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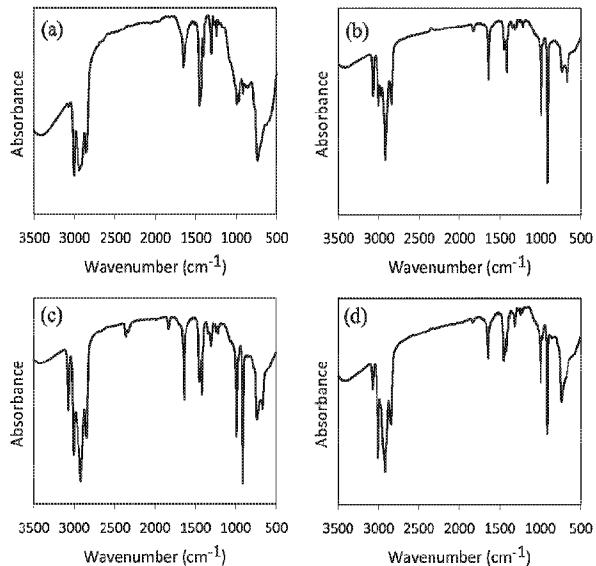
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(54) Titre : POLYBUTADIENES DIBLOCS STEREO-REGULIERS COMPRENNANT UNE STRUCTURE 1,4-CIS/ UNE  
STRUCTURE 1,2 SYNDIOTACTIQUE OBTENUE PAR POLYMERISATION STEREOESPECIFIQUE  
(54) Title: STEREOREGULAR DIBLOCK POLYBUTADIENES HAVING A 1,4-CIS/SYNDIOTACTIC 1,2 STRUCTURE  
FROM STEREOESPECIFIC POLYMERIZATION



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

(57) Abrégé/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.

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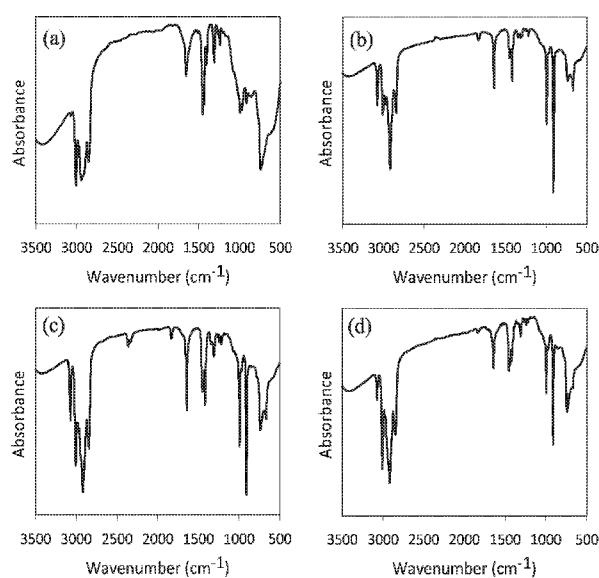
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[Continued on next page]

(54) Title: STEREOREGULAR DIBLOCK POLYBUTADIENES HAVING A 1,4-CIS/SYNDIOTACTIC 1,2 STRUCTURE FROM STEREOSPECIFIC POLYMERIZATION



**(57) 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 polybutadienes obtained: (a) MM46 (Example 6); (b) MM48 (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

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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  
10 a 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):



15 wherein:

- $\text{PB}_1$  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;

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

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 1,3-5 butadiene, and continuing said stereospecific polymerization.

The present invention also relates to a process for the preparation of a stereoregular diblock polybutadiene as defined above, comprising:

- 10 - 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;
- 15 - 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.

Said stereoregular diblock polybutadiene can be advantageously used in both the footwear industry (for 25 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), 4<sup>th</sup> 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), 2<sup>nd</sup> 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  $-100^\circ\text{C}$ , whose properties are extremely similar to those of natural rubber and whose main use is in the production of tires for motor vehicles 5 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 10 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 15 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, 20 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" 25 (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, Compounds, and

*Applications*" (2011), Lucas J. Vidmar Ed., Nova Science Publisher, Inc., USA, pages 39-81.

The catalytic system cobalt bis-acetylacetone/diethylaluminium chloride/water  $[\text{Co}(\text{acac})_2/\text{AlEt}_2\text{Cl}/\text{H}_2\text{O}]$ , 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-acetylacetone/methylaluminoxane  $[\text{Co}(\text{acac})_3/\text{MAO}]$  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-acetylacetone/tri-ethylaluminium/water  $[\text{Co}(\text{acac})_3/\text{AlEt}_3/\text{H}_2\text{O}]$ , 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: Ashitaka H. et al., "Journal of Polymer Science: Polymer Chemistry Edition" (1983), Vol. 21, pages 1853-1860; Ashitaka H. et al., "Journal of Polymer Science: Polymer Chemistry Edition" (1983), Vol. 21, pages 1951-1972;

Ashitaka H. et al., "Journal of Polymer Science: Polymer Chemistry Edition" (1983), Vol. 21, pages 1973-1988; Ashitaka H. et al., "Journal of Polymer Science: Polymer Chemistry Edition" (1983), Vol. 21, pages 1989-1995.

5 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  $(\eta^4\text{-C}_4\text{H}_6)(\eta^5\text{-C}_8\text{H}_{13})\text{Co}$  described, for example, in Natta G. et al., "Chemical Communications" 10 (1967), Issue 24, pages 1263-1265, with carbon disulfide ( $\text{CS}_2$ ), 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 15 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.

20 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 ( $\text{CoCl}_2$ ) or of cobalt 25 dibromide ( $\text{CoBr}_2$ ) 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

patents: US 5,879,805, US 4,324,939, US 3,966,697, US 4,285,833, US 3,498,963, US 3,522,332, US 4,182,813, US 5,548,045, US 7,009,013; or by Shiono T. et al., in "Macromolecular Chemistry and Physics" (2002), Vol. 203, 5 pages 1171-1177, "Applied Catalysis A: General" (2003), Vol. 238, pages 193-199, "Macromolecular Chemistry and Physics" (2003), Vol. 204, pages 2017-2022, "Macromolecules" (2009), Vol. 42, pages 7642-7643. The regioregularity and crystallinity of the polybutadienes 10 obtained with said catalytic systems are much lower (e.g., 80% - 90% of 1,2, units, melting point ( $T_m$ ) ranging from 75°C to 90°C) with respect to those of the polybutadienes obtained with the catalytic system described in Ricci G. et al., "Polymer Communication" 15 (1988), Vol. 29, pages 305-307, indicated above.

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, 20 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-

2769; Freixa Z. et al., "Dalton Transactions" (2003), pages 1890-1901; Tolman C., "Chemical Reviews" (1977), Vol. 77, pages 313-348.

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.,  $P^tBu_3$ ,  $P^iPr_3$ ,  $P^tBu_2^iPr$ ,  $P^tBu_2Me$ ,  $P^iBu_2Cy$ ,  $P^iBuCy_2$ ,  $PCy_3$ ,  $PCyp_3$  wherein P = phosphorous,  $tBu$  = tert-butyl,  $iPr$  = 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.,  $PCy_2H$ ;  $P^tBu_2H$ ;  $PEt_3$ ;  $P^nPr_3$  wherein P = phosphorous, Cy = cyclohexyl,  $tBu$  = tert-butyl, Et = ethyl and  $nPr$  = n-propyl), as described, for example, in international patent application WO 2003/1018649.

Polybutadienes with a high content of 1,4-cis units ( $\geq 96\%$ ) have been obtained with catalytic systems comprising complexes of cobalt with bidentate phosphines

[e.g.,  $\text{CoCl}_2[\text{R}_2\text{P}(\text{CH}_2)_n\text{PR}_2]/\text{MAO}$ , 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.,  $\text{CoCl}_2(\text{PRPh}_2)_2/\text{MAO}$  (wherein Co = cobalt, Cl = chlorine, P = phosphorous, R = methyl, n-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  $^{13}\text{C}$ -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.,  $\text{PMePh}_2$ ;  $\text{PEtPh}_2$ ;  $\text{P}^n\text{PrPh}_2$  wherein  $\text{P}$  = phosphorous,  $\text{Me}$  = methyl,  $\text{Et}$  = ethyl,  $\text{Ph}$  = phenyl,  $^n\text{Pr}$  = *n*-propyl) have proved to have a low crystallinity and with a content of syndiotactic triads  $[(\text{rr})\%]$  ranging from 20% to 50%, whereas the polybutadienes obtained with catalytic systems using phosphine ligands with a higher steric hindrance (e.g.,  $\text{P}^i\text{PrPh}_2$ ,  $\text{PCyPh}_2$  wherein  $\text{P}$  = phosphorous,  $^i\text{Pr}$  = *iso*-propyl,  $\text{Ph}$  = phenyl,  $\text{Cy}$  = cyclohexyl) have proved to be crystalline, with a melting point ( $T_m$ ) ranging from 100°C to 140°C and with a content of syndiotactic triads  $[(\text{rr})\%]$  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  $\text{CoCl}_2(\text{PR}_2\text{Ph})_2/\text{MAO}$  (wherein  $\text{Co}$  = cobalt,  $\text{Cl}$  = chlorine,  $\text{R}$  = methyl, ethyl, cyclohexyl,  $\text{Ph}$  = phenyl,  $\text{MAO}$  = 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  $\text{CoCl}_2(\text{PRPh}_2)_2/\text{MAO}$  described above: the content of syndiotactic triads [(rr)%], 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

M. et al., "Journal of the American Chemical Society" (1956), Vol. 78, para. 2656; Hsieh H. L. et al., "Anionic polymerization: principles and practical applications" (1996), 1<sup>st</sup> Ed., Marcel Dekker, New York; Lovell P. A. et al., "Emulsion polymerization and emulsion polymers" (1997), Wiley New York; Xie H. et al., "Journal of Macromolecular Science: Part A - Chemistry" (1985), Vol. 22 (10), pages 1333-1346; Wang Y. et al., "Journal of Applied Polymer Science" (2003), Vol. 88, pages 1049-1054.

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(ethyleneglycol)ethylether/tri-*iso*-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 5 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*-HTPBs obtained consisted of the LCPB block with a 1,4-*trans* content 10 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 ( $T_g$ ) equal to about -92°C and, 15 only in the presence of a 1,4-*trans* content >70%, a crystallization temperature ( $T_c$ ) 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 20 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) 25 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-*b*-high-1,4-*trans*-polybutadiene-*b*-medium 3,4-polyisoprene copolymers and the polystyrene-*b*-high-1,4-*trans*-polybutadiene-*b*-polystyrene copolymers had a block of polybutadiene 5 having a high content of 1,4-*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* + *trans*) units ranging from 72% to 80%, whereas the blocks of polystyrene proved 10 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 15 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 20 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 25 patent application EP 1,013,683, indicate the use of the catalytic complex  $CpTiCl_3/MAO$  (wherein  $Cp$  = cyclopentadienyl,  $Ti$  = titanium,  $Cl$  = chlorine,  $MAO$  = 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 5 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  $\text{Cp}^*\text{TiMe}_3/\text{B}(\text{C}_6\text{F}_5)_3/\text{AlR}_3$  (wherein 10  $\text{Cp}^*$  = cyclopentadienyl, Ti = titanium, Me = methyl,  $\text{B}(\text{C}_6\text{F}_5)_3$  = tris(pentafluorophenyl)borane,  $\text{AlR}_3$  = trialkylaluminium) and Caprio M. et al. in "Macromolecules" (2002), Vol. 35, pages 9315-9322, using a similar catalytic complex, i.e.  $\text{CpTiCl}_3/\text{Ti}(\text{OR}_4)/\text{MAO}$  15 (wherein Cp = cyclopentadienyl, Ti = titanium, Cl = chlorine, R = alkyl, MAO = methylaluminoxane), obtained, operating under specific polymerization conditions, multi-block copolymers containing blocks of polystyrene with a syndiotactic structure and blocks of polybutadiene 20 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 25 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

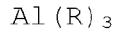
$\approx 70\%$ ), which showed a melting point ( $T_m$ ) equal to 270°C, attributed to the block of syndiotactic polystyrene. Caprio M. et al., on the other hand, operating at a polymerization temperature ranging from 25°C to 70°C, 5 obtained, with low yields, a multi-block copolymer having sequences 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 10 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 15 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 20 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 25 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, 5 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 10 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:



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

(b) dialkoxy molybdenum trichloride having formula:



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 25 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 5 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 10 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, 15 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 20 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 25 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 5 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, 10 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 15 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 20 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. 25 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 5 syndiotactic triads [(rr)%]] to be modulated and, consequently, the melting point ( $T_m$ ), in the stereoregular diblock polybutadiene obtained, depending on the characteristics of the end-product to be obtained.

SUMMARY OF THE INVENTION

10 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):

15  $PB_1-PB_2$  (I)

wherein:

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

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

Another object of the present application is a process for the preparation of a stereoregular diblock 25 polybutadiene as defined herein, 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;

5 - 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  
10 having a *1,4-cis* structure and a polybutadiene block having a *1,2* syndiotactic structure.

For the aim of the present description and of the following claims, the term "stereoregular diblock polybutadiene" means a polybutadiene in which only two  
15 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.

BRIEF DESCRIPTION OF THE FIGURES

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

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

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

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

Figure 2 shows the DSC diagram of the stereoregular

diblock polybutadiene obtained.

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

Figure 4 shows the  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra of the 5 stereoregular diblock polybutadiene obtained.

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

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

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

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

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

Figure 7 shows the DSC diagram of the polybutadiene obtained.

Figure 8 shows the  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra of the stereoregular diblock polybutadiene obtained.

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

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

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

Figure 10(c) shows the FT-IR spectrum 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.

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

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

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

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

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

Figure 16 shows the DSC diagram of the polybutadiene obtained.

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

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

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

Figure 18 shows the  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  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.

#### DETAILED DESCRIPTION

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 5 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 10 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".

15 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  $\text{cm}^{-1}$  and at 911 20  $\text{cm}^{-1}$ , respectively;
- upon  $^{13}\text{C}$ -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.

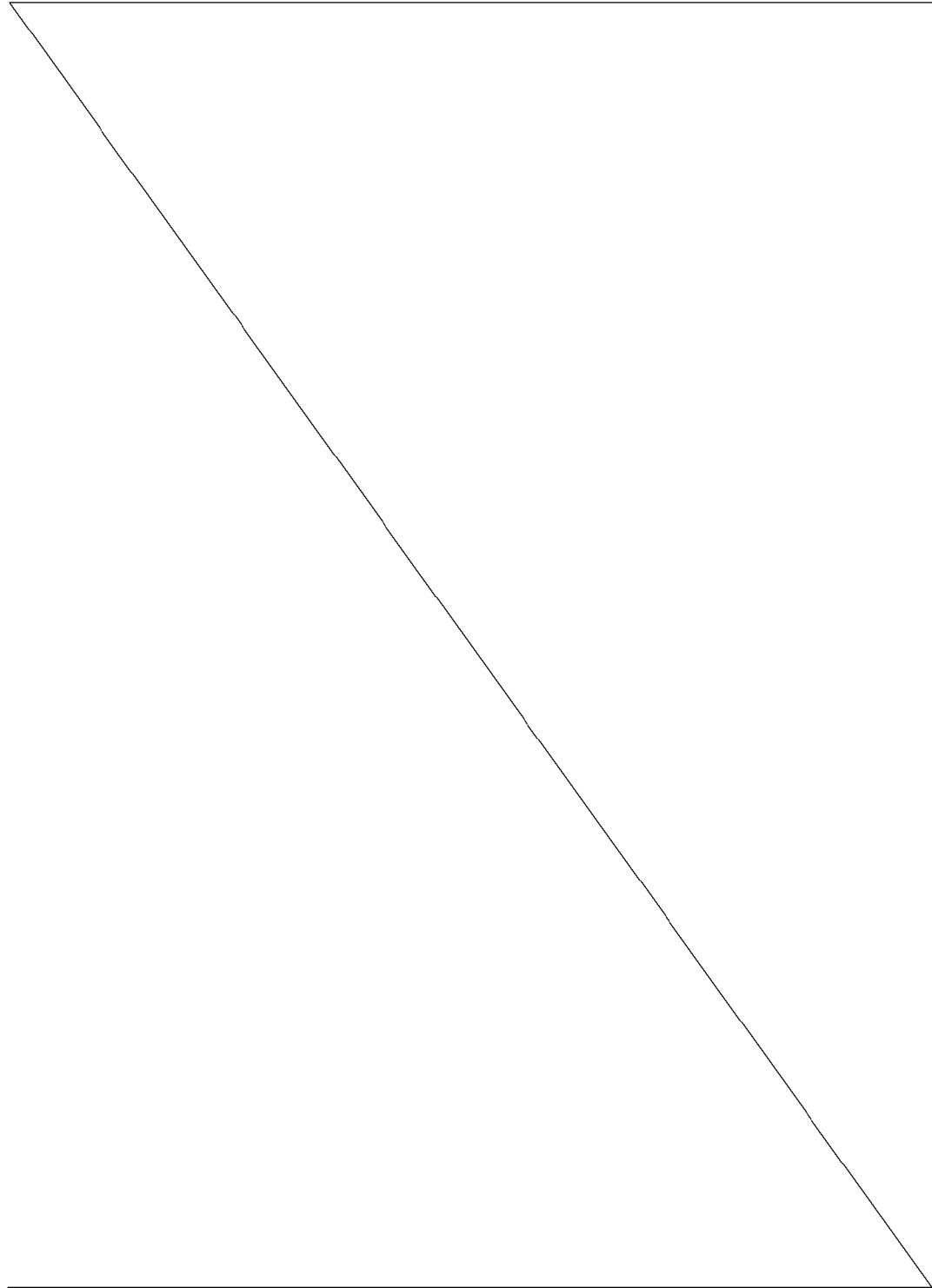
25 The infrared analysis (FT-IR) and the  $^{13}\text{C}$ -NMR analysis were carried out as indicated hereunder in the paragraph "Analysis and characterization methods".

According to a further preferred embodiment of the

20d

present invention, in said stereoregular diblock

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polybutadiene:

- the block having a 1,4-*cis* structure can have 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 syndiotactic 1,2 structure can have 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.

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 5 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 10 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<sup>®</sup> BR 40 of Versalis Spa) as shown in Figure 15 provided hereunder.

15 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, 20 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 25 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.

5 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 10 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%.

15 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, 20 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  $^{13}\text{C}$ -NMR spectroscopy analysis which 25 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 5 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 10 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 15 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 20 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 25 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);

5 - 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

10 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

15 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

20 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

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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).

5 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  
10 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  
15 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  
20 B. Ed., Marcel Dekker; ASTM D3189; ASTM D3186; ISO 2476:  
25 2009, and subsequent updates).

As already indicated above, the present invention also relates to a process for the preparation of a

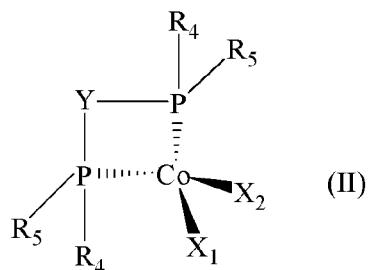
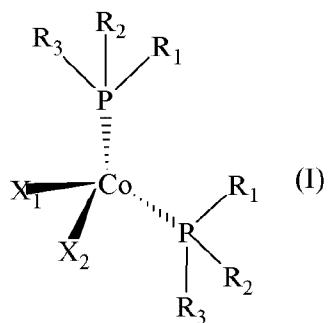
stereoregular diblock polybutadiene composed of a polybutadiene block having a 1,4-*cis* structure and a polybutadiene block having a syndiotactic 1,2 structure.

A further object of the present invention therefore 5 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:

10 - 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 15 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 25 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):



wherein:

5 -  $R_1$  and  $R_2$ , the same or different, are selected from linear or branched  $C_1-C_{20}$ , preferably  $C_1-C_{15}$ , alkyl groups,  $C_3-C_{30}$ , preferably  $C_4-C_{15}$ , cycloalkyl groups, more preferably are selected from *iso*-propyl, *tert*-butyl, cyclopentyl, cyclohexyl;

10 -  $R_3$  is selected from linear or branched  $C_1-C_{20}$ , preferably  $C_1-C_{15}$ , alkyl groups,  $C_3-C_{30}$ , preferably  $C_4-C_{15}$ , cycloalkyl groups, more preferably is selected from methyl, ethyl, *n*-propyl, *iso*-propyl, *tert*-butyl, cyclopentyl, cyclohexyl;

15 -  $R_4$  and  $R_5$ , the same or different, are selected from linear or branched  $C_1-C_{20}$ , preferably  $C_1-C_{15}$ , alkyl groups,  $C_3-C_{30}$ , preferably  $C_4-C_{15}$ , cycloalkyl groups,  $C_6-C_{30}$ , preferably  $C_6-C_{15}$ , aryl groups, more

preferably are selected from methyl, ethyl, *n*-propyl, *iso*-propyl, *tert*-butyl, cyclopentyl, cyclohexyl, phenyl;

- Y represents a divalent group  $-(\text{CH}_2)_n-$ , wherein n is an integer ranging from 1 to 5; or a divalent group  $-\text{NR}_6-$  wherein R<sub>6</sub> represents a hydrogen atom, or a linear or branched C<sub>1</sub>-C<sub>20</sub>, preferably C<sub>1</sub>-C<sub>15</sub>, alkyl group, more preferably is a hydrogen atom; or a divalent group  $-(\text{CH}_2)_m-\text{R}'-(\text{CH}_2)_m-$  wherein R' represents an aryl group optionally substituted, preferably a phenyl group optionally substituted, and m is 0, 1 or 2;
- X<sub>1</sub> and X<sub>2</sub>, 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<sub>1</sub>-C<sub>20</sub>, preferably C<sub>1</sub>-C<sub>15</sub>, alkyl groups, preferably methyl, ethyl, -OCOR<sub>7</sub> groups or -OR<sub>7</sub> groups wherein R<sub>7</sub> is selected from linear or branched C<sub>1</sub>-C<sub>20</sub>, preferably C<sub>1</sub>-C<sub>15</sub>, 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: International patent application WO 2003/018649; Italian patents IT 1,349,143, IT 1,349,142, IT 1,349,141; Ricci

G. et al., "Journal of Molecular Catalysis A: Chemical" (2005), Vol. 226, pages 235-241; Ricci G. et al., "Macromolecules" (2005), Vol. 38, pages 1064-1070; Ricci G. et al., "Journal of Organometallic Chemistry" (2005), Vol. 690, pages 1845-1854; Ricci G. et al., "Advanced in Organometallic Chemistry Research" (2007), K. Yamamoto 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, Compounds, and Applications" (2011), Lucas J. Vidmar Ed., Nova Science Publisher, Inc., USA, pages 39-81; Ricci G. et al., "Phosphorus: Properties, Health effects and the Environment" (2012), Ming Yue Chen and Da-Xia Yang Eds., Nova Science Publisher, Inc., USA, pages 53-94.

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

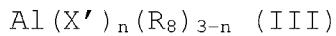
general formula (I) or (II) can be prepared *in situ*, i.e. directly in the polymerization environment. In this respect, said complex of cobalt with at least one phosphine ligand selected from hindered aliphatic phosphines or bidentate phosphines having general formula (I) or (II) can be prepared by separately introducing the ligand (obtained as described, for example, in the following examples), the compound containing cobalt [for example, cobalt dichloride ( $\text{CoCl}_2$ )] and the preselected 5 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 10 element  $M'$  different from carbon, said element  $M'$  being selected from elements belonging to groups 2, 12, 13 or 15 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 20 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 25 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 5 present invention, said co-catalyst can be selected from aluminium alkyls having general formula (III):



wherein  $\text{X}'$  represents a halogen atom such as, for example, chlorine, bromine, iodine, fluorine;  $\text{R}_8$  is 10 selected from linear or branched  $\text{C}_{1-\text{C}_{20}}$  alkyl groups, cycloalkyl groups, aryl groups, said groups being optionally substituted with one or more silicon or germanium atoms; and  $n$  is an integer ranging from 0 to 2.

According to a further preferred embodiment of the 15 present invention, said co-catalyst can be selected from organo-oxygenated compounds of an element  $\text{M}'$  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 20 compounds can be defined as organic compounds of  $\text{M}'$ , 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 25 present invention, said co-catalyst can be selected from organometallic compounds or mixtures of organometallic compounds of an element  $\text{M}'$  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 5 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.

10 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  
15 [www.iupac.org/fileadmin/user\\_upload/news/IUPAC\\_Periodic\\_Table-1Jun12.pdf](http://www.iupac.org/fileadmin/user_upload/news/IUPAC_Periodic_Table-1Jun12.pdf).

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.

20 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-

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-(2-5 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)-10 aluminium, tri-(2-ethyl-3,3-di-methyl-butyl)-aluminium, tri-(2-ethyl-3,3-di-methyl-pentyl)-aluminium, tri-(2-*iso*-propyl-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-(2-15 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-*iso*-propyl-phenyl-tri-(2-phenyl-butyl)-aluminium, tri-(3-methyl-2-phenyl-butyl)-20 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-25 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*-

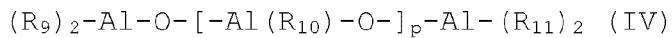
octyl-aluminium hydride, ethyl-aluminium di-hydride, *n*-propyl-aluminium di-hydride, iso-butyl-aluminium di-hydride, di-ethyl-aluminium chloride (DEAC), mono-ethyl-aluminium dichloride (EADC), di-methyl-aluminium chloride, di-*iso*-butyl-aluminium chloride, iso-butyl-aluminium dichloride, ethylaluminium 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.

5 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 10 can be selected from aluminoxanes having general formula (IV) :



wherein R<sub>9</sub>, R<sub>10</sub> and R<sub>11</sub>, the same or different, represent a hydrogen atom, a halogen atom such as, for example, 15 chlorine, bromine, iodine, fluorine; or they are selected from linear or branched C<sub>1</sub>-C<sub>20</sub> 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.

20 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 25 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, 5 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 10 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 15 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 20 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 25 contact with each other, is not particularly critical.

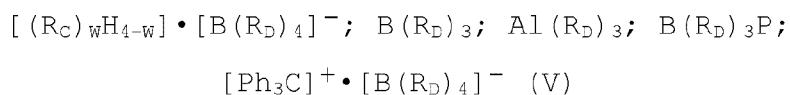
In addition to the above preferred aluminoxanes having general formula (IV), the definition of the compound according to the present invention can also

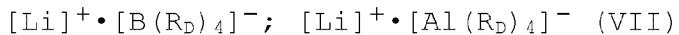
include galloxanes, wherein, in general formula (IV), gallium is present in substitution of aluminium, and stannoxyanes, wherein, in general formula (IV), tin is present in substitution of aluminium, whose use as co-catalysts in the polymerization of olefins in the presence of metallocene complexes, is known. Further details relating to said galloxanes and stannoxyanes can be found, for example, in American patents US 5,128,295 and US 5,258,475.

10 Specific examples of aluminoxanes having general formula (IV) which are particularly useful for the aim of the present invention are: methylaluminoxane (MAO), ethyl-aluminoxane, *n*-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 (TDMBAO), tetra-(2,3,3-tri-methyl-butyl)-aluminoxane (TTMBAO). Methylaluminoxane (MAO) is particularly preferred.

20 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):





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

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 5 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 aluminoxane having general formula (IV) such as, for example, methylaluminoxane (MAO), or, preferably, with an 10 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).

15 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 20 list, which however in no way limits the overall scope of the present invention:

(m<sub>1</sub>) contact of a complex of cobalt with at least one 25 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;

(m<sub>2</sub>) 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);

(m<sub>3</sub>) 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 AlR'''<sub>m</sub>Z<sub>3-m</sub> wherein R''' is a linear or branched C<sub>1</sub>-C<sub>8</sub> 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),  
5 (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),  
10 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 metallocene complexes, in the following publications:

- W. Beck et al., "Chemical Reviews" (1988), Vol. 88, pages 1405-1421;
- S. H. Stares, "Chemical Reviews" (1993), Vol. 93, pages 927-942;
- 25 - European patent applications EP 277 003, EP 495 375, EP 520 732, EP 427 697, EP 421 659, EP 418044;
- published International patent applications WO

92/00333, WO 92/05208.

Specific examples of compounds or mixtures of compounds having general formulae (V), (VI) or (VII), particularly useful for the aim of the present invention 5 are: tributylammonium-tetrakis-pentafluorophenyl-borate tributylammonium-tetrakis-pentafluorophenyl-aluminate, tributylammonium-tetrakis-[ (3,5-di- (trifluorophenyl) ]- borate, tributylammonium-tetrakis- (4-fluorophenyl) ]- borate, N,N-dimethylbenzyl-ammonium-tetrakis-pentafluoro-10 phenyl-borate, N,N-di-methyl-hexylammonium-tetrakis- pentafluorophenyl-borate, N,N-dimethylanilinium-tetrakis- (pentafluorophenyl) -borate, N,N-dimethylanilinium- tetrakis- (pentafluoro-phenyl) -aluminate, di- (propyl)- ammonium-tetrakis- (pentafluorophenyl) -borate, di-15 (cyclohexyl)-ammonium-tetrakis- (pentafluorophenyl) - borate, tri-phenyl-carbenium-tetrakis- (pentafluorophenyl) -borate, tri-phenylcarbenium-tetrakis- (penta-fluorophenyl) -aluminate, tris(pentafluorophenyl)boron, tris(penta-fluorophenyl)-20 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 25 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 5 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 10 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.

15 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 20 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 25 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 5 *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 10 (I) or (II), the co-catalyst and the preselected 1,3-butadiene 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 15 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 20 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 25 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

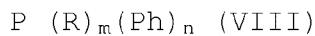
components to be supported, as either the complex of cobalt with at least one phosphine ligand selected from hindered aliphatic phosphines or bidentate phosphines having general formula (I) or (II) alone, or the co-  
5 catalyst, can be present on the surface of the carrier. In the latter case, the missing 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.

10 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  
15 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.

20 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  
25 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 5 (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 10 invention, said monodentate aromatic phosphine can be selected from aromatic phosphines having general formula (VIII) :



wherein:

15 - R is selected from linear or branched C<sub>1</sub>-C<sub>16</sub>, preferably C<sub>1</sub>-C<sub>8</sub>, alkyl groups, C<sub>3</sub>-C<sub>16</sub>, preferably C<sub>3</sub>-C<sub>8</sub>, cycloalkyl groups, optionally substituted, allyl groups, phenyl optionally substituted;

- Ph is phenyl optionally substituted;

20 - 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 (PCyPh<sub>2</sub>), iso-25 propyl-diphenylphosphine (P<sup>i</sup>PrPh<sub>2</sub>), methyl-diphenylphosphine (PMePh<sub>2</sub>), ethyl-diphenylphosphine (PEtPh<sub>2</sub>), n-propyl-diphenylphosphine (P<sup>n</sup>PrPh<sub>2</sub>), dimethyl-phenylphosphine (PMe<sub>2</sub>Ph), diethyl-phenylphosphine

( $\text{PEt}_2\text{Ph}$ ), dicyclohexyl-phenylphosphine ( $\text{PCy}_2\text{Ph}$ ), tri-phenylphosphine ( $\text{PPh}_3$ ). Cyclohexyl-diphenylphosphine ( $\text{PCyPh}_2$ ), *iso*-propyl-diphenylphosphine ( $\text{P}^i\text{PrPh}_2$ ), are preferred.

5 It should be pointed out that when a monodentate aromatic phosphine with a high steric hindrance is used, such as, for example, cyclohexyl-diphenylphosphine ( $\text{PCyPh}_2$ ) having a cone angle ( $\theta$ ) equal to  $153^\circ$ , *iso*-propyl-diphenylphosphine ( $\text{P}^i\text{PrPh}_2$ ) having a cone angle ( $\theta$ )  
10 equal to  $150^\circ$ , 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  
15 a melting point ( $T_m$ ) higher than or equal to  $70^\circ\text{C}$ , preferably ranging from  $95^\circ\text{C}$  to  $140^\circ\text{C}$ , when a monodentate aromatic phosphine with a lower steric hindrance is used, such as, for example, methyl-diphenylphosphine ( $\text{PMePh}_2$ ) having a cone angle ( $\theta$ ) equal to  $136^\circ$ , ethyl-  
20 diphenylphosphine ( $\text{PEtPh}_2$ ) having a cone angle ( $\theta$ ) equal to  $141^\circ$ , *n*-propyl-diphenylphosphine ( $\text{P}^n\text{PrPh}_2$ ) having a cone angle ( $\theta$ ) equal to  $142^\circ$ , dimethyl-phenylphosphine ( $\text{PMe}_2\text{Ph}$ ) having a cone angle ( $\theta$ ) equal to  $127^\circ$ , diethyl-phenylphosphine ( $\text{PEt}_2\text{Ph}$ ) having a cone angle ( $\theta$ ) equal to  
25  $136^\circ$ , 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.

5 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 10 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 15 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 20 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".

25 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 5 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 10 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 15 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 20 examples of the invention are indicated in the following list, together with their optional pretreatments and their supplier:

- cobalt dichloride (CoCl<sub>2</sub>) (Strem Chemicals): used as such;
- 25 - 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;
- 5 - 1,2-bis-(diphenylphosphine)ethane (Strem Chemicals): used as such;
- ethanol (Carlo Erba, RPE): used as such, or anhydriified by distillation on magnesium (Mg);
- pentane (Aldrich): pure,  $\geq$  99.5%, distilled on sodium (Na) in an inert atmosphere;
- 10 - 1,3-butadiene (Air Liquide): pure,  $\geq$  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,  $\geq$  99.5%, distilled on sodium (Na) in an inert atmosphere;
- methylaluminoxane (MAO) (toluene solution at 10% by weight) (Aldrich): used as such;
- 15 - hydrochloric acid in aqueous solution at 37% (Aldrich): used as such;
- *iso*-propyl-diphenylphosphine ( $P^iPrPh_2$ ) (Strem Chemicals): used as such;
- methyl-diphenylphosphine ( $PMePh_2$ ) (Strem Chemicals): used as such;
- 20 - tetrahydrofuran (THF) (Carlo Erba, RPE): maintained at reflux temperature on postassium/benzophenone and then distilled under nitrogen;
- 25 -

- deuterated tetrachloroethane ( $C_2D_2Cl_4$ ) (Acros): used as such;
- deuterated chloroform ( $CDCl_3$ ) (Acros): used as such.

Analysis and characterization methods

5 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 ( $H_2SO_4$ ) at 96% and 1 ml of nitric acid ( $HNO_3$ ) 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 ( $HNO_3$ ) 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 ( $HNO_3$ ) 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 5 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 10 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 15 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 - 20 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 25 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.

$^{13}\text{C}$ -HMR and  $^1\text{H}$ -HMR spectra

The  $^{13}\text{C}$ -HMR and  $^1\text{H}$ -HMR spectra were registered by means of a nuclear magnetic resonance spectrometer mod. 10 Bruker Avance 400, using deuterated tetrachloroethane ( $\text{C}_2\text{D}_2\text{Cl}_4$ ) at  $103^\circ\text{C}$ , and hexamethyldisiloxane (HDMS) as internal standard, or using deuterated chloroform ( $\text{CDCl}_3$ ), at  $25^\circ\text{C}$ , 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.

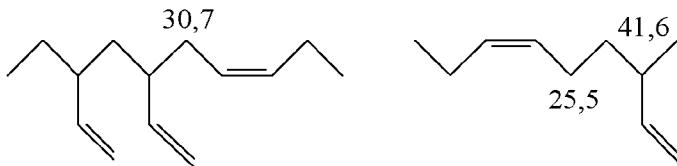
Two-dimensional  $^{13}\text{C}$ -NMR spectra

25 The two-dimensional  $^{13}\text{C}$ -NMR spectra were registered by means of a nuclear magnetic resonance spectrometer mod. Bruker Avance 400, using deuterated tetrachloroethane ( $\text{C}_2\text{D}_2\text{Cl}_4$ ) at  $103^\circ\text{C}$ , 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.

5 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 (" $^1\text{H}$ - $^{13}\text{C}$  long 10 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 15 figure A):



15

Figura A

Furthermore, the two-dimensional  $^1\text{H}$ - $^1\text{H}$  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 \*) 20 "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  $^1\text{H}$ - $^1\text{H}$  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 5 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) 10 (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 15 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- 20 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") 25 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:

$$dH/dt = Cp (dT/dt) + f(T, t)$$

5 wherein:

- $dH/dt$  is the total heat flow;
- $Cp$  is the heat capacity;
- $(dT/dt)$  is the heating rate;
- $Cp(dT/dt)$  is the reversing heat flow;
- 10 -  $f(T, t)$  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 15 crystallization phenomenon from the glass transition temperature(s) ( $T_g$ ).

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

20 For this purpose, the thermal cycle applied to the samples was the following ( $T$  = temperature;  $v$  = scanning rate):

- conditioning of the sample: heating from  $T = 25^\circ\text{C}$  to  $T = 155^\circ\text{C}$  at  $v = 10^\circ\text{C}/\text{min}$  in standard scanning 25 followed by a cooling profile from  $T = 155^\circ\text{C}$  to  $T = -130^\circ\text{C}$  at  $v = 3^\circ\text{C}/\text{min}$  in a modulation of  $+/-0.47^\circ\text{C}$  every 60 seconds with TMDSC (i.e. Modulated DSC) (1<sup>st</sup> cycle);

- subsequent heating from  $T = -130^{\circ}\text{C}$  to  $T = 155^{\circ}\text{C}$  at  $v = 10^{\circ}\text{C}/\text{min}$  (standard scanning) (2<sup>nd</sup> cycle);
- maintaining the sample at  $T = 155^{\circ}\text{C}$  for 2 minutes and subsequent cooling with the same procedure as the 1<sup>st</sup> cycle (TMDSC) (3<sup>rd</sup> cycle);
- tail heating  $T = -130^{\circ}\text{C}$  to  $T = 155^{\circ}\text{C}$  with the same procedure as the 2<sup>nd</sup> cycle (standard scanning) (4<sup>th</sup> cycle).

Molecular weight determination

10 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;
- 15 - I.R. Agilent 1100 detector;
- PL Mixed-A columns;
- solvent/eluent: tetrahydrofuran (THF);
- flow-rate: 1 ml/min;
- temperature: 25°C;
- 20 - 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 25 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 5 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* 10 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 15 (MM57) and for the polybutadiene reference samples of Example 19 (G1168) and Europrene NEOCIS® BR 40 (BR40).

#### EXAMPLE 1

##### Synthesis of $\text{CoCl}_2(\text{P}^t\text{Bu}_3)_2$

A solution of tri-*tert*-butylphosphine (1.14 g, 5.6 20 mmoles) in ethanol (20 ml) was added dropwise, under stirring, to a solution of anhydrous cobalt dichloride ( $\text{CoCl}_2$ ) (0.293 g, 2.26 mmoles) in ethanol (30 ml). A light blue precipitate was formed.

The suspension obtained was kept, under stirring, at 25 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 (CoCl<sub>2</sub>).

The solid residue obtained was dried under vacuum, 5 overnight, obtaining 0.75 g of a light-blue solid (yield equal to 62.1% based on the cobalt dichloride (CoCl<sub>2</sub>) charged).

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

10 FT-IR (KBr):  $\nu$  (cm<sup>-1</sup>) 2954 (m); 2924 (s); 2854 (m); 1465 (s); 1378 (m).

#### EXAMPLE 2

##### Synthesis of CoCl<sub>2</sub>(P<sup>t</sup>Bu<sub>2</sub>Me)<sub>2</sub>

A solution of di-*tert*-butylmethylphosphine (1.35 g, 15 8.4 mmoles) in ethanol (10 ml) was added to a solution of anhydrous cobalt dichloride (CoCl<sub>2</sub>) (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 20 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 25 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 (CoCl<sub>2</sub>) charged).

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

FT-IR (KBr):  $\nu$  (cm<sup>-1</sup>) 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 CoCl<sub>2</sub>(PCy<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>

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 (CoCl<sub>2</sub>) (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 20 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 g of a blue microcrystalline solid (yield equal to 76.5% based on the cobalt dichloride (CoCl<sub>2</sub>) charged).

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

EXAMPLE 4Synthesis of  $\text{CoCl}_2(\text{PCy}_2^t\text{Bu})_2$ 

Di-cyclohexyl-*tert*-butylphosphine (2.0 g, 7.9 mmoles) was added to a solution of anhydrous cobalt dichloride ( $\text{CoCl}_2$ ) (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 ( $25^\circ\text{C}$ ), 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 ( $\text{CoCl}_2$ ) charged).

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

EXAMPLE 5Synthesis of  $\text{CoCl}_2(\text{dppe})$ 

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 ( $\text{CoCl}_2$ ) (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 ( $25^\circ\text{C}$ ), 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<sub>2</sub>) charged).

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

FT-IR (KBr):  $\nu$  (cm<sup>-1</sup>) 3053 (m); 1485 (m); 1435 (s); 1159 (m); 1104 (s); 998 (m); 966 (m); 744 (s); 694 (s); 546 (m); 509 (sm).

10 EXAMPLE 6 (MM46)

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. 15 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<sup>-2</sup> moles, equal to about 0.58 g) was then added, and subsequently the complex CoCl<sub>2</sub>(P<sup>t</sup>Bu<sub>3</sub>)<sub>2</sub> (2.68 ml of toluene solution at a concentration of 2 mg/ml; 1x10<sup>-5</sup> moles, equal to about 5.4 mg), obtained as described in 20 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 25 obtained was then coagulated by the addition of 40 ml of a methanol solution containing 4% of antioxidant Irganox<sup>®</sup> 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 5 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 10 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; 1×10<sup>-2</sup> moles, equal to about 0.58 g), was then added and 15 subsequently the complex CoCl<sub>2</sub>(P<sup>t</sup>Bu<sub>3</sub>)<sub>2</sub> (2.68 ml of toluene solution at a concentration of 2 mg/ml; 1×10<sup>-5</sup> 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- 20 diphenylphosphine (P<sup>i</sup>PrPh<sub>2</sub>) in a toluene solution (0.55 ml; 1.2×10<sup>-5</sup> 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 25 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<sup>®</sup> 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 5 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 10 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 15 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; 1×10<sup>-2</sup> moles, equal to about 0.58 g), was then added and 20 subsequently the complex CoCl<sub>2</sub>(P<sup>t</sup>Bu<sub>3</sub>)<sub>2</sub> (2.68 ml of toluene solution at a concentration of 2 mg/ml; 1×10<sup>-5</sup> 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- 25 diphenylphosphine (P<sup>i</sup>PrPh<sub>2</sub>) in a toluene solution (0.55 ml; 1.2×10<sup>-5</sup> 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<sup>®</sup> 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 <sup>1</sup>H-NMR and <sup>13</sup>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 20 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<sup>-2</sup> moles, equal to about 0.58 g), was then added and 25 subsequently the complex CoCl<sub>2</sub>(P<sup>t</sup>Bu<sub>3</sub>)<sub>2</sub> (2.68 ml of toluene solution at a concentration of 2 mg/ml; 1x10<sup>-5</sup> 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 ( $P^iPrPh_2$ ) in a toluene solution (0.55 ml;  $1.2 \times 10^{-5}$  moles, equal to about 2.7 mg; molar ratio P/Co = 1.2), was added. The polymerization was left to 5 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 10 (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 15 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  $^1H$ -NMR and  $^{13}C$ -NMR spectra of the stereoregular diblock polybutadiene obtained.

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

EXAMPLE 10 (MM53)

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

25 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;  $1 \times 10^{-2}$  moles, equal to about 0.58 g) was then added, and subsequently the complex  $\text{CoCl}_2(\text{P}^t\text{Bu}_2\text{Me})_2$  (2.25 ml of toluene solution at a concentration of 2 mg/ml;  $1 \times 10^{-5}$  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.

20 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°) 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;  $1 \times 10^{-2}$  moles, equal to about 0.58 g), was then added and

subsequently the complex  $\text{CoCl}_2(\text{P}^t\text{Bu}_2\text{Me})_2$  (2.25 ml of toluene solution at a concentration of 2 mg/ml;  $1 \times 10^{-5}$  moles, equal to about 4.5 mg), obtained as described in Example 2. The whole mixture was kept under magnetic stirring, at  $20^\circ\text{C}$ , for 12 minutes, after which isopropyl-diphenylphosphine ( $\text{P}^i\text{PrPh}_2$ ) in a toluene solution (0.55 ml;  $1.2 \times 10^{-5}$  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<sup>®</sup> 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  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  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;  $1 \times 10^{-2}$  moles, equal to about 0.58 g), was then added and subsequently the complex  $\text{CoCl}_2(\text{P}^t\text{Bu}_2\text{Me})_2$  (2.25 ml of 5 toluene solution at a concentration of 2 mg/ml;  $1 \times 10^{-5}$  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 25 minutes, after which *iso*-propyl-diphenylphosphine ( $\text{P}^i\text{PrPh}_2$ ) in a toluene solution 10 (0.55 ml;  $1.2 \times 10^{-5}$  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 15 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 20 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.

25 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 5 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  $\text{CoCl}_2(\text{P}^t\text{Bu}_2\text{Me})_2$  (2.25 ml of toluene solution at a concentration of 2 mg/ml;  $1 \times 10^{-5}$  10 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 ( $\text{PMePh}_2$ ) in a toluene solution (0.48 ml;  $1.2 \times 10^{-5}$  moles, equal to about 2.4 mg; molar ratio P/Co = 15 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 20 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): 25 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; 1×10<sup>-2</sup> moles, equal to about 0.58 g) was then added, and subsequently the complex  $\text{CoCl}_2(\text{PCy}_2^t\text{Bu})_2$  (3.2 ml of toluene solution at a concentration of 2 mg/ml; 1×10<sup>-5</sup> 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)

25 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;  $1\times10^{-2}$  moles, equal to about 0.58 g) was then added, and 5 subsequently the complex  $\text{CoCl}_2(\text{PCy}_2^t\text{Bu})_2$  (3.2 ml of toluene solution at a concentration of 2 mg/ml;  $1\times10^{-5}$  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 *iso*-propyl-10 diphenylphosphine ( $\text{P}^i\text{PrPh}_2$ ) in a toluene solution (0.55 ml;  $1.2\times10^{-5}$  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 15 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 1,4-20 *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.

25 Figure 6(d) 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 5 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  $\text{CoCl}_2(\text{PCy}_2^t\text{Bu})_2$  (3.2 ml of toluene solution at a concentration of 2 mg/ml;  $1 \times 10^{-5}$  moles, 10 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 ( $\text{P}^i\text{PrPh}_2$ ) in a toluene solution (0.55 ml;  $1.2 \times 10^{-5}$  moles, equal to about 2.7 mg; molar ratio P/Co = 15 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 20 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): 25 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)

5        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; 10       $1 \times 10^{-2}$  moles, equal to about 0.58 g) was then added, and subsequently the complex  $\text{CoCl}_2(\text{PCy}_2^t\text{Bu})_2$  (3.2 ml of toluene solution at a concentration of 2 mg/ml;  $1 \times 10^{-5}$  moles, equal to about 6.4 mg), obtained as described in Example 4. The whole mixture was kept under magnetic stirring, at 15      20°C, for 5 minutes, after which methyl-diphenylphosphine (PMePh<sub>2</sub>) in a toluene solution (0.48 ml;  $1.2 \times 10^{-5}$  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 20      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<sup>®</sup> 1076 (Ciba), obtaining 1,4 g of stereoregular diblock 25      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.

5 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°) 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. 10 Methylaluminoxane (MAO) in a toluene solution (6.3 ml; 1x10<sup>-2</sup> moles, equal to about 0.58 g) was then added, and subsequently the complex CoCl<sub>2</sub>(PCy<sub>2</sub><sup>t</sup>Bu)<sub>2</sub> (3.2 ml of toluene solution at a concentration of 2 mg/ml; 1x10<sup>-5</sup> moles, equal to about 6.4 mg), obtained as described in Example 15 4. The whole mixture was kept under magnetic stirring, at 20°C, for 25 minutes, after which methyl-diphenylphosphine (PMePh<sub>2</sub>) in a toluene solution (0.48 ml; 20 1.2x10<sup>-5</sup> 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 25 coagulated by the addition of 40 ml of a methanol solution containing 4% of antioxidant Irganox<sup>®</sup> 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.

5 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)

10 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; 15  $1 \times 10^{-2}$  moles, equal to about 0.58 g) was then added, and subsequently the complex  $\text{CoCl}_2(\text{PCy}^t\text{Bu}_2)_2$  (2.9 ml of toluene solution at a concentration of 2 mg/ml;  $1 \times 10^{-5}$  moles, equal to about 5.9 mg), obtained as described in Example 3. The whole mixture was kept under magnetic stirring, at 20 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 25 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.

5 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 ( $-20^{\circ}$ ) in a 25 ml test-tube. 6.5 ml of toluene were subsequently added and the temperature of the solution obtained was brought to  $20^{\circ}\text{C}$ . 10 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  $\text{CoCl}_2(\text{PCy}^t\text{Bu}_2)_2$  (2.9 ml of toluene solution at a concentration of 2 mg/ml;  $1 \times 10^{-5}$  moles, equal to about 5.9 mg), obtained as described in Example 15 3. The whole mixture was kept under magnetic stirring, at  $20^{\circ}\text{C}$ , for 5 minutes, after which *iso*-propyl-diphenylphosphine ( $\text{P}^i\text{PrPh}_2$ ) in a toluene solution (0.55 ml;  $1.2 \times 10^{-5}$  moles, equal to about 2.7 mg; molar ratio 20  $\text{P/Co} = 1.2$ ), 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 25 then coagulated by the addition of 40 ml of a methanol solution containing 4% of antioxidant Irganox<sup>®</sup> 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 5 indicated in Table 1.

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

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

10 Figure 15 shows the elastic modulus ( $\text{G}'$ ) of the stereoregular diblock polybutadiene obtained.

EXAMPLE 21 (MM57)

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

15 2 ml of 1,3-butadiene, equal to about 1.4 g, were condensed at a low temperature ( $-20^\circ\text{C}$ ) in a 25 ml test-tube. 6.5 ml of toluene were subsequently added and the temperature of the solution obtained was brought to  $20^\circ\text{C}$ . Methylaluminoxane (MAO) in a toluene solution (6.3 ml; 20  $1\times 10^{-2}$  moles, equal to about 0.58 g) was then added, and subsequently the complex  $\text{CoCl}_2(\text{PCy}^t\text{Bu}_2)_2$  (2.9 ml of toluene solution at a concentration of 2 mg/ml;  $1\times 10^{-5}$  moles, equal to about 5.9 mg), obtained as described in Example 3. The whole mixture was kept under magnetic stirring, at 25  $20^\circ\text{C}$ , for 25 minutes, after which iso-propyl-diphenylphosphine ( $\text{P}^i\text{PrPh}_2$ ) in a toluene solution (0.55 ml;  $1.2\times 10^{-5}$  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 5 solution containing 4% of antioxidant Irganox<sup>®</sup> 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): 10 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.

15 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)

20 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 25 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  $\text{CoCl}_2(\text{PCy}^t\text{Bu}_2)_2$  (2.9 ml of toluene

solution at a concentration of 2 mg/ml;  $1 \times 10^{-5}$  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-  
5 diphenylphosphine ( $P^iPrPh_2$ ) in a toluene solution (0.55 ml;  $1.2 \times 10^{-5}$  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  
10 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-  
15 *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.

20 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)

25 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;  $1\times10^{-2}$  moles, equal to about 0.58 g) was then added, and 5 subsequently the complex  $\text{CoCl}_2(\text{PCy}^t\text{Bu}_2)_2$  (2.9 ml of toluene solution at a concentration of 2 mg/ml;  $1\times10^{-5}$  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 10 (PMePh<sub>2</sub>) in a toluene solution (0.48 ml;  $1.2\times10^{-5}$  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 15 hydrochloric acid. The polymer obtained was then coagulated by the addition of 40 ml of a methanol solution containing 4% of antioxidant Irganox<sup>®</sup> 1076 (Ciba), obtaining 1,4 g of stereoregular diblock polybutadiene having a block of polybutadiene with a 1,4- 20 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.

25 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 5 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  $\text{CoCl}_2(\text{PCy}^t\text{Bu}_2)_2$  (2.9 ml of toluene solution at a concentration of 2 mg/ml;  $1 \times 10^{-5}$  moles, 10 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 ( $\text{PMePh}_2$ ) in a toluene solution (0.48 ml;  $1.2 \times 10^{-5}$  moles, equal to about 2.4 mg; molar ratio P/Co = 15 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 20 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 25 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 5 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;  $1 \times 10^{-2}$  moles, equal to about 0.58 g) was then added, and 10 subsequently the complex  $\text{CoCl}_2(\text{dppe})$  (2.65 ml of toluene solution at a concentration of 2 mg/ml;  $1 \times 10^{-5}$  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 15 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 20 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.

25 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. 5 Methylaluminoxane (MAO) in a toluene solution (6.3 ml; 1×10<sup>-2</sup> moles, equal to about 0.58 g) was then added, and subsequently the complex CoCl<sub>2</sub>(dppe) (2.65 ml of toluene solution at a concentration of 2 mg/ml; 1×10<sup>-5</sup> moles, equal to about 5.3 mg), obtained as described in Example 5. The whole mixture was kept under magnetic stirring, at 10 20°C, for 12 minutes, after which iso-propyl-diphenylphosphine (P<sup>i</sup>PrPh<sub>2</sub>) in a toluene solution (0.55 ml; 1.2×10<sup>-5</sup> 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 15 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<sup>®</sup> 1076 (Ciba), obtaining 1,4 g of stereoregular diblock 20 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 25 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;  $1 \times 10^{-2}$  moles, equal to about 0.58 g) was then added, and subsequently the complex  $\text{CoCl}_2(\text{dppe})$  (2.65 ml of toluene solution at a concentration of 2 mg/ml;  $1 \times 10^{-5}$  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 ( $\text{P}^i\text{PrPh}_2$ ) in a toluene solution (0.55 ml;  $1.2 \times 10^{-5}$  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  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra of the stereoregular diblock polybutadiene obtained.

5 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.

TABLE 1

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

5

Example	T (°C)	Time (min)	Yield (g)	Conversion (%)	1,4-cis/1,2 (molar ratio)	(rr) <sup>(b)</sup> (%)	T <sub>m</sub> <sup>(c)</sup> (°C)	T <sub>c</sub> <sup>(d)</sup> (°C)	T <sub>g</sub> <sup>(e)</sup> (°C)	M <sub>w</sub> (g/mol)	M <sub>w</sub> /M <sub>n</sub>
6 (MM46)	20	40	1.04	74	96.8 <sup>(a)</sup>	-	-11.1	-33.5	-108.0	220000	1.9
7 (MM48)	20	105	1.4	100	35.9/64.1	72.7	-12.8 <sup>(cs)</sup> 121.9 <sup>(ch)</sup>	-42.4 <sup>(ds)</sup> 93.2 <sup>(dh)</sup>	-107 <sup>(es)</sup> -15.8 <sup>(eh)</sup>	187000	2.1
8 (MM49)	20	105	1.4	100	54.5/45.5	69.2	-14.9 <sup>(cs)</sup> 116.1 <sup>(ch)</sup>	-47.6 <sup>(ds)</sup> 90.1 <sup>(dh)</sup>	-107.5 <sup>(es)</sup> -20.2 <sup>(eh)</sup>	125000	2.3
9 (MM47)	20	105	1.4	100	68/32	68.5	-16.5 <sup>(cs)</sup> 112.5 <sup>(ch)</sup>	-56.5 <sup>(ds)</sup> 86.3 <sup>(dh)</sup>	-106.8 <sup>(es)</sup> -19.8 <sup>(eh)</sup>	130500	2.4
10 (MM53)	20	40	1.035	73.9	96.9 <sup>(a)</sup>	-	-14.7	-38.4	-109	300500	2.2
11 (MM54)	20	105	1.4	100	39.4/60.6	70.9	-13.1 <sup>(cs)</sup> 113.8 <sup>(ch)</sup>	-45.8 <sup>(ds)</sup> 99.8 <sup>(dh)</sup>	-108.0 <sup>(es)</sup> -17.8 <sup>(eh)</sup>	226800	2.3
12 (G1173)	20	55	1.4	100	48/52	68.5	-10.7 <sup>(cs)</sup> 107.0 <sup>(ch)</sup>	-50.0 <sup>(ds)</sup> 77.1 <sup>(dh)</sup>	-108.2 <sup>(es)</sup> -19.6 <sup>(eh)</sup>	230000	2.2
13 (MM64)	20	385	1.4	100	45.4/54.6	17.9	-14.1 <sup>(cs)</sup> n.d. <sup>(ch)</sup>	-37.2 <sup>(ds)</sup> n.d. <sup>(dh)</sup>	-107.6 <sup>(es)</sup> -23.9 <sup>(eh)</sup>	215500	2.3
14 (MM50)	20	180	1.4	100	97.1	-	-10.6	-29.9	-110	170000	1.9
15 (MM60)	20	15	1.4	100	26.7/73.3	74.7	-11.8 <sup>(cs)</sup> 126.5 <sup>(ch)</sup>	-32.1 <sup>(ds)</sup> 110.4 <sup>(dh)</sup>	-106.8 <sup>(es)</sup> -16.8 <sup>(eh)</sup>	157000	2.1

16 (G1174)	20	50	1.4	100	58.7/41.3	72.9	-12.7 <sup>(es)</sup>	-35.3 <sup>(ds)</sup>	-107.0 <sup>(es)</sup>	152000	2.0
17 (MM65)	20	252	1.4	100	28.4/71.6	18.7	-12.5 <sup>(es)</sup>	-34.8 <sup>(ds)</sup>	n.d. <sup>(es)</sup>	-15.4 <sup>(eh)</sup>	
18 (MM66)	20	252	1.4	100	75/25	20.3	-13.0 <sup>(es)</sup>	-37.0 <sup>(ds)</sup>	-108.9 <sup>(es)</sup>	165000	2.0
19 (G1168)	20	200	1.4	100	97	-	-8.2	-32.8	-109.5	160000	1.9
20 (MM59)	20	15	1.4	100	31.4/68.6	73.9	-9.4 <sup>(es)</sup>	-32.6 <sup>(ds)</sup>	-107.9 <sup>(es)</sup>	145700	2.2
21 (MM57)	20	105	1.4	100	62.5/37.5	71.8	-12.6 <sup>(es)</sup>	-41.2 <sup>(ds)</sup>	-108.5 <sup>(es)</sup>	139500	2.1
22 (MM58)	20	105	1.4	100	85.1/14.9	70.3	-14.8 <sup>(es)</sup>	99.8 <sup>(ch)</sup>	-18.6 <sup>(eh)</sup>	137000	2.0
23 (MM68)	20	150	1.4	100	33.9/66.1	20.1	-10.6 <sup>(es)</sup>	-49.3 <sup>(ds)</sup>	-109.0 <sup>(es)</sup>	150000	2.1
24 (MM69)	20	150	1.4	100	84/16	19.5	-10.3 <sup>(es)</sup>	-31.5 <sup>(ds)</sup>	-108.4 <sup>(es)</sup>	160000	2.2
25 (MM67)	20	120	0.765	54.6	97.2	-	-8.8	-28.7	-111.0	165000	2.0
26 (MM70)	20	150	1.4	100	35.9/64.1	76.4	-9.5 <sup>(es)</sup>	-29.8 <sup>(ds)</sup>	-110.2 <sup>(es)</sup>	350000	1.8
27 (MM71)	20	150	1.4	100	55.5/44.5	75.7	-9.4 <sup>(es)</sup>	-29.5 <sup>(ds)</sup>	-110.8 <sup>(es)</sup>	330000	1.9
										328000	2.1

(a). % 1,4-*cis*;

(b). content of syndiotactic triads [(r) %] in the polybutadiene block with a 1,2 syndiotactic structure determined by means of  $^{13}\text{C}$ -NMR analysis;

(c). melting point;

(d). crystallization temperature;

(e). glass transition temperature;

(f). melting point of the block having a 1,4-*cis* structure;

(g). melting point of the block having a 1,2 syndiotactic structure;

(h). crystallization temperature of the block having a 1,4-*cis* structure;

(i). crystallization temperature of the block having a 1,2 syndiotactic structure;

(j). glass transition temperature of the block having a 1,4-*cis* structure;

(k). glass transition temperature of the block having a 1,2 syndiotactic structure;

(l). not determined.

## CLAIMS

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

PB<sub>1</sub>–PB<sub>2</sub> (I)

wherein:

10 - PB<sub>1</sub> corresponds to the polybutadiene block having  
a 1,4-*cis* structure;

15 - PB<sub>2</sub> corresponds to the polybutadiene block having  
a 1,2 syndiotactic structure;  
having a content of 1,4-*trans* units lower than 3%  
molar.

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

20 - upon infrared analysis (FT-IR), bands typical of  
the 1,4-*cis* and 1,2 sequences centered at 737 cm<sup>-1</sup>  
and at 911 cm<sup>-1</sup>, respectively;

25 - upon <sup>13</sup>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:

25 - the block having a 1,4-*cis* structure has a glass

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

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

10   4. The stereoregular diblock polybutadiene according to any one of claims 1 to 3, 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.

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

20   6. The stereoregular diblock polybutadiene according to any one of claims 1 to 5, wherein in said stereoregular diblock polybutadiene, the

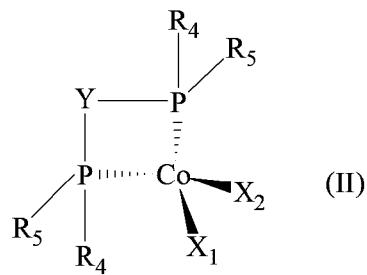
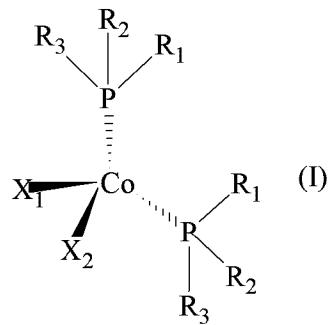
polybutadiene block having a 1,2 syndiotactic structure has a content of syndiotactic triads [(rr) %] higher than or equal to 15%.

7. The stereoregular diblock polybutadiene according to  
5 any one of claims 1 to 6, wherein in said stereoregular diblock polybutadiene, the 1,4-*cis*/1,2 molar ratio ranges from 15:85 to 80:20.

8. The stereoregular diblock polybutadiene according to  
10 any one of claims 1 to 7, wherein said stereoregular diblock polybutadiene has a weight average molecular weight ( $M_w$ ) ranging from 100,000 g/mol to 800,000 g/mol.

9. A process for the preparation of a stereoregular diblock polybutadiene as defined in any one of  
15 claims 1 to 8, 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  
20 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  
25 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 catalytic system comprises a 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):



wherein:

- R<sub>1</sub> and R<sub>2</sub>, the same or different, are selected from linear or branched C<sub>1</sub>-C<sub>20</sub> alkyl groups, C<sub>3</sub>-C<sub>30</sub> cycloalkyl groups;
- R<sub>3</sub> is selected from linear or branched C<sub>1</sub>-C<sub>20</sub> alkyl groups and C<sub>3</sub>-C<sub>30</sub> cycloalkyl groups;
- R<sub>4</sub> and R<sub>5</sub>, the same or different, are selected from linear or branched C<sub>1</sub>-C<sub>20</sub> alkyl groups, C<sub>3</sub>-C<sub>30</sub> cycloalkyl groups, and C<sub>6</sub>-C<sub>30</sub> aryl groups;

- Y represents a divalent group  $-(CH_2)_n-$ , wherein n is an integer ranging from 1 to 5; or a divalent group  $-NR_6-$  wherein R<sub>6</sub> represents a hydrogen atom, or a linear or branched C<sub>1</sub>-C<sub>20</sub> alkyl group;

5        - X<sub>1</sub> and X<sub>2</sub>, the same or different, represent a halogen atom; or they are selected from linear or branched C<sub>1</sub>-C<sub>20</sub> alkyl groups, -OCOR<sub>7</sub> groups and -OR<sub>7</sub> groups wherein R<sub>7</sub> is selected from linear or branched C<sub>1</sub>-C<sub>20</sub> and alkyl groups.

10      11. The process according to claim 10, wherein R<sub>4</sub> and R<sub>5</sub> are selected from the group consisting of methyl, ethyl, n-propyl, iso-propyl, tert-butyl, cyclopentyl, cyclohexyl and phenyl.

12. The process according to claim 10 or 11, wherein Y is a hydrogen atom or a divalent group  $-(CH_2)_m-R'-$   $(CH_2)_m-$  wherein R' represents an aryl group optionally substituted.

15      13. The process according to any one of claims 9 to 12, 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, 20      12, 13 or 14 of the Periodic Table of the Elements.

14. The process according to claim 13, wherein said co-catalyst is selected from aluminium alkyls having general formula (III):

25



wherein X' represents a halogen atom selected from

the group consisting of chlorine, bromine, iodine and fluorine; R<sub>8</sub> is selected from linear or branched C<sub>1</sub>-C<sub>20</sub> 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.

15. The process according to claim 13, 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.

16. The process according to claim 15, wherein the co-catalyst is an aluminoxane having general formula (IV):

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

wherein  $R_9$ ,  $R_{10}$  and  $R_{11}$ , the same or different, represent a hydrogen atom, a halogen atom selected from the groups consisting of chlorine, bromine, iodine and fluorine; or they are selected from linear or branched  $C_{1-C_{20}}$  alkyl groups, cycloalkyl groups and 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.

17. The process according to claim 13, wherein said co-  
25 catalyst is an organometallic compound 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 hindered aliphatic phosphines or bidentate phosphines, as defined in 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.

10 18. The process according to claim 17, wherein the non-coordinating organic anion containing the metal M' is an organic compound of aluminium or boron, and is represented by the following general formulae (V), (VI) or (VII):

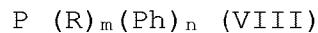
15  $[(R_C)_w H_{4-w}]^+ \bullet [B(R_D)_4]^-; B(R_D)_3; Al(R_D)_3; B(R_D)_3 P; [Ph_3 C]^+ \bullet [B(R_D)_4]^-$  (V)  
 $[(R_C)_3 PH]^+ \bullet [B(R_D)_4]^-$  (VI)  
 $[Li]^+ \bullet [B(R_D)_4]^-; [Li]^+ \bullet [Al(R_D)_4]^-$  (VII)

wherein w is an integer ranging from 0 to 3, each group R<sub>C</sub> independently represents an alkyl group or an aryl group having from 1 to 10 carbon atoms and each group R<sub>D</sub> independently represents an aryl group partially or totally fluorinated, having from 6 to 20 carbon atoms, P represents a pyrrole radical optionally substituted.

20 19. The process according to claim 18, wherein the aryl group is totally fluorinated.

25 20. The process according to any one of claims 9 to 19, wherein said monodentate aromatic phosphine is an

aromatic phosphine having general formula (VIII) :



wherein:

- R is selected from linear or branched C<sub>1</sub>-C<sub>16</sub> alkyl groups, C<sub>3</sub>-C<sub>16</sub> cycloalkyl groups, optionally substituted, allyl groups, phenyl optionally substituted;
- Ph is phenyl optionally substituted;
- m and n, different from each other, are 1 or 2, m+n being = 3.

21. The process according to any one of claims 9 to 20, wherein said process is carried out in the presence of an inert organic solvent selected from: saturated aliphatic hydrocarbons; saturated cycloaliphatic hydrocarbons; mono-olefins; aromatic hydrocarbons; halogenated hydrocarbons.

22. The process of claim 21, wherein the saturated aliphatic hydrocarbons are butane, pentane, hexane, heptane, or mixtures thereof.

23. The process of claim 21 or 22, wherein the saturated cycloaliphatic hydrocarbons are cyclopentane, cyclohexane, or mixtures thereof.

24. The process of any one of claims 21 to 23, wherein mono-olefins are 1-butene, 2-butene, or mixtures thereof.

25. The process of any one of claims 21 to 24, wherein aromatic hydrocarbons are benzene, toluene, xylene, or mixtures thereof.

26. The process of any one of claims 21 to 25, wherein  
the halogenated hydrocarbons are methylene chloride,  
chloroform, carbon tetrachloride, trichloroethylene,  
perchloroethylene, 1,2-dichloroethane,  
5 chlorobenzene, bromobenzene, chlorotoluene, or  
mixtures thereof.
27. The process according to any one of claims 21 to 26,  
wherein the concentration of 1,3-butadiene to be  
polymerized in said inert organic solvent ranges  
10 from 5% by weight to 50% with respect to the total  
weight of the mixture of 1,3-butadiene and inert  
organic solvent.
28. The process according to any one of claims 9 to 27,  
wherein said process is carried out at a temperature  
15 ranging from -70°C to +120°C.

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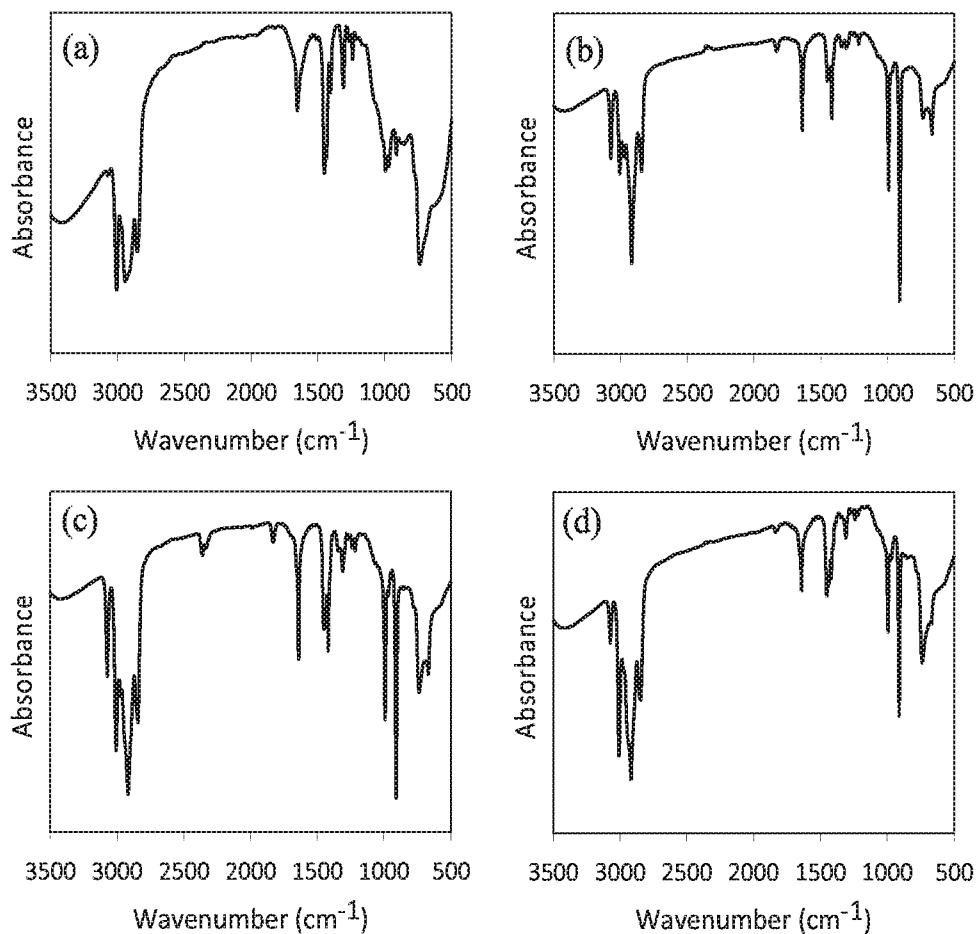


Figure 1

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

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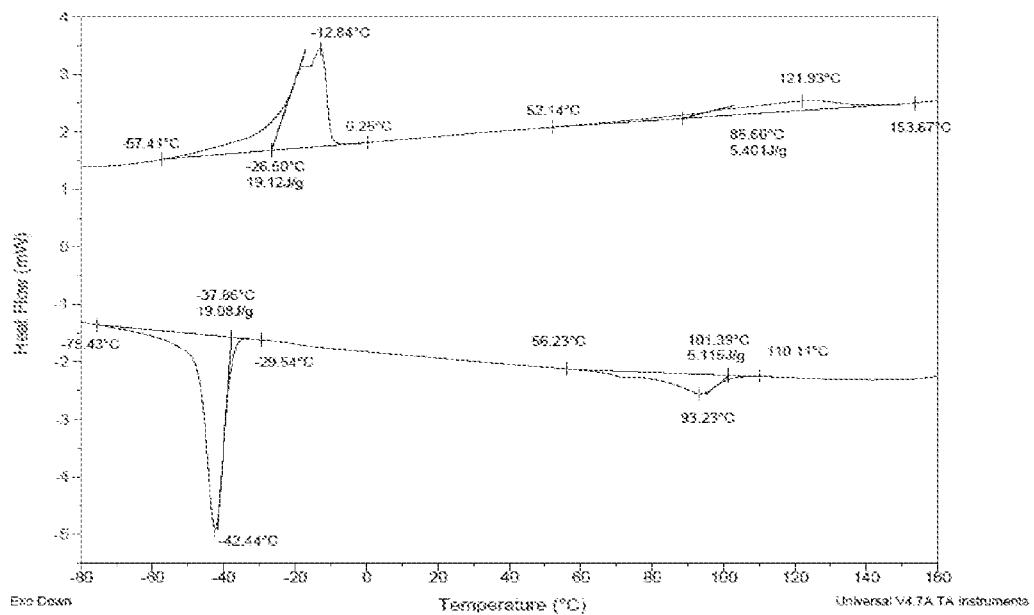


Figure 2

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

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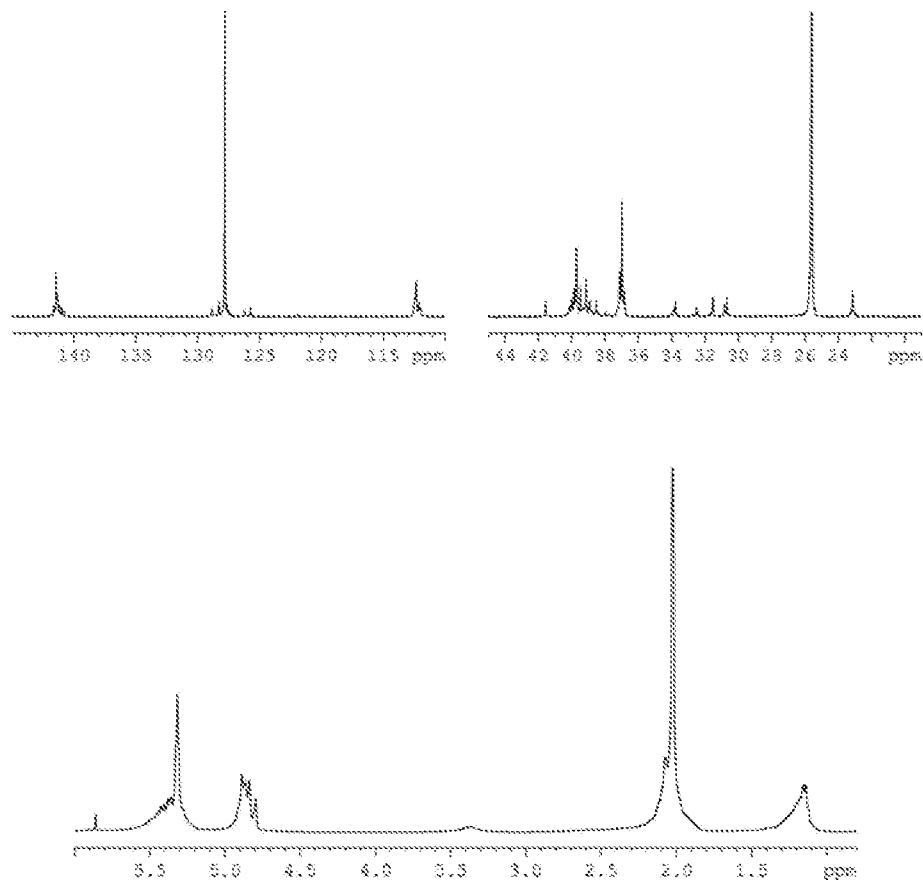


Figure 3

<sup>13</sup>C-NMR spectrum (above) and <sup>1</sup>H-NMR spectrum (below) of the stereoregular diblock polybutadiene of Example 8 (MM49)

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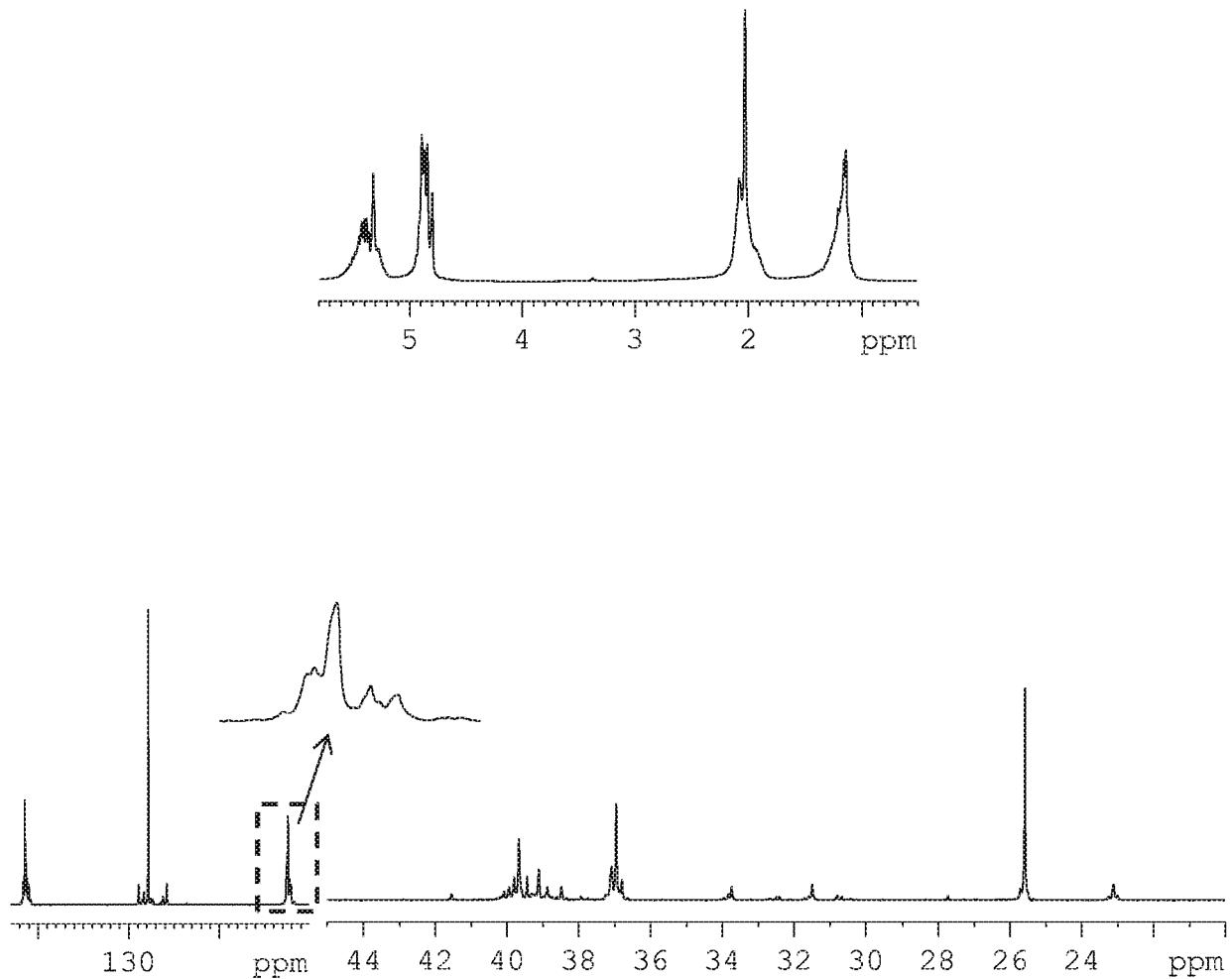


Figure 4

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

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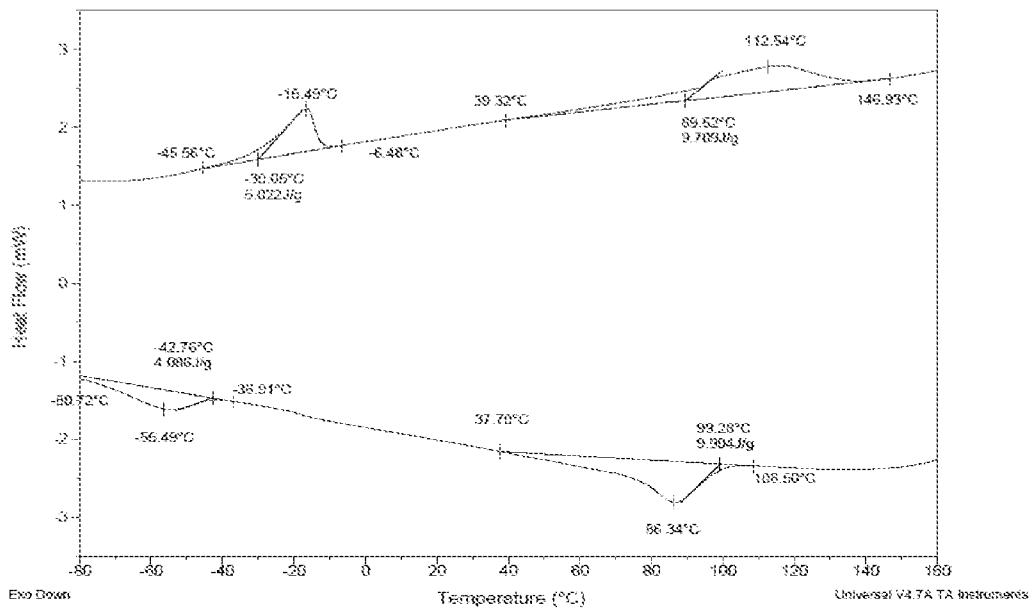


Figure 5

DSC diagram of the stereoregular diblock polybutadiene  
of Example 9 (MM47)

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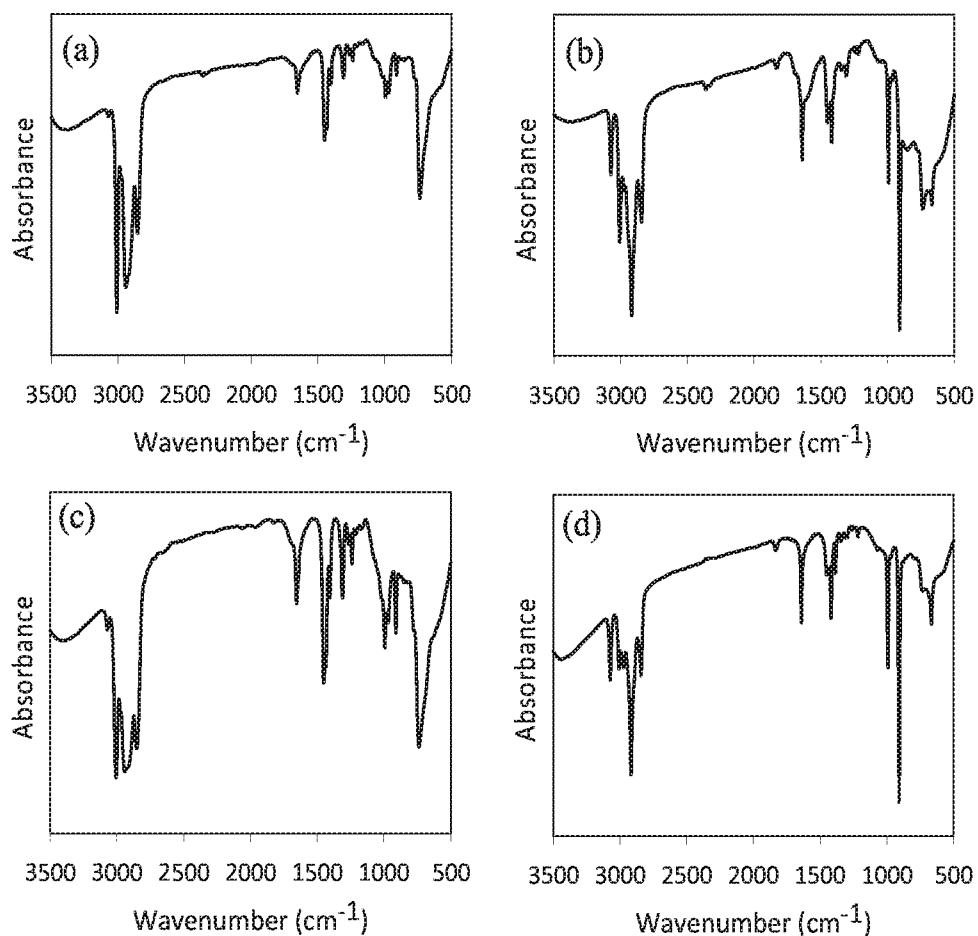


Figure 6

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

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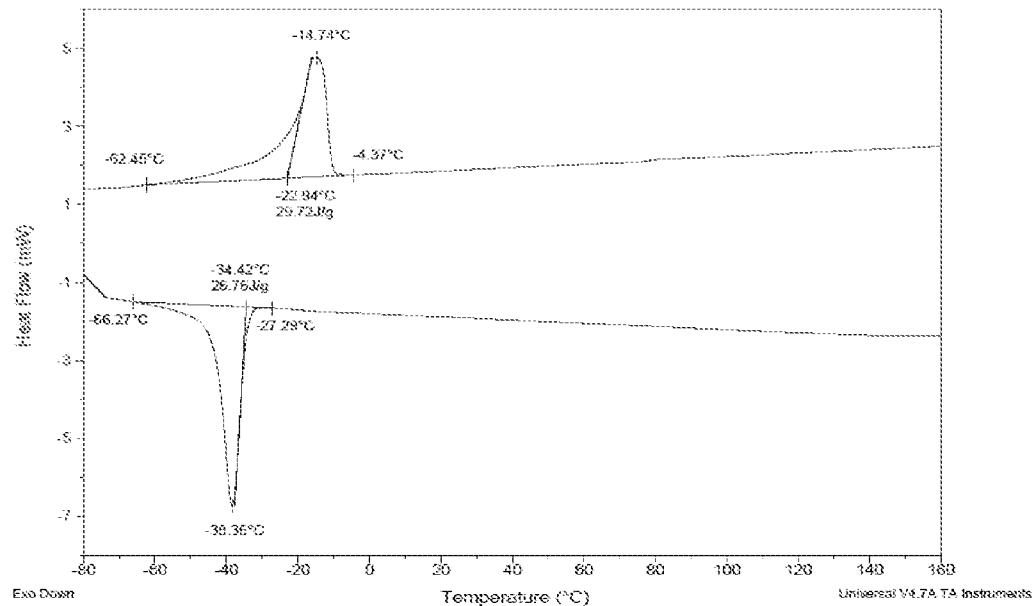


Figure 7

DSC diagram of the stereoregular diblock polybutadiene  
of Example 10 (MM53)

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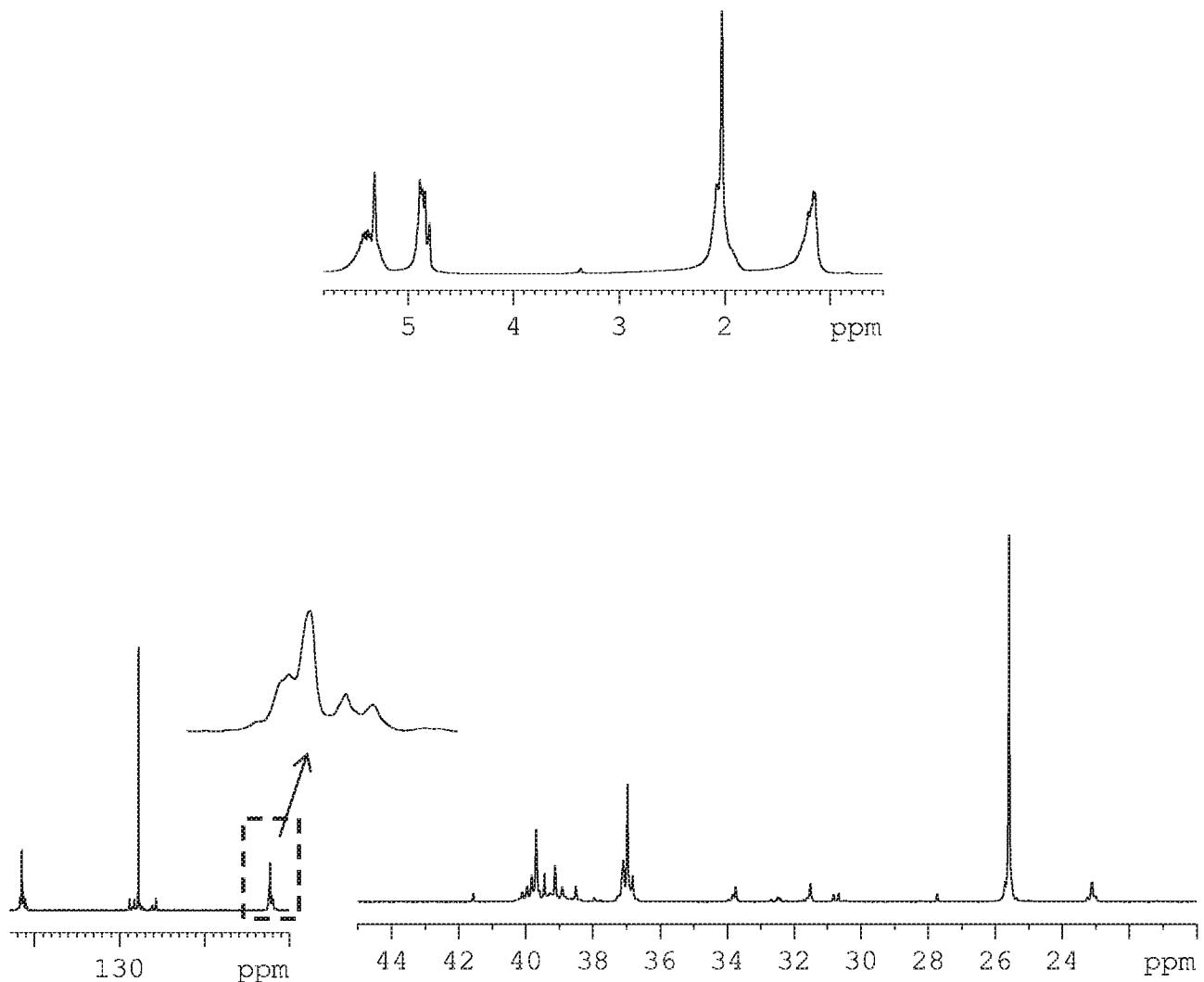


Figure 8

<sup>13</sup>C-NMR spectrum (above) and <sup>1</sup>H-NMR spectrum (below) of the stereoregular diblock polybutadiene of Example 11 (MM54)

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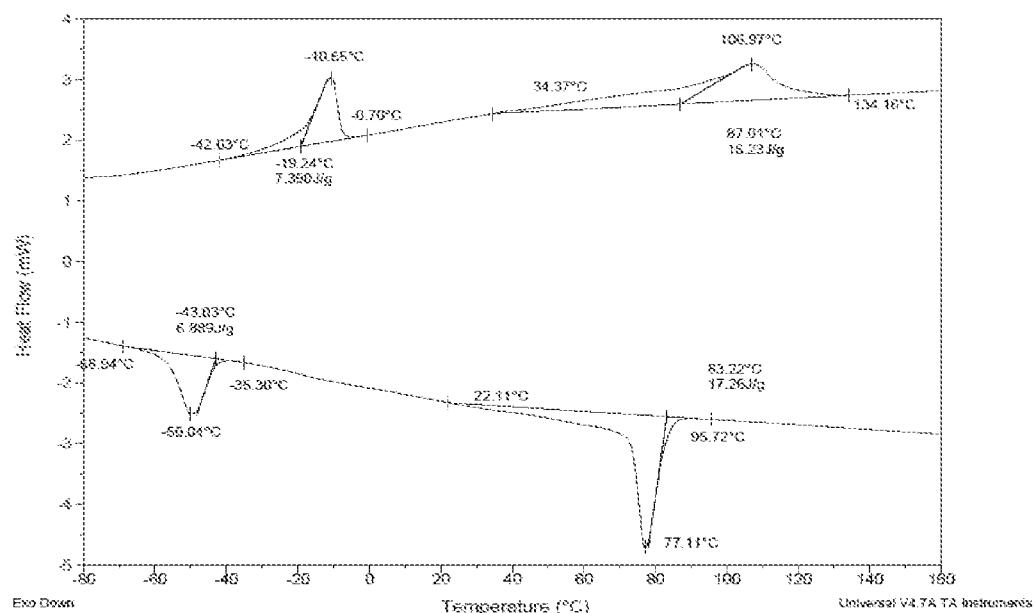


Figure 9

DSC diagram of the stereoregular diblock polybutadiene  
of Example 12 (G1173)

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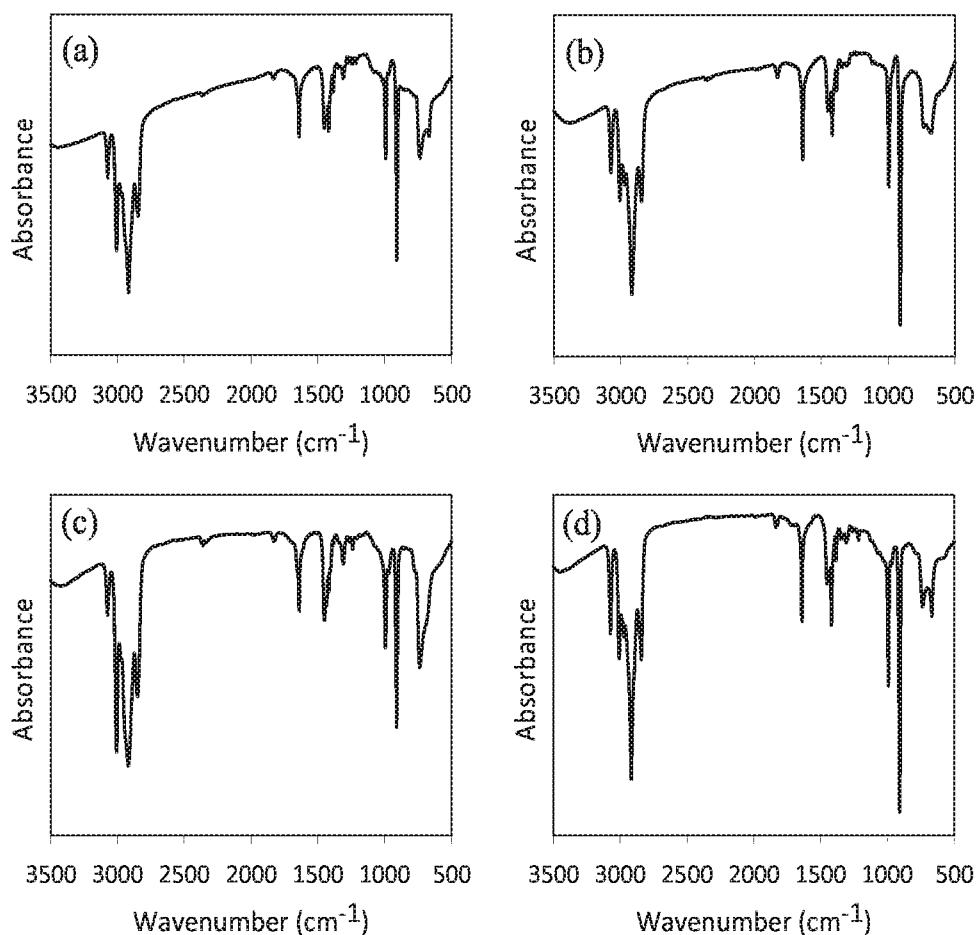


Figure 10

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

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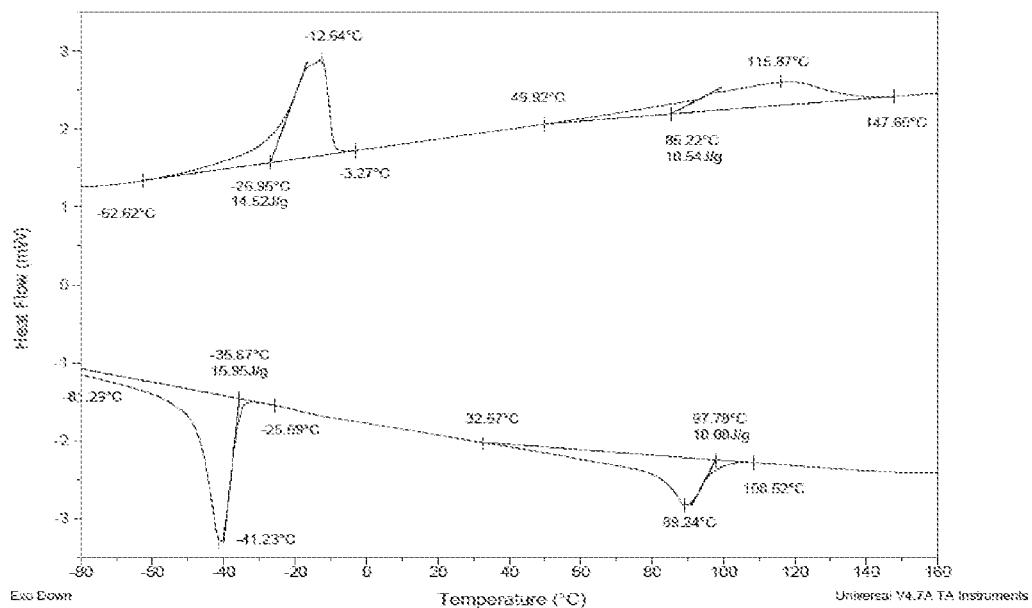


Figure 11

DSC diagram of the stereoregular diblock polybutadiene  
of Example 21 (MM57)

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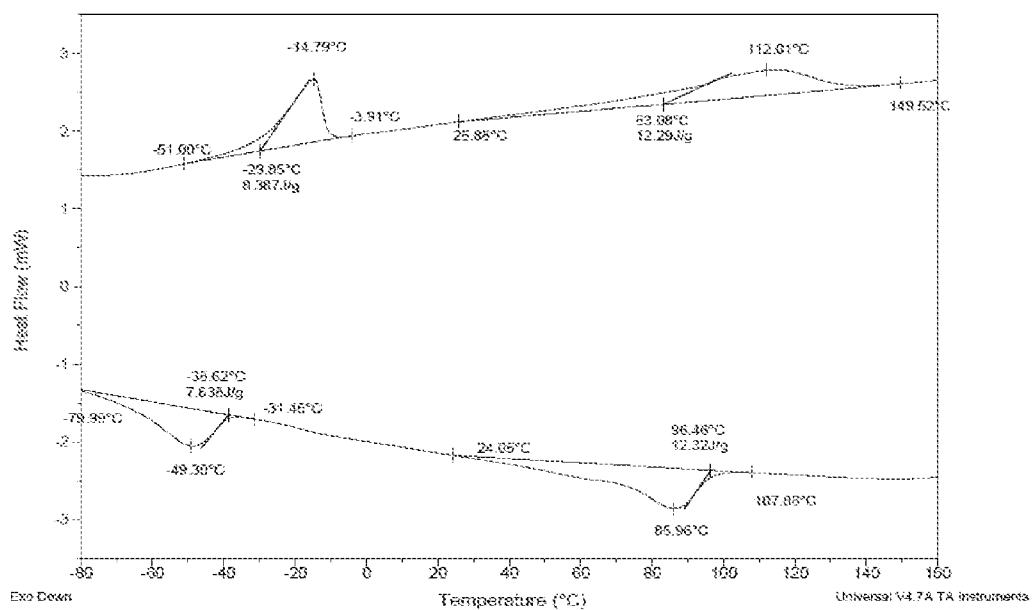


Figure 12

DSC diagram of the stereoregular diblock polybutadiene

of Example 22 (MM58)

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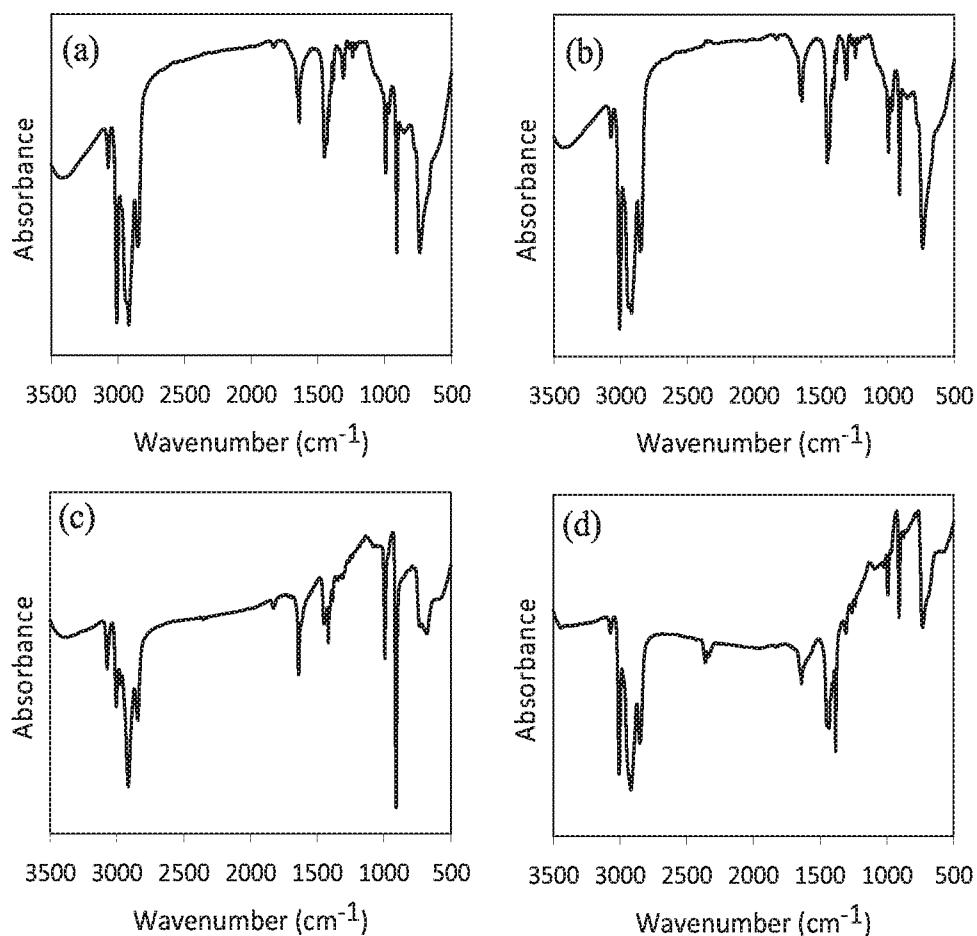


Figure 13

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

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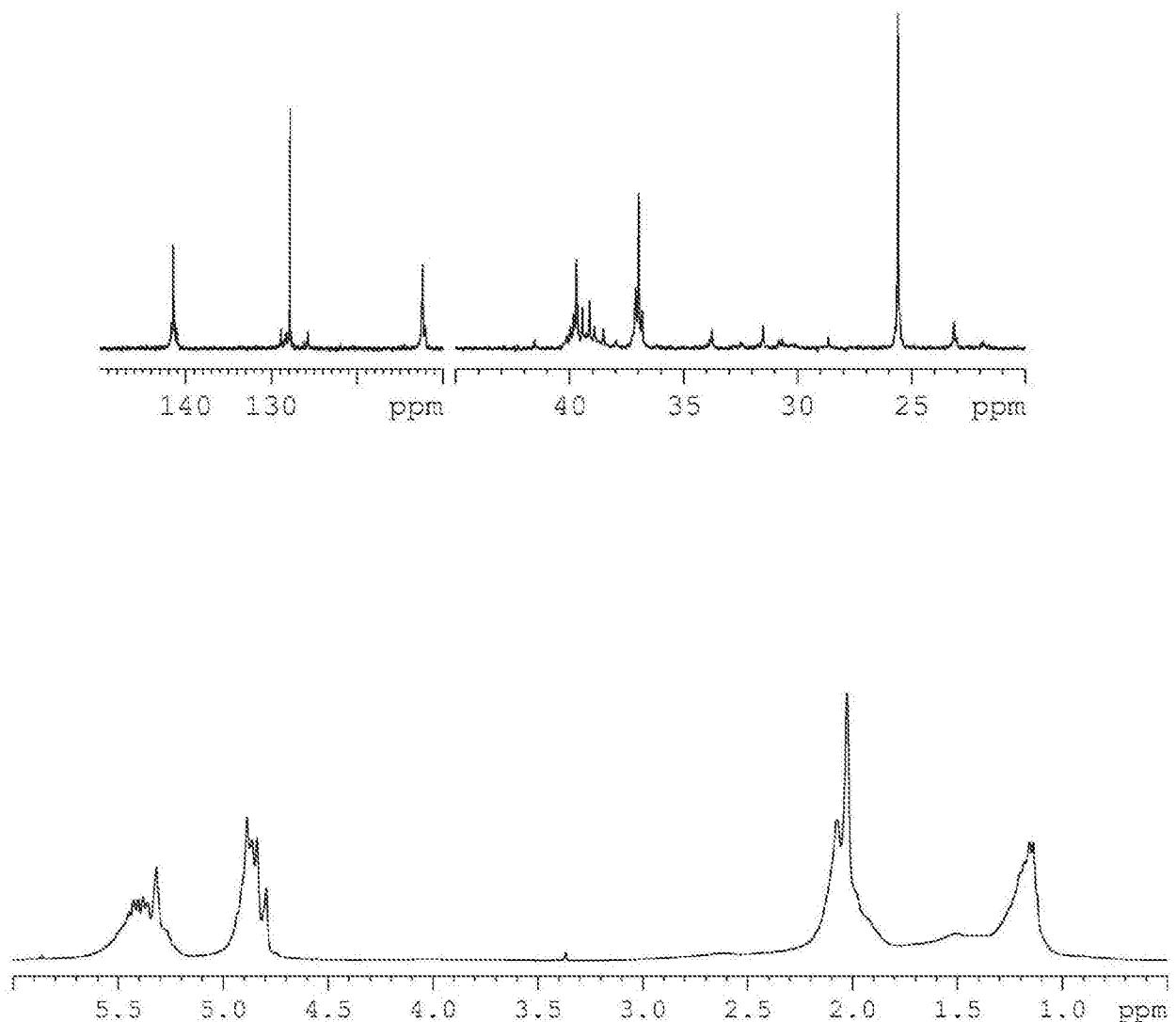


Figure 14

$^{13}\text{C}$ -NMR spectrum (above) and  $^1\text{H}$ -NMR spectrum (below) of the diblock polybutadiene of Example 20 (MM59)

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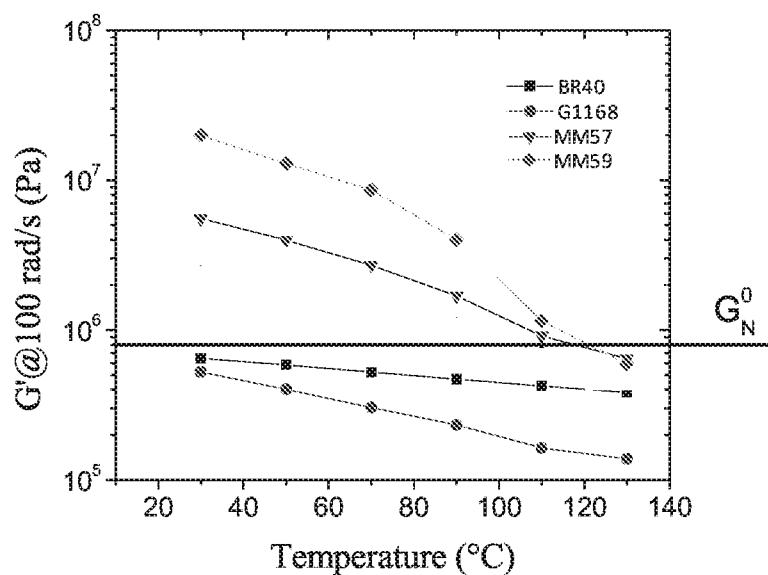


Figure 15

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

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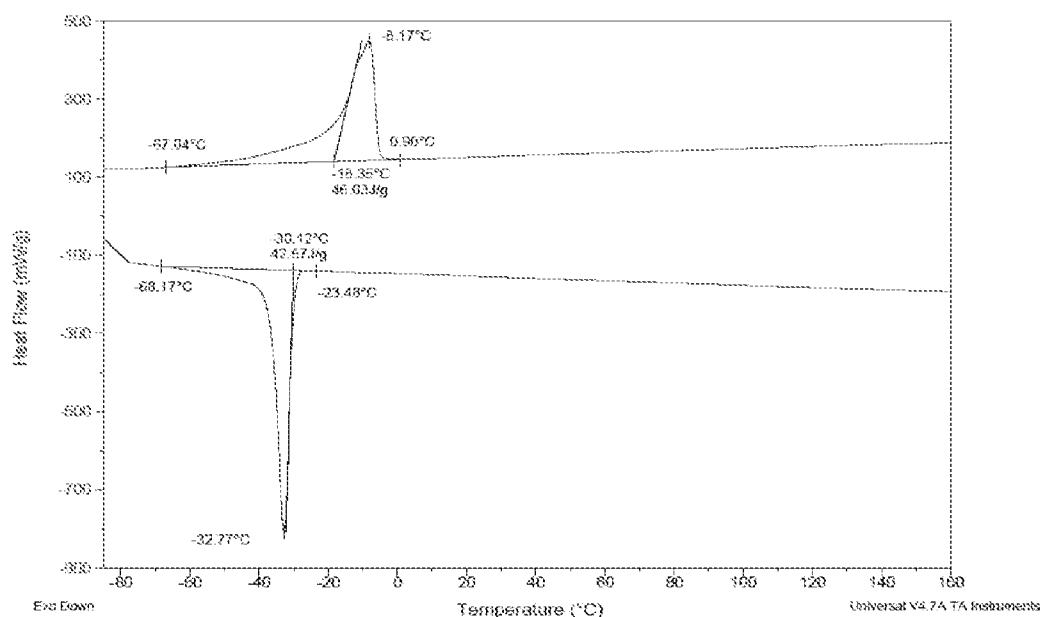


Figure 16  
DSC diagram of the stereoregular diblock polybutadiene  
of Example 19 (G1168)

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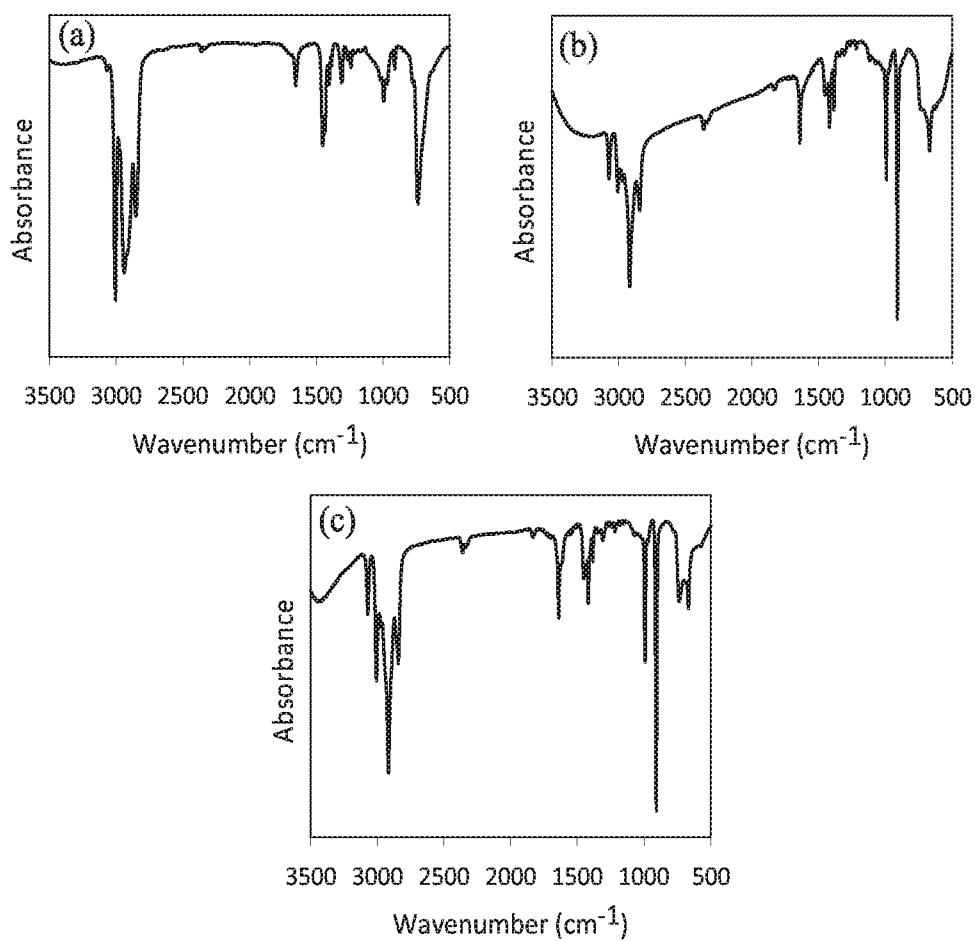


Figure 17

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

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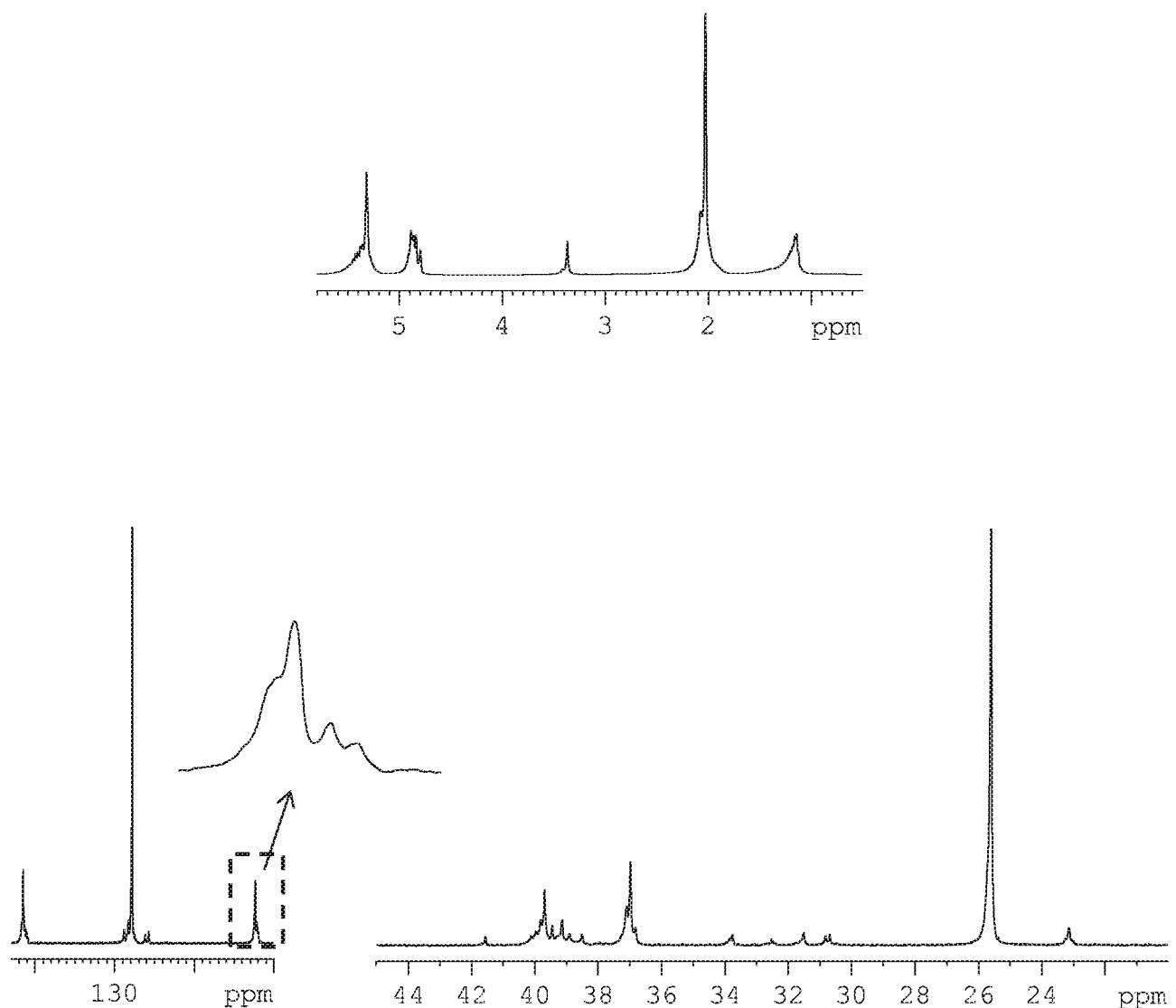
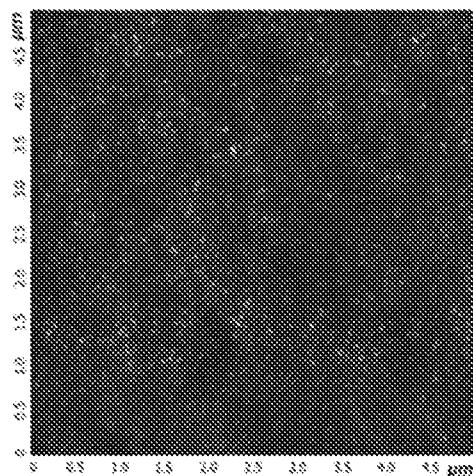


Figure 18

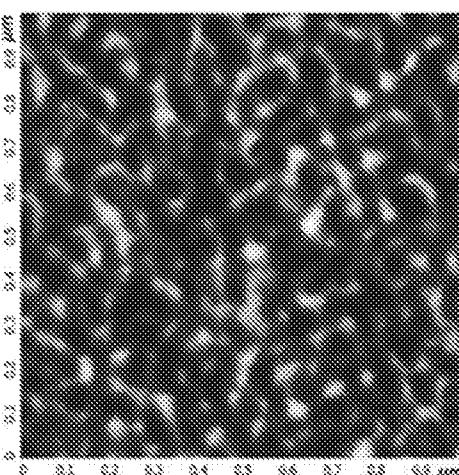
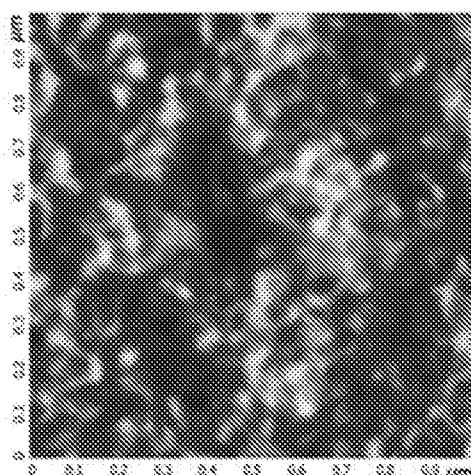
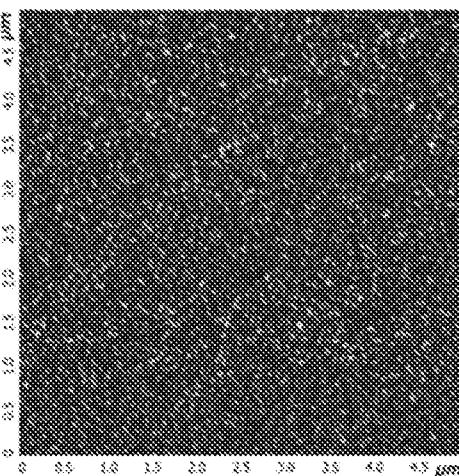
$^{13}\text{C}$ -NMR spectrum (above) and  $^1\text{H}$ -NMR spectrum (below) of the stereoregular diblock polybutadiene of Example 27 (MM71)

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HEIGHT IMAGE



PHASE IMAGE



Root Mean Square, Sq. 0.7 nm

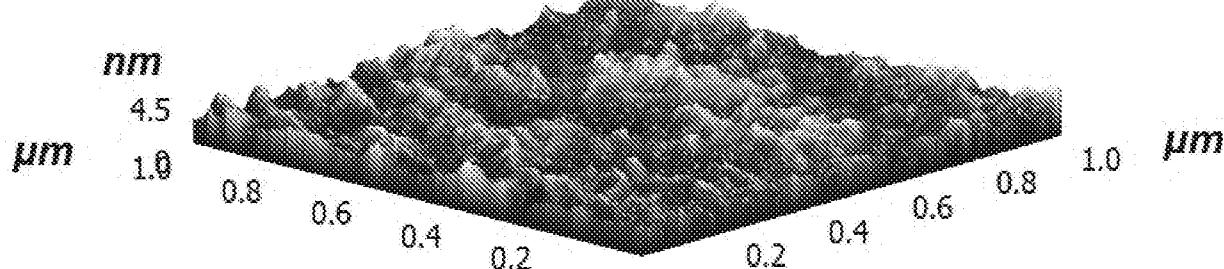
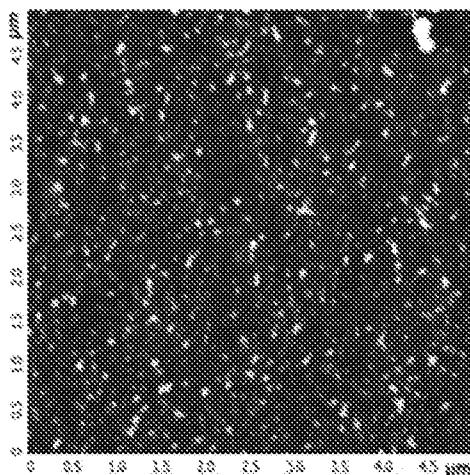


Figure 19

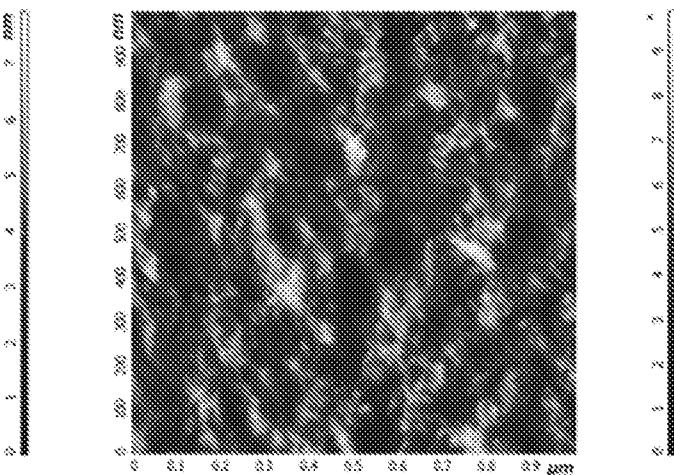
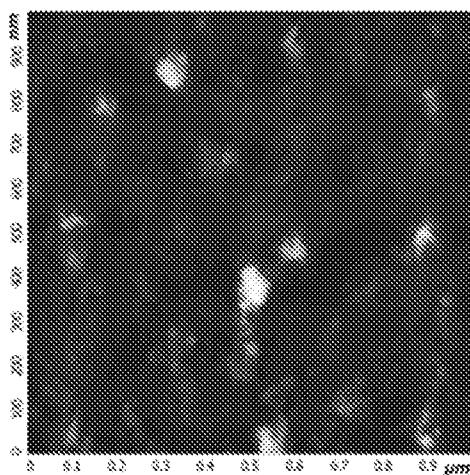
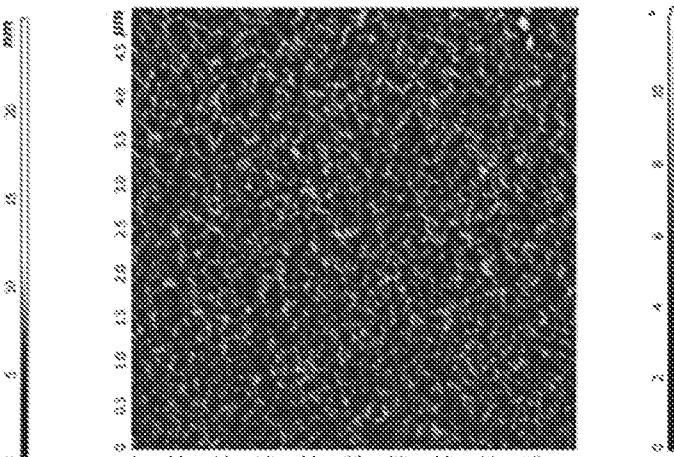
Atomic Force Microscopy (AFM) of the stereoregular diblock polybutadiene of Example 27 (MM71)

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HEIGHT IMAGE



PHASE IMAGE



Root Mean Square, Sq 1.6 nm

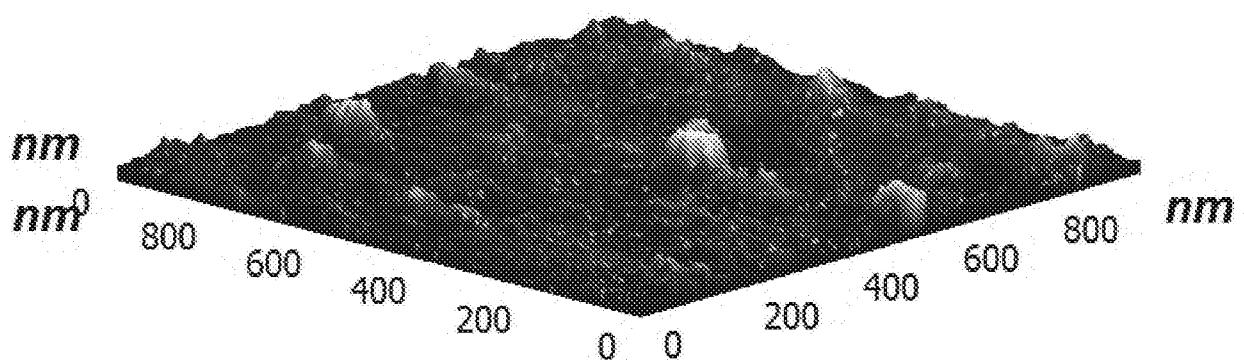
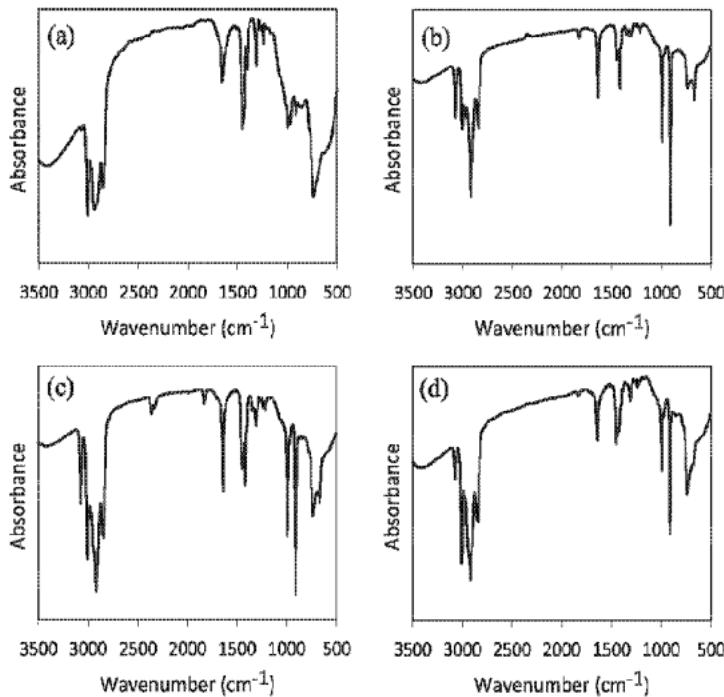


Figure 20

Atomic Force Microscopy (AFM) of the stereoregular diblock polybutadiene of Example 27 (MM71)



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