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(54) **Eljárás konjugált diének (ko)polimerjeinek előállítására kobalt bisz-imin komplexét tartalmazó katalitikus rendszer jelenlétében**

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(54) **PROCESS FOR THE PREPARATION OF (CO) POLYMERS OF CONJUGATED DIENES IN THE PRESENCE OF A CATALYTIC SYSTEM COMPRISING A BIS-IMINE COMPLEX OF COBALT**

VERFAHREN FÜR DIE HERSTELLUNG VON (CO)POLYMEREN VON KONJUGIERTEN DIEN-MONOMEREN IN ANWESENHEIT EINES KATALYTISCHEN SYSTEMS, BEINHALTEND EINEN BIS-IMINO-KOBALTKOMPLEX

PROCESSUS DE PRÉPARATION DE (CO)POLYMÈRES DE DIÈNE CONJUGUÉS EN PRÉSENCE D'UN SYSTÈME CATALYTIQUE COMPRENANT UN COMPLEXE DE COBALT AYANT UNE LIAISON BIS-IMINO

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- **SUYUN JIE ET AL: "Highly active and stereospecific polymerization of 1,3-butadiene catalyzed by dinuclear cobalt(ii) complexes bearing 3-aryliminomethyl-2-hydroxybenzaldehydes", DALTON TRANSACTIONS, vol. 40, no. 41, 2011, page 10975, XP055061366, ISSN: 1477-9226, DOI: 10.1039/c1dt11073j**
- **KIM BU UNG ET AL: "Highly cis-selectivity and low molecular weight distribution polymerization of 1,3-butadiene with cobalt (II) pyridyl bis(imine) complexes in the presence of ethylaluminum sesquichloride: effect of methyl position in the ligand", STUDIES IN SURFACE SCIENCE AND CATALYSIS, ELSEVIER B.V, vol. 159, 2006, pages 873-876, XP009169226, ISSN: 0167-2991**

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Description

[0001] The present invention relates to a process for the preparation of (co)polymers of conjugated dienes.

[0002] More specifically, the present invention relates to a process for the preparation of (co)polymers of conjugated dienes which comprises polymerizing at least one conjugated diene in the presence of a catalytic system comprising a bis-imine complex of cobalt.

[0003] It is known that the stereospecific (co)polymerization of conjugated dienes is an extremely important process in the chemical industry for obtaining products which are among the most widely-used rubbers.

[0004] It is also known that among the various polymers which can be obtained from the stereospecific polymerization of 1,3-butadiene (i.e. 1,4-cis, 1,4-trans, 1,2 syndiotactic, 1,2 isotactic, 1,2 atactic, mixed 1,4-cis/1,2 structure having a variable content of 1,2 units), only 1,4-cis polybutadiene and 1,2 syndiotactic polybutadiene are produced industrially and commercially available. Further details relating to these polymers can be found, for example, in: Takeuchi Y. et al., "New Industrial Polymers", "American Chemical Society Symposium Series" (1974), Vol. 4, pages 15-25; Halasa A. F. et al., "Kirk-Othmer Encyclopedia of Chemical Technology" (1989), 4th Ed., Kroschwitz J. I. Ed., John Wiley and Sons, New York, Vol. 8, pages 1031-1045; Tate D. et al., "Encyclopedia of Polymer Science and Engineering (1989), 2nd Ed., Mark H. F. Ed., John Wiley and Sons, New York, Vol. 2, pages 537-590; Kerns M. et al., "Butadiene Polymers", in "Encyclopedia of Polymer Science and Technology" (2003), Mark H. F. Ed., Wiley, Vol. 5, pages 317-356.

[0005] 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°C and a glass transition temperature (T_g) below -100°C, whose properties are very similar to those of natural rubber and whose main use is in the production of tyres for motor vehicles and/or trucks. In particular, in the production of tyres, polybutadiene with a high content of 1,4-cis units is used.

[0006] 1,4-cis polybutadiene is generally prepared through polymerization processes which use various catalytic systems comprising catalysts based on titanium (Ti), cobalt (Co), nickel (Ni), neodymium (Nd). Catalytic systems comprising catalysts based on cobalt have a high catalytic activity and stereospecificity and can be considered as being the most versatile among those listed above as, by varying their formulation, they are capable of providing all the possible stereoisomers of polybutadiene indicated above, as described, for example, in: Porri L. et al., "Comprehensive Polymer Science" (1989), Eastmond G.C. et al. Eds., Pergamon Press, Oxford, UK, Vol. 4, Part II, pages 53-108; Thiele S. K. H. et al., "Macromolecular Science. Part C: Polymer Reviews" (2003), C43, pages 581-628; Osakada, K. et al., "Advanced Polymer Science" (2004), Vol. 171, pages 137-194; Ricci G. et al., "Advances in Organometallic Chemistry Research" (2007), Yamamoto K. Ed., Nova Science Publisher, Inc., USA, pages 1-36; Ricci G. et al., "Coordination Chemistry Reviews" (2010), Vol. 254, pages 661-676; Ricci G. et al., "Cobalt: Characteristics, Compounds, and Applications" (2011), Lucas J. Vidmar Ed., Nova Science Publisher, Inc., USA, pages 39-81.

[0007] The catalytic system cobalt bis-acetylacetonate/diethylaluminium chloride/water [$Co(acac)_2/AlEt_2Cl/H_2O$], for example, provides a polybutadiene having a content of 1,4-cis units equal to about 97%, and it is that normally used for the industrial production of this polymer as described, for example, in Racanelli P. et al., "European Polymer Journal" (1970), Vol. 6, pages 751-761. The catalytic system cobalt tris-acetylacetonate/methylaluminoxane [$Co(acac)_3$/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.

[0008] The catalytic system cobalt tris-acetylacetonate/tri-ethylaluminium/water [$Co(acac)_3/AlEt_3/H_2O$], 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 (CS_2), is used, on the other hand, in processes for the industrial production of highly crystalline 1,2 syndiotactic 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.

[0009] An extremely active and stereospecific catalytic system for the preparation of 1,2-syndiotactic polybutadiene can be obtained by the combination of the cobalt allyl complex (η^4-C_4H_6) (η^5-C_5H_{13}) Co described, for example, by Natta G. et al., "Chemical Communications" (1967), Issue 24, pages 1263-1265, with carbon disulfide (CS_2), as described, for example, in: Ricci G. et al., "Polymer Communication" (1988), Vol. 29, pages 305-307. Said catalytic system is capable of dimerizing 1,3-butadiene at room temperature, as described, for example, in American patent US 5,879,805, but is only capable of giving 1,2-syndiotactic polymers when operating at low temperatures (-30°C) as described, for example, in: Ricci G. et al., "Polymer Communication" (1988), Vol. 29, pages 305-307.

[0010] 1,2 syndiotactic polybutadienes can also be produced using catalytic systems obtained by a combination of cobalt dichloride ($CoCl_2$) or cobalt dibromide ($CoBr_2$) with organic compounds of aluminium (e.g., alkyl compounds of aluminium), water and phosphines (e.g., triphenylphosphine) as described, for example, in the following American pat-

ents: 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. The regioregularity and crystallinity of the polybutadienes 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" (1988), Vol. 29, pages 305-307, indicated above.

[0011] Further details relating to the polymerization of 1,3-butadiene with catalytic systems comprising complexes of cobalt with various phosphines are provided, for example, in: 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; Takeuchi M. et al., "Polymer International" (1992), Vol. 29, pages 209-212; Takeuchi M. et al., "Polymer International" (1995), Vol. 36, pages 41-45; Takeuchi M. et al., "Macromolecular Chemistry and Physics" (1996), Vol. 197, pages 729-743; or in Italian patents IT 1,349,141, IT 1,349,142, IT 1,349,143. The use of various phosphines derives from the fact that it is well known that the 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 Previews" (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.

[0012] The documents relating to the use of phosphines indicated above, show how the use of phosphine complexes of cobalt combined with methylaluminoxane (MAO) can allow the microstructure of polybutadiene to be managed, thus allowing polybutadienes with **different** structures to be obtained, depending on the type of phosphine coordinated with the cobalt atom.

[0013] The polymerization of 1,3-butadiene with catalytic systems comprising complexes of cobalt with sterically hindered aliphatic phosphines (e.g., P^tBu_3, P^iPr_3, P^tBu_2Me, PCy_3, $PCyp_3$ wherein P = phosphorous, ^{t}Bu = tert-butyl, ^{i}Pr = *iso*-propyl, Cy = cyclohexyl and Cyp = cyclopentyl), provides polybutadienes with a prevalently 1,4-cis structure, whereas polybutadienes having a mixed 1,4-cis/1,2 structure have been obtained using catalytic systems comprising complexes of cobalt with phosphines having a lower steric hindrance (e.g., PCy_2H; P^tBu_2H; PEt_3; P^nPr_3 wherein P = phosphorous, Cy = cyclohexyl, ^{t}Bu = *tert*-butyl, Et = ethyl and ^{n}Pr - *n*-propyl), as described, for example, in: Ricci G. et al., "Advances in Organometallic Chemistry Research" (2007), Yamamoto K. Ed., Nova Science Publisher, Inc., USA, pages 1-36; Ricci G. et al., "Coordination Chemistry Reviews" (2010), Vol. 254, pages 661-676; Ricci G. et al., "Journal of Molecular Catalysis A: Chemical" (2005), Vol. 226, pages 235-241; and in Italian patent application IT 1,349,141.

[0014] Polybutadienes with a high content of 1,4-cis units (about 95%) have been obtained with catalytic systems comprising complexes of cobalt with bidentate phosphines [e.g., $CoCl_2[R_2P(CH_2)_nPR_2]$/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., "Advances in Organometallic Chemistry Research" (2007), Yamamoto K. Ed., Nova Science Publisher, Inc., USA, pages 1-36; Ricci G. et al., "Coordination Chemistry Reviews" (2010), Vol. 254, pages 661-676; and in Italian patent application IT 1,349,141.

[0015] Catalytic systems comprising complexes of cobalt with ligands selected from aromatic phosphines [e.g., $CoCl_2(PRPh_2)_2$/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: Ricci G. et al., "Advances in Organometallic Chemistry Research" (2007), Yamamoto K. Ed., Nova Science Publisher, Inc., USA, pages 1-36; Ricci G. et al., "Coordination Chemistry Reviews" (2010), Vol. 254, pages 661-676; Ricci G. et al., "Macromolecules" (2005), Vol. 38, pages 1064-1070; Ricci G. et al., "Journal of Organometallic Chemistry" (2005), Vol. 690, pages 1845-1854; or in Italian patent application IT 1,349,143. Using these catalytic systems, in fact, polybutadienes with an essentially 1,2 structure have been obtained (within a range of 70% to 88%), having a variable content of 1,2 units in relation to the type of complex and polymerization conditions. It has also been observed 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 a percentage of syndiotactic triads "rr"), determined by the ^{13}C-NMR spectra, increases with an increase in the steric requirement of the alkyl group bound to the phosphorous atom.

[0016] The 1,2 polybutadienes obtained with cobalt systems with less sterically hindered phosphine ligands (e.g., $PMePh_2$; $PEtPh_2$; P^nPrPh_2 wherein P = phosphorous, Me = methyl, Ph = phenyl, ^{n}Pr = n-propyl) have proved to be amorphous, whereas the polybutadienes obtained with catalytic systems using phosphine ligands with a higher steric hindrance (e.g., P^iPrPh_2, $PCyPh_2$ wherein P = phosphorous, ^{i}Pr = iso-propyl, Ph = phenyl, Cy = cyclohexyl), have proved to be crystalline, with a melting point (T_m) of 110°C - 120°C, depending on the polymerization conditions.

[0017] The polymerization of 1,3-butadiene with catalytic systems comprising complexes of cobalt with aromatic phosphines having the formula $CoCl_2(PR_2Ph)_2$/MAO (wherein Co = cobalt, Cl = chlorine, R = methyl, ethyl, cyclohexyl, Ph = phenyl, MAO = methylaluminoxane), has also been studied, as described, for example, in: Ricci G. et al., "Advances in Organometallic Chemistry Research" (2007), Yamamoto K. Ed., Nova Science Publisher, Inc., USA, pages 1-36; Ricci G. et al., "Coordination Chemistry Reviews" (2010), Vol. 254, pages 661-676; Ricci G. et al., "Journal of Organometallic Chemistry" (2005), Vol. 690, pages 1845-1854; or in Italian patent application IT 1,349,143. Using these catalytic systems,

essentially 1,2-polybutadienes have been obtained, but the syndiotacticity index of the polymers, with the same polymerization conditions, has generally proved to be slightly lower with respect to that of the 1,2-polybutadienes obtained with catalytic systems comprising complexes of cobalt with aromatic phosphines having the formula $CoCl_2(PRPh)_2$/MAO described above.

[0018] More recently, following the success obtained using the above catalytic systems comprising phosphine complexes of cobalt, also various catalytic systems comprising complexes of cobalt with ligands containing nitrogen or oxygen as donor atom, have been studied.

[0019] Kim J. S. et al., in "e-Polymer" (European Polymer Federation) (2006), No. 27, for example, describe the polymerization of 1,3-butadiene with catalytic systems comprising complexes of cobalt with bis(imine)pyridine and ethylaluminiumsesquichloride [$Al_2Et_3Cl_3$ (EASC)] **ligands.** These catalytic systems have proved to be particularly active, providing high-molecular-weight polybutadienes having a content of 1,4-cis units equal to 96.4%.

[0020] Catalytic systems comprising complexes of cobalt having the formula (Salen)Co(II) (wherein Salen = bis(salicylaldehyde)ethylenediiminate, Co = cobalt) and methylaluminoxane (MAO), characterized by a high activity and 1,4-cis selectivity, are described, for example by Endo K. et al., in "Journal of Polymer Science: Part A: Polymer Chemistry" (2006), vol. 44, pages 4088-4094.

[0021] Cariou R. et al., in "Dalton Transactions" (2010), Vol. 39, pages 9039-9045, describe the synthesis and characterization of a series of complexes of cobalt (II) [Co(II)] with bis(benzimidazole) which, when combined with methylaluminoxane (MAO), have proved to be highly selective for the 1,4-cis polymerization of 1,3-butadiene.

[0022] The synthesis and characterization of a series of complexes of cobalt (II) [Co(II)] with dibenzimidazole **ligands** and their use, combined with ethylaluminiumsesquichloride (EASC), for the polymerization of 1,3-butadiene, are described by Appukuttan et al., in "Polymer" (2009), Vol. 50, pages 1150-1158: the catalytic systems obtained are characterized by a high catalytic activity and also a high 1,4-cis selectivity (up to 97%).

[0023] Complexes of cobalt with 2,6-bis[1-(iminophenyl)ethyl]pyridine ligands were synthesized and characterized by Gong D. et al., as described in "Polymer" (2009), Vol. 50, pages 6259-6264. Said complexes, combined with methylaluminoxane (MAO), were tested for the polymerization of 1,3-butadiene, providing catalytic systems capable of giving 1,4-cis or 1,4-trans polybutadiene, in relation to the MAO/Co ratio. When operating with a MAO/Co molar ratio equal to 50, in fact, an essentially 1,4 trans polybutadiene was obtained (about 94.4%), whereas, when operating with a MAO/Co molar ratio equal to 100, a prevalently 1,4-cis polybutadiene was obtained (about 79%).

[0024] In "Journal of Molecular Catalysis A: Chemical (2010), Vol. 325, pages 84-90, Appukuttan V. et al., describe a series of complexes having general formula $[Py(Bm\text{-}R)_2]CoCl_2$ (wherein Py = pyridyl, Bm = benzimidazolyl, R = hydrogen, methyl, benzimidazole, Co = cobalt, Cl = chlorine), capable of providing, when combined with methylaluminoxane (MAO), high-molecular-weight 1,4-cis polybutadiene.

[0025] In "Journal of Organometallic Chemistry" (2011), Vol. 696, pages 1584-1590, Gong D. et al., describe a series of 2,6-bis(imine)pyridine complexes of cobalt (II) [Co(II)] which, when combined with methylaluminoxane (MAO) as co-catalyst, show a relatively good activity in the polymerization of 1,3-butadiene, allowing a polybutadiene to be obtained, having a 1,4-cis microstructure within a range of 77.5% to 97%, with control of both the molecular weight and also the molecular weight distribution.

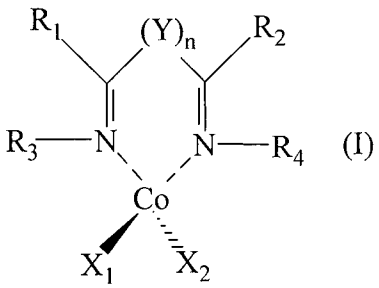
[0026] Finally, Jie S. et al., in "Dalton Transactions" (2011), Vol. 40, pages 10975-10982 and Ai P. et al., in "Journal of Organometallic Chemistry" (2012), Vol. 705, pages 51-58, have recently described the possibility of obtaining polybutadiene with a high content of 1,4-cis units (> 96%) with catalytic systems comprising catalysts based on complexes of cobalt with 3-aryliminomethyl-2-hydroxybenzaldehyde ligands, or with **ligands** of the NNO type (imino- or amino-pyridyl alcohols), respectively.

[0027] As already indicated above, as (co)polymers of conjugated dienes, in particular polybutadiene with a high content of 1,4-cis units, are the most widely-used polymers on an industrial scale, in particular for the production of tyres, the study of new processes capable of providing **said** (co)polymers is still of great interest.

[0028] The Applicant has considered the problem of finding a new process for the preparation of (co)polymers of conjugated dienes, such as, for example, polybutadiene, polyisoprene, in particular linear or branched polybutadiene with a high content of 1,4-cis units, i.e. a content of 1,4-cis units $\geq$ 98%.

[0029] The Applicant has now found that the preparation of (co)polymers of conjugated dienes, such as, for example, polybutadiene, polyisoprene, in particular linear or branched polybutadiene with a high content of 1,4-cis units, i.e. a content of 1,4-cis units $\geq$ 98%, can be advantageously carried out in the presence of a catalytic system comprising at least one bis-imine complex of cobalt having general formula (I) defined hereunder.

[0030] An object of the present invention therefore relates to a process for the preparation of (co)polymers of conjugated dienes which comprises polymerizing at least one conjugated diene in the presence of a catalytic system comprising at least one bis-imine complex of cobalt having general formula (I):



(I)

wherein:

- n is 0 or 1;
- Y represents a group -CR'R'' wherein R' and R'', equal to or different from each other, represent a hydrogen atom, or a linear or branched C_1-C_{20}, preferably C_1-C_{15}, alkyl group; or a divalent aromatic group optionally substituted;
- R_1 and R_2, equal to or different from each other, represent a hydrogen atom, or they are selected from a linear or branched C_1-C_{20}, preferably C_1-C_{15}, alkyl group optionally halogenated, cycloalkyl groups optionally substituted; or R_1 and R_2 can be optionally bound to each other to form, together with the other atoms to which they are bound, a cycle containing from 4 to 6 carbon atoms, saturated, unsaturated, or aromatic, optionally substituted with linear or branched C_1-C_{20}, preferably C_1-C_{15}, alkyl groups, said cycle optionally containing heteroatoms such as, for example, oxygen, sulfur, nitrogen, silicon, phosphorous, selenium;
- R_3 and R_4, equal to or different from each other, represent a hydrogen atom, or they are selected from a linear or branched C_1-C_{20}, preferably C_1-C_{15}, alkyl group optionally halogenated, cycloalkyl groups optionally substituted; aryl groups optionally substituted;
- or R_2 and R_4 can be optionally bound to each other to form, together with the other atoms to which they are bound, a cycle containing from 3 to 6 carbon atoms, saturated, unsaturated, or aromatic, optionally substituted with linear or branched C_1-C_{20}, preferably C_1-C_{15}, alkyl groups, said cycle optionally containing other heteroatoms such as, for example, oxygen, sulfur, nitrogen, silicon, phosphorous, selenium;
- or R_1 and R_3 can be optionally bound to each other to form, together with the other atoms to which they are bound, a cycle containing from 3 to 6 carbon atoms, saturated, unsaturated, or aromatic, optionally substituted with linear or branched C_1-C_{20}, preferably C_1-C_{15}, alkyl groups, said cycle optionally containing other heteroatoms such as oxygen, sulfur, nitrogen, silicon, phosphorous, selenium;
- X_1 and X_2, equal to or different from each other, represent a halogen atom such as, for example, chlorine, bromine, iodine; or they are selected from linear or branched C_1-C_{20} preferably C_1-C_{15}, alkyl groups, -$OCOR_5$ groups or -OR_5 groups wherein R_5 is selected from linear or branched C_1-C_{20} preferably C_1-C_{15}, alkyl groups.

[0031] For the **aim** of the present description and of the following claims, the definitions of the numerical intervals always include the extremes, unless otherwise specified.

[0032] For the aim of the present description and of the following claims, the term "comprising" also includes the terms "which essentially consist of" or "which consists of".

[0033] According to a preferred embodiment of the present invention, said catalytic system can comprise at least one co-catalyst (b) selected from organic compounds of an element M' different from carbon, said element M' being selected from elements belonging to groups 2, 12, 13 or 14, of the Periodic Table of Elements, preferably from: boron, aluminium, zinc, magnesium, gallium, tin, even more preferably from aluminium, boron.

[0034] The formation of the catalytic system comprising the bis-imine complex of cobalt having general formula (I) and the co-catalyst (b), is generally and preferably carried out in an inert liquid medium, more preferably in a hydrocarbon solvent. The choice of bis-imine complex of cobalt having general formula (I) and of co-catalyst (b), as well as the particular method used, can vary in relation to the molecular structures and **to the** desired result, according to what is analogously described in specific literature available to experts in the field for other complexes of transition metals with imine ligands, as described, for example, by L. K. Johnson et al. in "Journal of the American Chemical Society" (1995), Vol. 117, pages 6414-6415, and G. van Koten et al. in "Advances in Organometallic Chemistry" (1982), Vol. 21, pages 151-239.

[0035] According to a further preferred embodiment of the present invention, said co-catalyst (b) can be selected from (b_1) aluminium alkyls having general formula (II):

$$Al(X')_n(R_6)_{3-n} \qquad (II)$$

wherein X' represents a halogen atom such as, for example, chlorine, bromine, iodine, fluorine; R_6 is selected from linear or branched C_1-C_{20} alkyl groups, cycloalkyl groups, aryl groups, said groups being optionally substituted with one or more silicon or germanium atoms; and n is an integer ranging from 0 to 2.

[0036] According to a further preferred embodiment of the present invention, said co-catalyst (b) can be selected from (b_2) organo-oxygenated compounds of an element M' different from carbon belonging to groups 13 or 14 of the Periodic Table of Elements, preferably organo-oxygenated compounds of aluminium, gallium, tin. Said organo-oxygenated compounds (b_2) can be defined as organic compounds of M', wherein the latter is bound to at least one oxygen atom and to at least one organic group consisting of an alkyl group having from 1 to 6 carbon atoms, preferably methyl.

[0037] According to a further preferred embodiment of the present invention, said co-catalyst (b) can be selected from (b_3) organometallic compounds or mixtures of organometallic compounds of an element M' different from carbon capable of reacting with the bis-imine complex of cobalt having general formula (I), extracting therefrom a substituent X_1 or X_2 σ-bound, 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.

[0038] It should be noted that, for the aim of the present invention and of the following claims, the term "Periodic Table of Elements" refers to the IUPAC version of the "Periodic Table of Elements" dated June 22, 2007, provided in the following Internet website www.iupac.org/fileadmin/user upload/news/IUPAC Periodic Table-1Jun12.pdf.

[0039] The term "divalent aromatic group" refers to an aromatic carbocyclic group containing one or more aromatic rings. Said divalent aromatic group can be optionally substituted with one or more groups, equal to or different from each other, selected from: halogen atoms such as, for example, fluorine, chlorine, bromine; hydroxyl groups; C_1-C_{12} alkyl groups; C_1-C_{12} alkoxyl groups; cyano groups; amino groups; nitro groups. Specific examples of divalent aromatic group are: *orto*-phenylene, meta-phenylene methylphenylene, trimethylphenylene, methoxyphenylene, hydroxyphenylene, phenyloxyphenylene, fluorophenylene, chlorophenylene, bromophenylene, nitrophenylene, dimethylaminophenylene, naphtylene, phenylnaphtylene, phenantrenylene, antracenylene.

[0040] The term "C_1-C_{20} alkyl groups" refers to linear or branched alkyl groups having from 1 to 20 carbon atoms. Specific examples of C_1-C_{20} alkyl groups are: methyl, ethyl, *n*-propyl, *iso*-propyl, *n*-butyl, *s*-butyl, *iso*-butyl, *tert*-butyl, pentyl, hexyl, heptyl, octyl, *n*-nonyl, *n*-decyl, 2-butyloctyl, 5-methylhexyl, 4-ethylhexyl, 2-ethylheptyl, 2-ethylhexyl.

[0041] The term "C_1-C_{20} alkyl groups optionally halogenated" refers to linear or branched alkyl groups having from 1 to 20 carbon atoms, linear or branched, saturated or unsaturated, wherein at least one of the hydrogen atoms is substituted with a halogen atom such as, for example, fluorine, chlorine, bromine, preferably fluorine, chlorine. Specific examples of C_1-C_{20} alkyl groups optionally halogenated are: fluoromethyl, difluoromethyl, trifluoromethyl, trichloromethyl, 2,2,2-trifluoroethyl, 2,2,2-trichloroethyl, 2,2,3,3-tetrafluoropropyl, 2,2,3,3,3-pentafluoropropyl, perfluoropentyl, perfluorooctyl, perfluorodecyl.

[0042] The term "cycloalkyl groups" refers to cycloalkyl groups having from 3 to 30 carbon atoms. Said cycloalkyl groups can be optionally substituted with one or more groups, equal to or different from each other, selected from: halogen atoms; hydroxyl groups; C_1-C_{12} alkyl groups; C_1-C_{12} alkoxyl groups; cyano groups; amino groups; nitro groups. Specific examples of cycloalkyl groups are: cyclopropyl, 2,2-difluorocyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, hexamethylcyclohexyl, pentamethyl-cyclopentyl, 2-cyclooctylethyl, methylcyclohexyl, methoxycyclohexyl, fluorocyclohexyl, phenylcyclohexyl.

[0043] The term "aryl groups" refers to aromatic carbocyclic groups. Said aromatic carbocyclic groups can be optionally substituted by one or more groups, equal to or different from each other, selected from: halogen atoms such as, for example, fluorine, chlorine, bromine; hydroxyl groups; C_1-C_{12} alkyl groups; C_1-C_{12} alkoxyl groups, cyano groups; amino groups; nitro groups. Specific examples of aryl groups are: phenyl, methylphenyl, trimethylphenyl, methoxyphenyl, hydroxyphenyl, phenyloxyphenyl, fluorophenyl, chlorophenyl, bromophenyl, nitrophenyl, dimethylaminophenyl, naphthyl, phenylnaphthyl, phenanthrene, anthracene.

[0044] The term "cyclo" refers to a system containing a ring containing from 3 to 6 carbon atoms or from 4 to 6 carbon atoms, optionally containing, in addition to the nitrogen atom, other heteroatoms selected from nitrogen, oxygen, sulfur, silicon, selenium, phosphorous. Specific examples of cyclo are: pyridine, thiadiazole.

[0045] According to a further preferred embodiment of the present invention, said conjugated diene can be selected, for example, from: 1,3-butadiene, 2-methyl-1,3-butadiene (isoprene), 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, 1,3-hexadiene, cyclo-1,3-hexadiene, or mixtures thereof. 1,3-Butadiene, isoprene, are preferred.

[0046] According to a preferred embodiment of the present invention, in said bis-imine complex of cobalt having general formula (I):

- n is 0;
- R_1 and R_2, equal to or different from each other, are a hydrogen atom; or they are selected from linear or branched C_1-C_{20} alkyl groups, preferably **are** a methyl group;
- R_3 and R_4, equal to or different from each other, are selected from phenyl groups optionally substituted with linear

or branched C_1-C_{20} alkyl groups, preferably substituted with one or more methyl, ethyl, iso-propyl, tert-butyl groups;
- X_1 and X_2, the same as each other, are a halogen atom such as, for example, chlorine, bromine, iodine, preferably chlorine.

[0047] According to a further preferred embodiment of the present invention, in said bis-imine complex of cobalt having general formula (I):

- n is 1;
- Y is a group CR'R" wherein R' and R", equal to or different from each other, are a hydrogen atom, or they are selected from linear or branched C_1-C_{20} alkyl groups, preferably are a propyl group;
- R_1 and R_2, equal to or different from each other, are a hydrogen atom, or they are selected from linear or branched C_1-C_{20} alkyl groups, preferably **are** a methyl group;
- R_3 and R_4, equal to or different from each other, are selected from phenyl groups optionally substituted with linear or branched C_1-C_{20} alkyl groups, preferably substituted with one or more methyl, ethyl, iso-propyl, tert-butyl groups;
- X_1 and X_2, the same as each other, are a halogen atom such as, for example, chlorine, bromine, iodine, preferably chlorine.

[0048] According to a further preferred embodiment of the present invention, in said bis-imine complex of cobalt having general formula (I):

- n is 0;
- R_1 and R_3, are bound to each other and, together with the other atoms to which they are bound, form a pyridine;
- R_2 is a hydrogen atom, or it is selected from linear or branched C_1-C_{20} alkyl groups, preferably **is** a methyl group;
- R_4 is selected from phenyl groups optionally substituted with linear or branched C_1-C_{20} alkyl groups, preferably a phenyl group substituted with one or more methyl, ethyl, iso-propyl, tert-butyl groups;
- X_1 and X_2, the same as each other, are a halogen atom such as, for example, chlorine, bromine, iodine, preferably chlorine.

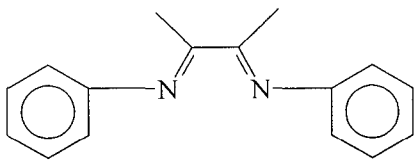
[0049] According to a further preferred embodiment of the present invention, in said bis-imine complex of cobalt formula (I):

- n is 1;
- Y is a divalent aromatic group optionally substituted, preferably a meta-phenylene group;
- R_1 and R_2, equal to or different from each other, are a hydrogen atom, or they are selected from linear or branched C_1-C_{20} alkyl groups, preferably **are** a methyl group;
- R_3 and R_4, equal to or different from each other, are selected from phenyl groups optionally substituted with linear or branched C_1-C_{20} alkyl groups, preferably a phenyl group substituted with a methyl group;
- X_1 and X_2, the same as each other, are a halogen atom such as, for example, chlorine, bromine, iodine, preferably chlorine.

[0050] The bis-imine complex of cobalt having general formula (I) should be considered, according to the present invention, as being in any physical form such as, for example, in the form of an isolated and purified solid, solvated with a suitable solvent, or supported on suitable organic or inorganic solids, preferably having a granular or powder physical form.

[0051] The bis-imine complex of cobalt having general formula (I) is prepared starting from ligands known in the art.

[0052] Specific examples of ligands which can be used for the aim of the present invention are those having the following formulae (L1)-(L22):



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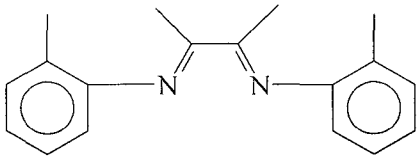

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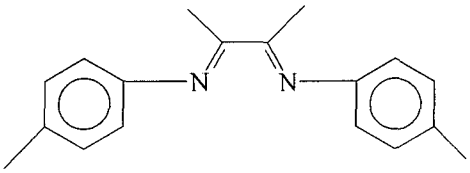
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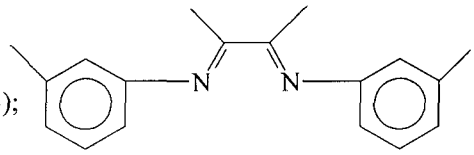
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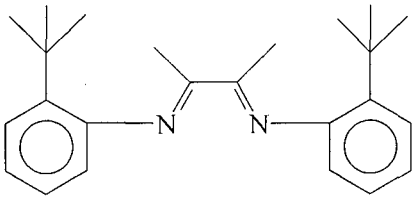
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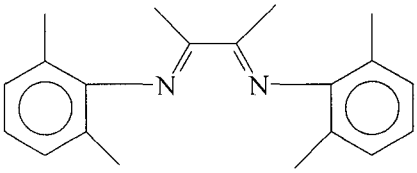
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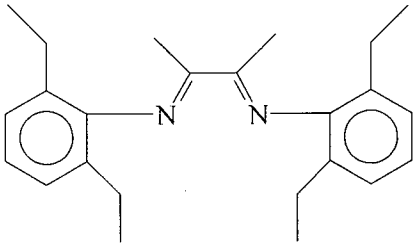
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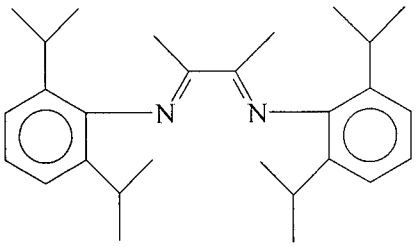
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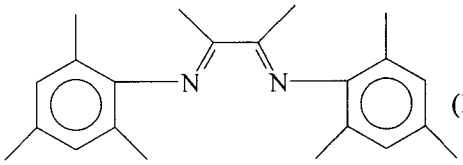
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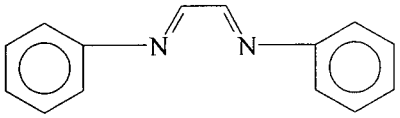
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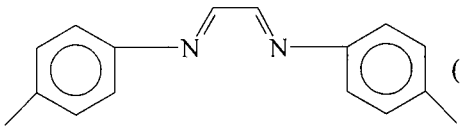
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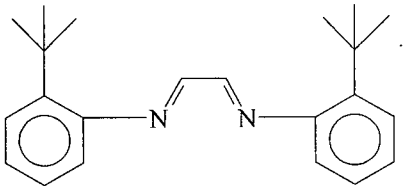
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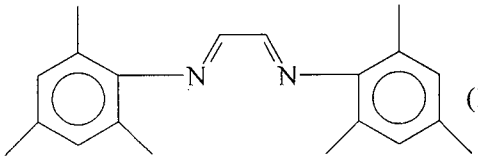
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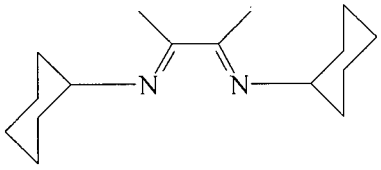
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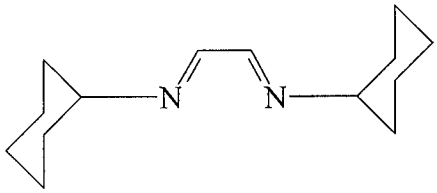
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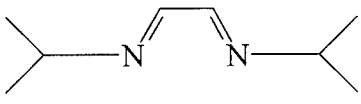
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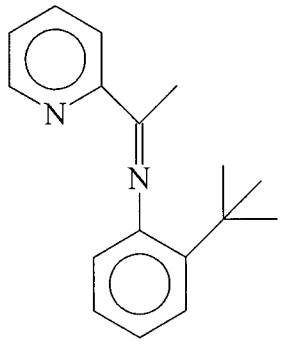
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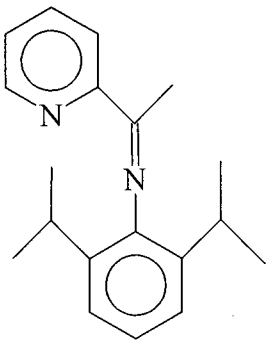
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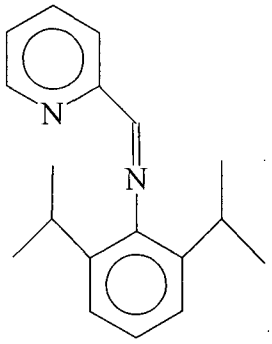
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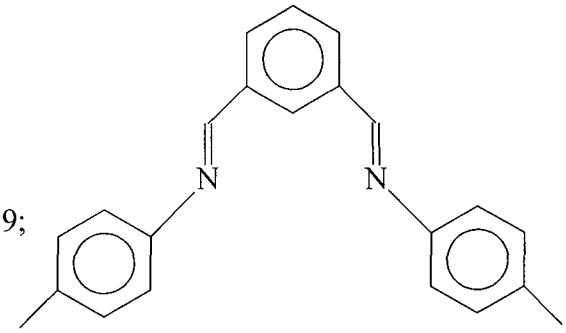
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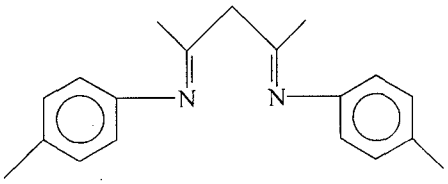
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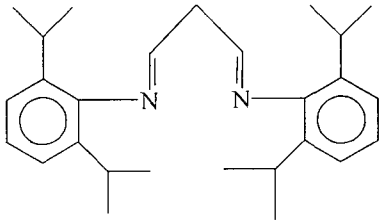

(L22).

[0053] Said ligands having formulae (L1)-(L22) can be prepared by means of processes known in the art. Said ligands having formulae (L1)-(L22) can be prepared, for example, by means of:

- condensation reactions between primary amines and α,β-diketones, as described, for example, by: van der Poel H. et al., in "Synthetic Communication" (1978), Vol. 8, pages 305; Svoboda M. et al., in "Zeitschrift fuer Naturfoschung" (1981), Teil B, pages 814-822; Dieck H. et al., in "Zeitschrift fuer Naturfoschung" (1981), Teil B, pages 823-832; Dieck H. et al., in "Zeitschrift fuer Naturfoschung" (1975), Teil B, pages 922-925;
- condensation reactions between primary amines and glyoxals as described, for example, by: Kliegman J. M. et al., in "Tetrahedron" (1970), Vol. 26, pages 2555-2560; Kliegman J. M. et al., in "The Journal of Organic Chemistry" (1970), Vol. 35(9), pages 3140-3143; Barney V. C. et al., in "Journal of Chemical Society" (1953), pages 3610-3612; Horner L. et al., in "Chemische Berichte" (1957), Vol. 90, pages 2184-2189; Carson J. F. et al., in "Journal of the American Chemical Society" (1953), Vol. 75, pages 4337-4338;
- condensation reactions between primary amines and α-ketoaldehydes as described, for example, by: van der Poel H. et al., in "Synthetic Communication" (1978), Vol. 8, pages 305; Svoboda M. et al., in "Zeitschrift fuer Naturfoschung" (1981), Teil B, pages 814-822; Dieck H. et al., in "Zeitschrift fuer Naturfoschung" (1981), Teil B, pages 823-832;
- condensation reactions between primary amines and β-diketones or β-dialdehydes as described, for example, by: Dove A. P. et al., in "Dalton Transactions" (2004), Issue 4, pages 570-578; Bourget-Merle L. et al., in "Chemical Reviews" (2002), Vol. 102, pages 3031-3065; Budzelaar P. H. et al., in "European Journal of Inorganic Chemistry" (2000), Issue 4, pages 753-769.

[0054] The bis-imine complex of cobalt having general formula (I) can be prepared by means of processes known in the art. Said bis-imine complex of cobalt can be prepared, for example, by the reaction between cobalt compounds having general formula $Co(X)_2$ wherein X is a halogen atom such as, for example, chlorine, bromine, iodine, preferably

chlorine, as such or complexed with ethers [for example, diethylether, tetrahydrofuran (THF), dimethoxyethane], with the **ligands** having formulae (L1)-(L22) indicated above, in a **ligand** (L)/cobalt (Co) molar ratio ranging from 1 to 1.5, preferably operating in the presence of at least one solvent which can be selected, for example, from: chlorinated solvents (for example, methylene chloride), ether solvents [for example, tetrahydrofuran (THF)], alcohol solvents (for example, butanol), hydrocarbon solvents (for example, toluene), or mixtures thereof, at room temperature or higher. The bis-imine complex of cobalt thus obtained can be subsequently recovered by means of methods known in the art such as, for example, precipitation by means of a non-solvent (for example, pentane), followed by separation by means of filtration or decanting and optional subsequent dissolution in a suitable solvent followed by crystallization at a low temperature

[0055] 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.

[0056] Specific examples of aluminium alkyls having general formula (II) 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-methylbutyl)-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-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-methylpentyl)-aluminium, tri-(2,3,3-tri-methyl-pentyl)-aluminium, tri-(2,3,3-tri-methyl-hexyl)-aluminium, tri-(2-ethyl-3,3-di-methyl-butyl)-aluminium, tri-(2-ethyl-3,3-di-methyl-pentyl)-aluminium, tri-(2-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-(2,3-di-methyl-3-phenyl-butyl)-aluminium, tri-(2-phenyl-propyl)-aluminium, tri-[2-(4-fluoro-phenyl)-propyl]-aluminium, tri-[2-(4-chloro-phenyl)-propyl]-aluminium, tri-[2-(3-*iso*-propyl-phenyl-tri-(2-phenylbutyl)-aluminium, tri-(3-methyl-2-phenyl-butyl)-aluminium, tri-(2-phenyl-pentyl)-aluminium, tri-[2-(pentafluoro-phenyl)-propyl]-aluminium, tri-(2,2-diphenyl-ethyl]-aluminium, tri-(2-phenyl-methylpropyl)-aluminium, tri-pentyl-aluminium, tri-hexyl-aluminium, tri-cyclohexyl-aluminium, tri-octyl-aluminium, di-ethyl-aluminium hydride, di-*n*-propyl-aluminium hydride, di-*n*-butyl-aluminium hydride, di-*iso*-butyl-aluminium hydride (DIBAH), di-hexyl-aluminium hydride, di-*iso*-hexyl-aluminium hydride, di-octyl-aluminium hydride, di-*iso*-octyl-aluminium hydride, ethyl-aluminium di-hydride, *n*-propyl-aluminium di-hydride, *iso*-butyl-aluminium di-hydride, di-ethyl-aluminium chloride (DEAC), mono-ethyl-aluminium dichloride (EADC), di-methyl-aluminium chloride, di-*iso*-butyl-aluminium chloride, *iso*-butyl-aluminium dichloride, ethyl-aluminium 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), ethyl-aluminium sesquichloride (EASC), are particularly preferred.

[0057] When used for the formation of a catalytic (co)polymerization system according to the present invention, the aluminium alkyls having general formula (II) may preferably be put in contact with a bis-imine complex of cobalt having general formula (I), in such proportions that the molar ratio between the cobalt present in the bis-imine complex of cobalt having general formula (I) and the aluminium present in the aluminium alkyls having general formula (II) can range from 5 to 5,000, preferably from 10 to 1,000. The sequence with which the bis-imine complex of cobalt having general formula (I) and aluminium alkyl having general formula (II) are put in contact with each other, is not particularly critical.

[0058] Further details relating to the aluminium alkyls having general formula (II) can be found in international patent application WO 2011/061151.

[0059] According to a particularly preferred embodiment, said organo-oxygenated compounds (b_2) can be selected from aluminoxanes having general formula (III):

$$(R_7)_2\text{-Al-O-[-Al}(R_8)\text{-O-]}_p\text{-Al-}(R_9)_2 \qquad \text{(III)}$$

wherein R_7, R_8 and R_9, equal to or different from each other, represent a hydrogen atom, a halogen atom such as, for example, chlorine, bromine, iodine, fluorine; or they are selected from linear or branched C_1-C_{20} alkyl groups, cycloalkyl groups, aryl groups, said groups being optionally substituted with one or more silicon or germanium atoms; and p is an integer ranging from 0 to 1,000.

[0060] 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 of an aluminium alkyl halide, with water or with other compounds containing predetermined quantities of available water, such as, for example, in the case of the reaction of aluminium trimethyl with aluminium sulfate hexahydrate, copper sulfate pentahydrate or iron sulfate pentahydrate.

[0061] Said aluminoxanes, and particularly methyl aluminoxane (MAO), are compounds which can be obtained by means of known organometallic chemical processes such as, for example, by the addition of aluminium trimethyl to a suspension in hexane of aluminium sulfate hydrate.

[0062] When used for the formation of a catalytic (co)polymerization system according to the present invention, the aluminoxanes having general formula (III) may preferably be put in contact with a bis-imine complex of cobalt having general formula (I), in such proportions that the molar ratio between the aluminium (Al) present in the aluminoxane having general formula (III) and the cobalt present in the bis-imine complex of cobalt having general formula (I) can range from 10 to 10,000, preferably from 100 to 5,000. The sequence with which the bis-imine complex of cobalt having general formula (I) and the aluminoxane having general formula (III) are put in contact with each other, is not particularly critical.

[0063] In addition to the above preferred aluminoxanes having general formula (III), the definition of the compound (b_2) according to the present invention can also include galloxanes, wherein, in general formula (III), gallium is present in substitution of the aluminium, and stannoxanes, wherein, in general formula (III), tin is present in substitution of the aluminium, whose use as co-catalysts in the polymerization of olefins in the presence of metallocene complexes, is known. Further details relating to said galloxanes and stannoxanes can be found, for example, in American patents US 5,128,295 and US 5,258,475.

[0064] Specific examples of aluminoxanes having general formula (III) 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.

[0065] Further details relating to the aluminoxanes having general formula (III) can be found in international patent application WO 2011/061151.

[0066] According to a preferred embodiment of the present invention, said compounds or mixtures of compounds (b_3) can be selected from organic compounds of aluminium and especially **of** boron, such as, for example, those represented by the following general formulae:

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

$$[Ph_3Cl^+\bullet[B(R_D)_4]^-;\ [(R_C)_3PH]^+\bullet[B(R_D)_4]^-;$$

$$[Li]^+\bullet[B(R_D)_4]^-;\ [Li]^+\bullet[Al(R_D)_4]^-$$

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.

[0067] When used for the formation of a catalytic (co)polymerization system according to the present invention, the compounds or mixtures of compounds (b_3) may preferably be put in contact with a bis-imine complex of cobalt having general formula (I), in such proportions that the molar ratio between the metal (M') present in the compounds or mixtures of compounds (b_3) and the cobalt present in the bis-imine complex of cobalt having general formula (I) ranges from 0.1 to 15, preferably from 0.5 to 10, more preferably from 1 to 6. The sequence with which the bis-imine complex of cobalt having general formula (I) and the compound or mixture of compounds (b_3) are put in contact with each other, is not particularly critical.

[0068] Said compounds or mixtures of compounds (b_3), especially when X_1 and X_2 in the bis-imine complex of cobalt having general formula (I) are different from alkyl, must be used in a combination with an aluminoxane having general formula (III) such as, for example, methylaluminoxane (MAO), or, preferably, with an aluminium alkyl having general formula (II), 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).

[0069] Examples of the methods generally used for the formation of a catalytic (co)polymerization system according to the present invention, when compounds or mixtures of compounds (b_3) are used, are qualitatively schematized in the following list, which however in no way limits the overall scope of the present invention:

(m_1) contact of a bis-imine complex of cobalt having general formula (I) wherein at least one of X_1 and X_2 is an alkyl group, with at least one compound or mixture of compounds (b_3) 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_2) reaction of a bis-imine complex of cobalt having general formula (I) with at least one aluminium alkyl having general formula (II), preferably an aluminium trialkyl, used in a molar excess of 10/1 to 300/1, followed by reaction with a strong Lewis acid, such as, for example, tris (pentafluorophenyl)boron [compound (b_3)], in an almost stoichiometric quantity or in slight excess with respect to the cobalt (Co);

(m_3) contact and reaction of a bis-imine complex of cobalt having general formula (I) 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 an alkyl aluminium halide represented by the formula $AlR'''_{4-m}Z_{3-m}$ wherein R''' is a linear or branched C_1-C_8 alkyl group, or a mixture thereof, Z is a halogen, preferably chlorine or bromine, and m is a decimal number ranging from 1 to 3, followed by addition, to the composition thus obtained, of at least one compound or mixture of compounds (b_3) in such quantities that the ratio between said compound or mixture of compounds (b_3) or the aluminium of said compound or mixture of compounds (b_3) and the cobalt of the bis-imine complex of cobalt having general formula (I) ranges from 0.1 to 15, preferably from 1 to 6.

[0070] Examples of compounds or mixtures of compounds (b_3) capable of producing an ionic catalytic system by reaction with a bis-imine complex of cobalt having general formula (I) according to the present invention, are described, although with reference to the formation of ionic metallocene complexes, in the following publications, whose contents are incorporated herein as reference:

- W. Beck et al., "Chemical Reviews" (1988), Vol. 88, pages 1405-1421;
- S. H. Stares, "Chemical Reviews" (1993), Vol. 93, pages 927-942;
- European patent applications EP 277 003, EP 495 375, EP 520 732, EP 427 697, EP 421 659, EP 418044;
- published international patent applications WO 92/00333, WO 92/05208.

[0071] Specific examples of a compound or mixture of compounds (b_3) particularly useful for the aim of the present invention are: tributylammonium-tetrakis-pentafluorophenyl-borate tributylammonium-tetrakis-pentafluorophenyl-aluminate, tributylammonium-tetrakis-[(3,5-di-(trifluorophenyl)]-borate, tributylammonium-tetrakis-(4-fluorophenyl)]-borate, N,N-dimethylbenzyl-ammonium-tetrakis-pentafluoro-phenyl-borate, N,N-di-methyl-hexylammonium-tetrakis-pentafluorophenyl-borate, N,N-dimethylanilinium-tetrakis-(pentafluorophenyl)-borate, N,N-dimethylanilinium-tetrakis-(pentafluorophenyl)-aluminate, di-(propyl)-ammonium-tetrakis-(pentafluorophenyl)-borate, di-(cyclohexyl)-ammonium-tetrakis-(pentafluorophenyl)-borate, tri-phenyl-carbenium-tetrakis-(pentafluorophenyl)-borate, tri-phenylcarbenium-tetrakis-(penta-fluorophenyl)-aluminate, tris(pentafluorophenyl)boron, tris(pentafluorophenyl)-aluminium, or mixtures thereof. Tetrakis-pentafluorophenyl-borates are preferred.

[0072] For the aim of the present description and of the following claims, the term "mole" and "molar ratio" are used with reference to compounds consisting of molecules and also with reference to atoms and ions, omitting, for the latter, the terms gram atom or atomic ratio, even if scientifically more correct.

[0073] Other additives or components can be optionally added to the above catalytic system in order to adapt it so as to satisfy specific practical requirements. The catalytic systems thus obtained should therefore be considered as being included in the scope of the present invention. Additives and/or components which can be added in the preparation and/or formulation of the above catalytic system are, for example: inert solvents, such as, for example, aliphatic and/or aromatic hydrocarbons; aliphatic and/or aromatic ethers; weakly coordinating additives (e.g., Lewis bases) selected, for example, from non-polymerizable olefins; sterically hindered or electronically poor ethers; halogenating agents such as, for example, silicon halides, halogenated hydrocarbons, preferably chlorinated; or mixtures thereof.

[0074] As already specified above, said catalytic system can be prepared according to methods known in the art.

[0075] Said catalytic system, for example, can be prepared separately (preformed) and subsequently introduced into the (co)polymerization environment. In this respect, said catalytic system can be prepared by reacting at least one bis-imine complex of cobalt having general formula (I) with at least one co-catalyst (b), optionally in the presence of other additives or components selected from those listed above, in the presence of a solvent such as, for example, toluene, heptane, at a temperature ranging from 20°C to 60°C, for a time ranging from 10 seconds to 10 hours, preferably from 30 seconds to 5 hours. Further details on the preparation of said catalytic system can be found in the examples provided hereunder.

[0076] Alternatively, said catalytic system can be prepared *in situ*, i.e. directly in the (co)polymerization environment. In this respect, said catalytic system can be prepared by introducing the bis-imine complex of cobalt having general formula (I), the co-catalyst (b) and the preselected conjugated diene(s) to be (co)polymerized, separately, operating under the conditions in which the (co)polymerization is carried out.

[0077] For the aim of the process object of the present invention, said catalytic systems can also be supported on inert solids, preferably consisting of silicon and/or aluminium oxides, such as, for example, silica, alumina or silico-aluminates. The known supporting techniques can be used for supporting said catalytic systems, generally comprising contact, in a suitable inert liquid medium, between the carrier, optionally activated by heating to temperatures higher than 200°C, and one or both of components, i.e. the bis-imine complex of cobalt having general formula (I) and the co-catalyst (b), 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 the bis-imine complex of cobalt having general formula (I) alone, or the co-catalyst (b) alone, 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.

[0078] The bis-imine complex of cobalt having general formula (I), and the catalytic systems based thereon, which have been supported on a solid by the functionalization of the latter and formation of a covalent bond between the solid and bis-imine complex of cobalt having general formula (I), are also included in the scope of the present invention.

[0079] The quantity of bis-imine complex of cobalt having general formula (I) and co-catalyst (b) that can be used in the process object of the present invention, varies according to the (co)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 bis-imine complex of cobalt having general formula (I) and the metal present in the co-catalyst (b), e.g., aluminium when the co-catalyst (b) is selected from aluminium alkyls (b_1) or aluminoxanes (b_2), boron when the co-catalyst (b) is selected from compounds or mixtures of compounds (b_3) having general formula (III), included within the values indicated above.

[0080] According to a preferred embodiment of the present invention, said process can be carried out in the presence of an inert organic solvent selected, for example, from: saturated aliphatic hydrocarbons such as, for example, butane, pentane, hexane, heptane, or mixtures thereof; saturated cycloaliphatic hydrocarbons such as, for example, cyclopentane, cyclohexane, or mixtures thereof; mono-olefins such as, for example, 1-butene, 2-butene, or mixtures thereof; aromatic hydrocarbons such as, for example, benzene, toluene, xylene, or mixtures thereof; halogenated hydrocarbons such as, for example, methylene chloride, chloroform, carbon tetrachloride, trichloroethylene, perchloroethylene, 1,2-dichloroethane, chlorobenzene, bromobenzene, chlorotoluene, or mixtures thereof. Said solvent is preferably selected from saturated aliphatic hydrocarbons.

[0081] Alternatively, said process can be carried out using, as solvent, the same conjugated diene(s) to be (co)polymerized, according to the process known as "bulk process".

[0082] According to a preferred embodiment of the present invention, the concentration of the conjugated diene to be (co)polymerized in said inert organic solvent ranges from 5% by weight to 50% by weight, preferably from 10% by weight to 20% by weight, with respect to the total weight of the mixture of conjugated diene and inert organic solvent.

[0083] According to a preferred embodiment of the present invention, said process can be carried out at a temperature ranging from -70°C to +100°C, preferably from -20°C to +80°C.

[0084] As far as the pressure is concerned, it is preferable to operate at the pressure of the components of the mixture to be (co)polymerized.

[0085] Said process can be carried out either in continuous or batchwise.

[0086] As indicated above, said process allows (co)polymers of conjugated dienes to be obtained, such as, for example, polybutadiene, polyisoprene, in particular, linear or branched polybutadiene, with a high content of 1,4-cis units, i.e. a content of 1,4-cis units ≥ 98%.

[0087] Some illustrative and non-limiting examples are provided hereunder for a better understanding of the present invention and for its practical embodiment.

EXAMPLES

Reagents and materials

[0088] The reagents and materials used in the following examples of the invention are indicated in the following list, together with their **optional** pretreatments and their supplier:

- cobalt dichloride ($CoCl_2$) (Stream Chemicals); used as such;
- tetrahydrofuran (THF) (Carlo Erba, RPE): kept at reflux temperature on potassium/benzophenone and then distilled under nitrogen;
- formic acid (85%) (Carlo Erba, RPE): used as such;
- 2,3-butandione (Aldrich): used as such;
- 2-*tert*-butylaniline (Aldrich): used as such;
- 2,6-diethylaniline (Aldrich): used as such;
- 2,4,6-trimethylaniline (Aldrich): used as such;
- 2,6-di-*iso*-propylaniline (Aldrich): used as such;
- p-toluidine (Aldrich): used as such;
- benzene-1,3-carboxyaldehyde (Aldrich): used as such;
- acetylpyridine (Aldrich): used as such;
- glyoxal (aqueous solution at 40%) (Aldrich): used as such;
- toluene (Aldrich): pure, ≥ 99.5%, distilled on sodium (Na) in an inert atmosphere;
- pentane (Aldrich): pure, ≥ 99.5%, distilled on sodium (Na) in an inert atmosphere;
- methylaluminoxane (MAO) (toluene solution at 10% by weight) (Aldrich): used as such;
- acetylacetone (Aldrich): used as such;
- 1,3-butadiene (Air Liquide): pure, ≥ 99.5%, evaporated from the container before each production, dried by passing

it through a column packed with molecular sieves and condensed inside the reactor which has been pre-cooled **at** -20°C;
- hydrochloric acid in aqueous solution at 37% (Aldrich): used as such;
- p-toluenesulfonic acid (Aldrich): used as such;
- sodium carbonate decahydrate ($Na_2CO_3 \cdot 10H_2O$) (Aldrich): used as such;
- magnesium sulfate ($MgSO_4$) (Aldrich): used as such;
- methanol (Carlo Erba, RPE): used as such;
- ethanol (Carlo Erba, RPE): used as such or optionally anhydrified by distillation on magnesium (Mg) ;
- dichloromethane (Carlo Erba, RPE): used as such;
- deuterated tetrachloroethylene ($C_2D_2Cl_4$) (Acros): used as such;
- deuterated chloroform ($CDCl_3$) (Acros): used as such.

[0089] The analyses and characterization methods indicated hereunder, were used.

Elemental analysis

a) Determination of Co

[0090] For the determination of the weight quantity of cobalt (Co) in the bis-imine 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 **mg** - 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 reappearance 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 added, without heat, 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 analytical instrumental determination was carried out using an ICP-OES (optical detection plasma) Thermo Optek IRIS Advantage Duo spectrometer, by comparison with solutions at a known concentration. For this aim, a calibration curve 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.

[0091] The solution of the sample prepared as described above was diluted again by weight so as to obtain concentrations close to those used as reference, before carrying out spectrophotometric analysis. All the samples were prepared in duplicate. The results were considered acceptable if the single data of the tests in duplicate did not differ by more than 2% relative with respect to their average value.

b) Chlorine determination

[0092] For this aim, samples of the bis-imine complexes of cobalt used for the aim of the present invention, about 30 mg - 50 mg, were weighed exactly in 100 ml glasses in a dry-box under a stream of nitrogen. 2 g of sodium carbonate (Na_2CO_3) and 50 ml of MilliQ water were added, outside the dry-box. The mixture was brought to boiling point on a plate, under magnetic stirring, for about 30 minutes. It was left to cool, diluted sulfuric acid (H_2SO_4) 1/5 was added until the reaction became acid and the mixture was titrated with silver nitrate ($AgNO_3$) 0.1 N with a potentiometer titrator.

c) Determination of carbon, hydrogen and nitrogen

[0093] The determination of the carbon, hydrogen and nitrogen, in the bis-imine complexes of cobalt, used for the aim of the present invention, and also in the ligands used for the aim of the present invention, was carried out by means of a Carlo Erba automatic analyzer Mod. 1106.

^{13}C-HMR and ^{1}H-HMR spectra

[0094] The ^{13}C-HMR and ^{1}H-HMR spectra were registered by means of a nuclear magnetic resonance spectrometer mod. Bruker Avance 400, using deuterated tetrachloroethylene ($C_2D_2Cl_4$) at 103°C, and hexamethyldisiloxane (HDMS) as internal standard, or using deuterated chloroform ($CDCl_3$), at 25°C, and tetramethylsilane (TMS) as internal standard. Polymeric solutions having concentrations equal to 10% by weight with respect to the total weight of the polymeric solution, were used for the aim.

[0095] The microstructure of the polymers [i.e. content of 1,4-cis units (%)] 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.

I.R. Spectra

[0096] The I.R. spectra (FT-IR) were registered by means of Thermo Nicolet Nexus 670 and Bruker IFS 48 spectrophotometers.

[0097] The I.R. spectra (FT-IR) of the ligands used in the present invention, were obtained by dispersing the ligand to be analyzed in anhydrous potassium bromide (KBr) (disks of KBr), or in a suspension of nujol.

[0098] The I.R. spectra (FT-IR) of the bis-imine complexes of cobalt used in the present invention, were obtained by dispersing the bis-imine complex of cobalt to be analyzed in anhydrous potassium bromide (KBr) (disks of KBr), or in a suspension of nujol.

[0099] The I.R. spectra (FT-IR) of the polymers were obtained from polymeric films on tablets of potassium bromide (KBr), said films being obtained by deposition of a solution of the polymer to be analyzed in hot o-dichlorobenzene. The concentration of the polymeric solutions analyzed was equal to 10% by weight with respect to the total weight of the polymeric solution.

Thermal Analysis (DSC)

[0100] The DSC ("Differential Scanning Calorimetry") thermal analysis, for determining the melting point (T_m) and **the** crystallization temperature (T_c) of the polymers obtained, was carried out using a Perkin Elmer Pyris differential scanning calorimeter. For this **aim,** 5 mg of polymer were analyzed, with a scanning rate ranging from 1°C/min to 20°C/min, in an inert nitrogen atmosphere.

[0101] The DSC ("Differential Scanning Calorimetry") thermal analysis, for determining the glass transition temperature (T_g) of the polymers obtained was carried out by means of the above calorimeter, using the following thermal program: isotherm for 3 minutes at +70°C; cooling from +70°C to -90°C at a rate of 10°C/min; isotherm for 3 min at -90°C; heating from -90°C to +70°C at a rate of 10°C/min.

Molecular weight determination

[0102] The determination of the molecular weight (MW) of the polymers obtained was carried out by means of GPC ("Gel Permeation Chromatography") operating under the following conditions:

- Agilent 1100 pump;
- I.R. Agilent 1100 detector;
- PL Mixed-A columns;
- solvent/eluent: tetrahydrofuran (THF);
- flow-rate: 1 ml/min;
- temperature: 25°C;
- molecular mass calculation: Universal Calibration method.

[0103] The weight average molecular weight (M_w) and polydispersion Index" (PDI) corresponding to the M_w/M_n ratio (M_n = number average molecular weight), are specified.

Determination of the branching

[0104] The determination of the branching of the polymers obtained was carried out by means of the GPC/MALLS technique obtained by coupling a multi-angle light scattering detector (MALLS) with a traditional SEC/RI elution, operating under the following conditions:

- Agilent 1050 pump;
- I.R. Agilent 1050 detector;
- MALLS Dawn-DSP Wyatt detector - Technology, = 632.8 nm;
- PL GEL Mixed-A (x4) columns;
- solvent/eluent: tetrahydrofuran (THF);
- flow-rate: 1 ml/min;
- temperature: 25°C.

[0105] Operating as described above, the absolute measurement can be contemporaneously carried out of the molecular weight and of the gyration radius of the macromolecules that are separated by the chromatographic system: the quantity of light scattered from a macromolecular species in solution can in fact be used directly for obtaining its molecular weight, whereas the angular variation in the scattering is directly correlated to its average dimensions. The fundamental relation which is used is represented by the following equation (1):

$$\frac{K^{*}c}{R_{\theta}} = \frac{1}{M_{w}P_{\theta}} + 2A_{2}c \quad (1)$$

wherein:

- K* is the optical constant which depends on the wavelength of the light used, on the refraction index (dn/dc) of the polymer, on the solvent used;
- M_w is the weight average molecular weight;
- c is the concentration of the polymeric solution;
- R_θ is the intensity of the light scattered, measured at the angle θ (excess Rayleigh factor);
- P_θ is the function describing the variation of the light scattered with the angle at which it is measured, equal to 1, for an angle θ equal to 0;
- A_2 is the second virial coefficient.

[0106] For very low concentrations (typical of a GPC system), the equation (1) indicated above is reduced to the following equation (2):

$$\frac{K^{*}c}{R_{\theta}} = \frac{1}{M_{w}P_{\theta}} \quad (2)$$

wherein K*, c, R_θ, M_w and P_θ, have the same meanings defined above, and by carrying out the measurement on several angles, the extrapolation at angle null of the function K^*c/R_θ in relation to $sen^2\theta/2$ directly provides the molecular weight of the intercept value and the gyration radius of the slope.

[0107] Furthermore, as this measurement is carried out for every slice of the chromatogram, it is possible to obtain a distribution of both the molecular weight and the gyration radius.

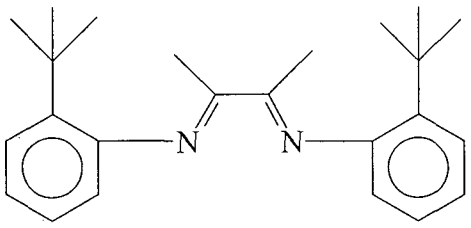
[0108] The macromolecular dimensions in solution are directly correlated to their branching degree: for the same molecular weight, the smaller the dimensions of the macromolecule with respect to the linear correspondent, the higher the branching degree will be.

[0109] The informations relating to the macrostructure of the polymer are qualitatively deduced from the value of the parameter α, which represents the slope of the curve which correlates the gyration radius with the molecular weight: when, under the same analysis conditions, this value decreases with respect to a macrostructure of the linear type, there is the presence of a polymer having a branched-type macrostructure. The typical value of the parameter α for linear polybutadiene having a high content of 1,4-cis units, in tetrahydrofuran (THF), is equal to 0.58-0.60.

EXAMPLE 1

Synthesis of the ligand having formula (L5)

[0110]



(L5).

[0111] A few drops of formic acid were added to a solution of 13.49 g (90 mmoles) of 2-tert-butylaniline in 50 ml of methanol, obtaining a yellow solution. A solution of 2,3-butandione (3.875 g - 45 mmoles) in 30 ml of methanol were added, dropwise, under stirring, to said solution.

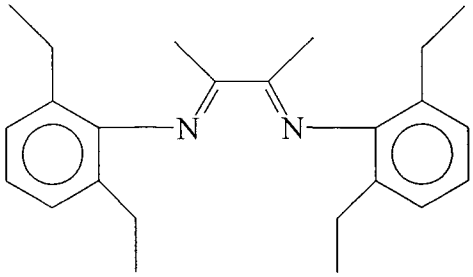
[0112] The whole was left, under stirring, at room temperature, for about 2 hours, until the formation of a yellow precipitate had been observed. The whole was left to rest for 14 hours and was subsequently filtered and dried under vacuum, at room temperature, obtaining 14.1 g of a yellowish solid product (yield = 90%) having formula (L5).

FT-IR (nujol): 1636 cm^{-1} $v_{(C=N)}$.
Molecular weight (MW): 348.53.
Elemental analysis [found (calculated)]: C: 81.95% (82.71%); H: 9.26% (9.25%); N: 8.02% (8.01%).

EXAMPLE 2

Synthesis of the ligand having formula (L7)

[0113]



(L7).

[0114] A few drops of formic acid were added to a solution of 21.81 g (180 mmoles) of 2,6-diethylaniline in 80 ml of methanol, obtaining a yellow solution. A solution of 2,3-butandione (7.75 g - 90 mmoles) in 100 ml of methanol were added, dropwise, under stirring, to said solution.

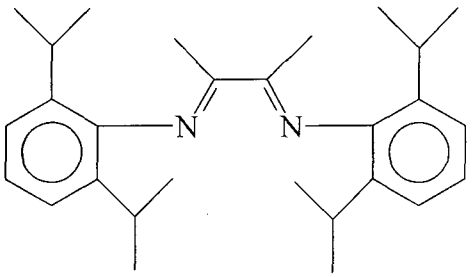
[0115] The whole was left, under stirring, at room temperature, for about 2 hours, until the formation of a yellow precipitate had been observed. The whole was left to rest for 14 hours and was subsequently filtered and dried under vacuum, at room temperature, obtaining 27 g of a yellowish solid product (yield = 86%) having formula (L7).

FT-IR (nujol): 1644 cm^{-1} $v_{(C=N)}$.
Molecular weight (MW): 348.53.
Elemental analysis [found (calculated)]: C: 82.6% (82.71%); H: 9.29% (9.25%); N: 8.04% (8.04%).

EXAMPLE 3

Synthesis of the ligand having formula (L8)

[0116]



(L8).

[0117] A few drops of formic acid were added to a solution of 15.96 g (90 mmoles) di 2,6-di-*iso*-propylaniline in 80 ml of methanol, obtaining a yellow solution. A solution of 2,3-butandione (3.875 g - 45 mmoles) in 80 ml of methanol were added, dropwise, under stirring, to said solution.

[0118] The whole was left, under stirring, at room temperature, for about 2 hours, until the formation of a yellow

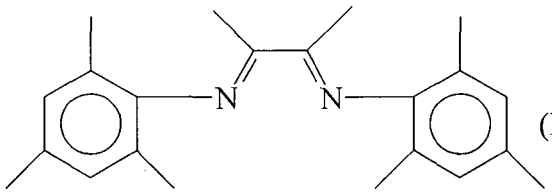
precipitate had been observed. The whole was left to rest for 14 hours and was subsequently filtered and dried under vacuum, at room temperature, obtaining 15.4 g of a yellowish solid product (yield = 84%) having formula (L8).

FT-IR (nujol): 1640 cm^{-1} $\nu_{(C=N)}$.
Molecular weight (MW): 404.64.
Elemental analysis [found (calculated)]: C: 82.86% (83.11%); H: 9.97% (9.96%); N: 6.94% (6.92%).

EXAMPLE 4

Synthesis of the ligand having formula (L9)

[0119]



(L9).

[0120] A few drops of formic acid were added to a solution of 24.34 g (180 mmoles) of 2,4,6-trimethylaniline in 60 ml of methanol, obtaining a yellow solution. A solution of 2,3-butandione (7.75 g - 90 mmoles) in 100 ml of methanol were added, dropwise, under stirring, to this solution.

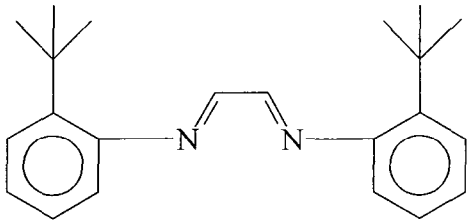
[0121] The whole was left, under stirring, at room temperature, for about 2 hours, until the formation of a yellow precipitate had been observed. The whole was left to rest for 14 hours and was subsequently filtered and dried under vacuum, at room temperature, obtaining 27.25 g of a yellowish solid product (yield = 94.5%) having formula (L9).

FT-IR (nujol): 1637 cm^{-1} $\nu_{(C=N)}$.
Molecular weight (MW): 320.48.
Elemental analysis [found (calculated)]: C: 81.620 (82.45%); H: 8.80% (8.81%); N: 8.66% (8.74%).

EXAMPLE 5

Synthesis of the **ligand** having formula (L12)

[0122]



(L12).

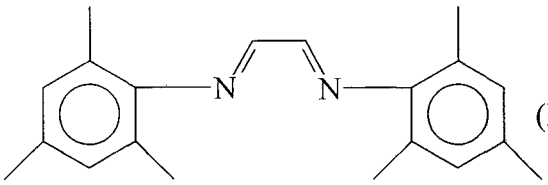
[0123] 14.924 g (100 mmoles) of 2-tert-butylaniline were dissolved in a mixture of methanol and distilled water (50 ml + 100 ml). 7.26 g (50 mmoles) of glyoxal (40% by weight of aqueous solution) were added, under vigorous stirring, to the solution thus obtained, cooled to 0°C with a water/ice bath. The yellow solution obtained was left, under stirring, at room temperature, until the precipitation of a solid had been obtained, which was filtered, washed with methanol, re-crystallized from pentane and dried under vacuum, at room temperature, obtaining 12 g of **a** yellow microcrystalline product (yield = 75%) having formula (L12).

FT-IR (nujol): 1608 $cm^{-1}\nu_{(C=N)}$.
Molecular weight (MW): 320.47.
Elemental analysis [found (calculated)]: C: 82.42% (82.45%); H: 8.80% (8.81%); N: 8.76% (8.74%).

EXAMPLE 6

Synthesis of the ligand having formula (L13)

[0124]



(L13).

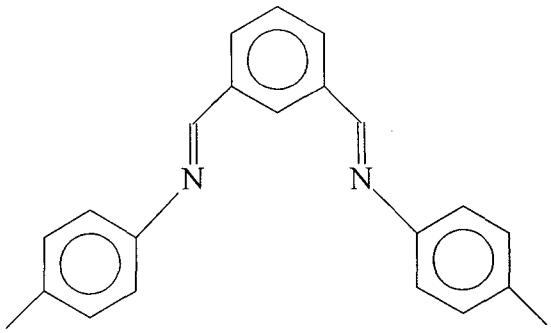
[0125] 13.52 g (100 mmoles) of 2,4,6-trimethylaniline were dissolved in a mixture of methanol and distilled water (50 ml + 100 ml). 7.26 g (50 mmoles) of glyoxal (40% by weight of aqueous solution) were added, under vigorous stirring, to the solution thus obtained, cooled to 0°C with a water/ice bath. The yellow solution obtained was left, under stirring, at room temperature, until the precipitation of a solid had been obtained, which was filtered, washed with methanol, re-crystallized from pentane and dried under vacuum, at room temperature, obtaining 12 g of a yellow microcrystalline product (yield = 82%) having formula (L13).

FT-IR (nujol): 1616 $cm^{-1}\nu_{(C=N)}$.
Molecular weight (MW): 292.42.
Elemental analysis [found (calculated)]: C: 82.0% (82.15%); H: 8.28% (8.27%); N: 9.5% (9.58%).

EXAMPLE 7

Synthesis of the ligand having formula (L20)

[0126]



L20.

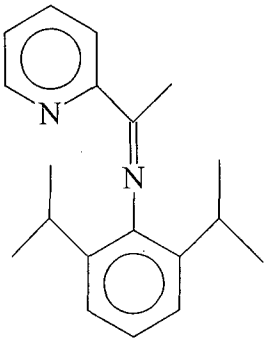
1 g (7.4 mmoles) of benzene-1,3-carboxyaldehyde (diisophthalaldehyde) was dissolved in 20 ml of anhydrous ethanol. 1.75 g of p-toluidine (16.3 mmoles) and a few drops of formic acid were added to the solution thus obtained. The yellow solution obtained was left, under stirring, at room temperature, for 4 hours, obtaining the precipitation of a solid, which was filtered, washed with ethanol and pentane and dried under vacuum, at room temperature, obtaining 2 g of a yellow solid product (yield = 86%) having formula (L20).

FT-IR (nujol): 1625 $cm^{-1}\nu_{(C=N)}$.
Molecular weight (MW): 312.41.
Elemental analysis [found (calculated)]: C:84.4% (84.58%); H: 6.4% (6.45%); N: 9.0% (8.97%).

EXAMPLE 8

Synthesis of the ligand having formula (L18)

[0127]



L18.

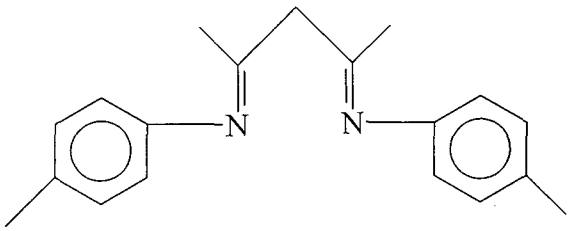
[0128] 15.96 g (90 mmoles) of 2,6-di-isopropylaniline were introduced into a flask together with 50 ml of methanol and 0.25 ml of formic acid. 50 ml of methanol containing 10.9 g (90 mmoles) of acetylpyridine were added dropwise, at room temperature, to the solution thus obtained. The solution obtained was left under stirring, at room temperature, until the precipitation of a solid was obtained, which was filtered, washed with cold methanol and dried under vacuum, at room temperature, obtaining 12.6 g of a white microcrystalline, product (yield = 53%) having formula (L18).

FT-IR (nujol): 1652 $cm^{-1}\nu_{(C=N)}$.
Molecular weight (MW): 280.41.
Elemental analysis [found (calculated)]: C: 81.52% (81.38%); H: 8.57% (8.63%); N: 9.90% (9.99%).

EXAMPLE 9

Synthesis of the ligand having formula (L21)

[0129]



(L21).

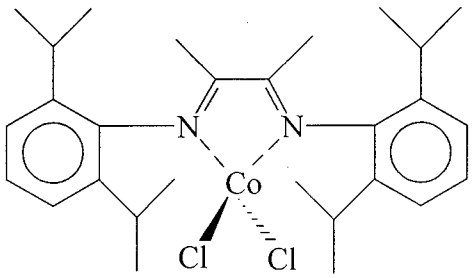
[0130] A mixture of p-toluidine (2.68 g, 25 mmoles), 2,4-pentadione (1.24 g, 12 mmoles) and p-toluenesulfonic acid (2.13 g) in toluene (35 ml), was heated to reflux temperature, for 24 hours, in a Dean-Stark apparatus. At the end, the toluene was decanted and the residue obtained was treated with diethylether (30 ml), water (25 ml) and sodium carbonate decahydrate (Na_2CO_3•$10H_2O$). The mixture obtained was left, under stirring, at room temperature, for 30 minutes and, the ether layer was subsequently separated from the aqueous layer and anhydrified with magnesium sulfate ($MgSO_4$). The solvent was then removed by vacuum evaporation. The residue obtained was dried under vacuum, at 100°C, and subsequently re-crystallized from hexane, obtaining 2.7 g of a microcrystalline product (yield = 78%), having formula (L21).

FT-IR (nujol): 1611 cm^{-1} $\nu_{(C=N)}$.
^{1}H-NMR ($CDCl_3$) : δ = 12.66 (s, 1H), 7.10 (d, 4H, ArH), 6.86 (d, 4H), 4.85 (s, 1H), 2.30 (s, 6H), 1.98 (s, 6H) ppm.
Molecular weight (MW): 278.41.
Elemental analysis [found (calculated)]: C: 81.80% (81.97%); H: 7.90% (7.96%); N: 10.20% (10.60%).

EXAMPLE 10

Synthesis of $CoCl_2$(L8) [sample GL648]

[0131]



(GL648).

[0132] Cobalt dichloride ($CoCl_2$) (0.334 g; 2.577 mmoles) was introduced into a 100 ml reaction flask together with 70 ml of tetrahydrofuran (THF). The whole was kept, under stirring, at room temperature, for a few minutes and the ligand having formula (L8) (1.25 g; 3.08 mmoles; molar ratio L8/Co = 1.2) obtained as described in Example 3, was subsequently added. A green suspension was immediately formed, which was kept, under stirring, at room temperature, for 24 hours. The solvent was then removed under vacuum and the solid dark green residue obtained was dried under vacuum, at room temperature, and subsequently charged onto the porous septum of a hot extractor for solids and was extracted, in continuous, with pentane at boiling point, for 24 hours, in order to remove the non-reacted ligand. The residue remaining on the porous septum was subsequently extracted again, in continuous, with toluene at boiling point, for 24 hours, obtaining a green-coloured solution. The toluene was removed under vacuum and the solid residue remaining on the porous septum was recovered and dried under vacuum, at room temperature, obtaining 1.03 g of a light green solid product corresponding to the complex $CoCl_2$(L8), equal to a conversion of 75% with respect to the cobalt dichloride charged.

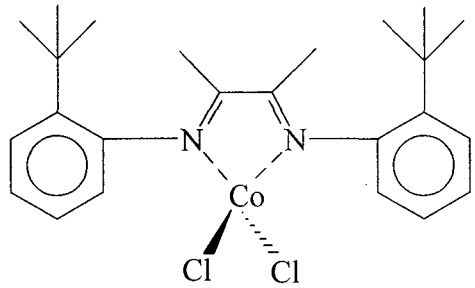
Elemental analysis [found (calculated)]: C: 62.30% (62.92%); H: 7.44% (7.54%); N: 5.36% (5.24%); Cl: 12.80% (13.27%); Co: 10.90% (11.03%).
Molecular weight (MW): 534.47.
FT-IR (nujol): 1639 cm^{-1} $\nu_{(C=N)}$; 1585 $cm^{-1}\nu_{(C=N)}$.

[0133] Figure 1 shows the FT-IR spectrum of the complex $CoCl_2$(L8) obtained (the nujol bands having been subtracted).

EXAMPLE 11

Synthesis of $CoCl_2$(L5) [sample GL649]

[0134]



(GL649).

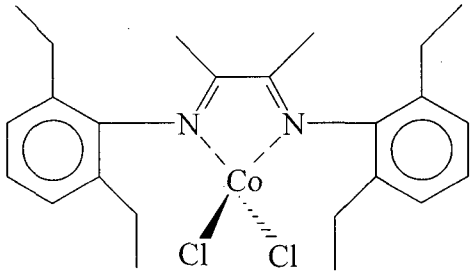
[0135] Cobalt dichloride ($CoCl_2$) (0.369 g; 2.84 mmoles) was introduced into a 100 ml reaction flask together with 70 ml of tetrahydrofuran (THF). The whole was kept, under stirring, at room temperature, for a few minutes and the ligand having formula (L5) (1.14 g; 3.27 mmoles; molar ratio L5/Co = 1.15) obtained as described in Example 1, was subsequently added. The green/light blue suspension obtained was kept under stirring, at room temperature, for 48 hours. The solvent was then removed under vacuum and the solid residue obtained was dried under vacuum, at room temperature, and subsequently charged onto the porous septum of a hot extractor for solids and was extracted, in continuous, with pentane at boiling point, for 24 hours, in order to remove the non-reacted ligand. The residue remaining on the porous septum was subsequently extracted again, in continuous, with dichloromethane at boiling point, for 24 hours, obtaining a green solution. The dichloromethane was removed under vacuum and the solid residue remaining on the porous septum was recovered and dried under vacuum, at room temperature, obtaining 1.107 g of a green solid product corresponding to the complex $CoCl_2$(L5), equal to a conversion of 81.5% with respect to the cobalt dichloride charged.

Elemental analysis [found (calculated)]: C: 59.80% (60.26%); H: 6.60% (6.74%); N: 5.70% (5.86%); Cl: 14.20% (14.82%); Co: 11.90% (12.32%).
Molecular weight (MW): 478.36.
FT-IR (nujol): 1633 cm^{-1} $\nu_{(C=N)}$; 1587 cm^{-1} $\nu_{(C=N)}$.

EXAMPLE 12

Synthesis of $CoCl_2$(L7) [sample GL546]

[0136]



(GL546).

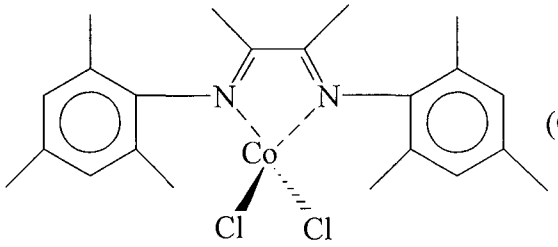
[0137] Cobalt dichloride ($CoCl_2$) (0.439 g; 3.4 mmoles) was introduced into a 100 ml reaction flask together with 70 ml of tetrahydrofuran (THF). The whole was kept under stirring, at room temperature, for a few minutes and the ligand having formula (L7) (1.4 g; 4.08 mmoles; molar ratio L7/Co = 1.2) obtained as described in Example 2, was subsequently added. A dark green suspension was immediately formed, which was kept, under stirring, at room temperature, for 24 hours. The solvent was then removed under vacuum and the dark green solid residue obtained was dried under vacuum, at room temperature, and subsequently charged onto the porous septum of a hot extractor for solids and was extracted, in continuous, with pentane at boiling point, for 24 hours, in order to remove the non-reacted ligand. The residue remaining on the porous septum was subsequently extracted again, in continuous, with dichloromethane at boiling point, for 24 hours, obtaining a green solution. The dichloromethane was removed under vacuum and the solid residue remaining on the porous septum was recovered and dried under vacuum, at room temperature, obtaining 0.921 g of a green solid product corresponding to the complex $CoCl_2$(L7), equal to a conversion of 56.6% with respect to the cobalt dichloride charged.

Elemental analysis [found (calculated)]: C: 60.0% (60.26%); H: 6.30% (6.64%); N: 5.70% (5.86%); Cl: 13.90% (14.82%); Co: 12.10% (12.32%).
Molecular weight (MW): 478.36.
FT-IR (nujol): 1642 cm^{-1} $\nu_{(C=N)}$; 1585 cm^{-1} $\nu_{(C=N)}$.

EXAMPLE 13

Synthesis of $CoCl_2$(L9) [sample GL651]

[0138]



(GL651).

[0139] Cobalt dichloride ($CoCl_2$) (0.444 g; 3.46 mmoles) was introduced into a 100 ml reaction flask together with 70 ml of tetrahydrofuran (THF). The whole was kept, under stirring, at room temperature, for a few minutes and the ligand having formula (L9) (1.33 g; 4.15 mmoles; molar ratio L9/Co = 1.2) obtained as described in Example 4, was subsequently added. A green suspension was immediately formed, which was kept, under stirring, at room temperature, for 24 hours.

The solvent was then removed under vacuum and the solid residue obtained was dried under vacuum, at room temperature, and subsequently charged onto the porous septum of a hot extractor for solids and was extracted, in continuous, with pentane at boiling point, for 24 hours, in order to remove the non-reacted ligand. The residue remaining on the porous septum was subsequently extracted again, in continuous, with dichloromethane at boiling point, for 24 hours, obtaining a green solution. The dichloromethane was removed under vacuum and the solid residue remaining on the porous septum was recovered and dried under vacuum, at room temperature, obtaining 1.10 g of a dark green solid product corresponding to the complex $CoCl_2$(L9), equal to a conversion of 70% with respect to the cobalt dichloride charged.

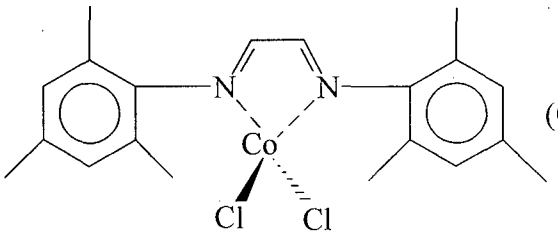
Elemental analysis [found (calculated)]: C: 58.40% (58.68%); H: 6.24% (6.27%); N: 6.45% (6.22%); Cl: 16.30% (15.75%); Co: 12.70% (13.09%).
Molecular weight (MW): 450.31.
FT-IR (nujol): 1635 cm^{-1} $\nu_{(C=N)}$; 1585 cm^{-1} $\nu_{(C=N)}$.

[0140] Figure 2 shows the FT-IR spectrum of the complex $CoCl_2$(L9) obtained (the nujol bands having been subtracted).

EXAMPLE 14

Synthesis of $CoCl_2$(L13) [sample GL769]

[0141]



(GL769).

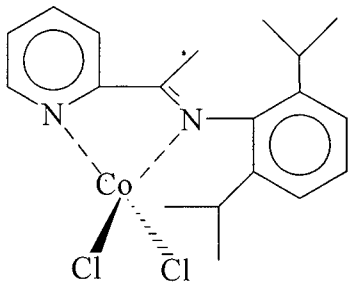
[0142] Cobalt dichloride ($CoCl_2$) (0.284 g; 2.19 mmoles) was introduced into a 100 ml reaction flask together with 50 ml of tetrahydrofuran (THF). The whole was kept under stirring, at room temperature, for a few minutes and the ligand having formula (L13) (0.690 g; 2.36 mmoles; molar ratio L13/Co = 1.1) obtained as described in Example 6, was subsequently added. A dark green suspension was immediately formed, which was kept, under stirring, at room temperature, for 24 hours. The solvent was then removed under vacuum and the light green solid residue obtained was dried under vacuum, at room temperature, and subsequently charged onto the porous septum of a hot extractor for solids and was extracted, in continuous, with pentane at boiling point, for 24 hours, in order to remove the non-reacted ligand. The residue remaining on the porous septum was subsequently extracted again, in continuous, with dichloromethane at boiling point, for 24 hours, obtaining a green solution. The dichloromethane was removed under vacuum and the solid residue remaining on the porous septum was recovered and dried under vacuum, at room temperature, obtaining 0.750 g of a brown/bordeaux solid product corresponding to the complex $CoCl_2$(L13), equal to a conversion of 81% with respect to the cobalt dichloride charged.

Elemental analysis [found (calculated)]: C: 56.20% (56.89%); H: 5.60% (5.73%); N: 6.40% (6.63%); Cl: 16.20% (16.79%); Co: 13.40% (13.96%).
Molecular weight (MW): 422.26.
FT-IR (nujol): 1612 cm^{-1} $\nu_{(C=N)}$.

EXAMPLE 15

Synthesis of $CoCl_2$(L18) [sample GL774]

[0143]



(GL774).

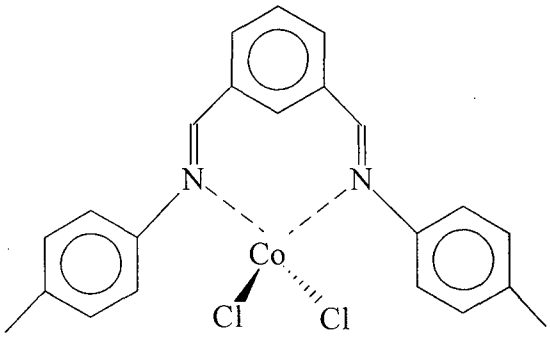
[0144] Cobalt dichloride ($CoCl_2$) (0.366 g; 2.82 mmoles) was introduced into a 100 ml reaction flask together with 50 ml of tetrahydrofuran (THF). The whole was kept under stirring, at room temperature, for a few minutes and the ligand having formula (L18) (0.908 g; 3.24 mmoles; molar ratio L18/Co = 1.15) obtained as described in Example 8, was subsequently added. A purple suspension was immediately formed, which was kept, under stirring, at room temperature, for 24 hours. The solvent was then removed under vacuum and the solid residue obtained was dried under vacuum, at room temperature, and subsequently charged onto the porous septum of a hot extractor for solids and was extracted, in continuous, with pentane at boiling point, for 24 hours, in order to remove the non-reacted **ligand.** The residue remaining on the porous septum was subsequently extracted again, in continuous, with dichloromethane at boiling point, for 24 hours, obtaining a green solution. The dichloromethane was removed under vacuum and the solid residue remaining on the porous septum was recovered and dried under vacuum, at room temperature, obtaining 0.824 g of a purple solid product corresponding to the complex $CoCl_2$(L18), equal to a conversion of 71% with respect to the cobalt dichloride charged.

Elemental analysis [found (calculated)]: C: 54.90% (55.63%); H: 5.80% (5.90%); N: 6.70% (6.83%); Cl: 16.90% (17.28%); Co: 13.90% (14.37%).
Molecular weight (MW): 410.25.
FT-IR (nujol) : 1648 cm^{-1} $\nu_{(C=N)}$.

EXAMPLE 16

Synthesis of $CoCl_2$(L20) [sample GL907]

[0145]



(GL907).

[0146] Cobalt dichloride ($CoCl_2$) (0.160 g; 1.23 mmoles) was introduced into a 100 ml reaction flask together with 50 ml of tetrahydrofuran (THF). The whole was kept under stirring, at room temperature, for a few minutes and the ligand having formula (L20) (0.416 g; 1.33 mmoles; molar ratio L20/Co = 1.1) obtained as described in Example 7, was subsequently added. A green/light blue suspension was immediately formed, which was kept, under stirring, at room temperature, for 24 hours. The solvent was then removed under vacuum and the solid residue obtained was dried under vacuum, at room temperature, and subsequently charged onto the porous septum of a hot extractor for solids and was extracted, in continuous, with pentane at boiling point, for 24 hours, in order to remove the non-reacted ligand. The residue remaining on the porous septum was subsequently extracted again, in continuous, with dichloromethane at boiling point, for 24 hours, obtaining a green solution. The dichloromethane was removed under vacuum and the solid residue remaining on the porous septum was recovered and dried under vacuum, at room temperature, obtaining 0.435 g of a green solid product corresponding to the complex $CoCl_2$(L20), equal to a conversion of 80% with respect to the

cobalt dichloride charged.

Elemental analysis [found (calculated)]: C: 59.50% (59.75%); H: 4.40% (4.56%); N: 6.10% (6.33%); Cl: 15.60% (16.03%); Co: 13.0% (13.33%).
Molecular weight (MW): 442.25.
FT-IR (nujol): 1622 cm^{-1} $\nu_{(C=N)}$.

EXAMPLE 17 (GL659)

[0147] 2 ml of 1, 3-butadiene equal to about 1.4 g were condensed at a low temperature (-20°C) in a 25 ml test-tube. 7.05 ml of toluene were then added, and the temperature of the solution thus obtained was brought to 20°C. Methylaluminoxane (MAO) in a toluene solution (6.3 ml; 1×10^{-2} moles, equal to about 0.58 g) was then added, and subsequently the complex $CoCl_2$(L8) [sample GL648] (2.65 ml of a toluene solution at a concentration equal to 2 mg/ml; 1×10^{-5} moles, equal to about 5.3 mg) obtained as described in Example 10. The whole was kept, under magnetic stirring, at 20°C, for 30 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 Irganox® 1076 antioxidant (Ciba), obtaining 0.985 g of polybutadiene having a content of 1,4-cis units equal to 98%: further characteristics of the process and of the polybutadiene obtained are shown in Table 1.
[0148] Figure 4 shows the FT-IR spectrum of the polybutadiene obtained.
[0149] Figure 9 shows the DSC diagrams of the polybutadiene obtained.

EXAMPLE 18 (GL661)

[0150] 2 ml of 1, 3-butadiene equal to about 1.4 g were condensed at a low temperature (-20°C) in a 25 ml test-tube. 7.3 ml of toluene were then added, and the temperature of the solution thus obtained was brought to 20°C. Methylaluminoxane (MAO) in a toluene solution (6.3 ml; 1×10^{-2} moles, equal to about 0.58 g) was then added, and subsequently the complex $CoCl_2$(L5) [sample GL649] (2.4 ml of a toluene solution at a concentration equal to 2 mg/ml; 1×10^{-5} moles, equal to about 4.8 mg) obtained as described in Example 11. The whole was kept, under magnetic stirring, at 20°C, for 30 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 Irganox® 1076 antioxidant (Ciba), obtaining 1.4 g of polybutadiene having a content of 1,4-cis units equal to 98.1%: further characteristics of the process and of **the** polybutadiene obtained are shown in Table 1.
[0151] Figure 4 shows the FT-IR spectrum of the polybutadiene obtained.

EXAMPLE 19 (GL640)

[0152] 2 ml of 1,3-butadiene equal to about 1.4 g were condensed at a low temperature (-20°C) in a 25 ml test-tube. 7.3 ml of toluene were then added, and the temperature of the solution thus obtained was brought to 20°C. Methylaluminoxane (MAO) in a toluene solution (6.3 ml; 1×10^{-2} moles, equal to about 0.58 g) was then added, and subsequently the complex $CoCl_2$(L7) [sample GL546] (2.4 ml of a toluene solution at a concentration equal to 2 mg/ml; 1×10^{-5} moles, equal to about 4.8 mg) obtained as described in Example 12. The whole was kept, under magnetic stirring, at 20°C, for 90 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 Irganox® 1076 antioxidant (Ciba), obtaining 0.56 g of polybutadiene having a content of 1,4-cis units equal to 98.1%: further characteristics of the process and **of the** polybutadiene obtained are shown in Table 1.
[0153] Figure 3 shows the FT-IR spectrum of the polybutadiene obtained.

EXAMPLE 20 (GL662)

[0154] 2 ml of 1, 3-butadiene equal to about 1.4 g were condensed at a low temperature (-20°C) in a 25 ml test-tube. 7.45 ml of toluene were then added, and the temperature of the solution thus obtained was brought to 20°C. Methylaluminoxane (MAO) in a toluene solution (6.3 ml; 1×10^{-2} moles, equal to about 0.58 g) was then added, and subsequently the complex $CoCl_2$(L9) [sample GL651] (2.25 ml of a toluene solution at a concentration equal to 2 mg/ml; 1×10^{-5} moles, equal to about 4.5 mg) obtained as described in Example 13. The whole was kept, under magnetic stirring, at 20°C, for 30 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 Irganox® 1076 antioxidant (Ciba), obtaining 0.77 g of polybutadiene having a content of 1,4-cis units equal to 98.2%: further characteristics of the process and **of the** polybutadiene obtained are shown in Table 1.

[0155] Figure 3 shows the FT-IR spectrum of the polybutadiene obtained.

EXAMPLE 21 (GL779)

[0156] 2 ml of 1, 3-butadiene equal to about 1.4 g were condensed at a low temperature (-20°C) in a 25 ml test-tube. 7.6 ml of toluene were then added, and the temperature of the solution thus obtained was brought to 20°C. Methylaluminoxane (MAO) in a toluene solution (6.3 ml; 1×10^{-2} moles, equal to about 0.58 g) was then added, and subsequently the complex $CoCl_2$(L13) [sample GL769] (2.1 ml of a toluene solution at a concentration equal to 2 mg/ml; 1×10^{-5} moles, equal to about 4.2 mg) obtained as described in Example 14. The whole was kept, under magnetic stirring, at 20°C, for 140 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 Irganox® 1076 antioxidant (Ciba), obtaining 0.59 g of polybutadiene having a content of 1,4-cis units equal to 98.2%: further characteristics of the process and of the polybutadiene obtained are shown in Table 1.

[0157] Figure 3 shows the FT-IR spectrum of the polybutadiene obtained

[0158] Figure 5 shows the ^{1}H-NMR and ^{13}C-NMR spectra of the polybutadiene obtained.

[0159] Figure 7 shows the DSC diagrams of the polybutadiene obtained.

EXAMPLE 22 (GL820)

[0160] 2 ml of 1, 3-butadiene equal to about 1.4 g were condensed at a low temperature (-20°C) in a 25 ml test-tube. 7.6 ml of toluene were then added, and the temperature of the solution thus obtained was brought to 20°C. Methylaluminoxane (MAO) in a toluene solution (6.3 ml; 1×10^{-2} moles, equal to about 0.58 g) was then added, and subsequently the complex $CoCl_2$(L13) [sample GL769] (2.1 ml of a toluene solution at a concentration equal to 2 mg/ml; 1×10^{-5} moles, equal to about 4.2 mg) obtained as described in Example 14. The whole was kept, under magnetic stirring, at 50°C, for 240 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 Irganox® 1076 antioxidant (Ciba), obtaining 1.4 g of polybutadiene having a content of 1,4-cis units equal to 98%: further characteristics of the process and of the polybutadiene obtained are shown in Table 1.

[0161] Figure 3 shows the FT-IR spectrum of the polybutadiene obtained.

[0162] Figure 6 shows the ^{1}H-NMR and ^{13}C-NMR spectra of the polybutadiene obtained.

[0163] Figure 8 shows the DSC diagrams of the polybutadiene obtained.

EXAMPLE 23 (GL781)

[0164] 2 ml of 1,3-butadiene equal to about 1.4 g were condensed at a low temperature (-20°C) in a 25 ml test-tube. 7.65 ml of toluene were then added, and the temperature of the solution thus obtained was brought to 20°C. Methylaluminoxane (MAO) in a toluene solution (6.3 ml; 1×10^{-2} moles, equal to about 0.58 g) was then added, and subsequently the complex $CoCl_2$(L18) [sample GL774] (2.05 ml of a toluene solution at a concentration equal to 2 mg/ml; 1×10^{-5} moles, equal to about 4.1 mg) obtained as described in Example 15. The whole was kept, under magnetic stirring, at 20°C, for 360 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 Irganox® 1076 antioxidant (Ciba), obtaining 0.91 g of polybutadiene having a content of 1,4-cis units equal to 98.1%: further characteristics of the process and of the polybutadiene obtained are shown in Table 1.

[0165] Figure 4 shows the FT-IR spectrum of the polybutadiene obtained.

EXAMPLE 24 (GL980)

[0166] 2 ml of 1, 3-butadiene equal to about 1.4 g were condensed at a low temperature (-20°C) in a 25 ml test-tube. 7.5 ml of toluene were then added, and the temperature of the solution thus obtained was brought to 20°C. Methylaluminoxane (MAO) in a toluene solution (6.3 ml; 1×10^{-2} moles, equal to about 0.58 g) was then added, and subsequently the complex $CoCl_2$(L20) [sample GL907] (2.2 ml of a toluene solution at a concentration equal to 2 mg/ml; 1×10^{-5} moles, equal to about 4.4 mg) obtained as described in Example 16. The whole was kept, under magnetic stirring, at 20°C, for 120 minutes. The polymerization was then quenched by the addition of 2 ml of methanol containing a few drops of hydrochloric acid. The polymer obtained was then coagulated by the addition of 40 ml of a methanol solution containing 4% of Irganox® 1076 antioxidant (Ciba), obtaining 0.83 g of polybutadiene having a content of 1,4-cis units equal to 98%: further characteristics of the process and **of the** polybutadiene obtained are shown in Table 1.

[0167] Figure 4 shows the FT-IR spectrum of the polybutadiene obtained.

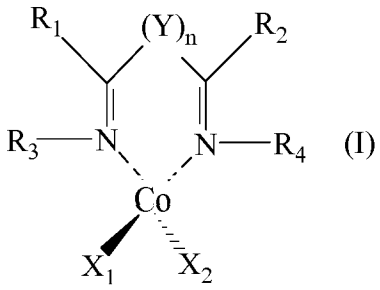
Table 1: Polymerization of 1,3-butadiene with catalytic systems comprising complexes of cobalt.

Example	Times (min)	Conversion (%)	N[(a)] (h^{-1})	T_m[(b)] (°C)	T_c[(c)] (°C)	M_w ($gxmol^{-1}$)	M_w/M_n	α[(e)]
17	30	70	3648	-7.7	-26.5	410000	2.0	0.60
18	30	100	5185	-7.9	-26.3	287000	2.1	0.60
19	90	40	691	-9.0	-26.4	350000	1.9	0.59
20	30	55	2852	-9.3	-31.1	650000	2.5	0.61
21	140	42	468	-12.1	-34.9	630000	2.6	0.60
22	240	100	648	-13.7	-40.9	296000	2.4	0.59
23	360	65	281	-13.2	-32.2	272000	1.8	0.55
24	120	59	769	-12.8	-36.2	228000	2.0	0.59

([a]): number of moles of 1,3-butadiene polymerized, per hour, per mole of cobalt;
([b]): melting point;
([c]): crystallization temperature;
([e]): linearity index of polybutadiene.

Claims

1. A process for the preparation of (co)polymers of conjugated dienes which comprises polymerizing at least one conjugated diene in the presence of a catalytic system comprising at least one bis-imine complex of cobalt having general formula (I):



(I)

wherein:

n is 0 or 1;

- Y represents a group -CR'R" wherein R' and R", equal to or different from each other, represent a hydrogen atom, or a linear or branched C_1-C_{20} alkyl group; or a divalent aromatic carbocyclic group optionally substituted;
- R_1 and R_2, equal to or different from each other, represent a hydrogen atom; or they are selected from a linear or branched C_1-C_{20} alkyl groups optionally halogenated, cycloalkyl groups optionally substituted; or R_1 and R_2 can be **optionally** bound to each other to form, together with the other atoms to which they are bound, a cycle containing from 4 to 6 carbon atoms, saturated, unsaturated, or aromatic, optionally substituted with linear or branched C_1-C_{20} alkyl groups, said cycle optionally containing heteroatoms such as oxygen, sulfur, nitrogen, silicon, phosphorous, selenium;
- R_3 and R_4, equal to or different from each other, represent a hydrogen atom; or they are selected from a linear or branched C_1-C_{20} alkyl groups optionally halogenated, cycloalkyl groups optionally substituted; aryl groups optionally substituted;
- or R_2 and R_4 can be **optionally** bound to each other to form, together with the other atoms to which they are bound, a cycle containing from 3 to 6 carbon atoms, saturated, unsaturated, or aromatic, optionally

substituted with linear or branched C_1-C_{20} alkyl groups, said cycle optionally containing other heteroatoms such as oxygen, sulfur, nitrogen, silicon, phosphorous, selenium;
- or R_1 and R_3 can be **optionally** bound to each other to form, together with the other atoms to which they are bound, a cycle containing from 3 to 6 carbon atoms, saturated, unsaturated, or aromatic, optionally substituted with linear or branched C_1-C_{20} alkyl groups, said cycle optionally containing other heteroatoms such as oxygen, sulfur, nitrogen, silicon, phosphorous, selenium;
- X_1 and X_2, equal to or different from each other, represent a halogen atom such as chlorine, bromine, iodine; or they are selected from linear or branched C_1-C_{20} alkyl groups, -$OCOR_5$ groups or -OR_5 groups wherein R_5 is selected from linear or branched C_1-C_{20} alkyl groups.

2. The process for the preparation of (co)polymers of conjugated dienes according to claim 1, wherein said catalytic system comprises at least one co-catalyst (b) selected from organic compounds of an element M' different from carbon, said element M' being selected from elements belonging to groups 2, 12, 13 or 14 of the Periodic Table of Elements, such as: boron, aluminium, zinc, magnesium, gallium, tin.

3. The process for the preparation of (co)polymers of conjugated dienes according to claim 2, wherein said co-catalyst (b) is selected from (b_1) aluminium alkyls having general formula (II):

$$Al(X')_n(R_6)_{3-n} \qquad (II)$$

wherein X' represents a halogen atom such as chlorine, bromine, iodine, fluorine; R_6 is selected from linear or branched C_1-C_{20} alkyl groups, cycloalkyl groups, aryl groups, said groups being optionally substituted with one or more silicon or germanium atoms; and n is an integer ranging from 0 to 2.

4. The process for the preparation of (co)polymers of conjugated dienes according to claim 2, wherein said co-catalyst (b) is selected from (b_2) organo-oxygenated compounds of an element M' different from carbon belonging to groups 13 or 14 of the Periodic Table of Elements.

5. The process for the preparation of (co)polymers of conjugated dienes according to claim 2, wherein said co-catalyst (b) is selected from (b_3) organometallic compounds or mixtures of organometallic compounds of an element M' different from carbon capable of reacting with the bis-imine complex of cobalt having general formula (I), extracting therefrom a substituent X_1 or X_2 σ-bound, 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.

6. The process for the preparation of (co)polymers of conjugated dienes according to any of the previous claims, wherein said conjugated diene is selected from: 1,3-butadiene, 2-methyl-1,3-butadiene (isoprene), 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, 1,3-hexadiene, cyclo-1,3-hexadiene, or mixtures thereof.

7. The process for the preparation of (co)polymers of conjugated dienes according to any of the previous claims, wherein in said bis-imine complex of cobalt having general formula (I):

n is 0;

- R_1 and R_2; equal to or different from each other, are a hydrogen atom, or they are selected from linear or branched C_1-C_{20} alkyl groups, preferably **are** a methyl group;
- R_3 and R_4, equal to or different from each other, are selected from phenyl groups optionally substituted with linear or branched C_1-C_{20} alkyl groups, preferably substituted with one or more methyl, ethyl, iso-propyl, tert-butyl groups;
- X_1 and X_2, the same as each other, are a halogen atom such as chlorine, bromine, iodine, preferably chlorine.

8. The process for the preparation of (co)polymers of conjugated dienes according to any of the claims from 1 to 6, wherein in said bis-imine complex of cobalt having general formula (I):

n is 1;

- Y is a group CR'R" wherein R' and R", equal to or different from each other, are a hydrogen atom; or they

are selected from linear or branched C_1-C_{20} alkyl groups, preferably **are** a propyl group
- R_1 and R_2, equal to or different from each other, are a hydrogen atom; or they are selected from linear or branched C_1-C_{20} alkyl groups, preferably **are** a methyl group;
- R_3 and R_4, equal to or different from each other, are selected from phenyl groups optionally substituted with linear or branched C_1-C_{20} alkyl groups, preferably substituted with one or more methyl, ethyl, iso-propyl, tert-butyl groups;
- X_1 and X_2, the same as each other, are a halogen atom such as chlorine, bromine, iodine, preferably chlorine.

9. The process for the preparation of (co)polymers of conjugated dienes according to any of the claims from 1 to 6, wherein in said bis-imine complex of cobalt having general formula (I):

n is 0;

- R_1 and R_3, are bound to each other and, together with the other atoms to which they are bound, form a pyridine;
- R_2 is a hydrogen atom, or it is selected from linear or branched C_1-C_{20} alkyl groups, preferably **is** a methyl group;
- R_4 is selected from phenyl groups optionally substituted with linear or branched C_1-C_{20} alkyl groups, preferably a phenyl group substituted with one or more methyl, ethyl, iso-propyl, tert-butyl groups;
- X_1 and X_2, the same as each other, are a halogen atom such as chlorine, bromine, iodine, preferably chlorine.

10. The process for the preparation of (co)polymers of conjugated dienes according to any of the claims from 1 to 6, wherein in said bis-imine complex of cobalt having general formula (I):

n is 1;

- Y is a divalent aromatic group optionally substituted, preferably a meta-phenylene group
- R_1 and R_2, equal to or different from each other, are a hydrogen atom, or they are selected from linear or branched C_1-C_{20} alkyl groups, preferably are a methyl group;
- R_3 and R_4, equal to or different from each other, are selected from phenyl groups optionally substituted with linear or branched C_1-C_{20} alkyl groups, preferably a phenyl group substituted with a methyl group;
- X_1 and X_2, the same as each other, are a halogen atom such as chlorine, bromine, iodine, preferably chlorine.

11. The process for the preparation of (co)polymers of conjugated dienes according to claim 3, wherein said aluminium alkyls (b_1) having general formula (II) are diethyl-aluminium chloride, mono-ethyl-aluminium dichloride, ethylaluminiumsesquichloride (EASC).

12. The process for the preparation of (co)polymers of conjugated dienes according to claim 4, wherein said organo-oxygenated compounds (b_2) are selected from aluminoxanes having general formula (III):

$$(R_7)_2\text{-Al-O-[-Al}(R_8)\text{-O-]}_p\text{-Al-}(R_9)_2 \qquad \text{(III)}$$

wherein R_7, R_8 and R_9, equal to or different from each other, represent a hydrogen atom, a halogen atom such as chlorine, bromine, iodine, fluorine; or they are selected from linear or branched C_1-C_{20} alkyl groups, cycloalkyl groups, aryl groups, said groups being optionally substituted with one or more silicon or germanium atoms; and p is an integer ranging from 0 to 1,000.

13. The process for the preparation of (co)polymers of conjugated dienes according to claim 12, wherein said organo-oxygenated compound (b_2) is methylaluminoxane (MAO).

14. The process for the preparation of (co)polymers of conjugated dienes according to claim 5, wherein said compounds or mixtures of compounds (b_3) are selected from organic compounds of aluminium and especially boron, such as those represented by the following general formulae:

$$[(R_C)_W H_{4-W}]^{\bullet}[B(R_D)_4]^{-};\ B(R_D)_3;\ Al(R_D)_3;\ B(R_D)_3P;$$

$[Ph_3C]^+\bullet[B(R_D)_4]^-$; $[(R_C)_3PH]^+\bullet[B(R_D)_4]^-$;

$[Li]^+\bullet[B(R_D)_4]^-$; $[Li]^+\bullet[Al(R_D)_4]$

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

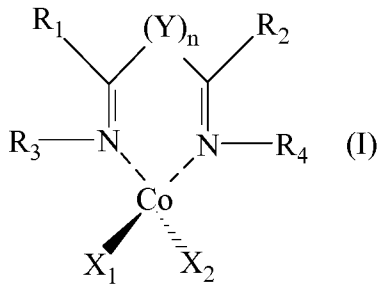
15. The process for the preparation of (co)polymers of conjugated dienes according to any of the previous claims, wherein said process is carried out in the presence of an inert organic solvent selected from: saturated aliphatic hydrocarbons such as butane, pentane, hexane, heptane, or mixtures thereof;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

16. The process for the preparation of (co)polymers of conjugated dienes according to claim 15, wherein the concentration of the conjugated diene to be (co)polymerized in said inert organic solvent ranges from 5% by weight to 50% by weight with respect to the total weight of the mixture of conjugated diene and inert organic solvent.

17. The process for the preparation of (co)polymers of conjugated dienes according to any of the previous claims, wherein said process is carried out at a temperature ranging from -70°C to +100°C.

Patentansprüche

1. Ein Verfahren für die Herstellung von (Co)polymeren konjugierter Diene, welches das Polymerisieren mindestens eines konjugierten Diens in Gegenwart eines katalytischen Systems, das mindestens einen Bisimin-Komplex von Kobalt mit der allgemeinen Formel (I) beinhaltet, beinhaltet:



(I)

wobei:

n 0 oder 1 ist;

- Y eine Gruppe -CR'R" darstellt, wobei R' und R", einander gleich oder voneinander verschieden, ein Wasserstoffatom oder eine lineare oder verzweigte C_1-C_{20}-Alkylgruppe darstellen; oder eine optional substituierte bivalente aromatische carbocyclische Gruppe;
- R_1 und R_2, einander gleich oder voneinander verschieden, ein Wasserstoffatom darstellen; oder sie ausgewählt sind aus einer linearen oder verzweigten, optional halogenierten C_1-C_{20}-Alkylgruppen, optional substituierten Cycloalkylgruppen; oder R_1 und R_2 optional aneinander gebunden sein können, um zusammen mit den anderen Atomen, an die sie gebunden sind, einen Ring zu bilden, der 4 bis 6 Kohlenstoffatome enthält, gesättigt, ungesättigt oder aromatisch, optional substituiert mit linearen oder verzweigten C_1-C_{20}-Alkylgruppen, wobei der Ring optional Heteroatome wie etwa Sauerstoff, Schwefel, Stickstoff, Silicium, Phosphor, Selen enthält;
- R_3 und R_4, einander gleich oder voneinander verschieden, ein Wasserstoffatom darstellen; oder sie ausgewählt sind aus einer linearen oder verzweigten, optional halogenierten C_1-C_{20}-Alkylgruppen, optional

substituierten Cycloalkylgruppen; optional substituierten Arylgruppen;
- oder R_2 und R_4 optional aneinander gebunden sein können, um zusammen mit den anderen Atomen, an die sie gebunden sind, einen Ring zu bilden, der 3 bis 6 Kohlenstoffatome enthält, gesättigt, ungesättigt oder aromatisch, optional substituiert mit linearen oder verzweigten C_1-C_{20}-Alkylgruppen, wobei der Ring optional andere Heteroatome wie etwa Sauerstoff, Schwefel, Stickstoff, Silicium, Phosphor, Selen enthält;
- oder R_1 und R_3 optional aneinander gebunden sein können, um zusammen mit den anderen Atomen, an die sie gebunden sind, einen Ring zu bilden, der 3 bis 6 Kohlenstoffatome enthält, gesättigt, ungesättigt oder aromatisch, optional substituiert mit linearen oder verzweigten C_1-C_{20}-Alkylgruppen, wobei der Ring optional andere Heteroatome wie etwa Sauerstoff, Schwefel, Stickstoff, Silicium, Phosphor, Selen enthält;
- X_1 und X_2, einander gleich oder voneinander verschieden, ein Halogenatom wie etwa Chlor, Brom, Iod darstellen; oder sie ausgewählt sind aus linearen oder verzweigten C_1-C_{20}-Alkylgruppen, -$OCOR_5$-Gruppen oder-OR_5-Gruppen, wobei R_5 aus linearen oder verzweigten C_1-C_{20}-Alkylgruppen ausgewählt ist.

2. Verfahren für die Herstellung von (Co)polymeren konjugierter Diene gemäß Anspruch 1, wobei das katalytische System mindestens einen Cokatalysator (b) beinhaltet, der aus organischen Verbindungen eines Elements M', das sich von Kohlenstoff unterscheidet, ausgewählt ist, wobei das Element M' aus Elementen ausgewählt ist, die zu den Gruppen 2, 12, 13 oder 14 des Periodensystems der Elemente gehören, wie etwa: Bor, Aluminium, Zink, Magnesium, Gallium, Zinn.

3. Verfahren für die Herstellung von (Co)polymeren konjugierter Diene gemäß Anspruch 2, wobei der Cokatalysator (b) ausgewählt ist aus (b_1) Aluminiumalkylen mit der allgemeinen Formel (II):

$$Al(X')_n(R_6)_{3-n} \qquad (II)$$

wobei X' ein Halogenatom wie etwa Chlor, Brom, Iod, Fluor darstellt; R_6 ausgewählt ist aus linearen oder verzweigten C_1-C_{20}-Alkylgruppen, Cycloalkylgruppen, Arylgruppen, wobei die Gruppen optional mit einem oder mehreren Silicium- oder Germaniumatomen substituiert sind; und n eine ganze Zahl im Bereich von 0 bis 2 ist.

4. Verfahren für die Herstellung von (Co)polymeren konjugierter Diene gemäß Anspruch 2, wobei der Cokatalysator (b) ausgewählt ist aus (b_2) organo-oxygenierten Verbindungen eines Elements M', das sich von Kohlenstoff unterscheidet, das zu den Gruppen 13 oder 14 des Periodensystems der Elemente gehört.

5. Verfahren für die Herstellung von (Co)polymeren konjugierter Diene gemäß Anspruch 2, wobei der Cokatalysator (b) ausgewählt ist aus (b_3) organometallischen Verbindungen oder Mischungen organometallischer Verbindungen eines Elements M', das sich von Kohlenstoff unterscheidet, in der Lage, mit dem Bisimin-Komplex von Kobalt mit der allgemeinen Formel (I) zu reagieren, wobei ein σ-gebundener Substituent X_1 oder X_2 extrahiert wird, um einerseits mindestens eine neutrale Verbindung und andererseits eine ionische Verbindung, bestehend aus einem Kation, welches das durch den Liganden koordinierte Metall (Co) enthält, und einem nicht koordinierenden organischen Anion, welches das Metall M' enthält, wobei die negative Ladung auf einer polyzentrischen Struktur delokalisiert ist, zu bilden.

6. Verfahren für die Herstellung von (Co)polymeren konjugierter Diene gemäß einem der vorhergehenden Ansprüche, wobei das konjugierte Dien aus Folgendem ausgewählt ist: 1,3-Butadien, 2-Methyl-1,3-butadien (Isopren), 2,3-Dimethyl-1,3-butadien, 1,3-Pentadien, 1,3-Hexadien, Cyclo-1,3-hexadien oder Mischungen davon.

7. Verfahren für die Herstellung von (Co)polymeren konjugierter Diene gemäß einem der vorhergehenden Ansprüche, wobei bei dem Bisimin-Komplex von Kobalt mit der allgemeinen Formel (I):

n 0 ist;

- R_1 und R_2, einander gleich oder voneinander verschieden, ein Wasserstoffatom sind oder sie ausgewählt sind aus linearen oder verzweigten C_1-C_{20}-Alkylgruppen, vorzugsweise eine Methylgruppe sind;
- R_3 und R_4, einander gleich oder voneinander verschieden, ausgewählt sind aus Phenylgruppen, optional substituiert mit linearen oder verzweigten C_1-C_{20}-Alkylgruppen, vorzugsweise substituiert mit einer oder mehreren Methyl-, Ethyl-, *iso*-Propyl-, *tert*-Butyl-Gruppen;
- X_1 und X_2, einander gleich, ein Halogenatom wie etwa Chlor, Brom, Iod, vorzugsweise Chlor, sind.

8. Verfahren für die Herstellung von (Co)polymeren konjugierter Diene gemäß einem der Ansprüche 1 bis 6, wobei

bei dem Bisimin-Komplex von Kobalt mit der allgemeinen Formel (I):

n 1 ist;

- Y eine Gruppe CR'R" ist, wobei R' und R", einander gleich oder voneinander verschieden, ein Wasserstoffatom sind; oder sie ausgewählt sind aus linearen oder verzweigten C_1-C_{20}-Alkylgruppen, vorzugsweise eine Propylgruppe sind;
- R_1 und R_2, einander gleich oder voneinander verschieden, ein Wasserstoffatom sind; oder sie ausgewählt sind aus linearen oder verzweigten C_1-C_{20}-Alkylgruppen, vorzugsweise eine Methylgruppe sind;
- R_3 und R_4, einander gleich oder voneinander verschieden, ausgewählt sind aus Phenylgruppen, optional substituiert mit linearen oder verzweigten C_1-C_{20}-Alkylgruppen, vorzugsweise substituiert mit einer oder mehreren Methyl-, Ethyl-, *iso*-Propyl-, *tert*-Butyl-Gruppen;
- X_1 und X_2, einander gleich, ein Halogenatom wie etwa Chlor, Brom, Iod, vorzugsweise Chlor, sind.

9. Verfahren für die Herstellung von (Co)polymeren konjugierter Diene gemäß einem der Ansprüche 1 bis 6, wobei bei dem Bisimin-Komplex von Kobalt mit der allgemeinen Formel (I):

n 0 ist;

- R_1 und R_3 aneinander gebunden sind und zusammen mit den anderen Atomen, an die sie gebunden sind, ein Pyridin bilden;
- R_2 ein Wasserstoffatom ist oder er ausgewählt ist aus linearen oder verzweigten C_1-C_{20}-Alkylgruppen, vorzugsweise eine Methylgruppe ist;
- R_4 ausgewählt ist aus Phenylgruppen, optional substituiert mit linearen oder verzweigten C_1-C_{20}-Alkylgruppen, vorzugsweise einer mit einer oder mehreren Methyl-, Ethyl-, *iso*-Propyl-, *tert*-Butyl-Gruppen substituierten Phenylgruppe;
- X_1 und X_2, einander gleich, ein Halogenatom wie etwa Chlor, Brom, Iod, vorzugsweise Chlor, sind.

10. Verfahren für die Herstellung von (Co)polymeren konjugierter Diene gemäß einem der Ansprüche 1 bis 6, wobei bei dem Bisimin-Komplex von Kobalt mit der allgemeinen Formel (I):

n 1 ist;

- Y eine bivalente aromatische Gruppe, optional substituiert, vorzugsweise eine meta-Phenylen-Gruppe ist;
- R_1 und R_2, einander gleich oder voneinander verschieden, ein Wasserstoffatom sind oder sie ausgewählt sind aus linearen oder verzweigten C_1-C_{20}-Alkylgruppen, vorzugsweise eine Methylgruppe sind;
- R_3 und R_4, einander gleich oder voneinander verschieden, ausgewählt sind aus Phenylgruppen, optional substituiert mit linearen oder verzweigten C_1-C_{20}-Alkylgruppen, vorzugsweise einer mit einer Methylgruppe substituierten Phenylgruppe;
- X_1 und X_2, einander gleich, ein Halogenatom wie etwa Chlor, Brom, Iod, vorzugsweise Chlor, sind.

11. Verfahren für die Herstellung von (Co)polymeren konjugierter Diene gemäß Anspruch 3, wobei die Aluminiumalkyle (b_1) mit der allgemeinen Formel (II) Diethylaluminiumchlorid, Monoethylaluminiumdichlorid, Ethylaluminiumsesquichlorid (EASC) sind.

12. Verfahren für die Herstellung von (Co)polymeren konjugierter Diene gemäß Anspruch 4, wobei die organo-oxygenierten Verbindungen (b_2) ausgewählt sind aus Aluminoxanen mit der allgemeinen Formel (III):

$$(R_7)_2\text{-Al-O-[-Al}(R_8)\text{-O-]}_p\text{-Al-}(R_9)_2 \qquad \text{(III)}$$

wobei R_7, R_8 und R_9, einander gleich oder voneinander verschieden, ein Wasserstoffatom, ein Halogenatom wie etwa Chlor, Brom, Iod, Fluor darstellen; oder sie ausgewählt sind aus linearen oder verzweigten C_1-C_{20}-Alkylgruppen, Cycloalkylgruppen, Arylgruppen, wobei die Gruppen optional mit einem oder mehreren Silicium- oder Germaniumatomen substituiert sind; und p eine ganze Zahl im Bereich von 0 bis 1000 ist.

13. Verfahren für die Herstellung von (Co)polymeren konjugierter Diene gemäß Anspruch 12, wobei die organo-oxygenierte Verbindung (b_2) Methylaluminoxan (MAO) ist.

14. Verfahren für die Herstellung von (Co)polymeren konjugierter Diene gemäß Anspruch 5, wobei die Verbindungen oder Mischungen von Verbindungen (b_3) ausgewählt sind aus organischen Verbindungen von Aluminium und insbesondere Bor, wie etwa den durch die folgenden allgemeinen Formeln dargestellten:

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

$[Ph_3C]^+\bullet[B(R_D)_4]^-$; $[(R_C)_3PH]^+\bullet[B(R_D)_4]^-$;

$[Li]^+\bullet[B(R_D)_4]^-$; $[Li]^+\bullet[Al(R_D)_4]^-$

wobei w eine ganze Zahl im Bereich von 0 bis 3 ist, jede Gruppe R_C unabhängig eine Alkylgruppe oder eine Arylgruppe mit 1 bis 10 Kohlenstoffatomen darstellt und jede Gruppe R_D unabhängig eine teilweise oder gänzlich, vorzugsweise gänzlich, fluorierte Arylgruppe mit 6 bis 20 Kohlenstoffatomen darstellt, P einen optional substituierten Pyrrolrest darstellt.

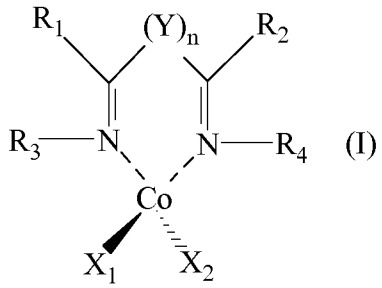
15. Verfahren für die Herstellung von (Co)polymeren konjugierter Diene gemäß einem der vorhergehenden Ansprüche, wobei das Verfahren in Gegenwart eines inerten organischen Lösungsmittels ausgeführt wird, welches aus Folgendem ausgewählt ist: gesättigten aliphatischen Kohlenwasserstoffen wie etwa Butan, Pentan, Hexan, Heptan oder Mischungen davon; gesättigten cycloaliphatischen Kohlenwasserstoffen wie etwa Cyclopentan, Cyclohexan oder Mischungen davon; Monoolefinen wie etwa 1-Buten, 2-Buten oder Mischungen davon; aromatischen Kohlenwasserstoffen wie etwa Benzen, Toluen, Xylen oder Mischungen davon; halogenierten Kohlenwasserstoffen wie etwa Methylenchlorid, Chloroform, Kohlenstofftetrachlorid, Trichlorethylen, Perchlorethylen, 1,2-Dichlorethan, Chlorbenzen, Brombenzen, Chlortoluen oder Mischungen davon.

16. Verfahren für die Herstellung von (Co)polymeren konjugierter Diene gemäß Anspruch 15, wobei die Konzentration des konjugierten Diens zur (Co)polymerisierung in dem inerten organischen Lösungsmittel im Bereich von 5 Gew.-% bis 50 Gew.-%, bezogen auf das Gesamtgewicht der Mischung von konjugiertem Dien und inertem organischem Lösungsmittel, liegt.

17. Verfahren für die Herstellung von (Co)polymeren konjugierter Diene gemäß einem der vorhergehenden Ansprüche, wobei das Verfahren bei einer Temperatur im Bereich von -70 °C bis +100 °C ausgeführt wird.

Revendications

1. Un procédé pour la préparation de (co)polymères de diènes conjugués, lequel comprend la polymérisation d'au moins un diène conjugué en présence d'un système catalytique comprenant au moins un complexe bis-imine de cobalt ayant la formule générale (I) :



(I)

dans laquelle :

n est 0 ou 1 ;

- Y représente un groupe -CR'R" dans lequel R' et R", égaux ou différents l'un de l'autre, représentent un atome d'hydrogène, ou un groupe alkyle en C_1-C_{20} linéaire ou ramifié ; ou un groupe carbocyclique aromatique divalent facultativement substitué ;
- R_1 et R_2, égaux ou différents l'un de l'autre, représentent un atome d'hydrogène ; ou ils sont sélectionnés

parmi un des groupes alkyle en C_1-C_{20} linéaires ou ramifiés facultativement halogénés, des groupes cycloalkyle facultativement substitués ; ou R_1 et R_2 peuvent être facultativement liés l'un à l'autre afin de former, conjointement avec les autres atomes auxquels ils sont liés, un cycle contenant de 4 à 6 atomes de carbone, saturé, insaturé, ou aromatique, facultativement substitué par des groupes alkyle en C_1-C_{20} linéaires ou ramifiés, ledit cycle contenant facultativement des hétéroatomes tels que l'oxygène, le soufre, l'azote, le silicium, le phosphore, le sélénium ;

- R_3 et R_4, égaux ou différents l'un de l'autre, représentent un atome d'hydrogène ; ou ils sont sélectionnés parmi un des groupes alkyle en C_1-C_{20} linéaires ou ramifiés facultativement halogénés, des groupes cycloalkyle facultativement substitués ; des groupes aryle facultativement substitués ;
- ou R_2 et R_4 peuvent être facultativement liés l'un à l'autre afin de former, conjointement avec les autres atomes auxquels ils sont liés, un cycle contenant de 3 à 6 atomes de carbone, saturé, insaturé, ou aromatique, facultativement substitué par des groupes alkyle en C_1-C_{20} linéaires ou ramifiés, ledit cycle contenant facultativement d'autres hétéroatomes tels que l'oxygène, le soufre, l'azote, le silicium, le phosphore, le sélénium ;
- ou R_1 et R_3 peuvent être facultativement liés l'un à l'autre afin de former, conjointement avec les autres atomes auxquels ils sont liés, un cycle contenant de 3 à 6 atomes de carbone, saturé, insaturé, ou aromatique, facultativement substitué par des groupes alkyle en C_1-C_{20} linéaires ou ramifiés, ledit cycle contenant facultativement d'autres hétéroatomes tels que l'oxygène, le soufre, l'azote, le silicium, le phosphore, le sélénium ;
- X_1 et X_2, égaux ou différents l'un de l'autre, représentent un atome d'halogène tel que le chlore, le brome, l'iode ; ou ils sont sélectionnés parmi des groupes alkyle en C_1-C_{20} linéaires ou ramifiés, des groupes $-OCOR_5$ ou des groupes $-OR_5$ dans lesquels R_5 est sélectionné parmi des groupes alkyle en C_1-C_{20} linéaires ou ramifiés.

2. Le procédé pour la préparation de (co)polymères de diènes conjugués selon la revendication 1, dans lequel ledit système catalytique comprend au moins un co-catalyseur (b) sélectionné parmi des composés organiques d'un élément M' différent du carbone, ledit élément M' étant sélectionné parmi des éléments appartenant aux groupes 2, 12, 13 ou 14 du Tableau Périodique des Éléments, tels que : le bore, l'aluminium, le zinc, le magnésium, le gallium, l'étain.

3. Le procédé pour la préparation de (co)polymères de diènes conjugués selon la revendication 2, dans lequel ledit co-catalyseur (b) est sélectionné parmi (b_1) des alkyles d'aluminium ayant la formule générale (II) :

$$Al(X')_n(R_6)_{3-n} \qquad (II)$$

dans laquelle X' représente un atome d'halogène tel que le chlore, le brome, l'iode, le fluor ; R_6 est sélectionné parmi des groupes alkyle en C_1-C_{20} linéaires ou ramifiés, des groupes cycloalkyle, des groupes aryle, lesdits groupes étant facultativement substitués par un ou plusieurs atomes de silicium ou de germanium ; et n est un entier compris dans la gamme allant de 0 à 2.

4. Le procédé pour la préparation de (co)polymères de diènes conjugués selon la revendication 2, dans lequel ledit co-catalyseur (b) est sélectionné parmi (b_2) des composés organo-oxygénés d'un élément M' différent du carbone appartenant aux groupes 13 ou 14 du Tableau Périodique des Éléments.

5. Le procédé pour la préparation de (co)polymères de diènes conjugués selon la revendication 2, dans lequel ledit co-catalyseur (b) est sélectionné parmi (b_3) des composés organométalliques ou mélanges de composés organométalliques d'un élément M' différent du carbone capables de réagir avec le complexe bis-imine de cobalt ayant la formule générale (I), extrayant de celui-ci un substituant X_1 ou X_2 σ-lié, afin de former d'un côté au moins un composé neutre, et de l'autre un composé ionique consistant en un cation contenant le métal (Co) coordonné par le ligand, et un anion organique non-coordinant contenant le métal M', dans lequel la charge négative est délocalisée sur une structure multicentrique.

6. Le procédé pour la préparation de (co)polymères de diènes conjugués selon n'importe lesquelles des revendications précédentes, dans lequel ledit diène conjugué est sélectionné parmi : le 1,3-butadiène, le 2-méthyl-1,3-butadiène (isoprène), le 2,3-diméthyl-1,3-butadiène, le 1,3-pentadiène, le 1,3-hexadiène, le cyclo-1,3-hexadiène, ou des mélanges de ceux-ci.

7. Le procédé pour la préparation de (co)polymères de diènes conjugués selon n'importe lesquelles des revendications

précédentes, dans lequel dans ledit complexe bis-imine de cobalt ayant la formule générale (I) :

n est 0 ;

- R_1 et R_2, égaux ou différents l'un de l'autre, sont un atome d'hydrogène, ou ils sont sélectionnés parmi des groupes alkyle en C_1-C_{20} linéaires ou ramifiés, préférablement sont un groupe méthyle ;
- R_3 et R_4, égaux ou différents l'un de l'autre, sont sélectionnés parmi des groupes phényle facultativement substitués par des groupes alkyle en C_1-C_{20} linéaires ou ramifiés, préférablement substitués par un ou plusieurs groupes méthyle, éthyle, *iso*-propyle, *tert*-butyle ;
- X_1 et X_2, identiques l'un à l'autre, sont un atome d'halogène tel que le chlore, le brome, l'iode, préférablement le chlore.

8. Le procédé pour la préparation de (co)polymères de diènes conjugués selon n'importe lesquelles des revendications 1 à 6, dans lequel dans ledit complexe bis-imine de cobalt ayant la formule générale (I) :

n est 1 ;

- Y est un groupe CR'R" dans lequel R' et R", égaux ou différents l'un de l'autre, sont un atome d'hydrogène ; ou ils sont sélectionnés parmi des groupes alkyle en C_1-C_{20} linéaires ou ramifiés, préférablement sont un groupe propyle ;
- R_1 et R_2, égaux ou différents l'un de l'autre, sont un atome d'hydrogène ; ou ils sont sélectionnés parmi des groupes alkyle en C_1-C_{20} linéaires ou ramifiés, préférablement sont un groupe méthyle ;
- R_3 et R_4, égaux ou différents l'un de l'autre, sont sélectionnés parmi des groupes phényle facultativement substitués par des groupes alkyle en C_1-C_{20} linéaires ou ramifiés, préférablement substitués par un ou plusieurs groupes méthyle, éthyle, *iso*-propyle, *tert*-butyle ;
- X_1 et X_2, identiques l'un à l'autre, sont un atome d'halogène tel que le chlore, le brome, l'iode, préférablement le chlore.

9. Le procédé pour la préparation de (co)polymères de diènes conjugués selon n'importe lesquelles des revendications 1 à 6, dans lequel dans ledit complexe bis-imine de cobalt ayant la formule générale (I) :

n est 0 ;

- R_1 et R_3, sont liés l'un à l'autre et, conjointement avec les autres atomes auxquels ils sont liés, forment une pyridine ;
- R_2 est un atome d'hydrogène, ou il est sélectionné parmi des groupes alkyle en C_1-C_{20} linéaires ou ramifiés, préférablement est un groupe méthyle ;
- R_4 est sélectionné parmi des groupes phényle facultativement substitués par des groupes alkyle en C_1-C_{20} linéaires ou ramifiés, préférablement un groupe phényle substitué par un ou plusieurs groupes méthyle, éthyle, *iso*-propyle, *tert*-butyle ;
- X_1 et X_2, identiques l'un à l'autre, sont un atome d'halogène tel que le chlore, le brome, l'iode, préférablement le chlore.

10. Le procédé pour la préparation de (co)polymères de diènes conjugués selon n'importe lesquelles des revendications 1 à 6, dans lequel dans ledit complexe bis-imine de cobalt ayant la formule générale (I) :

n est 1 ;

- Y est un groupe aromatique divalent facultativement substitué, préférablement un groupe méta-phénylène ;
- R_1 et R_2, égaux ou différents l'un de l'autre, sont un atome d'hydrogène, ou ils sont sélectionnés parmi des groupes alkyle en C_1-C_{20} linéaires ou ramifiés, préférablement sont un groupe méthyle ;
- R_3 et R_4, égaux ou différents l'un de l'autre, sont sélectionnés parmi des groupes phényle facultativement substitués par des groupes alkyle en C_1-C_{20} linéaires ou ramifiés, préférablement un groupe phényle substitué par un groupe méthyle ;
- X_1 et X_2, identiques l'un à l'autre, sont un atome d'halogène tel que le chlore, le brome, l'iode, préférablement le chlore.

11. Le procédé pour la préparation de (co)polymères de diènes conjugués selon la revendication 3, dans lequel lesdits

alkyles d'aluminium (b_1) ayant la formule générale (II) sont le chlorure de di-éthyl-aluminium, le dichlorure de mono-éthyl-aluminium, le sesquichlorure d'éthylaluminium (EASC).

12. Le procédé pour la préparation de (co)polymères de diènes conjugués selon la revendication 4, dans lequel lesdits composés organo-oxygénés (b_2) sont sélectionnés parmi des aluminoxanes ayant la formule générale (III) :

$$(R_7)_2\text{-Al-O-[-Al}(R_8)\text{-O-]}_p\text{-Al-}(R_9)_2 \qquad \text{(III)}$$

dans laquelle R_7, R_8 et R_9, égaux ou différents l'un de l'autre, représentent un atome d'hydrogène, un atome d'halogène tel que le chlore, le brome, l'iode, le fluor ; ou ils sont sélectionnés parmi des groupes alkyle en C_1-C_{20} linéaires ou ramifiés, des groupes cycloalkyle, des groupes aryle, lesdits groupes étant facultativement substitués par un ou plusieurs atomes de silicium ou de germanium ; et p est un entier compris dans la gamme allant de 0 à 1 000.

13. Le procédé pour la préparation de (co)polymères de diènes conjugués selon la revendication 12, dans lequel ledit composé organo-oxygéné (b_2) est le méthylaluminoxane (MAO).

14. Le procédé pour la préparation de (co)polymères de diènes conjugués selon la revendication 5, dans lequel lesdits composés ou mélanges de composés (b_3) sont sélectionnés parmi des composés organiques d'aluminium et surtout de bore, tels que ceux représentés par les formules générales suivantes :

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

$$[Ph_3C]^+\bullet[B(R_D)_4]^- \text{ ; } [(R_C)_3PH]^+\bullet[B(R_D)_4]^- \text{ ;}$$

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

dans lesquelles w est un entier compris dans la gamme allant de 0 à 3, chaque groupe R_C représente indépendamment un groupe alkyle ou un groupe aryle ayant de 1 à 10 atomes de carbone et chaque groupe R_D représente indépendamment un groupe aryle partiellement ou totalement, préférablement totalement, fluoré, ayant de 6 à 20 atomes de carbone, P représente un radical pyrrolique facultativement substitué.

15. Le procédé pour la préparation de (co)polymères de diènes conjugués selon n'importe lesquelles des revendications précédentes, ledit procédé étant mis en oeuvre en présence d'un solvant organique inerte sélectionné parmi : des hydrocarbures aliphatiques saturés tels que le butane, le pentane, l'hexane, l'heptane, ou des mélanges de ceux-ci ; des hydrocarbures cycloaliphatiques saturés tels que le cyclopentane, le cyclohexane, ou des mélanges de ceux-ci ; des mono-oléfines telles que le 1-butène, le 2-butène, ou des mélanges de ceux-ci ; des hydrocarbures aromatiques tels que le benzène, le toluène, le xylène, ou des mélanges de ceux-ci ; des hydrocarbures halogénés tel que le chlorure de méthylène, le chloroforme, le tétrachlorure de carbone, le trichloroéthylène, le perchloroéthylène, le 1,2-dichloroéthane, le chlorobenzène, le bromobenzène, le chlorotoluène, ou des mélanges de ceux-ci.

16. Le procédé pour la préparation de (co)polymères de diènes conjugués selon la revendication 15, dans lequel la concentration du diène conjugué devant être (co)polymérisé dans ledit solvant organique inerte est comprise dans la gamme allant de 5 % en poids à 50 % en poids par rapport au poids total du mélange de diène conjugué et de solvant organique inerte.

17. Le procédé pour la préparation de (co)polymères de diènes conjugués selon n'importe lesquelles des revendications précédentes, ledit procédé étant mis en oeuvre à une température comprise dans la gamme allant de -70 °C à +100 °C.

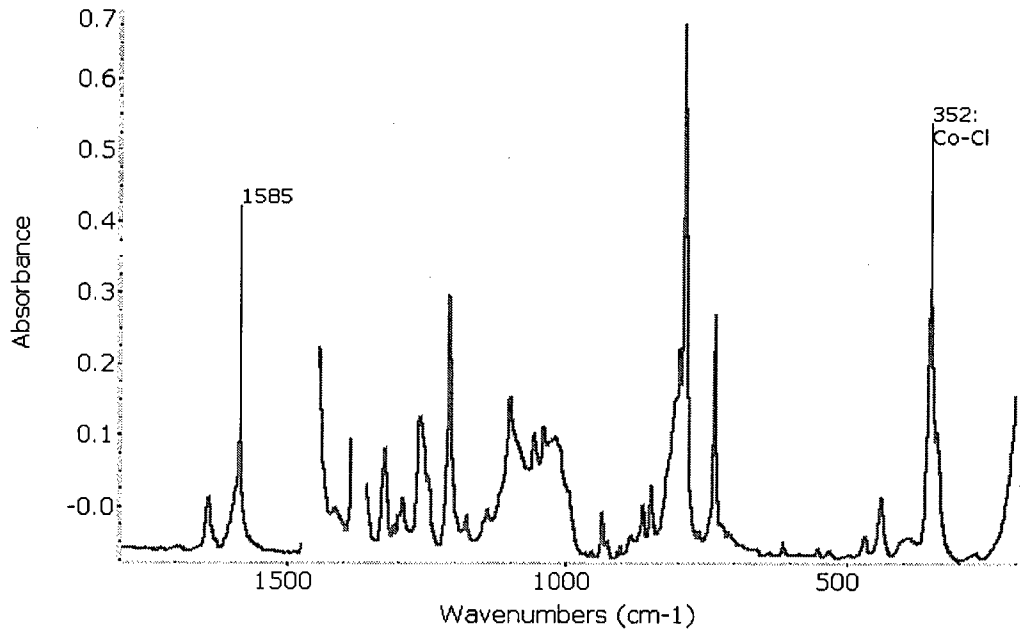


Figure 1

FT-IR spectrum of the $CoCl_2$(L8)complex [sample GL648] (Example 10)

(the nujol bands have been subtracted)

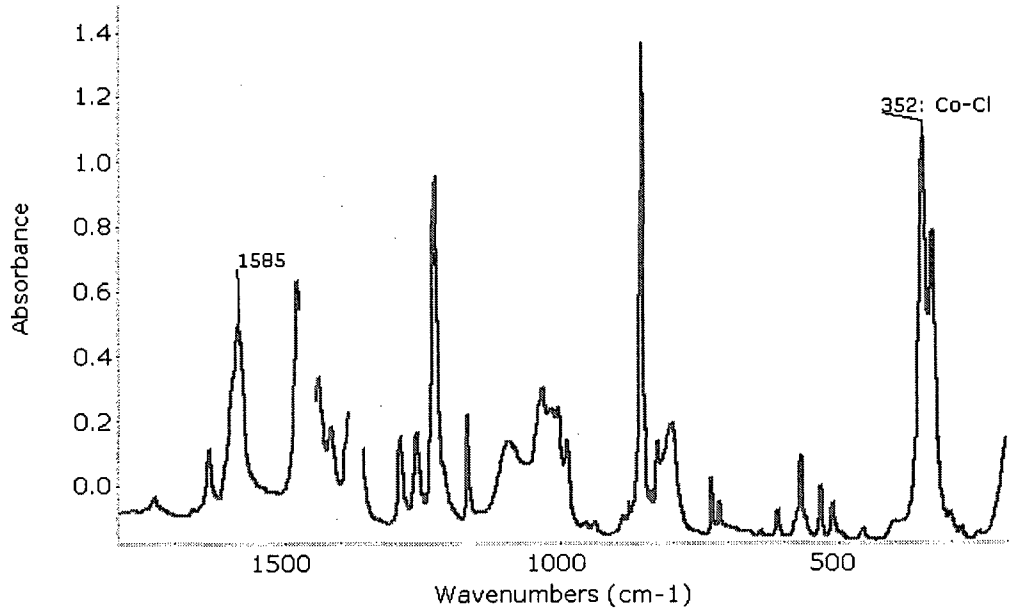


Figure 2

FT-IR spectrum of the $CoCl_2$(L9)complex [sample GL651] (Example 13) (the nujol bands have been subtracted)

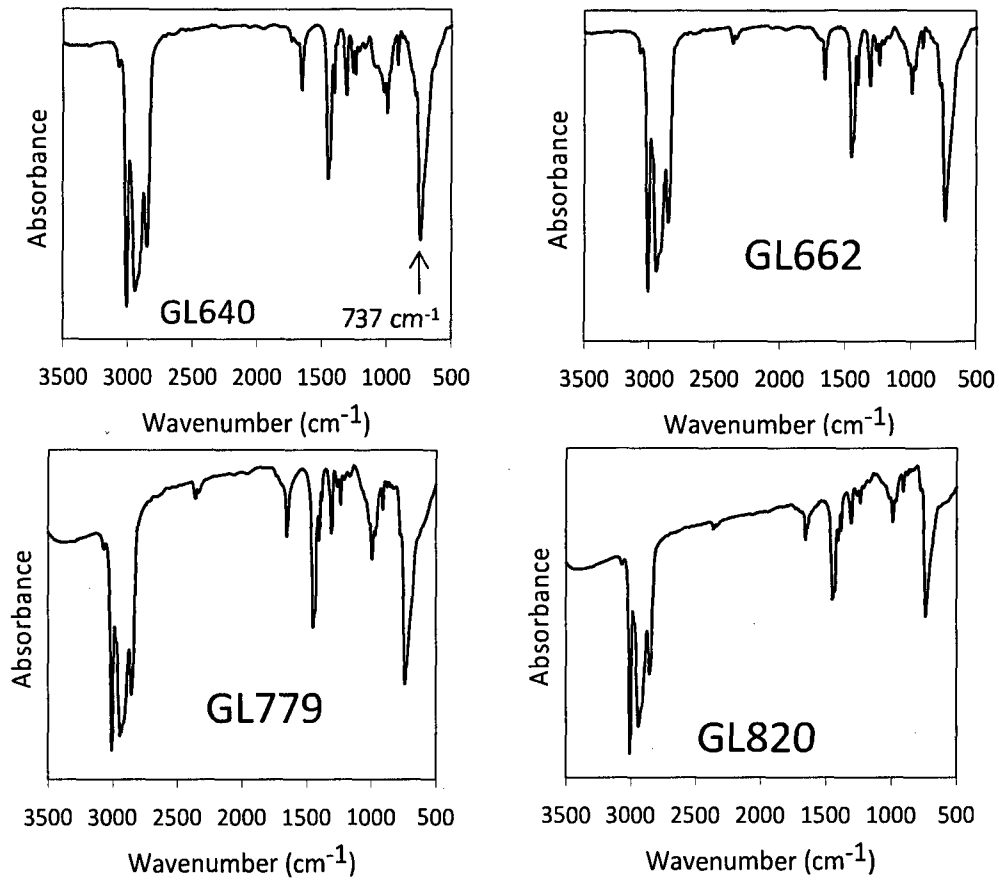


Figure 3

FT-IR spectra of polybutadienes indicated in Table 1: GL640 (Example 19); GL662 (Example 20); GL779 (Example 21); GL820 (Example 22)

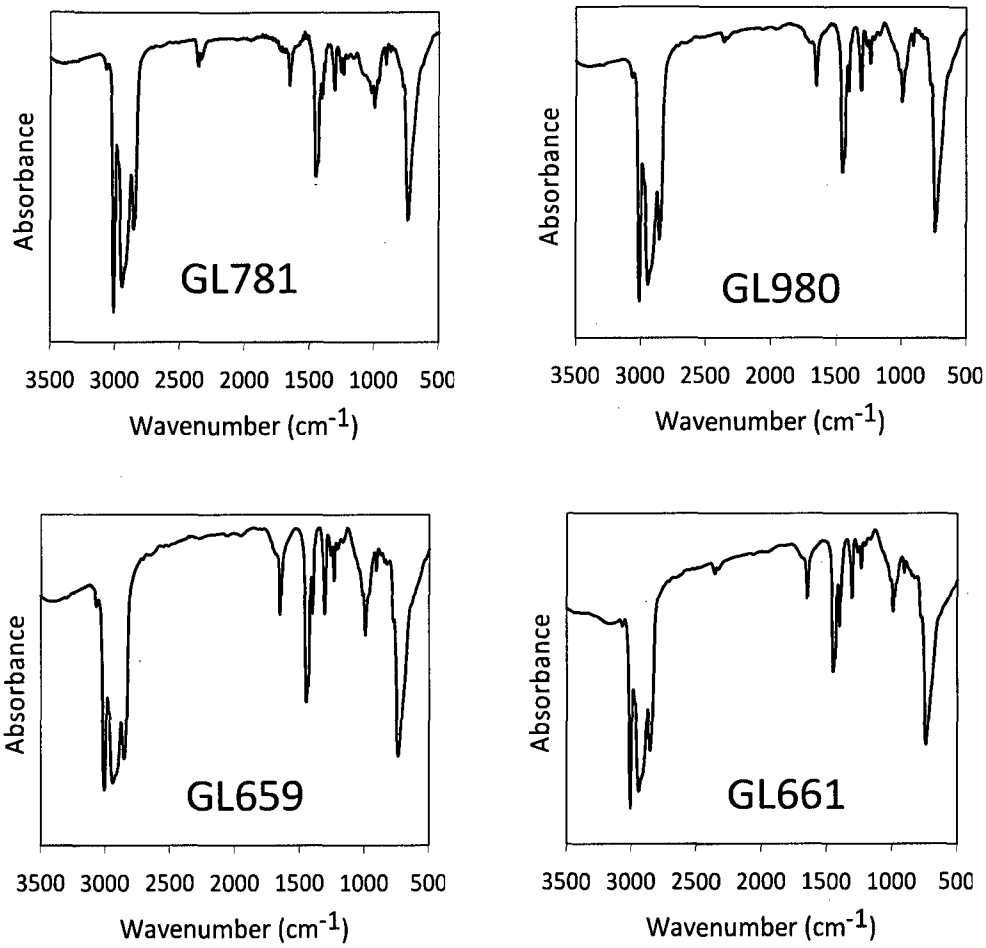


Figure 4

FT-IR spectra of polybutadienes indicated in Table 1: GL781 (Example 23); GL980 (Example 24); GL659 (Example 17); GL661 (Example 18)

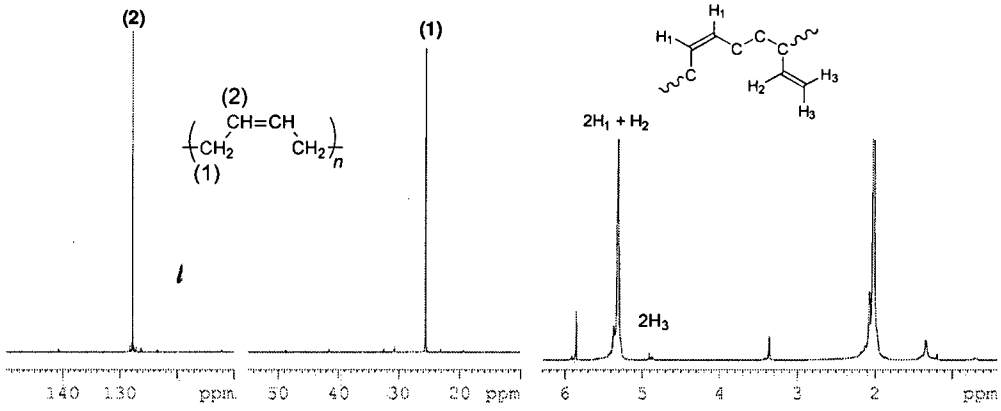


Figure 5

^{1}H-NMR (on the left) and ^{13}C-NMR (on the right) spectra of the polybutadiene of Example 21

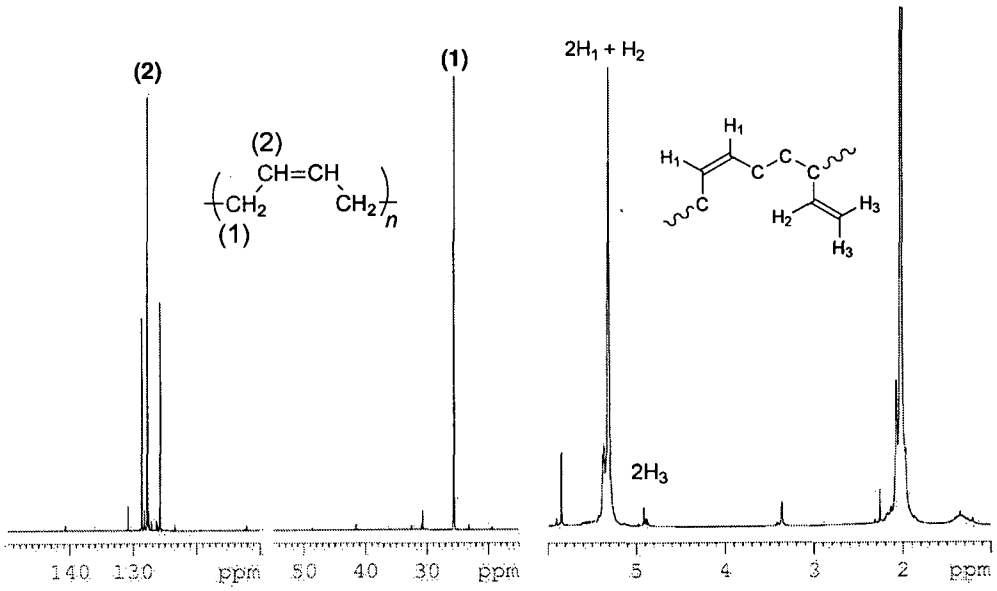
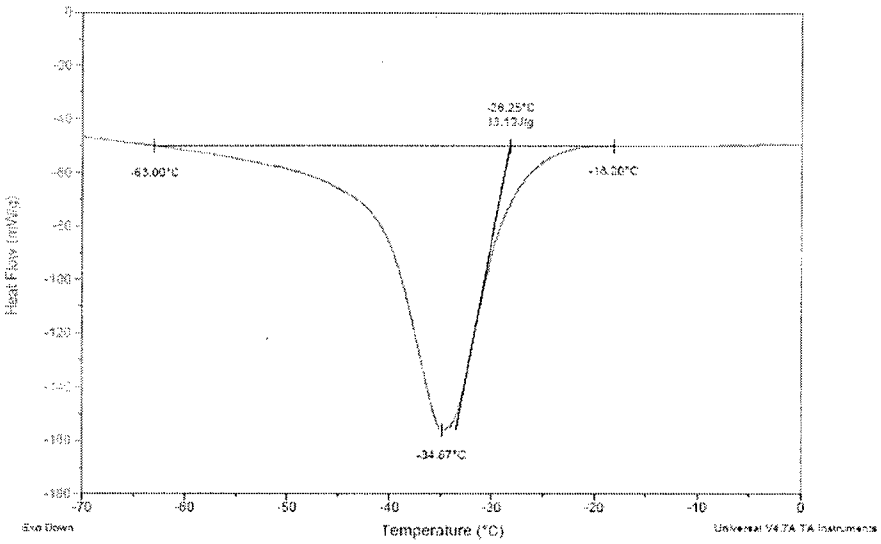
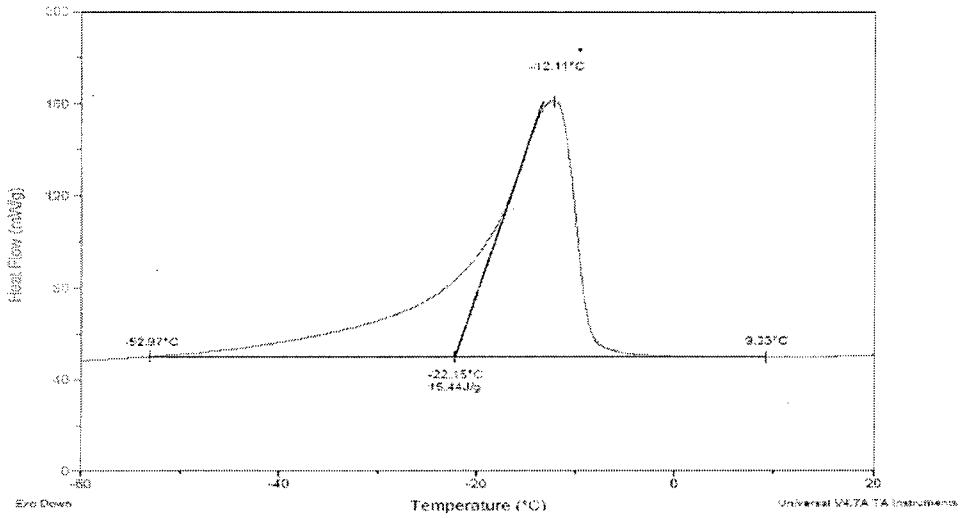


Figure 6

^{1}H-NMR (on the left) and ^{13}C-NMR (on the right) spectra of the polybutadiene of Example 22



(A)

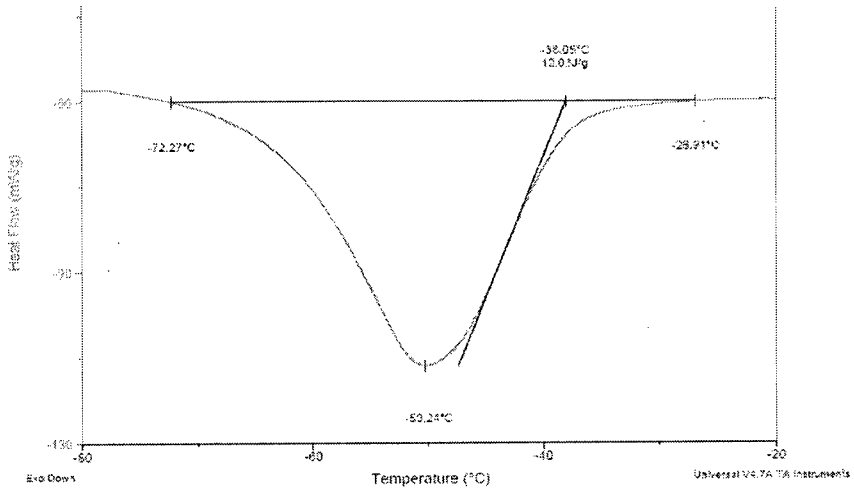


(B)

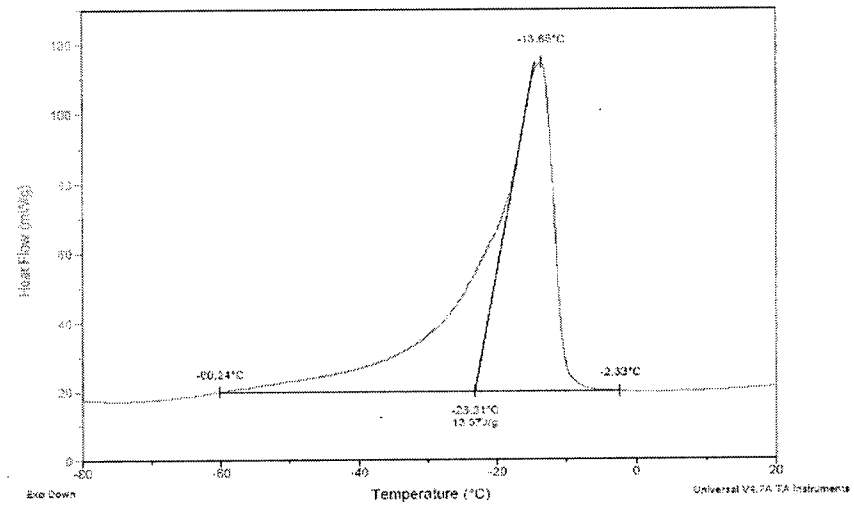
Figure 7

DSC diagrams of the polybutadiene of Example 21: (A) crystallization;

(B) melting



(A)

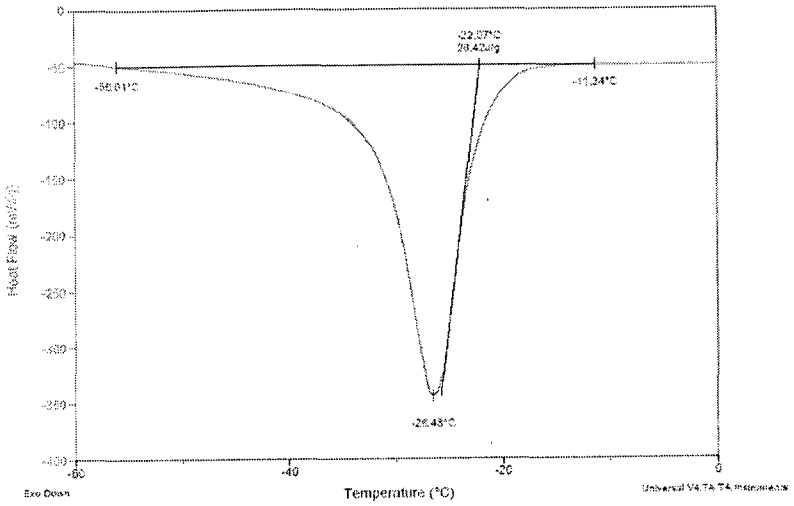


(B)

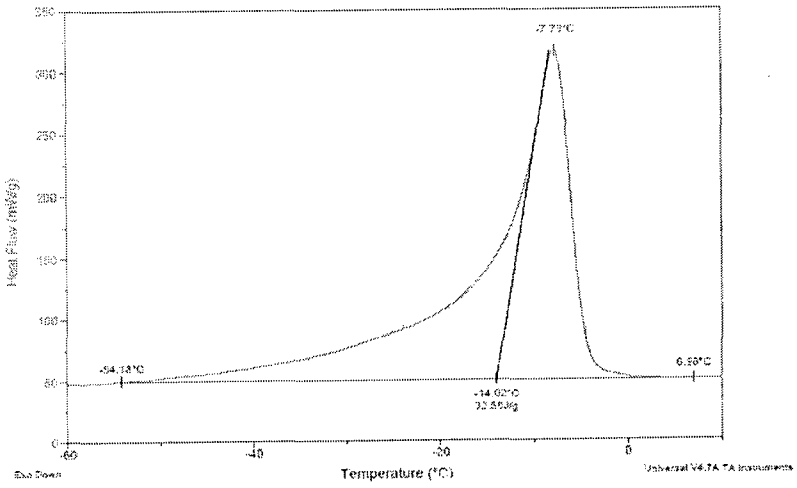
Figure 8

DSC diagrams of the polybutadiene of Example 22: (A) crystallization;

(B) melting



(A)



(B)

Figure 9

DSC diagrams of the polybutadiene of Example 17: (A) crystallization;

(B) melting

REFERENCES CITED IN THE DESCRIPTION

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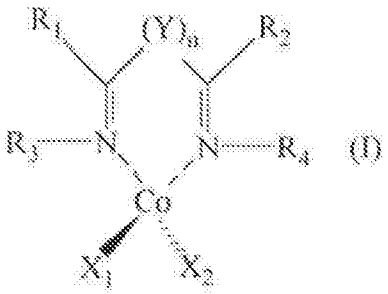
ELJÁRÁS KONJUGÁLT DIÉNEK (KO)POLIMERJEINEK ELŐÁLLÍTÁSÁRA KOBALT BISZ-IMIN KOMPLEXÉT TARTALMAZÓ KATALITIKUS RENDSZER JELENLÉTÉBEN

SZABADALMI IGÉNYPONTOK

1. Eljárás konjugált diének (ko)polimerjeinek előállítására, amely eljárás tartalmazza legalább egy konjugált dién polimerizálását egy katalitikus rendszer jelenlétében, ahol az tartalmazza kobalt legalább egy bisz-imin komplexét, amely a következő (I) általános képlettel bír:



(I)

ahol az általános képletben:

n értéke 0 vagy 1;

- Y jelentése -CR'R" általános képletű csoport, ahol R' és R" azonos vagy egymástól különböző, és jelentésük hidrogénatom vagy egyenes vagy elágazó láncú C_1-C_{20} alkil-csoport; vagy egy kétértékű aromás karbociklusos csoport, amely kívánt esetben szubsztituálva van;
- R_1 és R_2 jelentése azonos vagy egymástól különböző, és jelentésük hidrogénatom, vagy ezek a következők közül választhatók ki: egyenes vagy elágazó láncú C_1-C_{20} alkil-csoport, amely kívánt esetben halogénezve van, cikloalkil csoport, amely kívánt esetben szubsztituálva van; vagy R_1 és R_2 kívánt esetben össze vannak kötve egymással, és azokkal a további atomokkal, amelyekhez ezek kötődnek, kialakítanak egy gyűrűt (cycle), amely 4-6 szénatomot tartalmaz, és amely lehet telített, telítetlen vagy aromás, és kívánt esetben szubsztituálva lehet egyenes vagy elágazó láncú C_1-C_{20} alkil-csoportokkal, ahol az említett gyűrű kívánt esetben tartalmaz heteroatomokat, amilyenek az oxigén, kén, nitrogén, szilícium, foszfor és szelén;
- R_3 és R_4 jelentése azonos vagy egymástól különböző, és jelentésük hidrogénatom, vagy ezek a következők közül választhatók ki: egyenes vagy elágazó láncú C_1-C_{20} alkil-csoport, amely kívánt esetben halogénezve van, cikloalkil-csoport, amely kívánt esetben szubsztituálva van, aril-csoport, amely kívánt esetben szubsztituálva van;
- vagy R_2 és R_4 kívánt esetben össze vannak kötve egymással, és azokkal a további atomokkal, amelyekhez ezek kötődnek, kialakítanak egy gyűrűt, amely 3-6 szénatomot tartalmaz, és amely lehet telített, telítetlen vagy aromás, és kívánt esetben szubsztituálva lehet egyenes vagy elágazó láncú C_1-C_{20} alkil-csoportokkal, ahol az említett gyűrű kívánt esetben tartalmaz további heteroatomokat, amilyenek az oxigén, kén, nitrogén, szilícium, foszfor és szelén;
- vagy R_1 és R_3 kívánt esetben össze vannak kötve egymással, és azokkal a további atomokkal, amelyekhez ezek kötődnek, kialakítanak egy gyűrűt (cycle), amely 3-6 szénatomot tartalmaz, és amely lehet telített, telítetlen vagy aromás, és kívánt esetben szubsztituálva lehet egyenes vagy elágazó láncú C_1-C_{20} alkil-csoportokkal, ahol az említett gyűrű kívánt esetben tartalmaz további heteroatomokat, amilyenek az oxigén, kén, nitrogén, szilícium, foszfor és szelén;

- X_1 és X_2 jelentése azonos vagy egymástól különböző, és jelentése halogénatom, mint klór-, bróm- vagy jódatom, vagy ezek a következők közül választhatók ki: egyenes vagy elágazó láncú C_1-C_{20} alkil-csoport, $-OCOR_5$ csoport és $-OR_5$ csoport, ahol R_5 jelentése a következők közül választható ki: egyenes vagy elágazó láncú C_1-C_{20} alkil-csoportok.

2. Az 1. igénypont szerinti eljárás konjugált diének (ko)polimerjeinek előállítására, ahol az említett katalizátor rendszer tartalmaz legalább egy (b) ko-katalizátort, amely a széntől különböző M' elem szerves vegyületei közül választható ki, ahol az említett M' elem azon elemek közül választható ki, amelyek az Elemek Periódusos Táblázatának 2., 12., 13. vagy 14. csoportjaiba tartoznak,mint például a bór, alumínium, cink, magnézium, gallium és ón.

3. A 2. igénypont szerinti eljárás konjugált diének (ko)polimerjeinek előállítására, ahol az említett (b) ko-katalizátor (b_1) alumínium-alkilek közül választható ki, amelyek a (II) általános képlettel bírnak:

$$Al(X')_n(R_6)_{3-n} \qquad (II)$$

ahol az általános képletben X jelentése halogénatom, mint klór, bróm, jód, fluor; R_6 jelentése a következők közül választható ki: C_1-C_{20} alkil-csoport, cikloalkil-csoport és aril-csoport, ahol az említett csoportok kívánt esetben szubsztituálva vannak egy vagy több szilícium vagy germánium atommal; és n értéke egész szám 0-tól 2-ig.

4. A 2. igénypont szerinti eljárás konjugált diének (ko)polimerjeinek előállítására, ahol az említett (b) ko-katalizátor a széntől különböző M' elem (b_2) szerves-oxigénezett (organo-oxygenated) vegyületei közül választható ki, ahol az említett M' elem azon elemek közül választható ki, amelyek az Elemek Periódusos Táblázatának 13. vagy 14. csoportjaiba tartoznak.

5. A 2. igénypont szerinti eljárás konjugált diének (ko)polimerjeinek előállítására, ahol az említett (b) ko-katalizátor a széntől különböző M' elem (b_3) szerves-fém (organometallic) vegyületei vagy szerves-fém vegyületeinek keverékei közül választható ki, ahol ezek képesek reagálni a kobalt (I) általános képletű bisz-imin komplexével, ebből kivonunk egy X_1 szubsztituenst vagy egy X_2 σ-kötést, hogy így alakítsunk ki egyrészt legalább egy semleges vegyületet, és másrészt egy anionos vegyületet, amely olyan kationból áll, ahol ez tartalmazza a (Co) fémet egy ligandum által koordinálva, továbbá egy nem-koordináló szerves aniont, amely tartalmazza az M' fémet, ahol a negatív töltés delokalizálva van egy több-központú (multicentric) szerkezeten.

6. Az 1-5. igénypontok bármelyike szerinti eljárás konjugált diének (ko)polimerjeinek előállítására, ahol az említett konjugált dién a következők közül választható ki: 1,3-butadién, 2-metil-1,3-butadién (izoprén), 2,3-dimetil-1,3-butadién, 1,3-pentadién, 1,3-hexadién, ciklo-1,3-hexadién, és mindezek keverékei.

7. Az 1-6. igénypontok bármelyike szerinti eljárás konjugált diének (ko)polimerjeinek előállítására, ahol a kobalt említett (I) általános képlettel bíró bisz-imin komplexében:

n értéke 0;

- R_1 és R_2 jelentése azonos vagy egymástól különböző, és jelentésük hidrogénatom, vagy a következők közül választható ki: egyenes vagy elágazó láncú C_1-C_{20} alkil-csoportok, előnyösen metil-csoport;
- R_3 és R_4 jelentése azonos vagy egymástól különböző, és a következők közül választhatók ki: fenil-csoportok, amelyek kívánt esetben szubsztituálva vannak egyenes vagy elágazó láncú C_1-C_{20} alkil-csoportokkal, előnyösen szubsztituálva vannak egy vagy több metil-, etil-, izopropil- vagy terc-butil-csoporttal;
- X_1 és X_2 jelentése azonos vagy egymástól különböző, és jelentésük halogénatom, mint klór-, bróm- vagy jódatom, előnyösen klóratom.

8. Az 1-6. igénypontok bármelyike szerinti eljárás konjugált diének (ko)polimerjeinek előállítására, ahol a kobalt (I) általános képlettel bíró említett bisz-imin komplexében:

n értéke 1;

- Y jelentése CR'R" általános képletű csoport, ahol R' és R" jelentése azonos vagy egymástól különböző és ez hidrogénatom, vagy ezek a következők közül választhatók ki: egyenes vagy elágazó láncú C_1-C_{20} alkil-csoportok, előnyösen propil-csoport;
- R_1 és R_2 jelentése azonos vagy egymástól különböző és ez hidrogénatom, vagy ezek a következők közül választhatók ki: egyenes vagy elágazó láncú C_1-C_{20} alkil-csoportok, előnyösen metil-csoport;
- R_3 és R_4 jelentése azonos vagy egymástól különböző, és a következők közül választható ki: fenil-csoportok, amelyek kívánt esetben szubsztituálva vannak egyenes vagy elágazó láncú C_1-C_{20} alkil-csoportokkal, előnyösen szubsztituálva vannak egy vagy több metil-, etil-, izopropil- vagy terc-butil-csoporttal;
- X_1 és X_2 jelentése azonos vagy egymástól különböző, és jelentése halogénatom, mint klór-, bróm- vagy jódatom, előnyösen klóratom.

9. Az 1-6. igénypontok bármelyike szerinti eljárás konjugált diének (ko)polimerjeinek előállítására, ahol a kobalt (I) általános képlettel bíró említett bisz-imin komplexében:

n értéke 0;

- R_1 és R_3 össze vannak kapcsolva egymással, és azokkal a szénatomokkal együtt, amelyekhez hozzá vannak kapcsolva, piridint képeznek;
- R_2 jelentése hidrogénatom, vagy a következők közül választható ki: egyenes vagy elágazó láncú C_1-C_{20} alkil-csoportok, előnyösen metil-csoport;
- R_4 jelentése a következők közül választható ki: fenil-csoportok, amelyek kívánt esetben szubsztituálva vannak egyenes vagy elágazó láncú C_1-C_{20} alkil-csoportokkal, előnyösen fenil-csoport, amely szubsztituálva van egy vagy több metil-, etil-, izopropil- vagy terc-butil-csoporttal;
- X_1 és X_2 jelentése azonos vagy egymástól különböző, és jelentése halogénatom, mint klór-, bróm- vagy jódatom, előnyösen klóratom.

10. Az 1-6. igénypontok bármelyike szerinti eljárás konjugált diének (ko)polimerjeinek előállítására, ahol a kobalt (I) általános képlettel bíró említett bisz-imin komplexében:

n értéke 1;

- Y jelentése kétértékű aromás csoport, amely kívánt esetben szubsztituálva van, előnyösen meta-fenilén-csoport;
- R_1 és R_2 jelentése azonos vagy egymástól különböző és ez hidrogénatom, vagy ezek a következők közül választhatók ki: egyenes vagy elágazó láncú C_1-C_{20} alkil-csoportok, előnyösen metil-csoport;
- R_3 és R_4 jelentése azonos vagy egymástól különböző, és a következők közül választható ki: fenil-csoportok, amelyek kívánt esetben szubsztituálva vannak egyenes vagy elágazó láncú C_1-C_{20} alkil-csoportokkal, előnyösen fenil-csoport, amely szubsztituálva van metil-csoporttal;
- X_1 és X_2 jelentése azonos vagy egymástól különböző, és jelentése halogénatom, mint klór-,bróm- vagy jódatom, előnyösen klóratom.

11. A 3. igénypont szerinti eljárás konjugált diének (ko)polimerjeinek előállítására, ahol az említett (b_1) alumínium-alkil, amely (II) általános képlettel bír, dietil-alumínium-klorid, monoetil-alumínium-diklorid, etil-alumínium-szeszkviklorid (EASC).

12. A 4. igénypont szerinti eljárás konjugált diének (ko)polimerjeinek előállítására, ahol az említett (b_2) szerves-oxigénezett vegyületek a (III) általános képletű alumínoxánok közül választhatók ki:

$$(R_7)_2\text{-Al-O-}[\text{-Al}(R_8)\text{-O-}]_p\text{-Al-}(R_9)_2 \qquad \text{(III)}$$

ahol az általános képletben R_7, R_8 és R_9 jelentése azonos vagy egymástól különböző, és jelentése hidrogénatom vagy

halogénatom, mint klór-, bróm-, jód- és fluoratom, vagy ezek a következők közül választhatók ki: egyenes vagy elágazó láncú C_1-C_{20} alkil-csoportok, cikloalkil-csoportok és aril-csoportok, ahol az említett csoportok kívánt esetben szubsztituálva vannak egy vagy több szilícium vagy germánium atommal; és p értéke egész szám a 0 és 1000 közötti tartományban.

13. A 12. igénypont szerinti eljárás konjugált diének (ko)polimerjeinek előállítására, ahol az említett (b_2) szerves-oxigénezett vegyület metil-alumínoxán (MAO).

14. Az 5. igénypont szerinti eljárás konjugált diének (ko)polimerjeinek előállítására, ahol az említett (b_3) vegyületek vagy vegyületek keverékei a következők közül választhatók ki: alumínium, de elsősorban bór szerves vegyületei, amilyenekat például a következő általános képletek képviselnek:

$$[(R_7)_wH_{4-w}]^+[B(R_8)_4]^-;\ B(R_8)_3;\ Al(R_8)_3;\ B(R_8)_3P;$$

$$[Ph_3C]^+[B(R_8)_4]^-;\ [(R_7)_3PH]^+[B(R_8)_4]^-;$$

$$[(Li)^+]_q[B(R_8)_4]^-;\ [(Li)^+]_q[Al(R_8)_4]^-;$$

ahol az általános képletekben w értéke egész szám a 0 és 3 közötti tartományban, minden R_8 csoport egymástól függetlenül alkil-csoportot vagy aril-csoportot jelent, amelyek 1-10 szénatommal bírnak, és minden R_8 csoport egymástól függetlenül 6-20 szénatommal bíró aril-csoportot jelent, amely részlegesen vagy teljesen, előnyösen teljesen, fluorozva van, és P jelentése pirrolgyűrű, amely kívánt esetben szubsztituálva van.

15. Az 1-14. igénypontok bármelyike szerinti eljárás konjugált diének (ko)polimerjeinek előállítására, ahol az említett eljárást inert szerves oldószer jelenlétében hajtjuk végre, amely a következők közül választható ki: telített alifás szénhidrogének, mint bután, pentán, hexán, heptán, vagy mindezek keverékei; telített cikloalifás szénhidrogének, mint ciklopentán, ciklohexán, vagy mindezek keverékei; mono-olefinek, mint 1-butén, 2-butén, vagy mindezek keverékei; aromás szénhidrogének, mint benzol, toluol, xilol, vagy mindezek keverékei; halogénezett szénhidrogének, mint metilén-klorid, kloroform, szén-tetraklorid, triklór-etilén, perklór-etilén, 1,2-diklór-etán, klór-benzol, bróm-benzol, klór-toluol, vagy mindezek keverékei.

16. A 15. igénypont szerinti eljárás konjugált diének (ko)polimerjeinek előállítására, ahol a (ko)polimerizálandó konjugált dién koncentrációja az említett inert szerves oldószerben az 5 tömeg % és 50 tömeg % közötti tartományban van a konjugált dién és az inert szerves oldószer keverékének össztömegére vonatkoztatva.

17. Az 1-16. igénypontok bármelyike szerinti eljárás konjugált diének (ko)polimerjeinek előállítására, ahol az említett eljárást a -70°C és +100°C közötti hőmérséklet-tartományban hajtjuk végre.