dichloride (C0Cl2) charged).

Elemental analysis [found (calculated)]: Co: 13.70%
(13.09%); CI: 16.30% (15.75%); P: 13.50% (15.75%).

FT-IR (KBr): ν (cm⁻¹) 2963 (s), 2949 (s), 2905 (m),
2873 (m), 1475 (s), 1396 (m), 1372 (s), 1304 (s), 1182
(w), 1127 (s), 1101 (s), 1047 (m), 1025 (m), 943 (m), 886
(s), 818 (s), 759 (m), 726 (w), 641 (m), 485 (w), 471
(w), 455 (m), 414 (w).

EXAMPLE 3

Synthesis of CoCl₂(PCy₃·Bu₂)₂

A solution of di-tert-butylcyclohexylphosphine (2.0
g, 8.8 mmoles) in ethanol (20 ml) was added to a solution
of anhydrous cobalt dichloride (COCl₂) (0.53 g, 4.1
mmoles) in ethanol (40 ml). A blue suspension was formed,
which was kept, under stirring, at room temperature
(25°C), for 48 hours, and subsequently filtered on a
vacuum filter.

The blue residue remaining on the filter was washed
with small quantities of ethanol and pentane, dried under
vacuum, and subsequently subjected to extraction, in
continuous, with pentane at boiling point, obtaining 1.84
25 g of a blue microcrystalline solid (yield equal to 76.5%
based on the cobalt dichloride (COCl2) charged).

Elemental analysis [found (calculated)]: Co: 10.20%
(10.05%); CI: 12.30% (12.09%); P: 10.80% (10.56%).
EXAMPLE 4

Synthesis of CoCl₂(PCy₂Bu)₂

Di-cyclohexyl- tert-butylphosphine (2.0 g, 7.9 mmoles) was added to a solution of anhydrous cobalt dichloride (CoCl₂) (0.49 g, 3.8 mmoles) in ethanol (40 ml).

After a few minutes, a blue solution was formed, which was kept, under stirring, at room temperature (25°C), for 48 hours, and subsequently dried under vacuum. The residue obtained was washed with ethanol (3 x 10 ml) and dried again under vacuum obtaining 2.1 g of a blue microcrystalline solid (yield equal to 86.5% based on the cobalt dichloride (CoCl₂) charged).

Elemental analysis [found (calculated)]: Co: 9.10% (9.23%); Cl: 11.30% (11.10%); P: 9.90% (9.70%).

EXAMPLE 5

Synthesis of CoCl₂(dppe)

A suspension of 1,2-bis (diphenylphosphine) ethane (2.1 g, 5 mmoles) in ethanol (50 ml) was added to a solution of anhydrous cobalt dichloride (CoCl₂) (0.55 g, 4.2 mmoles) in ethanol (25 ml): the colour of the suspension rapidly changed from a dark-blue colour to turquoise.

The suspension obtained was heated to reflux temperature for 3 hours, cooled to room temperature (25°C), and subsequently filtered on a vacuum filter.

The residue remaining on the filter was washed several times with ethanol and subsequently with pentane,
and was then dried under vacuum, at room temperature (25°C), overnight, obtaining 1.96 g of a solid product (yield equal to 88% based on the cobalt dichloride (CoCl$_2$) charged).

Elemental analysis [found (calculated)]: Co: 11.20% (10.87%); Cl: 13.25% (13.08%); P: 11.30% (11.42%).

FT-IR (KBr): $\nu$ (cm$^{-1}$) 3053 (m); 1485 (m); 1435 (s); 1159 (m); 1104 (s); 966 (m); 744 (s); 694 (s); 546 (m); 509 (sm).

**EXAMPLE 6 (MM4 6)**

**Synthesis of 1,4-cis polybutadiene (reference homopolymer)**

2 ml of 1,3-butadiene, equal to about 1.4 g, were condensed at a low temperature (-20°C) in a 25 ml test-tube. 7.0 ml of toluene were subsequently added and the temperature of the solution thus obtained was brought to 20°C. Methylaluminoxane (MAO) in a toluene solution (6.3 ml; 1x10$^{-2}$ moles, equal to about 0.58 g) was then added, and subsequently the complex CoCl$_2$ (P)$_2$ (2.68 ml of toluene solution at a concentration of 2 mg/ml; 1x10$^{-5}$ moles, equal to about 5.4 mg), obtained as described in Example 1. The whole mixture was kept under magnetic stirring, at 20°C, for 40 minutes. The polymerization was then quenched by the addition of 2 ml of methanol containing a few drops of hydrochloric acid. The polymer obtained was then coagulated by the addition of 40 ml of a methanol solution containing 4% of antioxidant Irganox® 1076 (Ciba), obtaining 1.4 g of polybutadiene having a
content of 1,4-cis units equal to 96.8%: further characteristics of the process and of the polybutadiene obtained are indicated in Table 1.

Figure 1(a) shows the FT-IR spectrum of the polybutadiene obtained.

EXAMPLE 7 (MM48)

Synthesis of stereoregular diblock polybutadiene with a 1,4-cis/syndiotactic 1,2 structure (invention)

2 ml of 1,3-butadiene, equal to about 1.4 g, were condensed at a low temperature (-20°C) in a 25 ml test-tube. 7.0 ml of toluene were subsequently added and the temperature of the solution obtained was brought to 20°C. Methylaluminoxane (MAO) in a toluene solution (6.3 ml; 1x10^{-2} moles, equal to about 0.58 g), was then added and subsequently the complex COCl₂(P'B₄)₂ (2.68 ml of toluene solution at a concentration of 2 mg/ml; 1x10^{-5} moles, equal to about 5.4 mg), obtained as described in Example 1. The whole mixture was kept under magnetic stirring at 20°C, for 5 minutes, after which iso-propyl-diphenylphosphine (P'PPh₂) in a toluene solution (0.55 ml; 1.2x10^{-5} moles, equal to about 2.7 mg; molar ratio P/Co = 1.2), was added. The polymerization was left to proceed for a further 100 minutes and was subsequently quenched by the addition of 2 ml of methanol containing a few drops of hydrochloric acid. The polymer obtained was then coagulated by the addition of 40 ml of a methanol solution containing 4% of antioxidant Irganox® 1076 (Ciba), obtaining 1.4 g of stereoregular diblock
polybutadiene having a block of polybutadiene with a 1,4-cis structure and a block of polybutadiene with a syndiotactic 1,2 structure (molar ratio 35.9/64.1).

Further characteristics of the process and of the stereoregular diblock polybutadiene obtained, are indicated in Table 1.

Figure 1 (b) shows the FT-IR spectrum of the stereoregular diblock polybutadiene obtained.

Figure 2 shows the DSC diagram of the stereoregular diblock polybutadiene obtained.

**EXAMPLE 8 (MM49)**

Synthesis of stereoregular diblock polybutadiene with a 1,4-cis/syndiotactic 1,2 structure (invention)

2 ml of 1,3-butadiene, equal to about 1.4 g, were condensed at a low temperature (-20°) in a 25 ml test-tube. 7.0 ml of toluene were subsequently added and the temperature of the solution obtained was brought to 20°C. Methylaluminoxane (MAO) in a toluene solution (6.3 ml; 1x10⁻² moles, equal to about 0.58 g), was then added and subsequently the complex COCl₂ (P'B₄)₂ (2.68 ml of toluene solution at a concentration of 2 mg/ml; 1x10⁻⁵ moles, equal to about 5.4 mg), obtained as described in Example 1. The whole mixture was kept under magnetic stirring, at 20°C, for 12 minutes, after which iso-propyl-diphenylphosphine (P₂PrPh₂) in a toluene solution (0.55 ml; 1.2x10⁻⁵ moles, equal to about 2.7 mg; molar ratio P/Co = 1.2), was added. The polymerization was left to proceed for a further 93 minutes and was subsequently
quenched by the addition of 2 ml of methanol containing a few drops of hydrochloric acid. The polymer obtained was then coagulated by the addition of 40 ml of a methanol solution containing 4% of antioxidant Irganox® 1076 (Ciba), obtaining 1.4 g of stereoregular diblock polybutadiene having a block of polybutadiene with a 1,4-cis structure and a block of polybutadiene with a syndiotactic 1,2 structure (molar ratio 54.5/45.5): further characteristics of the process and of the stereoregular diblock polybutadiene obtained, are indicated in Table 1.

Figure 1 (c) shows the FT-IR spectrum of the stereoregular diblock polybutadiene obtained.

Figure 3 shows the $^1$H-NMR and $^{13}$C-NMR spectra of the stereoregular diblock polybutadiene obtained.

**EXAMPLE 9 (MM47)**

Synthesis of stereoregular diblock polybutadiene with a 1,4-cis/syndiotactic 1,2 structure (invention)

2 ml of 1,3-butadiene, equal to about 1.4 g, were condensed at a low temperature (-20°) in a 25 ml test-tube. 7.0 ml of toluene were subsequently added and the temperature of the solution obtained was brought to 20°C. Methylaluminoxane (MAO) in a toluene solution (6.3 ml; $1 \times 10^{-2}$ moles, equal to about 0.58 g), was then added and subsequently the complex $\text{COCI}_2(\text{P}-\text{Bu}_3)_2$ (2.68 ml of toluene solution at a concentration of 2 mg/ml; $1 \times 10^{-5}$ moles, equal to about 5.4 mg), obtained as described in Example 1. The whole mixture was kept under magnetic stirring, at
20°C, for 25 minutes, after which iso-propyl-diphenylphosphine \((\text{P}^3\text{PrPh}_2)\) in a toluene solution (0.55 ml; 1.2x1CT \(_5\) moles, equal to about 2.7 mg; molar ratio P/Co = 1.2), was added. The polymerization was left to proceed for a further 80 minutes and was subsequently quenched by the addition of 2 ml of methanol containing a few drops of hydrochloric acid. The polymer obtained was then coagulated by the addition of 40 ml of a methanol solution containing 4% of antioxidant Irganox\textsuperscript® 1076 (Ciba), obtaining 1.4 g of stereoregular diblock polybutadiene having a block of polybutadiene with a 1,4-cis structure and a block of polybutadiene with a syndiotactic 1,2 structure (molar ratio 68/32): further characteristics of the process and of the stereoregular diblock polybutadiene obtained, are indicated in Table 1.

Figure 1 (d) shows the FT-IR spectrum of the stereoregular diblock polybutadiene obtained.

Figure 4 shows the \(^1^H\text{-NMR} \) and \(^{13}C\text{-NMR} \) spectra of the stereoregular diblock polybutadiene obtained.

Figure 5 shows the DSC diagram of the stereoregular diblock polybutadiene obtained.

**EXAMPLE 10 (MM53)**

Synthesis\_of\ 1,4-cis\ polybutadiene\_ (reference homopolymer )

2 ml of 1,3-butadiene, equal to about 1.4 g, were condensed at a low temperature (-20°C) in a 25 ml test-tube. 7.5 ml of toluene were subsequently added and the temperature of the solution obtained was brought to 20°C.
Methylaluminoxane (MAO) in a toluene solution (6.3 ml; 1x1CT^2 moles, equal to about 0.58 g) was then added, and subsequently the complex COCl_2 (P'B^Me)_2 (2.25 ml of toluene solution at a concentration of 2 mg/ml; 1x1CT^5 moles, equal to about 4.5 mg), obtained as described in Example 2. The whole mixture was kept under magnetic stirring, at 20°C, for 40 minutes. The polymerization was then quenched by the addition of 2 ml of methanol containing a few drops of hydrochloric acid. The polymer obtained was then coagulated by the addition of 40 ml of a methanol solution containing 4% of antioxidant Irganox® 1076 (Ciba), obtaining 1.035 g of polybutadiene having a content of 1,4-cis units equal to 96.9%: further characteristics of the process and of the polybutadiene obtained are indicated in Table 1.

Figure 6(a) shows the FT-IR spectrum of the polybutadiene obtained.

Figure 7 shows the DSC diagram of the polybutadiene obtained.

EXAMPLE 11 (MM54)

Synthesis of stereoregular diblock polybutadiene with a 1,4-cis/syndiotactic 1,2 structure (invention)

2 ml of 1,3-butadiene, equal to about 1.4 g, were condensed at a low temperature (-20°C) in a 25 ml test-tube. 7.5 ml of toluene were subsequently added and the temperature of the solution obtained was brought to 20°C. Methylaluminoxane (MAO) in a toluene solution (6.3 ml; 1x10^{-2} moles, equal to about 0.58 g), was then added and
subsequently the complex \(	ext{CoCl}_2 (P^\text{Bu}_2\text{Me})_2\) (2.25 ml of toluene solution at a concentration of 2 mg/ml; 1x1C\text{t}^5 moles, equal to about 4.5 mg), obtained as described in Example 2. The whole mixture was kept under magnetic stirring, at 20°C, for 12 minutes, after which iso-propyl-diphenylphosphine \((P^i\text{PrPh}_2)\) in a toluene solution (0.55 ml; 1.2x1C\text{t}^5 moles, equal to about 2.7 mg; molar ratio \(P/\text{Co} = 1.2\)), was added. The polymerization was left to proceed for a further 93 minutes and was subsequently quenched by the addition of 2 ml of methanol containing a few drops of hydrochloric acid. The polymer obtained was then coagulated by the addition of 40 ml of a methanol solution containing 4% of antioxidant Irganox® 1076 (Ciba), obtaining 1.4 g of stereoregular diblock polybutadiene having a block of polybutadiene with a 1,4-cis structure and a block of polybutadiene with a syndiotactic 1,2 structure (molar ratio 39.4/60.6). Further characteristics of the process and of the stereoregular diblock polybutadiene obtained, are indicated in Table 1.

Figure 8 shows the \(_1^\text{H}-\text{NMR}\) and \(_{13}^\text{C}-\text{NMR}\) spectra of the stereoregular diblock polybutadiene obtained.

**EXAMPLE 12 (G1173)**

_Synthesis of stereoregular diblock polybutadiene with a 1,4-cis/syndiotactic 1,2 structure (invention)_

2 ml of 1,3-butadiene, equal to about 1.4 g, were condensed at a low temperature \((-20^\circ)\) in a 25 ml test-tube. 7.5 ml of toluene were subsequently added and the
temperature of the solution obtained was brought to 20°C. Methylaluminoxane (MAO) in a toluene solution (6.3 ml; 1x1CT² moles, equal to about 0.58 g), was then added and subsequently the complex \( \text{COCl}_2 (\text{P'}\text{B}^\text{Me})_2 \) (2.25 ml of toluene solution at a concentration of 2 mg/ml; 1x1CT⁵ moles, equal to about 4.5 mg), obtained as described in Example 2. The whole mixture was kept under magnetic stirring, at 20°C, for 25 minutes, after which iso-propyl-diphenylphosphine (\( \text{P}^d\text{Pr}^d\text{Ph}_2 \)) in a toluene solution (0.55 ml; 1.2x10⁻⁵ moles, equal to about 2.7 mg; molar ratio P/Co = 1.2), was added. The polymerization was left to proceed for a further 30 minutes and was subsequently quenched by the addition of 2 ml of methanol containing a few drops of hydrochloric acid. The polymer obtained was then coagulated by the addition of 40 ml of a methanol solution containing 4% of antioxidant Irganox® 1076 (Ciba), obtaining 1.4 g of stereoregular diblock polybutadiene having a block of polybutadiene with a 1,4-cis structure and a block of polybutadiene with a syndiotactic 1,2 structure (molar ratio 48/52): further characteristics of the process and of the stereoregular diblock polybutadiene obtained, are indicated in Table 1.

Figure 6 (b) shows the FT-IR spectrum of the stereoregular diblock polybutadiene obtained.

Figure 9 shows the DSC diagram of the stereoregular diblock polybutadiene obtained.

EXAMPLE 13 (MM64)

Synthesis of stereoregular diblock polybutadiene with a
1,4-cis/syndiotactic 1,2 structure (invention)

2 ml of 1,3-butadiene, equal to about 1.4 g, were condensed at a low temperature (-20°) in a 25 ml test-tube. 7.5 ml of toluene were subsequently added and the temperature of the solution obtained was brought to 20°C. Methylaluminoxane (MAO) in a toluene solution (6.3 ml; 1x1CT² moles, equal to about 0.58 g), was then added and subsequently the complex COCl₂(P'B²Me)₂ (2.25 ml of toluene solution at a concentration of 2 mg/ml; 1x1CT⁵ moles, equal to about 4.5 mg), obtained as described in Example 2. The whole mixture was kept under magnetic stirring, at 20°C, for 25 minutes, after which methyl-diphenylphosphine (PMePh²) in a toluene solution (0.48 ml; 1.2x10⁻⁵ moles, equal to about 2.4 mg; molar ratio P/Co = 1.2), was added. The polymerization was left to proceed for a further 360 minutes and was subsequently quenched by the addition of 2 ml of methanol containing a few drops of hydrochloric acid. The polymer obtained was then coagulated by the addition of 40 ml of a methanol solution containing 4% of antioxidant Irganox® 1076 (Ciba), obtaining 1.4 g of stereoregular diblock polybutadiene having a block of polybutadiene with a 1,4-cis structure and a block of polybutadiene with a syndiotactic 1,2 structure (molar ratio 45.4/54.6): further characteristics of the process and of the stereoregular diblock polybutadiene obtained, are indicated in Table 1.

EXAMPLE 14 (MM50)
Synthesis of 1,4-cis polybutadiene (reference homopolymer)

2 ml of 1,3-butadiene, equal to about 1.4 g, were condensed at a low temperature (-20°) in a 25 ml test-tube. 6.5 ml of toluene were subsequently added and the temperature of the solution obtained was brought to 20°C. Methylaluminoxane (MAO) in a toluene solution (6.3 ml; 1x1CT² moles, equal to about 0.58 g) was then added, and subsequently the complex COCl₂(PCy₂Bu)₂ (3.2 ml of toluene solution at a concentration of 2 mg/ml; 1x10⁻⁵ moles, equal to about 6.4 mg), obtained as described in Example 4. The whole mixture was kept under magnetic stirring, at 20°C, for 180 minutes. The polymerization was then quenched by the addition of 2 ml of methanol containing a few drops of hydrochloric acid. The polymer obtained was then coagulated by the addition of 40 ml of a methanol solution containing 4% of antioxidant Irganox® 1076 (Ciba), obtaining 1.4 g of polybutadiene having a content of 1,4-cis units equal to 97.1%; further characteristics of the process and of the polybutadiene obtained are indicated in Table 1.

Figure 6(c) shows the FT-IR spectrum of the polybutadiene obtained.

EXAMPLE 15 (MM60)

Synthesis of stereoregular diblock polybutadiene with a 1,4-cis/syndiotactic 1,2 structure (invention)

2 ml of 1,3-butadiene, equal to about 1.4 g, were condensed at a low temperature (-20°) in a 25 ml test-
tube. 6.5 ml of toluene were subsequently added and the temperature of the solution obtained was brought to 20°C. Methylaluminoxane (MAO) in a toluene solution (6.3 ml; 1x1CT² moles, equal to about 0.58 g) was then added, and subsequently the complex COCl₂(PCy₂Bu)₂ (3.2 ml of toluene solution at a concentration of 2 mg/ml; 1x1CT⁵ moles, equal to about 6.4 mg), obtained as described in Example 4. The whole mixture was kept under magnetic stirring, at 20°C, for 5 minutes, after which iso-propyl-diphenylphosphine (P²PrPh₂) in a toluene solution (0.55 ml; 1.2x10⁻⁵ moles, equal to about 2.7 mg; molar ratio P/Co = 1.2), was added. The polymerization was left to proceed for a further 10 minutes and was subsequently quenched by the addition of 2 ml of methanol containing a few drops of hydrochloric acid. The polymer obtained was then coagulated by the addition of 40 ml of a methanol solution containing 4% of antioxidant Irganox® 1076 (Ciba), obtaining 1.4 g of stereoregular diblock polybutadiene having a block of polybutadiene with a 1,4-cis structure and a block of polybutadiene with a syndiotactic 1,2 structure (molar ratio 26.7/73.3): further characteristics of the process and of the stereoregular diblock polybutadiene obtained, are indicated in Table 1. Figure 6 (a) shows the FT-IR spectrum of the stereoregular diblock polybutadiene obtained.

EXAMPLE 16 (G1174)

Synthesis of stereoregular diblock polybutadiene with a
1,4-cis/syndiotactic 1,2 structure (invention)

2 ml of 1,3-butadiene, equal to about 1.4 g, were condensed at a low temperature (-20°) in a 25 ml test-tube. 6.5 ml of toluene were subsequently added and the temperature of the solution obtained was brought to 20°C. Methylaluminoxane (MAO) in a toluene solution (6.3 ml; 1x1CT^2 moles, equal to about 0.58 g) was then added, and subsequently the complex COCl₂(PCy₂²Bu)₂ (3.2 ml of toluene solution at a concentration of 2 mg/ml; 1x1CT^5 moles, equal to about 6.4 mg), obtained as described in Example 4. The whole mixture was kept under magnetic stirring, at 20°C, for 25 minutes, after which iso-propyl-diphenylphosphine (P₂PrPh₂) in a toluene solution (0.55 ml; 1.2x10^-⁵ moles, equal to about 2.7 mg; molar ratio P/Co = 1.2), was added. The polymerization was left to proceed for a further 25 minutes and was subsequently quenched by the addition of 2 ml of methanol containing a few drops of hydrochloric acid. The polymer obtained was then coagulated by the addition of 40 ml of a methanol solution containing 4% of antioxidant Irganox® 1076 (Ciba), obtaining 1.4 g of stereoregular diblock polybutadiene having a block of polybutadiene with a 1,4-cis structure and a block of polybutadiene with a syndiotactic 1,2 structure (molar ratio 58.7/41.3):

Further characteristics of the process and of the stereoregular diblock polybutadiene obtained, are indicated in Table 1.

Figure 10 (a) shows the FT-IR spectrum of the
stereoregular diblock polybutadiene obtained.

**EXAMPLE 17 (MM65)**

Synthesis of stereoregular diblock polybutadiene with a
1,4-cis/syndiotactic 1,2 structure (invention)

2 ml of 1,3-butadiene, equal to about 1.4 g, were
condensed at a low temperature (-20°) in a 25 ml test-
tube. 6.5 ml of toluene were subsequently added and the
temperature of the solution obtained was brought to 20°C.
Methylaluminoxane (MAO) in a toluene solution (6.3 ml;
1xlCT² moles, equal to about 0.58 g) was then added, and
subsequently the complex COCl₂(PC₅₂Bu)₂ (3.2 ml of toluene
solution at a concentration of 2 mg/ml; 1xl10⁻⁵ moles,
equal to about 6.4 mg), obtained as described in Example
4. The whole mixture was kept under magnetic stirring, at
20°C, for 5 minutes, after which methyl-diphenylphosphine
(PMePh₂) in a toluene solution (0.48 ml; 1.2x10⁻⁵ moles,
equal to about 2.4 mg; molar ratio P/Co = 1.2), was
added. The polymerization was left to proceed for a
further 247 minutes and was subsequently quenched by the
addition of 2 ml of methanol containing a few drops of
hydrochloric acid. The polymer obtained was then
coagulated by the addition of 40 ml of a methanol
solution containing 4% of antioxidant Irganox® 1076
(Ciba), obtaining 1.4 g of stereoregular diblock
polybutadiene having a block of polybutadiene with a 1,4-
cis structure and a block of polybutadiene with a
syndiotactic 1,2 structure (molar ratio 28.4/71.6):

further characteristics of the process and of the
stereoregular diblock polybutadiene obtained, are indicated in Table 1.

Figure 10 (b) shows the FT-IR spectrum of the stereoregular diblock polybutadiene obtained.

EXAMPLE 18 (MM66)

Synthesis of stereoregular diblock polybutadiene with a 1,4-cis/syndiotactic 1,2 structure (invention)

2 ml of 1,3-butadiene, equal to about 1.4 g, were condensed at a low temperature (-20°C) in a 25 ml test-tube. 6.5 ml of toluene were subsequently added and the temperature of the solution obtained was brought to 20°C. Methylaluminoxane (MAO) in a toluene solution (6.3 ml; 1x10^-2 moles, equal to about 0.58 g) was then added, and subsequently the complex COCl₂(PCy₂Bu)₂ (3.2 ml of toluene solution at a concentration of 2 mg/ml; 1x10^-5 moles, equal to about 6.4 mg), obtained as described in Example 4. The whole mixture was kept under magnetic stirring, at 20°C, for 25 minutes, after which methyl-diphenylphosphine (PMePh₂) in a toluene solution (0.48 ml; 1.2x10^-5 moles, equal to about 2.4 mg; molar ratio P/Co = 1.2), was added. The polymerization was left to proceed for a further 227 minutes and was subsequently quenched by the addition of 2 ml of methanol containing a few drops of hydrochloric acid. The polymer obtained was then coagulated by the addition of 40 ml of a methanol solution containing 4% of antioxidant Irganox® 1076 (Ciba), obtaining 1.4 g of stereoregular diblock polybutadiene having a block of polybutadiene with a 1,4-
cis structure and a block of polybutadiene with a syndiotactic 1,2 structure (molar ratio 75/25): further characteristics of the process and of the stereoregular diblock polybutadiene obtained, are indicated in Table 1.

Figure 10 (c) shows the FT-IR spectrum of the stereoregular diblock polybutadiene obtained.

EXAMPLE 19 (G1168)

Synthesis of 1,4-cis polybutadiene (reference homopolymer)

2 ml of 1,3-butadiene, equal to about 1.4 g, were condensed at a low temperature (-20°) in a 25 ml test-tube. 6.5 ml of toluene were subsequently added and the temperature of the solution obtained was brought to 20°C. Methylaluminoxane (MAO) in a toluene solution (6.3 ml; 1x10^-2 moles, equal to about 0.58 g) was then added, and subsequently the complex COCl₂(PCy²Bu₂)₂ (2.9 ml of toluene solution at a concentration of 2 mg/ml; 1x10^-5 moles, equal to about 5.9 mg), obtained as described in Example 3. The whole mixture was kept under magnetic stirring, at 20°C, for 200 minutes. The polymerization was then quenched by the addition of 2 ml of methanol containing a few drops of hydrochloric acid. The polymer obtained was then coagulated by the addition of 40 ml of a methanol solution containing 4% of antioxidant Irganox® 1076 (Ciba), obtaining 1.4 g of polybutadiene having a content of 1,4-cis units equal to 97%: further characteristics of the process and of the polybutadiene obtained are indicated in Table 1.
Figure 15 shows the elastic modulus ($G'$) of the polybutadiene obtained.

Figure 16 shows the DSC diagram of the polybutadiene obtained.

**EXAMPLE 20 (MM59)**

Synthesis of stereoregular diblock polybutadiene with a 1,4-cis/syndiotactic 1,2 structure (invention)

2 ml of 1,3-butadiene, equal to about 1.4 g, were condensed at a low temperature (-20°) in a 25 ml test-tube. 6.5 ml of toluene were subsequently added and the temperature of the solution obtained was brought to 20°C. Methylaluminoxane (MAO) in a toluene solution (6.3 ml; 1x10^{-2} moles, equal to about 0.58 g) was then added, and subsequently the complex COCl$_2$ (PCy$_2$Bu$_2$)$_2$ (2.9 ml of toluene solution at a concentration of 2 mg/ml; 1x10^{-5} moles, equal to about 5.9 mg), obtained as described in Example 3. The whole mixture was kept under magnetic stirring, at 20°C, for 5 minutes, after which iso-propyl-diphenylphosphine ($P'PrPh_2$) in a toluene solution (0.55 ml; 1.2x10^{-5} moles, equal to about 2.7 mg; molar ratio P/Co = 1.2), was added. The polymerization was left to proceed for a further 10 minutes and was subsequently quenched by the addition of 2 ml of methanol containing a few drops of hydrochloric acid. The polymer obtained was then coagulated by the addition of 40 ml of a methanol solution containing 4% of antioxidant Irganox® 1076 (Ciba), obtaining 1.4 g of stereoregular diblock polybutadiene having a block of polybutadiene with a 1,4-
cis structure and a block of polybutadiene with a syndiotactic 1,2 structure (molar ratio 31.4/68.6): further characteristics of the process and of the stereoregular diblock polybutadiene obtained, are indicated in Table 1.

Figure 13 (a) shows the FT-IR spectrum of the stereoregular diblock polybutadiene obtained.

Figure 14 shows the $^1$H-NMR and $^{13}$C-NMR spectra of the stereoregular diblock polybutadiene obtained.

Figure 15 shows the elastic modulus ($G'$) of the stereoregular diblock polybutadiene obtained.

**EXAMPLE 21 (MM57)**

**Synthesis of stereoregular diblock polybutadiene with a 1,4-cis/syndiotactic 1,2 structure (invention)**

2 ml of 1,3-butadiene, equal to about 1.4 g, were condensed at a low temperature (-20°) in a 25 ml test-tube. 6.5 ml of toluene were subsequently added and the temperature of the solution obtained was brought to 20°C. Methylaluminoxane (MAO) in a toluene solution (6.3 ml; 1x10$^{-2}$ moles, equal to about 0.58 g) was then added, and subsequently the complex CoCl$_2$ ($^5$Cy$^+$Bu$_2$)$_2$ (2.9 ml of toluene solution at a concentration of 2 mg/ml; 1x10$^{-5}$ moles, equal to about 5.9 mg), obtained as described in Example 3. The whole mixture was kept under magnetic stirring, at 20°C, for 25 minutes, after which iso-propyl-diphenylphosphine ($^5$P$^+$PrPh$_2$) in a toluene solution (0.55 ml; 1.2x10$^{-5}$ moles, equal to about 2.7 mg; molar ratio P/Co = 1.2), was added. The polymerization was left to
proceed for a further 80 minutes and was subsequently quenched by the addition of 2 ml of methanol containing a few drops of hydrochloric acid. The polymer obtained was then coagulated by the addition of 40 ml of a methanol solution containing 4% of antioxidant Irganox® 1076 (Ciba), obtaining 1.4 g of stereoregular diblock polybutadiene having a block of polybutadiene with a 1,4-cis structure and a block of polybutadiene with a syndiotactic 1,2 structure (molar ratio 62.5/37.5):

Further characteristics of the process and of the stereoregular diblock polybutadiene obtained, are indicated in Table 1.

Figure 15 shows the elastic modulus ($G'$) of the stereoregular diblock polybutadiene obtained.

Figure 10 (d) shows the FT-IR spectrum of the stereoregular diblock polybutadiene obtained.

Figure 11 shows the DSC diagram of the stereoregular diblock polybutadiene obtained.

**EXAMPLE 22 (MM58)**

Synthesis of stereoregular diblock polybutadiene with a 1,4-cis/syndiotactic 1,2 structure (invention)

2 ml of 1,3-butadiene, equal to about 1.4 g, were condensed at a low temperature (-20°C) in a 25 ml test-tube. 6.5 ml of toluene were subsequently added and the temperature of the solution obtained was brought to 20°C. Methylaluminoxane (MAO) in a toluene solution (6.3 ml; 1x10^-2 moles, equal to about 0.58 g) was then added, and subsequently the complex COCl2 (PCy^5Bu2)2 (2.9 ml of toluene
solution at a concentration of 2 mg/ml; 1x1CT^5 moles, equal to about 5.9 mg), obtained as described in Example 3. The whole mixture was kept under magnetic stirring, at 20°C, for 45 minutes, after which iso-propyl-diphenylphosphine (P^3PrPh₂) in a toluene solution (0.55 ml; 1.2x1CT^5 moles, equal to about 2.7 mg; molar ratio P/Co = 1.2), was added. The polymerization was left to proceed for a further 60 minutes and was subsequently quenched by the addition of 2 ml of methanol containing a few drops of hydrochloric acid. The polymer obtained was then coagulated by the addition of 40 ml of a methanol solution containing 4% of antioxidant Irganox® 1076 (Ciba), obtaining 1.4 g of stereoregular diblock polybutadiene having a block of polybutadiene with a 1,4-cis structure and a block of polybutadiene with a syndiotactic 1,2 structure (molar ratio 85.1/14.9); further characteristics of the process and of the stereoregular diblock polybutadiene obtained, are indicated in Table 1.

Figure 13 (b) shows the FT-IR spectrum of the stereoregular diblock polybutadiene obtained.

Figure 12 shows the DSC diagram of the stereoregular diblock polybutadiene obtained.

**EXAMPLE 23 (MM68)**

Synthesis of stereoregular diblock polybutadiene with a 1,4-cis/syndiotactic 1,2 structure (invention)

2 ml of 1,3-butadiene, equal to about 1.4 g, were condensed at a low temperature (-20°) in a 25 ml test-
tube. 6.5 ml of toluene were subsequently added and the temperature of the solution obtained was brought to 20°C. Methylaluminoxane (MAO) in a toluene solution (6.3 ml; 1x1CT^2 moles, equal to about 0.58 g) was then added, and subsequently the complex COCl_2·(PCy^2Bu_2)_2 (2.9 ml of toluene solution at a concentration of 2 mg/ml; 1x1CT^5 moles, equal to about 5.9 mg), obtained as described in Example 3. The whole mixture was kept under magnetic stirring, at 20°C, for 5 minutes, after which methyl-diphenylphosphine (PMePh_2) in a toluene solution (0.48 ml; 1.2x10^{-5} moles, equal to about 2.4 mg; molar ratio P/Co = 1.2), was added. The polymerization was left to proceed for a further 145 minutes and was subsequently quenched by the addition of 2 ml of methanol containing a few drops of hydrochloric acid. The polymer obtained was then coagulated by the addition of 40 ml of a methanol solution containing 4% of antioxidant Irganox® 1076 (Ciba), obtaining 1.4 g of stereoregular diblock polybutadiene having a block of polybutadiene with a 1,4-cis structure and a block of polybutadiene with a syndiotactic 1,2 structure (molar ratio 33.9/66.1): further characteristics of the process and of the stereoregular diblock polybutadiene obtained, are indicated in Table 1.

Figure 13 (c) shows the FT-IR spectrum of the stereoregular diblock polybutadiene obtained.

**EXAMPLE 24 (MM69)**

Synthesis of stereoregular diblock polybutadiene with a
1,4-cis/syndiotactic 1,2 structure (invention)

2 ml of 1,3-butadiene, equal to about 1.4 g, were condensed at a low temperature (-20°) in a 25 ml test-tube. 6.5 ml of toluene were subsequently added and the temperature of the solution obtained was brought to 20°C. Methylaluminoxane (MAO) in a toluene solution (6.3 ml; 1x1CT² moles, equal to about 0.58 g) was then added, and subsequently the complex COCl₂(PCy₅Bu₂)₂ (2.9 ml of toluene solution at a concentration of 2 mg/ml; 1x1CT⁵ moles, equal to about 5.9 mg), obtained as described in Example 3. The whole mixture was kept under magnetic stirring, at 20°C, for 20 minutes, after which methyl-diphenylphosphine (PMePh₂) in a toluene solution (0.48 ml; 1.2x10⁻⁵ moles, equal to about 2.4 mg; molar ratio P/Co = 1.2), was added. The polymerization was left to proceed for a further 130 minutes and was subsequently quenched by the addition of 2 ml of methanol containing a few drops of hydrochloric acid. The polymer obtained was then coagulated by the addition of 40 ml of a methanol solution containing 4% of antioxidant Irganox® 1076 (Ciba), obtaining 1.4 g of stereoregular diblock polybutadiene having a block of polybutadiene with a 1,4-cis structure and a block of polybutadiene with a syndiotactic 1,2 structure (molar ratio 84/16); further characteristics of the process and of the stereoregular diblock polybutadiene obtained, are indicated in Table 1.

Figure 13 (d) shows the FT-IR spectrum of the stereoregular diblock polybutadiene obtained.
EXAMPLE 25 (MM67)

Synthesis of 1,4-cis polybutadiene (reference homopolymer)

2 ml of 1,3-butadiene, equal to about 1.4 g, were condensed at a low temperature (-20°) in a 25 ml test-tube. 7 ml of toluene were subsequently added and the temperature of the solution obtained was brought to 20°C. Methylaluminoxane (MAO) in a toluene solution (6.3 ml; 1x1CT² moles, equal to about 0.58 g) was then added, and subsequently the complex CoCl₂(dppe) (2.65 ml of toluene solution at a concentration of 2 mg/ml; 1x10⁻⁵ moles, equal to about 5.3 mg), obtained as described in Example 5. The whole mixture was kept under magnetic stirring, at 20°C, for 120 minutes. The polymerization was then quenched by the addition of 2 ml of methanol containing a few drops of hydrochloric acid. The polymer obtained was then coagulated by the addition of 40 ml of a methanol solution containing 4% of antioxidant Irganox® 1076 (Ciba), obtaining 0.765 g of polybutadiene having a content of 1,4-cis units of 97.2%. Further characteristics of the process and of the polybutadiene obtained are indicated in Table 1.

Figure 17(a) shows the FT-IR spectrum of the polybutadiene obtained.

EXAMPLE 26 (MM70)

Synthesis of stereoregular diblock polybutadiene with a 1,4-cis/syndiotactic 1,2 structure (invention)

2 ml of 1,3-butadiene, equal to about 1.4 g, were
condensed at a low temperature (-20°) in a 25 ml test-tube. 7 ml of toluene were subsequently added and the temperature of the solution obtained was brought to 20°C. Methylaluminoxane (MAO) in a toluene solution (6.3 ml; 1x1CT² moles, equal to about 0.58 g) was then added, and subsequently the complex CoCl₂(dppe) (2.65 ml of toluene solution at a concentration of 2 mg/ml; 1x1CT⁵ moles, equal to about 5.3 mg), obtained as described in Example 5. The whole mixture was kept under magnetic stirring, at 20°C, for 12 minutes, after which iso-propyl-diphenylphosphine (P₂PrPh₂) in a toluene solution (0.55 ml; 1.2x10⁻⁵ moles, equal to about 2.7 mg; molar ratio P/Co = 1.2), was added. The polymerization was left to proceed for a further 138 minutes and was subsequently quenched by the addition of 2 ml of methanol containing a few drops of hydrochloric acid. The polymer obtained was then coagulated by the addition of 40 ml of a methanol solution containing 4% of antioxidant Irganox® 1076 (Ciba), obtaining 1,4 g of stereoregular diblock polybutadiene having a block of polybutadiene with a 1,4-cis structure and a block of polybutadiene with a syndiotactic 1,2 structure (molar ratio 35.9/64.1): further characteristics of the process and of the stereoregular diblock polybutadiene obtained, are indicated in Table 1.

Figure 17 (b) shows the FT-IR spectrum of the stereoregular diblock polybutadiene obtained.

EXAMPLE 27 (MM71)
Synthesis of stereoregular diblock polybutadiene with a 1,4-cis/syndiotactic 1,2 structure (invention)

2 ml of 1,3-butadiene, equal to about 1.4 g, were condensed at a low temperature (-20°) in a 25 ml test-tube. 7 ml of toluene were subsequently added and the temperature of the solution obtained was brought to 20°C. Methylaluminoxane (MAO) in a toluene solution (6.3 ml; 1x10^2 moles, equal to about 0.58 g) was then added, and subsequently the complex CoCl₂(dppe) (2.65 ml of toluene solution at a concentration of 2 mg/ml; 1x10^-5 moles, equal to about 5.3 mg), obtained as described in Example 5. The whole mixture was kept under magnetic stirring, at 20°C, for 30 minutes, after which iso-propyl-diphenylphosphine (P₂P₃Ph₂) in a toluene solution (0.55 ml; 1.2x10^-5 moles, equal to about 2.7 mg; molar ratio P/Co = 1.2), was added. The polymerization was left to proceed for a further 120 minutes and was subsequently quenched by the addition of 2 ml of methanol containing a few drops of hydrochloric acid. The polymer obtained was then coagulated by the addition of 40 ml of a methanol solution containing 4% of antioxidant Irganox® 1076 (Ciba), obtaining 1.4 g of stereoregular diblock polybutadiene having a block of polybutadiene with a 1,4-cis structure and a block of polybutadiene with a syndiotactic 1,2 structure (molar ratio 55.5/44.5): further characteristics of the process and of the stereoregular diblock polybutadiene obtained, are indicated in Table 1.
Figure 17 (c) shows the FT-IR spectrum of the stereoregular diblock polybutadiene obtained.

Figure 18 shows the $^1$H-NMR and $^{13}$C-NMR spectra of the stereoregular diblock polybutadiene obtained.

Figure 19 and Figure 20 show the height image ("HEIGHT IMAGE") and phase image ("PHASE IMAGE") obtained by means of Atomic Force Microscopy (AFM), of the stereoregular diblock polybutadiene obtained.
Polymerization of 1,3-butadiene with catalytic systems comprising cobalt complexes with at least one phosphine ligand selected from hindered aliphatic phosphines or from bidentate phosphines and with aromatic phosphines.

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<th>T_g (°C)</th>
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(a) % 1,4-c/s;
(b) content of syndiotactic triads [(m) %] in the polybutadiene block with a 1,2 syndiotactic structure determined by means of $^{13}$C-NMR analysis;
(c) melting point;
(d) crystallization temperature;
(e) glass transition temperature;
(cs) melting point of the block having a 1,4-c/s structure;
(ch) melting point of the block having a 1,2 syndiotactic structure;
(ds) crystallization temperature of the block having a 1,4-c/s structure;
(dh) crystallization temperature of the block having a 1,2 syndiotactic structure;
(es) glass transition temperature of the block having a 1,4-c/s structure;
(eth) glass transition temperature of the block having a 1,2 syndiotactic structure;
n.d. not determined.
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):

   \[ \text{PBi-PB}_2 \] (I)

wherein:
- PBi corresponds to the polybutadiene block having a 1,4-cis structure;
- \( \text{PB}_2 \) corresponds to the polybutadiene block having a 1,2 syndiotactic structure;

essentially free of 1,4-trans units.

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, preferably ranging from -104°C to -113°C, a melting point \((T_m)\) lower than or equal to -2°C, preferably ranging from -5°C to -20°C, and a crystallization temperature \((T_c)\) lower than or equal to -25°C, preferably ranging from -30°C to -54°C;

- the block having a 1,2 syndiotactic structure has a glass transition temperature \((T_g)\) lower than or equal to -10°C, preferably ranging from -14°C to -24°C, a melting point \((T_m)\) higher than or equal to 70°C, preferably ranging from 95°C to 140°C, and a crystallization temperature \((T_c)\) higher than or equal to 55°C, preferably ranging from 60°C to 130°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 (i.e. not subjected to stress), and has a 1,4-cis content higher than or equal to 96% molar,
preferably ranging from 97% molar to 99% 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 \([rrr]\) higher than or equal to 15%, preferably ranging from 60% to 80%.

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, preferably ranging from 25:75 to 70:30.

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, preferably ranging from 120,000 g/mol to 600,000 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
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):

![Chemical structures](attachment:chemical_structures.png)
wherein:

- R₁ and R₂, the same or different, are selected from linear or branched C₁-C₂₀, preferably C₁-C₁₅, alkyl groups, C₃-C₃₀, preferably C₄-C₁₅, cycloalkyl groups, more preferably are selected from iso-propyl, tert-butyl, cyclopentyl, cyclohexyl;

- R₃ is selected from linear or branched C₁-C₂₀, preferably C₁-C₁₅, alkyl groups, C₃-C₃₀, preferably C₄-C₁₅, cycloalkyl groups, more preferably is selected from methyl, ethyl, n-propyl, iso-propyl, tert-butyl, cyclopentyl, cyclohexyl;

- R₄ and R₅, the same or different, are selected from linear or branched C₁-C₂₀, preferably C₁-C₁₅, alkyl groups, C₃-C₃₀, preferably C₄-C₁₅, cycloalkyl groups, C₆-C₃₀, preferably C₆-C₁₅, aryl groups, more preferably are selected from methyl, ethyl, n-propyl, iso-propyl, tert-butyl, cyclopentyl, cyclohexyl, phenyl;

- Y represents a divalent group -(C₄)n-, wherein n is an integer ranging from 1 to 5; or a divalent group -N-R₆- wherein R₆ represents a hydrogen atom, or a linear or branched C₁-C₂₀, preferably C₁-C₁₅, alkyl group, more preferably is a hydrogen atom; or a divalent group -(CH₂)m-R'- (CH₂)m- wherein R' represents an aryl group optionally substituted, preferably a phenyl group optionally substituted, and m is 0, 1 or 2;

- X₁ and X₂, the same or different, represent a
halogen atom such as, for example, chlorine, bromine, iodine, preferably chlorine; or they are selected from linear or branched C\textsubscript{1}-C\textsubscript{20}, preferably C\textsubscript{1}-C\textsubscript{15}, alkyl groups, preferably methyl, ethyl, -OCOR\textsubscript{7} groups or -OR\textsubscript{7} groups wherein R\textsubscript{7} is selected from linear or branched C\textsubscript{1}-C\textsubscript{20}, preferably C\textsubscript{1}-C\textsubscript{15}, alkyl groups, preferably methyl, ethyl.

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, such as: boron, aluminium, zinc, magnesium, gallium, tin, even more preferably from aluminium, boron.

12. The process according to claim 11, wherein said co-catalyst is selected from aluminium alkyls having general formula (III):

\[
\text{Al}(X')_n(R_\text{S})_{3-n}\quad \text{(HI)}
\]

wherein X' represents a halogen atom such as chlorine, bromine, iodine, fluorine; Rs is selected from linear or branched C\textsubscript{1}-C\textsubscript{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, preferably from aluminoxanes having general formula (IV):

\[(R_9)_2\text{Al}-0-(-\text{Al}(R_{i0})-0-)_p\text{Al}-(R_n)_2\] (IV)

wherein \(R_9, R_{i0}\) and \(R_n\), 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, preferably organic
compounds of aluminium and especially boron, such as those represented by the following general formulae (V), (VI) or (VII):

\[
[(\text{R}_c)_{w}H_{4-w}]^{-}[\text{B}(\text{R}_D)_{4}]^{-} \quad \text{(V)}
\]

\[
[(\text{R}_c)_{3}\text{PH}]^{+}[\text{B}(\text{R}_D)_{4}]^{-} \quad \text{(VI)}
\]

\[
[\text{Li}]^{+}[\text{B}(\text{R}_D)_{4}]^{-}; [\text{Li}]^{+}[\text{Al}(\text{R}_D)_{4}]^{-} \quad \text{(VII)}
\]

wherein \(w\) is an integer ranging from 0 to 3, each group \(\text{R}_c\) independently represents an alkyl group or an aryl group having from 1 to 10 carbon atoms and each group \(\text{R}_D\) independently represents an aryl group partially or totally, preferably totally, fluorinated, having from 6 to 20 carbon atoms, \(\text{P}\) 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):

\[
\text{P} \quad (\text{R})_{m} (\text{Ph})_{n} \quad \text{(VIII)}
\]

wherein:

- \(\text{R}\) is selected from linear or branched \(\text{C}_{1}-\text{C}_{16}\), preferably \(\text{C}_{1}-\text{C}_{8}\), alkyl groups, \(\text{C}_{3}-\text{C}_{16}\), preferably \(\text{C}_{3}-\text{C}_{8}\), cycloalkyl groups, optionally substituted, allyl groups, phenyl optionally substituted;
- \(\text{Ph}\) 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%, preferably from 10% by weight to 20% by weight, 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, preferably ranging from -20°C to +100°C.
Figure 1

FT-IR spectra of the polybutadienes obtained: (a) MM46 (Example 6); (b) MM48 (Example 7); (c) MM49 (Example 8); (d) MM47 (Example 9)
Figure 2

DSC diagram of the stereoregular diblock polybutadiene of Example 7 (MM48)
Figure 3

$^{13}$C-NMR spectrum (above) and $^1$H-NMR spectrum (below) of the stereoregular diblock polybutadiene of Example 8 (MM49)
Figure 4

$^{13}$C-NMR spectrum (above) and $^1$H-NMR spectrum (below) of the stereoregular diblock polybutadiene of Example 9 (MM47)
Figure 5

DSC diagram of the stereoregular diblock polybutadiene

of Example 9 (MM47)
Figure 6

FT-IR spectra of the polybutadienes obtained: (a) MM53 (Example 10); (b) G1173 (Example 12);
(c) MM50 (Example 14); (d) MM60 (Example 15)
Figure 7

DSC diagram of the stereoregular diblock polybutadiene

of Example 10 (MM53)
$^{13}$C-NMR spectrum (above) and $^1$H-NMR spectrum (below) of the stereoregular diblock polybutadiene of Example 11 (MM54)
Figure 9

DSC diagram of the stereoregular diblock polybutadiene

of Example 12 (G1173)
Figure 10

FT-IR spectra of the polybutadienes obtained: (a) G1174 (Example 16); (b) MM65 (Example 17); (c) MM66 (Example 18); (d) MM57 (Example 21)
Figure 11

DSC diagram of the stereoregular diblock polybutadiene

of Example 21 (MM57)
Figure 12

DSC diagram of the stereoregular diblock polybutadiene of Example 22 (MM58)
Figure 13

FT-IR spectra of the polybutadienes obtained: (a) MM59 (Example 20); (b) MM58 (Example 22);
(c) MM68 (Example 23); (d) MM69 (Example 24)
Figure 14

$^{13}$C-NMR spectrum (above) and $^1$H-NMR spectrum (below) of the diblock polybutadiene of Example 20 (MM59)
Elastic moduli ($G'$) at 100 rad/s in relation to the temperature, for the reference polybutadiene of Example 19 (G1168), for the stereoregular diblock polybutadienes of Examples 20 (MM59) and 21 (MM57) and for the polybutadiene reference sample Europrene NEOCIS® BR40 (BR40)
Figure 16

DSC diagram of the stereoregular diblock polybutadiene of Example 19 (G1168)
Figure 17

FT-IR spectra of the polybutadienes obtained: (a) MM67 (Example 25); (b) MM70 (Example 26); (c) MM71 (Example 27)
Figure 18

$^{13}$C-NMR spectrum (above) and $^1$H-NMR spectrum (below) of the stereoregular diblock polybutadiene of Example 27 (MM71)
Figure 19

Atomic Force Microscopy (AFM) of the stereoregular diblock polybutadiene of Example 27 (MM71)
Figure 20
Atomic Force Microscopy (AFM) of the stereoregular diblock polybutadiene of Example 27 (MM71)
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08F295/00 C08F4/655

ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>EP 0 511 015 Al (JAPAN SYNTHETIC RUBBER CO LTD [JP]) 28 October 1992 (1992-10-28) page 6, line 19 - line 21; claims 1-19; example 53</td>
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<td>X</td>
<td>SUYUN JI ET AL: &quot;Highly active and stereospecific polymeric zation of 1,3-butadiene catalyzed by dinuclear cobalt (iii) complexes bearing 3-aryl iminomethyl-2-hydroxybenzaldehydes&quot;, DALTON TRANSACTIONS, vol. 40, no. 41, 1 January 2011 (2011-01-01), page 10975, XP055061366, ISSN: 1477-9226, DOI: 10.1039/cldtl073j page 10979; examples 7, 8</td>
<td>1-18</td>
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See patent family annex.

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Date of the actual completion of the international search

25 February 2015

Date of mailing of the international search report

03/03/2015

Name and mailing address of the ISA/
European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk
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Madalsinski, Maciej
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