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(54) **PROCEDE ET COMPOSITION D'UN CATALYSEUR A BASE DE
FER POUR LA PRODUCTION DE POLY(1,2-BUTADIENE)
SYNDIOTACTIQUE**

(54) **PROCESS AND IRON-BASED CATALYST COMPOSITION FOR
THE PRODUCTION OF SYNDIOTACTIC 1,2-
POLYBUTADIENE**

(57) A catalyst composition comprising (a) an iron-containing compound, (b) a dihydrocarbyl hydrogen phosphite, and (c) an organoaluminum compound is disclosed for polymerizing 1,3-butadiene into syndiotactic 1,2-polybutadiene. The use of the catalyst composition of this disclosure avoids the use of environmentally detrimental components such as carbon disulfide and halogenated solvents. The melting temperature of the syndiotactic 1,2-polybutadiene can be varied from about 100 to about 200 °C by variations in the catalyst components and the component ratios. The ability to vary the melting temperature over such a broad range with a single catalyst composition is very desirable. The syndiotactic 1,2-polybutadiene can be used as a plastic or as an additive for rubber compositions wherein it can crosslink with conventional rubbers using conventional crosslinking agents.

ABSTRACT

A catalyst composition comprising (a) an iron-containing compound, (b) a dihydrocarbyl hydrogen phosphite, and (c) an
5 organoaluminum compound is disclosed for polymerizing 1,3-butadiene into syndiotactic 1,2-polybutadiene. The use of the catalyst composition of this disclosure avoids the use of environmentally detrimental components such as carbon disulfide and halogenated solvents. The
melting temperature of the syndiotactic 1,2-polybutadiene can be varied
10 from about 100 to about 200 °C by variations in the catalyst components and the component ratios. The ability to vary the melting temperature over such a broad range with a single catalyst composition is very desirable. The syndiotactic 1,2-polybutadiene can be used as a plastic or as an additive for rubber compositions wherein it can crosslink
15 with conventional rubbers using conventional crosslinking agents.

PROCESS AND IRON-BASED CATALYST COMPOSITION FOR THE PRODUCTION OF SYNDIOTACTIC 1,2-POLYBUTADIENE

FIELD OF INVENTION

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The present invention relates to a catalyst composition comprising (a) an iron-containing compound, (b) a dihydrocarbyl hydrogen phosphite, and (c) an organoaluminum compound and its use to polymerize 1,3-butadiene into syndiotactic 1,2-polybutadiene. Syndiotactic 1,2-polybutadiene is a thermoplastic resin and is cocurable with conventional rubbers due to its residual unsaturation.

BACKGROUND OF THE INVENTION

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Syndiotactic 1,2-polybutadiene is a thermoplastic resin that has a stereoregular structure in which the vinyl groups as side chains are located alternately on the opposite sides in relation to the polymeric main chain consisting of carbon-carbon bonds. Syndiotactic 1,2-polybutadiene is a unique material that combines the properties of plastics and rubber. Accordingly, syndiotactic 1,2-polybutadiene has many uses. For example, films, fibers and molded articles can be made utilizing syndiotactic 1,2-polybutadiene. It can also be blended into rubbers and cocured therewith.

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Syndiotactic 1,2-polybutadiene can be made by solution, emulsion or suspension polymerization. The syndiotactic 1,2-polybutadiene from solution, emulsion or suspension polymerization typically has a melting temperature that is within the range of about 195 °C to 215 °C. However, for processability reasons it is generally desirable for syndiotactic 1,2-polybutadiene to have a melting temperature of less than about 195 °C to render it suitable for practical utilization.

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Various transition metal catalyst systems based on cobalt, titanium, vanadium, chromium, and molybdenum have been reported in the prior art for the preparation of syndiotactic 1,2-polybutadiene (see, e.g., L. Porri and A. Giarrusso, in *Comprehensive Polymer Science*,

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edited by G. C. Eastmond, A. Ledwith, S. Russo and P. Sigwalt, Pergamon Press: Oxford, 1989, Volume 4, Page 53). However, the majority of these catalyst systems have no practical utility because they have low catalytic activity or poor stereoselectivity and in some cases
5 produce low molecular weight polymers or crosslinked polymers unsuitable for commercial use.

The following cobalt-based catalyst systems are well known for the preparation of syndiotactic 1,2-polybutadiene on a commercial scale: (1) cobalt bis(acetylacetonate)/triethyl aluminum/water/triphenyl
10 phosphine (U.S. Pat. Nos. 3,498,963 and 4,182,813; Jap. Kokoku 44-32426, assigned to Japan Synthetic Rubber Co. Ltd.), and (2) cobalt tris(acetylacetonate)/triethyl aluminum/carbon disulfide (U.S. Pat. No. 3,778,424; Jap. Kokoku 72-19,892, 81-18,127, 74-17,666, and 74-17,667; Jap. Kokai 81-88,408, 81-88,409, 81-88,410, 75-59,480, 75-
15 121,380, and 75-121,379, assigned to Ube Industries Ltd.). These two catalyst systems also have serious disadvantages.

The cobalt bis(acetylacetonate)/triethyl aluminum/water/triphenyl phosphine system yields syndiotactic 1,2-polybutadiene having very low crystallinity. In addition, this catalyst system develops sufficient
20 catalytic activity only in halogenated hydrocarbon solvents as the polymerization medium, and halogenated solvents present the problems of toxicity.

The cobalt tris(acetylacetonate)/triethyl aluminum/carbon disulfide system uses carbon disulfide as one of the catalyst components.
25 Because of its high volatility, obnoxious smell, low flash point as well as toxicity, carbon disulfide is difficult and dangerous to use and requires expensive safety measures to prevent even minimal amounts escaping into the atmosphere. Furthermore, the syndiotactic 1,2-polybutadiene produced with this catalyst system has a very high melting temperature
30 within the range of 200-210 °C, which makes it difficult to process the polymer. Although the melting temperature of the syndiotactic 1,2-

polybutadiene can be reduced by the use of a catalyst modifier as a fourth catalyst component, the presence of such a catalyst modifier also has an adverse effect on the catalyst activity and polymer yields. Accordingly, many restrictions are required for the industrial utilization of the two aforesaid cobalt-based catalyst systems of the prior art.

Coordination catalyst systems based on iron-containing compounds such as iron(III) acetylacetonate/triethylaluminum have been known in the prior art for a long time, but they have very low catalytic activity and poor stereoselectivity for the polymerization of 1,3-butadiene and sometimes give rise to oligomers, low molecular weight liquid polymers or crosslinked polymers. Therefore, these iron-based catalyst systems of the prior art have no industrial utility.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide syndiotactic 1,2-polybutadiene having various melting temperatures and syndiotacticities without the above-mentioned disadvantages of the prior art.

It is another object of the present invention to provide a process for efficiently producing the aforesaid syndiotactic 1,2-polybutadiene.

It is a further object of the present invention to provide a versatile and inexpensive catalyst composition, which has high catalytic activity and stereoselectivity for use in the production of the aforesaid syndiotactic 1,2-polybutadiene.

It has been found that the polymerization of 1,3-butadiene by the use of a specified iron-based catalyst composition is capable of efficiently producing the objective syndiotactic 1,2-polybutadiene.

Specifically, the present invention relates to a catalyst composition which can be utilized in the stereospecific polymerization of 1,3-butadiene monomer into syndiotactic 1,2-polybutadiene, said catalyst composition being comprised of: (a) an iron-containing

compound, (b) a dihydrocarbyl hydrogen phosphite, and (c) an organoaluminum compound.

The present invention further relates to a process for the production of syndiotactic 1,2-polybutadiene, which comprises
5 polymerizing 1,3-butadiene monomer in the presence of a catalytically effective amount of the foregoing catalyst composition.

By utilizing the process and catalyst composition of the present invention, numerous distinct and highly beneficial advantages are realized. For example, by utilizing the process and catalyst composition
10 of the present invention, syndiotactic 1,2-polybutadiene can be produced in high yields with low catalyst levels after relatively short polymerization times. Additionally and more significantly, since the catalyst composition of the present invention does not contain the highly volatile, toxic and flammable carbon disulfide which is typically employed in some
15 of the prior-art catalyst systems, the toxicity, obnoxious smell, dangers and expense involved in the use of carbon disulfide are eliminated. Further, the catalyst composition of the present invention displays high catalytic activity in a wide range of solvents including nonhalogenated solvents, such as aliphatic and cycloaliphatic hydrocarbons, which are
20 environmentally preferred. In addition, the catalyst composition of the present invention is iron-based, and iron compounds are generally stable, non-toxic, inexpensive and readily available. Furthermore, the catalyst composition of the present invention is very versatile and capable of producing syndiotactic 1,2-polybutadiene having a wide range of melting
25 temperatures without the need to use a catalyst modifier as a fourth catalyst component.

DETAILED DESCRIPTION OF THE INVENTION

30 The catalyst composition of the present invention is comprised of the following components: (a) an iron-containing compound, (b) a

dihydrocarbyl hydrogen phosphite, and (c) an organoaluminum compound.

As the component (a) of the catalyst composition of the present invention, various iron-containing compounds can be utilized. It is
5 generally advantageous to employ iron-containing compounds that are soluble in a hydrocarbon solvent such as aromatic hydrocarbons, aliphatic hydrocarbons, or cycloaliphatic hydrocarbons. Nevertheless, insoluble iron-containing compounds may merely be suspended in the polymerization medium to form the catalytically active species.
10 Accordingly, no limitations should be placed on the iron-containing compounds to insure solubility.

The iron in the iron-containing compounds employed in the catalyst composition of the present invention can be in various oxidation states including, but not limited to, the 0, +2, +3, and +4 oxidation
15 states. It is preferable to use divalent iron compounds (also called ferrous compounds), wherein the iron is in the +2 oxidation state, and trivalent iron compounds (also called ferric compounds), wherein the iron is in the +3 oxidation state. Suitable types of iron-containing compounds that can be utilized in the catalyst composition of the
20 present invention include, but are not limited to, iron carboxylates, iron β -diketonates, iron alkoxides or aryloxides, iron halides, iron pseudo-halides, and organoiron compounds.

Some specific examples of suitable iron carboxylates include iron(II) formate, iron(III) formate, iron(II) acetate, iron(III) acetate, iron(II)
25 acrylate, iron(III) acrylate, iron(II) methacrylate, iron(III) methacrylate, iron(II) valerate, iron(III) valerate, iron(II) gluconate, iron(III) gluconate, iron(II) citrate, iron(III) citrate, iron(II) fumarate, iron(III) fumarate, iron(II) lactate, iron(III) lactate, iron(II) maleate, iron(III) maleate, iron(II) oxalate, iron(III) oxalate, iron(II) 2-ethylhexanoate, iron(III) 2-ethylhexanoate,
30 iron(II) neodecanoate, iron(III) neodecanoate, iron(II) naphthenate, iron(III) naphthenate, iron(II) stearate, iron(III) stearate, iron(II) oleate, iron(III)

oleate, iron(II) benzoate, iron(III) benzoate, iron(II) picolinate, and iron(III) picolinate.

Some specific examples of suitable iron β -diketonates include iron(II) acetylacetonate, iron(III) acetylacetonate, iron(II) trifluoroacetylacetonate, iron(III) trifluoroacetylacetonate, iron(II) hexafluoroacetylacetonate, iron(III) hexafluoroacetylacetonate, iron(II) benzoylacetonate, iron(III) benzoylacetonate, iron(II) 2,2,6,6-tetramethyl-3,5-heptanedionate, and iron(III) 2,2,6,6-tetramethyl-3,5-heptanedionate.

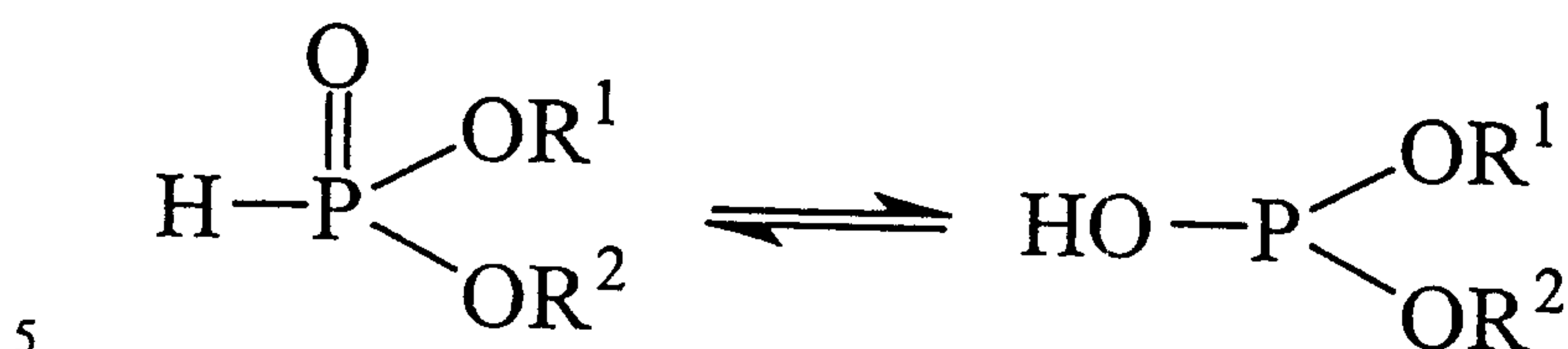
Some specific examples of suitable iron alkoxides or aryloxides include iron(II) methoxide, iron(III) methoxide, iron(II) ethoxide, iron(III) ethoxide, iron(II) isopropoxide, iron(III) isopropoxide, iron(II) 2-ethylhexoxide, iron(III) 2-ethylhexoxide, iron(II) phenoxide, iron(III) phenoxide, iron(II) nonylphenoxide, iron(III) nonylphenoxide, iron(II) naphthoxide, and iron(III) naphthoxide.

Some specific examples of suitable iron halides include iron(II) fluoride, iron(III) fluoride, iron(II) chloride, iron(III) chloride, iron(II) bromide, iron(III) bromide, and iron(II) iodide.

Some representative examples of suitable iron pseudo-halides include iron(II) cyanide, iron(III) cyanide, iron(II) cyanate, iron(III) cyanate, iron(II) thiocyanate, iron(III) thiocyanate, iron(II) azide, iron(III) azide, and iron(III) ferrocyanide (also called Prussian blue).

As used herein, the term "organoiron compounds" refers to any iron compound containing at least one covalent iron-carbon bond. Some specific examples of suitable organoiron compounds include bis(cyclopentadienyl)iron(II) (also called ferrocene), bis(pentamethylcyclopentadienyl)iron(II) (also called decamethylferrocene), bis(pentadienyl)iron(II), bis(2,4-dimethylpentadienyl)iron(II), bis(allyl)dicarbonyliron(II), (cyclopentadienyl)(pentadienyl)iron(II), tetra(1-norbornyl)iron(IV), (trimethylenemethane)tricarbonyliron(II), bis(butadiene)carbonyliron(II), (butadiene)tricarbonyliron(0), and bis(cyclooctatetraene)iron(0).

The component (b) of the catalyst composition of the present invention is a dihydrocarbyl hydrogen phosphite represented by the following keto-enol tautomeric structures:



Wherein R^1 and R^2 , which may be the same or different, are hydrocarbyl radicals selected from the group consisting of alkyl, cycloalkyl, aryl, aralkyl, alkaryl, and allyl groups; each group preferably containing from 1, or the appropriate minimum number of carbon atoms (often 3 or 6) to form such group, up to 20 carbon atoms. The dihydrocarbyl hydrogen phosphite exists mainly as the keto tautomer (shown on the left), with the enol tautomer (shown on the right) being the minor species. Either of the two tautomers or mixtures thereof can be used as the component (b) of the catalyst composition of the present invention. The equilibrium constant for the above-mentioned tautomeric equilibrium is dependent upon such factors as the temperature, the types of R^1 and R^2 groups, the type of solvent, and the like. Both tautomers may be associated in dimeric, trimeric or oligomeric forms by hydrogen bonding.

Some representative examples of suitable dihydrocarbyl hydrogen phosphites are dimethyl hydrogen phosphite, diethyl hydrogen phosphite, dibutyl hydrogen phosphite, dihexyl hydrogen phosphite, dioctyl hydrogen phosphite, didecyl hydrogen phosphite, didodecyl hydrogen phosphite, dioctadecyl hydrogen phosphite, bis(2,2,2-trifluoroethyl) hydrogen phosphite, diisopropyl hydrogen phosphite, bis(3,3-dimethyl-2-butyl) hydrogen phosphite, bis(2,4-dimethyl-3-pentyl) hydrogen phosphite, di-t-butyl hydrogen phosphite, bis(2-ethylhexyl) hydrogen phosphite, dineopentyl hydrogen phosphite, bis(cyclopropylmethyl) hydrogen phosphite, bis(cyclobutylmethyl) hydrogen phosphite,

bis(cyclopentylmethyl) hydrogen phosphite, bis(cyclohexylmethyl) hydrogen phosphite, dicyclobutyl hydrogen phosphite, dicyclopentyl hydrogen phosphite, dicyclohexyl hydrogen phosphite, dimethyl hydrogen phosphite, diphenyl hydrogen phosphite, dinaphthyl hydrogen phosphite, dibenzyl hydrogen phosphite, bis(1-naphthylmethyl) hydrogen phosphite, diallyl hydrogen phosphite, dimethallyl hydrogen phosphite, dicrotyl hydrogen phosphite, ethyl butyl hydrogen phosphite, methyl hexyl hydrogen phosphite, methyl neopentyl hydrogen phosphite, methyl phenyl hydrogen phosphite, methyl cyclohexyl hydrogen phosphite, methyl benzyl hydrogen phosphite, and the like. Mixtures of the above dihydrocarbyl hydrogen phosphites may also be utilized.

The catalyst composition of the present invention further comprises an organoaluminum compound as the component (c). As used herein, the term "organoaluminum compound" refers to any aluminum compound containing at least one covalent aluminum-carbon bond. It is generally advantageous to employ organoaluminum compounds that are soluble in the hydrocarbon polymerization medium. A preferred class of organoaluminum compounds that can be utilized in the catalyst composition of the present invention are represented by the general formula AlR_nX_{3-n} ($n = 1, 2$ or 3), wherein each R, which may be the same or different, is a hydrocarbyl radical selected from the group consisting of alkyl, cycloalkyl, aryl, aralkyl, alkaryl, and allyl groups and preferably contains from 1, or the appropriate minimum number of carbon atoms (often 3 or 6) to form such group, up to 20 carbon atoms, and each X, which may be the same or different, is a hydrogen; halogen, preferably chlorine or bromine; or alkoxide or aryloxy group having 1 or 6 to 20 carbon atoms. Thus suitable types of organoaluminum compounds that can be utilized in the catalyst composition of the present invention include, but are not limited to, trihydrocarbylaluminum, dihydrocarbylaluminum hydride, hydrocarbylaluminum dihydride, dihydrocarbylaluminum halide, hydrocarbylaluminum dihalide,

dihydrocarbylaluminum alkoxide, hydrocarbylaluminum dialkoxide, dihydrocarbylaluminum aryloxide, hydrocarbylaluminum diaryloxide, and the like, and mixtures thereof. Trihydrocarbylaluminum compounds are generally preferred.

5 Some specific examples of suitable organoaluminum compounds that can be utilized in the catalyst composition of the present invention include trimethylaluminum, triethylaluminum, triisobutylaluminum, tri-n-propylaluminum, triisopropylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum, tricyclohexylaluminum, triphenylaluminum, tri-p-
10 tolylaluminum, tribenzylaluminum, diethylphenylaluminum, diethyl-p-tolylaluminum, diethylbenzylaluminum, ethyldiphenylaluminum, ethyldi-p-tolylaluminum, ethyldibenzylaluminum, diethylaluminum hydride, di-n-propylaluminum hydride, diisopropylaluminum hydride, di-n-butylaluminum hydride, diisobutylaluminum hydride, di-n-octylaluminum
15 hydride, diphenylaluminum hydride, di-p-tolylaluminum hydride, dibenzylaluminum hydride, phenylethylaluminum hydride, phenyl-n-propylaluminum hydride, phenylisopropylaluminum hydride, phenyl-n-butylaluminum hydride, phenylisobutylaluminum hydride, phenyl-n-octylaluminum hydride, p-tolyethy-
20 laluminum hydride, p-tolylisopropylaluminum hydride, p-tolyl-n-butylaluminum hydride, p-tolylisobutylaluminum hydride, p-tolyl-n-octylaluminum hydride, benzylethylaluminum hydride, benzyl-n-propylaluminum hydride, benzylisopropylaluminum hydride, benzyl-n-butylaluminum hydride, benzylisobutylaluminum hydride, and benzyl-n-
25 octylaluminum hydride, ethylaluminum dihydride, n-propylaluminum dihydride, isopropylaluminum dihydride, n-butylaluminum dihydride, isobutylaluminum dihydride, n-octylaluminum dihydride, dimethylaluminum chloride, diethylaluminum chloride, dimethylaluminum bromide, diethylaluminum bromide, dimethylaluminum fluoride,
30 diethylaluminum fluoride, methylaluminum dichloride, ethylaluminum dichloride, methylaluminum dibromide, ethylaluminum dibromide,

5 methylaluminum difluoride, ethylaluminum difluoride, methylaluminum
sesquichloride, ethylaluminum sesquichloride, isobutylaluminum
sesquichloride, dimethylaluminum methoxide, diethylaluminum
methoxide, diisobutylaluminum methoxide, dimethylaluminum ethoxide,
10 diethylaluminum ethoxide, diisobutylaluminum ethoxide,
dimethylaluminum phenoxide, diethylaluminum phenoxide,
diisobutylaluminum phenoxide, methylaluminum dimethoxide,
ethylaluminum dimethoxide, isobutylaluminum dimethoxide,
methylaluminum diethoxide, ethylaluminum diethoxide, isobutylaluminum
15 diethoxide, methylaluminum diphenoxide, ethylaluminum diphenoxide,
isobutylaluminum diphenoxide, and the like, and mixtures thereof.

The catalyst composition of the present invention contains the
above-described three components (a), (b), and (c) as the main
components. In addition to the three catalyst components (a), (b), and
15 (c), other catalyst components such as other organometallic compounds,
which are known in the art, can also be added, if desired.

The catalyst composition of the present invention has very high
catalytic activity over a wide range of total catalyst concentrations and
catalyst component ratios. The three catalyst components (a), (b), and
20 (c) apparently interact to form the active catalyst species. Accordingly,
the optimum concentration for any one catalyst component is dependent
upon the concentrations of the other two catalyst components. While
polymerization will occur over a wide range of catalyst concentrations
and catalyst component ratios, the polymers having the most desirable
25 properties are obtained within a narrower range of catalyst
concentrations and catalyst component ratios.

The molar ratio of the dihydrocarbyl hydrogen phosphite to the
iron-containing compound (P/Fe) in the catalyst composition of the
present invention can be varied from about 0.5:1 to about 50:1, with a
30 more preferred range being from about 1:1 to about 25:1 and a most
preferred range being from about 2:1 to about 10:1. The molar ratio of

the organoaluminum compound to the iron-containing compound (Al/Fe) can be varied from about 1:1 to about 100:1. However, a more preferred range of Al/Fe molar ratio is from about 3:1 to about 50:1, and a most preferred range is from about 5:1 to about 20:1.

5 The total catalyst concentration in the polymerization mass depends on such factors as the purity of the components, the polymerization rate and conversion desired, the polymerization temperature, and the like. Accordingly, specific total catalyst concentrations cannot be definitively set forth except to say that
10 catalytically effective amounts of the respective catalyst components should be used. Generally, the amount of the iron-containing compound used can be varied from about 0.01 to about 2 mmol per 100 g of 1,3-butadiene, with a more preferred range being from about 0.02 to about 1.0 mmol per 100 g of 1,3-butadiene and a most preferred range being
15 from about 0.05 to about 0.5 mmol per 100 g of 1,3-butadiene. Certain specific total catalyst concentrations and catalyst component ratios that produce polymers having desired properties will be illustrated in the examples given to explain the teachings of the present invention.

 The three catalyst components of this invention may be
20 introduced into the polymerization system in several different ways. Thus, the catalyst may be formed in situ by adding the three catalyst components to the monomer/solvent mixture in either a stepwise or simultaneous manner; the sequence in which the components are added in a stepwise manner is not critical but the components are preferably
25 added in the sequence of iron-containing compound, dihydrocarbyl hydrogen phosphite, and finally organoaluminum compound. Alternatively, the three catalyst components may also be premixed outside the polymerization system at an appropriate temperature (e.g., from about -20 °C to about 80 °C), and the resulting mixture then
30 added to the polymerization system. Additionally, the catalyst may also be preformed, that is, the three catalyst components are premixed in the

presence of a small amount of 1,3-butadiene monomer at an appropriate temperature (e.g., from about -20 °C to about 80 °C), prior to being charged to the main portion of the monomer/solvent mixture that is to be polymerized. The amount of 1,3-butadiene monomer which is used for the catalyst preforming can range from about 1 to about 500 moles per mole of the iron-containing compound, and preferably should be from about 4 to about 50 moles per mole of the iron-containing compound. In addition, the three catalyst components may also be introduced to the polymerization system using a two-stage procedure. This procedure involves first reacting the iron-containing compound with the organoaluminum compound in the presence of a small amount, as specified above, of 1,3-butadiene monomer at an appropriate temperature (e.g., from about -20 °C to about 80 °C). The resultant reaction mixture and the dihydrocarbyl hydrogen phosphite are then added to the main portion of the monomer/solvent mixture in either a stepwise or simultaneous manner. Further, an alternative two-stage procedure may also be employed. This involves first reacting the iron-containing compound with the dihydrocarbyl hydrogen phosphite at an appropriate temperature (e.g., from about -20 °C to about 80 °C) to form an iron complex, followed by adding the resultant iron complex and the organoaluminum compound to the monomer/solvent mixture in either a stepwise or simultaneous manner.

When a solution of a catalyst component is prepared outside the polymerization system, the organic solvent usable for the catalyst component solution may be selected from aromatic hydrocarbons, aliphatic hydrocarbons and cycloaliphatic hydrocarbons, and mixtures of two or more of the above-mentioned hydrocarbons. Preferably, the organic solvent consists of at least one selected from benzene, toluene, xylene, hexane, heptane and cyclohexane.

As described hereinabove, the iron-based catalyst composition of the present invention containing the three catalyst components (a), (b),

and (c) exhibits a very high catalytic activity for the production of syndiotactic 1,2-polybutadiene. Hence, the present invention further provides a process for producing syndiotactic 1,2-polybutadiene by the use of the above-described iron-based catalyst composition.

5 The production of syndiotactic 1,2-polybutadiene according to the process of the present invention is put into practice by polymerizing 1,3-butadiene monomer in the presence of an iron-based catalyst composition comprising the foregoing three catalyst components (a), (b), and (c). As described above, there are available a variety of methods for
10 bringing the three components of the catalyst composition of the present invention into contact with 1,3-butadiene monomer.

In accordance with the process of the present invention, the polymerization of 1,3-butadiene monomer may be carried out by means of bulk polymerization, wherein no solvents are employed. Such bulk
15 polymerization can be conducted either in a condensed liquid phase or in a gas phase.

Alternatively and more typically, the polymerization of 1,3-butadiene according to the process of the present invention is carried out in an organic solvent as the diluent. In such cases, a solution
20 polymerization system may be employed in which both the 1,3-butadiene monomer to be polymerized and the polymer formed are soluble in the polymerization medium. Alternatively, a suspension polymerization system may be employed by choosing a solvent in which the polymer formed is insoluble. In both cases, an amount of the organic solvent in
25 addition to the organic solvent contained in the catalyst component solutions is usually added to the polymerization system. The additional organic solvent may be either the same as or different from the organic solvent contained in the catalyst component solutions. It is normally desirable to select an organic solvent that is inert with respect to the
30 catalyst composition employed to catalyze the polymerization. Suitable types of organic solvents that can be utilized as the diluent include, but

are not limited to, aliphatic, cycloaliphatic, and aromatic hydrocarbons. Some representative examples of suitable aliphatic solvents include n-pentane, n-hexane, n-heptane, n-octane, n-nonane, n-decane, isopentane, isohexanes, isoheptanes, isooctanes, 2,2-dimethylbutane, petroleum ether, kerosene, petroleum spirits, and the like. Some
5 representative examples of suitable cycloaliphatic solvents include cyclopentane, cyclohexane, methylcyclopentane, methylcyclohexane, and the like. Some representative examples of suitable aromatic solvents include benzene, toluene, xylenes, ethylbenzene,
10 diethylbenzene, mesitylene, and the like. Commercial mixtures of the above hydrocarbons may also be used. For environmental reasons, aliphatic and cycloaliphatic solvents are highly preferred.

The concentration of the 1,3-butadiene monomer to be polymerized is not limited to a special range. However, generally, it is
15 preferable that the concentration of the 1,3-butadiene monomer present in the polymerization medium at the beginning of the polymerization be in a range of from about 3% to about 80% by weight, but a more preferred range is from about 5% to about 50% by weight, and the most preferred range is from about 10% to about 30% by weight.

20 In performing the polymerization of 1,3-butadiene according to the process of the present invention, a molecular weight regulator may be employed to control the molecular weight of the syndiotactic 1,2-polybutadiene to be produced. As a result, the scope of the polymerization system can be expanded in such a manner that it can be
25 used for the production of syndiotactic 1,2-polybutadiene ranging from an extremely high molecular weight polymer to a low molecular weight polymer. Suitable types of molecular weight regulators that can be utilized include, but are not limited to, accumulated diolefins such as allene and 1,2-butadiene; nonconjugated diolefins such as 1,6-octadiene,
30 5-methyl-1,4-hexadiene, 1,5-cyclooctadiene, 3,7-dimethyl-1,6-octadiene, 1,4-cyclohexadiene, 4-vinylcyclohexene, 1,4-pentadiene, 1,4-hexadiene,

1,5-hexadiene, 1,6-heptadiene, 1,2-divinylcyclohexane, 5-ethylidene-2-norbornene, 5-methylene-2-norbornene, 5-vinyl-2-norbornene, dicyclopentadiene, and 1,2,4-trivinylcyclohexane; acetylenes such as acetylene, methylacetylene and vinylacetylene; and mixtures thereof.

5 The amount of the molecular weight regulator used, expressed in parts per hundred parts by weight of the 1,3-butadiene monomer (phm) employed in the polymerization, is in the range of about 0.01 to about 10 phm, preferably in the range of about 0.02 to about 2 phm, and most preferably in the range of about 0.05 to about 1 phm. In addition, the
10 molecular weight of the syndiotactic 1,2-polybutadiene product to be obtained can also be effectively controlled by performing the polymerization of the 1,3-butadiene monomer in the presence of hydrogen. In this case, the partial pressure of hydrogen is appropriately chosen within the range of about 0.01 to about 50 atmospheres.

15 In accordance with the process of the present invention, the polymerization 1,3-butadiene may be carried out as a batch process, on a semi-continuous basis, or on a continuous basis. In any case, the polymerization is conducted under anaerobic conditions using an inert protective gas such as nitrogen, argon or helium, with moderate to
20 vigorous agitation. The polymerization temperature employed in the practice of this invention may vary widely from a low temperature, such as -10 °C or below, to a high temperature such as 100 °C or above, with a preferred temperature range being from about 20 °C to about 90 °C. The heat of polymerization may be removed by external cooling, cooling
25 by evaporation of the 1,3-butadiene monomer or the solvent, or a combination of the two methods. Although the polymerization pressure employed in the practice of this invention also may vary widely, a preferred pressure range is from about 1 atmosphere to about 10 atmospheres.

30 The polymerization reaction of the present invention, on reaching a desired conversion, can be stopped by addition of a known

polymerization terminator into the polymerization system to inactivate the catalyst system, followed by the conventional steps of removing solvent and drying as are typically employed and are known to those skilled in the art in the production of conjugated diene polymers.

5 Typically, the terminator employed to inactivate the catalyst system is a protic compound, which includes, but is not limited to, an alcohol, a carboxylic acid, an inorganic acid, and water or a combination thereof. An antioxidant such as 2,6-di-*tert*-butyl-4-methylphenol may be added along with, before or after addition of the terminator. The amount of the
10 antioxidant employed is usually in the range of 0.2% to 1% by weight of the polymer product. When the polymerization reaction has been stopped, the syndiotactic 1,2-polybutadiene product may be isolated from the polymerization mixture by precipitation with an alcohol such as methanol, ethanol, or isopropanol or by steam distillation of the solvent
15 and the unreacted 1,3-butadiene monomer, followed by filtration. The product is then dried under a constant vacuum at a temperature within the range of about 25 °C to about 100 °C (preferably at about 60 °C).

The syndiotactic 1,2-polybutadiene made utilizing the catalyst composition of the present invention can have various melting
20 temperatures, which are dependent upon the catalyst components and the component ratios. Desirably, the melting temperature varies from about 90 to about 215 °C, more desirably from about 100 to about 200 °C, and preferably from about 110 to about 190 °C. The 1,2-linkage content is desirably from about 50 to about 99%, more desirably from
25 about 60 to about 98%, and preferably from about 70 to about 98%. The syndiotacticity is desirably from about 50 to about 99%, more desirably from about 60 or 70 to about 98%.

The syndiotactic 1,2-polybutadiene produced with the catalyst composition of the present invention has many uses. It can be blended
30 with various rubbers in order to improve the properties thereof. For

example, it can be incorporated into elastomers in order to improve the green strength of those elastomers, particularly in tires. The supporting carcass (reinforcing carcass) of tires is particularly prone to distortion during tire building and curing procedures. For this reason the
5 incorporation of the syndiotactic 1,2-polybutadiene into rubber compositions, which are utilized in the supporting carcass of tires, has particular utility in preventing or minimizing this distortion. In addition, the incorporation of the syndiotactic 1,2-polybutadiene into tire tread compositions can reduce the heat build-up and improve the wear
10 characteristics of tires. The syndiotactic 1,2-polybutadiene product is also useful in the manufacture of food films and in many molding applications.

The practice of the present invention is further illustrated by reference to the following examples which however, should not be
15 construed as limiting the scope of the invention. Parts and percentages shown in the examples are by weight unless otherwise indicated.

Example 1

20 An oven-dried 1-liter glass bottle was capped with a self-sealing rubber liner and a perforated metal cap and purged with a stream of dry nitrogen. The bottle was charged with 64 g of hexanes and 186 g of a 1,3-butadiene/hexanes blend containing 26.9% by weight of
25 1,3-butadiene. The following catalyst components were added to the bottle in the following order: (1) 0.050 mmol of iron(II) 2-ethylhexanoate, (2) 0.20 mmol of bis(2-ethylhexyl) hydrogen phosphite, and (3) 0.75 mmol of triisobutylaluminum. The bottle was tumbled for 4 hours in a water bath maintained at 50 °C. The
30 polymerization was terminated by addition of 10 ml of isopropanol containing 0.5 g of 2,6-di-*tert*-butyl-4-methylphenol. The polymerization

mixture was added into 3 liters of isopropanol. The polymer was isolated by filtration and dried to a constant weight under vacuum at 60 °C. The yield of the polymer was 47.5 g (95%). As measured by differential scanning calorimetry (DSC), the polymer had a melting
5 temperature of 187 °C. ¹H and ¹³C nuclear magnetic resonance (NMR) analysis of the polymer indicated a 1,2-linkage content of 90.9% and a syndiotacticity of 93.7%. As determined by gel permeation chromatography (GPC), the polymer had a weight average molecular weight (M_w) of 1,288,000, a number average molecular weight (M_n) of
10 650,000, and a polydispersity index (M_w/M_n) of 1.9. The monomer charge, the amounts of catalyst components and the properties of the resultant syndiotactic 1,2-polybutadiene are summarized in Table I.

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Examples 2-6

In Examples 2-6, the procedure in Example 1 was repeated except that the catalyst ratio was varied as shown in Table I. The monomer charge, the amounts of catalyst components, and the properties of the
20 resultant syndiotactic 1,2-polybutadiene produced in each example are summarized in Table I.

Table I

Example No.	1	2	3	4	5	6
Hexanes	64	64	64	64	64	64
26.9% 1,3-Bd/hexanes (g)	186	186	186	186	186	186
Fe(2-EHA) ₂ (mmol)	0.050	0.050	0.050	0.050	0.050	0.050
HP(O)(OCH ₂ CH(Et)(CH ₂) ₃ CH ₃) ₂ (mmol)	0.20	0.20	0.20	0.20	0.20	0.20
<i>i</i> -Bu ₃ Al (mmol)	0.75	0.60	0.65	0.70	0.80	0.85
Fe/P/Al molar ratio	1:4:15	1:4:12	1:4:13	1:4:14	1:4:16	1:4:17
Polymer yield (%) after 4 hr at 50 °C	95	95	96	94	95	95
Melting point (°C)	187	184	186	187	187	187
M _w	1,228,000	688,000	1,022,000	1,161,000	1,033,000	1,065,000
M _n	650,000	180,000	258,000	701,000	413,000	410,000
M _w /M _n	1.9	3.8	4.0	1.7	2.5	2.6

Examples 7-13

5 In Examples 7-13, the procedure in Example 1 was repeated
except that iron(III) 2-ethylhexanoate was substituted for iron(II)
2-ethylhexanoate, having the catalyst ratio varied as shown in Table II.
The monomer charge, the amounts of catalyst components, and the
properties of the resultant syndiotactic 1,2-polybutadiene produced in
10 each example are summarized in Table II.

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20

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Table II

Example No.	7	8	9	10	11	12	13
Hexanes	64	64	64	64	64	64	64
26.9% 1,3-Bd/hexanes (g)	186	186	186	186	186	186	186
Fe(2-EHA) ₃ (mmol)	0.050	0.050	0.050	0.050	0.050	0.050	0.050
HP(O)(OCH ₂ CH(Et)(CH ₂) ₃ CH ₃) ₂ (mmol)	0.20	0.20	0.20	0.20	0.20	0.20	0.20
<i>i</i> -Bu ₃ Al (mmol)	0.50	0.55	0.60	0.65	0.70	0.75	0.80
Fe/P/Al molar ratio	1:4:10	1:4:11	1:4:12	1:4:13	1:4:14	1:4:15	1:4:16
Polymer yield (%) after 4 hr at 50 °C	96	97	95	96	97	96	97
Melting point (°C)	182	185	186	187	188	188	188
M _w	422,000	464,000	599,000	664,000	855,000	916,000	971,000
M _n	155,000	159,000	239,000	310,000	491,000	365,000	545,000
M _w /M _n	2.7	2.9	2.5	2.1	1.7	2.5	1.8

Examples 14-20

In Examples 14-20, the procedure in Example 1 was repeated except
5 that iron(III) 2-ethylhexanoate was substituted for iron(II)
2-ethylhexanoate, and dineopentyl hydrogen phosphite was substituted
for bis(2-ethylhexyl) hydrogen phosphite, having the catalyst ratio varied
as shown in Table III. The monomer charge, the amounts of catalyst
components, and the properties of the resultant syndiotactic 1,2-
10 polybutadiene produced in each example are summarized in Table III.

Table III

Example No.	14	15	16	17	18	19	20
Hexanes	64	64	64	64	64	64	64
26.9% 1,3-Bd/hexanes (g)	186	186	186	186	186	186	186
Fe(2-EHA) ₃ (mmol)	0.050	0.050	0.050	0.050	0.050	0.050	0.050
HP(O)(OCH ₂ CMe ₃) ₂ (mmol)	0.20	0.20	0.20	0.20	0.20	0.20	0.20
<i>i</i> -Bu ₃ Al (mmol)	0.55	0.60	0.65	0.70	0.75	0.80	0.85
Fe/P/Al molar ratio	1:4:11	1:4:12	1:4:13	1:4:14	1:4:15	1:4:16	1:4:17
Polymer yield (%) after 4 hr at 50 °C	95	97	95	96	95	95	92
Melting point (°C)	168	183	188	191	191	191	191
M _w	704,000	1,027,000	1,050,000	956,000	1,185,000	1,190,000	1,198,000
M _n	228,000	564,000	609,000	419,000	657,000	623,000	592,000
M _w /M _n	3.1	1.8	1.7	2.3	1.8	1.90	2.0

Examples 21-26

In Examples 21-26, the procedure in Example 1 was repeated
5 except that iron(III) 2-ethylhexanoate was substituted for iron(II)
2-ethylhexanoate, and dibutyl hydrogen phosphite was substituted for
bis(2-ethylhexyl) hydrogen phosphite, having the catalyst ratio varied as
shown in Table IV. The monomer charge, the amounts of catalyst
components, and the properties of the resultant syndiotactic 1,2-
10 polybutadiene produced in each example are summarized in Table IV.

Table IV

Example No.	21	22	23	24	25	26
Hexanes	64	64	64	64	64	64
26.9% 1,3-Bd/hexanes (g)	186	186	186	186	186	186
Fe(2-EHA) ₃ (mmol)	0.050	0.050	0.050	0.050	0.050	0.050
HP(O)(OBu) ₂ (mmol)	0.20	0.20	0.20	0.20	0.20	0.20
<i>i</i> -Bu ₃ Al (mmol)	0.60	0.65	0.70	0.75	0.80	0.85
Fe/P/Al molar ratio	1:4:12	1:4:13	1:4:14	1:4:15	1:4:16	1:4:17
Polymer yield (%) after 4 hr at 50 °C	94	97	97	98	96	95
Melting point (°C)	181	181	181	181	182	181
M _w	750,000	956,000	853,000	756,000	858,000	869,000
M _n	287,000	548,000	477,000	467,000	463,000	548,000
M _w /M _n	2.6	1.8	1.8	1.6	1.9	1.6

Examples 27-31

In Examples 27-31, the procedure in Example 1 was repeated
5 except that iron(III) 2-ethylhexanoate was substituted for iron(II)
2-ethylhexanoate, and dimethyl hydrogen phosphite was substituted for
bis(2-ethylhexyl) hydrogen phosphite, having the catalyst ratio varied as
shown in Table V. The monomer charge, the amounts of catalyst
components, and the properties of the resultant syndiotactic 1,2-
10 polybutadiene produced in each example are summarized in Table V.

Table V

Example No.	27	28	29	30	31
Hexanes	64	64	64	64	64
26.9% 1,3-Bd/hexanes (g)	186	186	186	186	186
Fe(2-EHA) ₃ (mmol)	0.050	0.050	0.050	0.050	0.050
HP(O)(OCH ₃) ₂ (mmol)	0.20	0.20	0.20	0.20	0.20
<i>i</i> -Bu ₃ Al (mmol)	0.65	0.70	0.75	0.80	0.85
Fe/P/Al molar ratio	1:4:13	1:4:14	1:4:15	1:4:16	1:4:17
Polymer yield (%) after 4 hr at 50 °C	86	94	96	91	89
Melting point (°C)	177	176	176	176	177
M _w	780,000	851,000	861,000	802,000	815,000
M _n	409,000	460,000	580,000	466,000	497,000
M _w /M _n	1.9	1.8	1.5	1.7	1.6

Examples 32-38

5 In Examples 32-38, the procedure in Example 1 was repeated
except that iron(III) acetylacetonate was substituted for iron(II)
2-ethylhexanoate, having the catalyst ratio varied as shown in Table VI.
The monomer charge, the amounts of catalyst components, and the
properties of the resultant syndiotactic 1,2-polybutadiene produced in
10 each example are summarized in Table VI.

Table VI

Example No.	32	33	34	35	36	37	38
Hexanes	64	64	64	64	64	64	64
26.9% 1,3-Bd/hexanes (g)	186	186	186	186	186	186	186
Fe(acac) ₃ (mmol)	0.050	0.050	0.050	0.050	0.050	0.050	0.050
HP(O)(OCH ₂ CH(Et)(CH ₂) ₃ CH ₃) ₂ (mmol)	0.20	0.20	0.20	0.20	0.20	0.20	0.20
<i>i</i> -Bu ₃ Al (mmol)	0.55	0.60	0.65	0.70	0.75	0.80	0.85
Fe/P/Al molar ratio	1:4:11	1:4:12	1:4:13	1:4:14	1:4:15	1:4:16	1:4:17
Polymer yield (%) after 4 hr at 50 °C	96	96	96	95	96	95	97
Melting point (°C)	187	187	187	187	187	188	188
M _w	1,124,000	1,150,000	1,146,000	1,151,000	1,196,000	1,578,000	1,187,000
M _n	491,000	543,000	559,000	639,000	678,000	793,000	468,000
M _w /M _n	2.3	2.1	2.1	1.8	1.8	2.0	2.5

Examples 39-45

5 In Examples 39-45, the procedure in Example 1 was repeated
except that iron(III) acetylacetonate was substituted for iron(II)
2-ethylhexanoate, and dineopentyl hydrogen phosphite was substituted
for bis(2-ethylhexyl) hydrogen phosphite, having the catalyst ratio varied
as shown in Table VII. The monomer charge, the amounts of catalyst
10 components, and the properties of the resultant syndiotactic 1,2-
polybutadiene produced in each example are summarized in Table VII.

Table VII

Example No.	39	40	41	42	43	44	45
Hexanes	64	64	64	64	64	64	64
26.9% 1,3-Bd/hexanes (g)	186	186	186	186	186	186	186
Fe(acac) ₃ (mmol)	0.050	0.050	0.050	0.050	0.050	0.050	0.050
HP(O)(OCH ₂ CMe ₃) ₂ (mmol)	0.20	0.20	0.20	0.20	0.20	0.20	0.20
<i>i</i> -Bu ₃ Al (mmol)	0.55	0.60	0.65	0.70	0.75	0.80	0.85
Fe/P/Al molar ratio	1:4:11	1:4:12	1:4:13	1:4:14	1:4:15	1:4:16	1:4:17
Polymer yield (%) after 4 hr at 50 °C	97	95	93	92	90	88	87
Melting point (°C)	182	185	190	190	191	192	192
M _w	634,000	624,000	943,000	1,227,000	994,000	1,117,000	968,000
M _n	241,000	312,000	408,000	707,000	572,000	674,000	475,000
M _w /M _n	2.6	2.5	2.3	1.7	1.7	1.7	2.0

Examples 46-52

In Examples 46-52, the procedure in Example 1 was repeated
5 except that iron(III) acetylacetonate was substituted for iron(II)
2-ethylhexanoate, and triethylaluminum was substituted for
triisobutylaluminum, having the catalyst ratio varied as shown in Table
VIII. The monomer charge, the amounts of catalyst components, and
the properties of the resultant syndiotactic 1,2-polybutadiene produced
10 in each example are summarized in Table VIII. ^1H and ^{13}C NMR analysis
of the polymer produced in Example 48 indicated a 1,2-linkage content
of 84.6% and a syndiotacticity of 74.5%.

Table VIII

Example No.	46	47	48	49	50	51	52
Hexanes	64	64	64	64	64	64	64
26.9% 1,3-Bd/hexanes (g)	186	186	186	186	186	186	186
Fe(acac) ₃ (mmol)	0.050	0.050	0.050	0.050	0.050	0.050	0.050
HP(O)(OCH ₂ CH(Et)(CH ₂) ₃ CH ₃) ₂ (mmol)	0.20	0.20	0.20	0.20	0.20	0.20	0.20
AlEt ₃ (mmol)	0.55	0.60	0.65	0.70	0.75	0.80	0.85
Fe/P/Al molar ratio	1:4:11	1:4:12	1:4:13	1:4:14	1:4:15	1:4:16	1:4:17
Polymer yield (%) after 4 hr at 50 °C	92	97	95	98	88	83	54
Melting point (°C)	115	127	128	128	130	131	131
M _w	284,000	276,000	269,000	238,000	275,000	328,000	298,000
M _n	116,000	131,000	102,000	110,000	96,000	108,000	83,000
M _w /M _n	2.5	2.1	2.6	2.2	2.9	3.0	3.6

Examples 53-58

In Examples 53-58, the procedure in Example 1 was repeated
5 except that iron(III) acetylacetonate was substituted for iron(II)
2-ethylhexanoate, dineopentyl hydrogen phosphite was substituted for
bis(2-ethylhexyl) hydrogen phosphite, and triethylaluminum was
substituted for triisobutylaluminum, having the catalyst ratio varied as
shown in Table IX. The monomer charge, the amounts of catalyst
10 components, and the properties of the resultant syndiotactic
1,2-polybutadiene produced in each example are summarized in Table IX.

Table IX

Example No.	53	54	55	56	57	58
Hexanes	64	64	64	64	64	64
26.9% 1,3-Bd/hexanes (g)	186	186	186	186	186	186
Fe(acac) ₃ (mmol)	0.050	0.050	0.050	0.050	0.050	0.050
HP(O)(OCH ₂ CMe ₃) ₂ (mmol)	0.20	0.20	0.20	0.20	0.20	0.20
AlEt ₃ (mmol)	0.55	0.60	0.65	0.70	0.75	0.80
Fe/P/Al molar ratio	1:4:11	1:4:12	1:4:13	1:4:14	1:4:15	1:4:16
Polymer yield (%) after 4 hr at 50 °C	86	91	92	88	72	46
Melting point (°C)	129	129	132	132	133	133
M _w	162,000	180,000	203,000	243,000	298,000	356,000
M _n	67,000	81,000	86,000	103,000	129,000	154,000
M _w /M _n	2.4	2.2	2.4	2.3	2.3	2.3

Example 59

Inside a glovebox operated under a nitrogen atmosphere, 32.4 mg
5 (0.20 mmol) of anhydrous iron(III) chloride powder was charged to into
an oven-dried 1-liter glass bottle. The bottle was capped with a self-
sealing rubber liner and a perforated metal cap and then removed from
the glovebox. The bottle was charged with 132 g of hexanes and 368 g
of a 1,3-butadiene/hexanes blend containing 27.2% by weight of 1,3-
10 butadiene, followed by 0.80 mmol of bis(2-ethylhexyl) hydrogen
phosphite and 2.80 mmol of triisobutylaluminum. The bottle was
tumbled for 4 hours in a water bath maintained at 50 °C. Workup of the
polymerization mixture in a manner similar to that described in Example 1
gave 37.2 g (37% yield) of the polymer. As measured by DSC, the
15 polymer had a melting temperature of 168 °C. As determined by GPC,
the polymer had a weight average molecular weight (M_w) of 871,000, a
number average molecular weight (M_n) of 329,000, and a polydispersity
index (M_w/M_n) of 2.6.

Although the present invention has been described in the above
20 examples with reference to particular means, materials and
embodiments, it would be obvious to persons skilled in the art that
various changes and modifications may be made, which fall within the
scope claimed for the invention as set out in the appended claims. The
invention is therefore not limited to the particulars disclosed and extends
25 to all equivalents within the scope of the claims.

CLAIMS:

1. A catalyst composition comprising:
 - a) an iron-containing compound;
 - b) a dihydrocarbyl hydrogen phosphite; and
 - c) an organoaluminum compound.
2. The catalyst composition of claim 1 wherein the iron of said iron-containing compound has an oxidation state of 0, +2, +3, or +4.
3. The catalyst composition of any of claims 1 to 2 wherein said iron-containing compound comprises an iron carboxylate, iron β -diketonate, iron alkoxide, iron aryloxide, iron halide, iron pseudo-halide, or organoiron compound.
4. The catalyst composition of any of claims 1 to 3 wherein said dihydrocarbyl hydrogen phosphite has the keto-enol tautomeric structure



wherein R^1 and R^2 are independently selected from an alkyl group having 1 to 20 carbon atoms, an allyl or cycloalkyl group having 3 to 20 carbon atoms, or an aryl, aralkyl, or alkaryl group having 6 to 20 carbon atoms.

5. The catalyst composition of any of claims 1 to 4 wherein said organoaluminum compound has the formula $\text{AlR}_n\text{X}_{3-n}$, where n is 1, 2 or 3; each R individually is an alkyl group having 1 to 20 carbon atoms, an allyl or cycloalkyl group having 3 to 20 carbon atoms or an aryl, aralkyl, or alkaryl group having 6 to 20 carbon atoms; and each X individually is a hydrogen, halogen, alkoxide group having 1 to 20 carbon atoms, or aryloxide group having 6 to 20 carbon atoms.

6. The catalyst composition of any of claims 1 to 5 wherein the molar ratio of said dihydrocarbyl hydrogen phosphite to said iron-containing compound is from 1:1 to 25:1.

7. The catalyst composition of any of claims 1 to 6 wherein the molar ratio of said organoaluminum compound to said iron-containing compound is from 3:1 to 50:1.

8. The catalyst composition of any of claims 1 to 5 wherein the molar ratio of said dihydrocarbyl hydrogen phosphite to said iron-containing compound is from 0.5:1 to 50:1 and the molar ratio of said organoaluminum compound to said iron-containing compound is from 1:1 to 100:1.

9. A process for forming syndiotactic 1,2-polybutadiene comprising polymerizing 1,3-butadiene in the presence of a catalytically effective amount of the catalyst composition of any of claims 1 to 8, optionally in the presence of a molecular weight regulator.

10. The process of claim 9 wherein at least one of the following is true:
the iron-containing compound is present in the polymerization in an amount from about 0.01 to about 2 mmol per 100 g of said 1,3-butadiene, and
said syndiotactic 1,2-polybutadiene has

- (1) a melting temperature from 110° to 190°C,
- (2) a 1,2-linkage content from 60 to 98%, and
- (3) a syndiotacticity from about 60% to about 98%.