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(54) Title: SOLUTION POLYMERIZATION/CO-POLYMERIZATION OF DIENES, HYDROGENATION OF DIENERUBBERS AND HYDROGENATED DIENERUBBERS

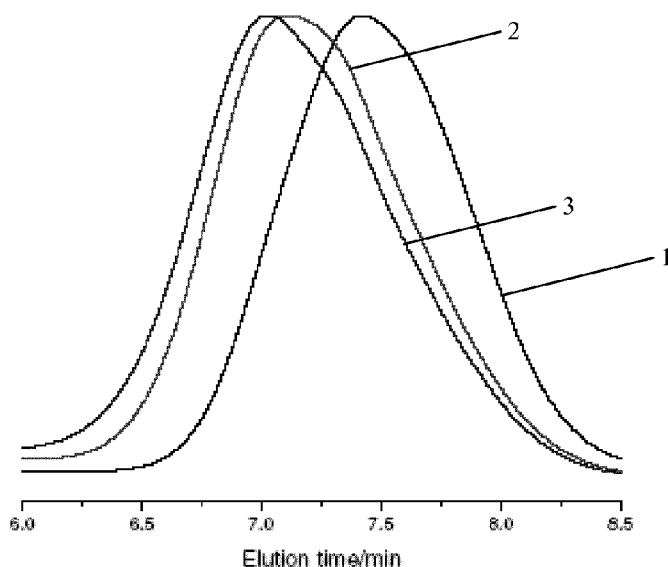


Fig. 1

(57) Abstract: The present invention relates to butadiene rubber polymers having low molecular weights and narrower molecular weight distributions than those known in the art. The present invention also relates to a metal-containing catalyst system, a solution polymerization process for the manufacture of said butadiene rubber, a one-pot process for the synthesis of the hydrogenated diene polymers, and a process for the hydrogenation of diene polymers.



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**SOLUTION POLYMERIZATION/CO-POLYMERIZATION OF DIENES,
HYDROGENATION OF DIENERUBBERS AND HYDROGENATED DIENERUBBERS**

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FIELD OF THE INVENTION

This invention generally relates to solution polymerization/co-polymerization of dienes, specifically relates to a catalyst system for the solution polymerization/co-polymerization of diene and vinyl monomers and/or the hydrogenation of the obtained diene rubbers based polymers either in a one-pot manner or in a two-step manner, a process for the solution
10 polymerization/co-polymerization of diene and vinyl monomers in the presence of metal catalysts system, as well as the hydrogenation of the obtained diene rubbers based polymers either in a one-pot manner or in a two-step manner, diene rubber polymers obtained by the solution polymerization and/or the hydrogenation of the obtained diene rubber based polymers either in a one-pot manner or in a two-step manner.

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BACKGROUND OF THE INVENTION

Butadiene rubber (BR) is a common synthetic rubber obtained by polymerizing monomer of 1,3-diene. Butadiene rubbers are commonly polymerized butadiene in solution, including anionic polymerization and coordination polymerization.

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Styrene-butadiene rubber (SBR) may be polymerized in solution (such as anionic polymerization), so-called SSBR. Styrene-butadiene rubber (SBR) may also be polymerized in emulsion, so-called ESBR.

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Nitrile butadiene rubber (NBR) is commonly produced by free-radical emulsion polymerization. Nitrile butadiene rubber (NBR), a co-polymer comprising at least one conjugated diene, butadiene, at least one unsaturated nitrile and optionally further comonomers, is a specialty
rubber, which has good chemical resistance, and excellent oil resistance. Coupled with the high level of mechanical properties of the rubber (in particular the high resistance to abrasion) it is not surprising that NBR has found widespread use in the automotive (seals, hoses, bearing pads), electrical (cable sheathing), mechanical engineering (wheels, rollers) and footwear industries, amongst others.

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Currently, NBR is made by a radical emulsion polymerization process which produces NBR polymer with a relatively broad molecular weight distribution and with a certain level of emulsifier residues. Generally, NBR obtained by this process has a Mooney viscosity in the arrange of from 30 to 90, an Mn in the range of from 80,000 to 150,000, an Mw in the arrange of from 250,000 to 350,000 and a polydispersity index greater than 3.2.

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A metal compound catalyzed solution polymerization process could produce NBR with higher purity and more controlled molecular structure.

Furthermore, hydrogenated nitrile butadiene rubber (HNBR) polymer is manufactured by the hydrogenation of NBR in a solution process - the NBR polymer was first coagulated from latex,

cleaned and dried then dissolved in a solvent for hydrogenation. When NBR polymer (which is made by a radical emulsion polymerization process) is hydrogenated, the Mooney viscosity of HNBR polymer will increase up to 60-120.

5 Since NBR is produced in latex form after the emulsion polymerization (E-NBR) and the hydrogenation of NBR in plant production is technically only feasible in organic solutions, the present commercial HNBR production involves a number of cumbersome steps to obtain clean solid NBR from the latex and subsequent dissolution of the NBR in organic solvents. Also, due to the limitation of the E-NBR finishing process, the supply of low Mooney Viscosity (MV) NBR feedstocks for making low MV HNBR is limited; LANXESS developed the metathesis
10 process to produce Therban AT with low MV for improved processibility. However, the additional metathesis process increases the production costs.

In the past two decades, controlled radical polymerization (CRP), including ATRP, NOMP, RAFT and iniferter, has attracted many attentions because it opens an avenue to the production of well-defined polymers with precisely designed molecular architectures in a relatively easy
15 way (not as sensitive to moisture/air/impurities as in the living anionic polymerization) (Chem. Rev. 2001, 101, 2921-2990; Chem. Rev. 2001, 101, 3689-3745; Chem. Rev., 2001, 101, 3661-3688; Prog. Polym. Sci. 2007, 32, 93-146).

In general, comparing to (meth)acrylic vinyl vinylidene type of monomers, dienes were considered to be much more difficult to be polymerized via CRP. There are only several reports
20 about the controlled radical homo- or co-polymerization of dienes. ((a) ATRP: *J. Ind. Eng. Chem.*, 2005, 11(6), 911-917; *J. Ind. Eng. Chem.*, 2006, 12(2), 241.; (b) RAFT: *Macromolecules*, 2007, 40, 1408; *J. Polymer Sci. Part A: Polymer Chem.* 2007, 45, 4100; *Macromol. Rapid Commun.* 2010, 31, 1616-1621. (c) NOMP: *Macromolecules*, 1998, 31, 7559; *Macromolecules*, 2000, 33, 363).

25 The mentioned polymerization processes used different types metal catalysts, it is needed to provide a catalyst system for the solution polymerization/co-polymerization of diene and vinyl monomers and/or the hydrogenation of the obtained diene rubbers based polymers either in a one-pot manner or in a two-step manner having controlled molecular weights, narrower molecular weight distributions and a Mooney viscosity in the arrange of from more than 0 to 30,
30 preferably more than 1 to 30.

In summary, it is an object of this invention therefore to provide a solution polymerization/co-polymerization process for producing nitrile rubber polymers having controlled molecular weights, a lower Mooney viscosity and narrower molecular weight distributions than those known in the art.

35 SUMMARY OF THE INVENTION

In the first aspect, the present invention provides a metal-containing catalyst system, which comprises (1) a metal-containing catalyst, (2) a co-catalyst, and optionally (3) an additive, for a solution polymerization process of diene and/or for hydrogenation of diene-containing polymers, wherein (1) the metal-containing catalyst is selected from ML_nX_m , MX_m , $MX_m \cdot pH_2O$,

M(OC(O)R)_m, or any combination thereof, wherein M represents a metal selected from Rh, Pd,

Ru, Ir, Mo, Co, Cu, Fe, or Ti, L is a group selected from $\begin{array}{c} \text{P} - \text{R}_1 \\ \quad \quad \quad \text{R}_2 \\ \quad \quad \quad \text{R}_3 \end{array}$, in which R₁, R₂, and R₃ may be same or different, and each R₁, R₂ and R₃ is independently selected from H, C₁-C₆ alkyl, C₅-C₇ aryl or C₃-C₆ cycloalkyl, substituted C₃-C₆ cycloalkyl, substituted C₅-C₇ aryl, with a proviso that R₁, R₂ and R₃ are not all of H, X is a halogen, n is a integer of 1 to 5, p is a integer of 1 to 7, and m is equal to the valence of M;

(2) the co-catalyst is selected from a halide, an azo-compound, or a peroxide; and optionally

(3) the additive is selected from a group consisting of a primary amine (R₁-NH₂), a second amine (R₁-NH-R₂), a tertiary amine (N(R₁)(R₂)(R₃)), $\begin{array}{c} \text{P} - \text{R}_1 \\ \quad \quad \quad \text{R}_2 \\ \quad \quad \quad \text{R}_3 \end{array}$, ascorbic acid, or an ammonium salt, or any combination thereof, in which R₁, R₂, and R₃ are defined as the above.

In the second aspect, the present invention provides a solution polymerization process of diene, comprising homopolymerization of diene or copolymerization of diene together with at least one of comonomers in the presence of at least one of the metal-containing catalyst system of the present application in at least one of organic solvents.

The solution polymerization provide a process for the synthesis of low molecular weight nitrile rubber having narrow molecular weight distribution by the direct solution copolymerization of at least one conjugated dienes monomers with at least one α,β -unsaturated nitrile and optionally further one or more copolymerizable monomers in the presence of metal-containing catalyst(s) and co-catalyst with or without suitable additive(s) in organic solvents.

The present invention is directed to a nitrile rubber having an Mn in the range of less than 1000 to 300000 g/mol, a Mooney viscosity (ML 1+4@100°C) of less than 1 to 30, and a polydispersity index of less than 5.

In the third aspect, the present invention provides a diene polymer, obtained by the solution polymerization, comprises in the range of from 40 to 85 weight part of repeating units derived from one or more dienes, in the range of from 0 to 70 weight part of repeating units derived from one or more α,β -unsaturated nitriles or styrene or any of derivatives of styrene, and in the range of from 0 to 40 weight part of repeating units derived from optional termonomers other than α,β -unsaturated nitrile or styrene and any of derivatives of styrene.

In the fourth aspect, the present invention provides a use of the dienes polymer obtained by the solution polymerization process of the invention in the hydrogenation in the present hydrogen and a catalyst of Rh, Ru, and/or Pd-based to obtain hydrogenated diene polymers.

In the fifth aspect, the present invention provides a one-pot process for synthesis of the hydrogenated diene polymers by directly introducing hydrogen into the reactor after the completion of solution polymerization and reacting at a desired temperature.

In the sixth aspect, the invention provides a hydrogenated diene polymer, obtained by the one-

pot process for the synthesis of the hydrogenated diene polymers of the invention.

5 In the seventh aspect, the present invention provides a process for hydrogenation of diene polymers, comprising a) solution homopolymerization of diene or copolymerization of diene together with at least one of comonomers in the presence of one of the metal-containing catalyst system of the present invention in at least one of organic solvents to obtain diene rubber, b) directly introducing hydrogen into the mixture of step a) after the completion of solution polymerization to obtain the hydrogenated diene-containing polymers.

In the eighth aspect, the present invention provides a process for hydrogenation of diene polymers, comprising:

- 10 a) dissolving at least one diene polymer into at least one organic solvent in a autoclave reactor,
- b) adding at least one of the metal-containing catalyst system of the invention into the solution obtained in step a),
- c) introducing hydrogen into the autoclave reactor and heating the autoclave reactor up to a predetermined temperature for a predetermined time.

15 In the ninth aspect, the present invention provides a process for hydrogenation of diene polymers, comprising a) adding the solution homopolymerization of diene or copolymerization of diene obtained by the solution polymerization process of the invention, and optionally at least one of organic solvents, b) directly introducing hydrogen into the mixture of step a) and heat up to a predetermined temperature to obtain the hydrogenated diene-containing polymers.

20 In the tenth aspect, the invention provides a hydrogenated diene rubber, obtained by the one-pot process for the synthesis of the hydrogenated diene-containing polymers of the invention.

In the eleventh aspect, the invention provides a use of the catalyst system of the invention in the manufacture of diene polymer.

25 In the twelfth aspect, the invention provides a use of the catalyst system of the invention in the manufacture of hydrogenated diene-containing polymer.

In the thirteenth aspect, the invention provides a use of glass tube reactor and/or autoclave in the solution polymerization process of the invention or in the one-pot process for the synthesis of the hydrogenated diene polymers of the invention.

30 In the fourteenth aspect, the invention provides a use of glass tube reactor and/or autoclave in process for the synthesis of the hydrogenated diene polymers of the invention.

The diene rubber polymers provided by the solution polymerization of the present application have a Mn in the range of less than 1000 to 300000 g/mol, a Mooney viscosity (ML 1+4@100 °C) of less than 1 to 30, and a polydispersity index of less than 5, preferably in the range from 1.1 to 5.0 and in particular in the range from 1.1 to 4.0, more preferably in the range from 1.1 to 2.0. Meanwhile, the diene rubber polymers provided by the solution polymerization of the

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present application may be hydrogenated directly in the presence of hydrogen. The hydrogenated diene rubber polymers, obtained by the one-pot process for the synthesis of the hydrogenated diene-containing polymers of the present application or by the process for hydrogenation of diene polymers, have a M_n in the range of less than 1000 to 300000 g/mol, a Mooney viscosity (ML 1+4@100 °C) of 10 to 60, and a polydispersity index of less than 5, preferably in the range from 1.1 to 5.0 and in particular in the range from 1.1 to 4.0, more preferably in the range from 1.1 to 3.0, still more preferably in the range from 1.1 to 2.0.

BRIEF DESCRIPTION TO THE FIGURES

The above and other aspects, features and advantages of the invention will become apparent from the following detailed description in conjunction with the accompanying drawings, in which the number represents the number of the example hereinafter and:

Figure 1 is the GPC curves of Examples 1-3, wherein numbers of 1-3 represent Examples 1-3;

Figure 2 is the GPC curves of Examples 4-6, wherein numbers of 4-6 represent Examples 4-6;

Fig. 3a is M_n and PDI of Examples 6-15;

Fig. 3b is conversions of the samples of Example 6 and 8-15;

Fig. 3c is FT-IR spectra of the samples of Examples 6-16, wherein numbers of 6-16 represent Examples 6-16;

Fig. 3d is ^1H NMR spectra of the samples of Examples 6-16, wherein numbers of 6-16 represent Examples 6-16;

Fig. 3e is ^1H NMR spectrum of the sample of Example 6 alone;

Fig. 3f is DSC curves of the samples of Examples 6-15, wherein numbers of 6-15 represent the samples of Examples 6-15;

Fig. 4a is FT-IR spectra of the samples of Examples 3, 6, 17 and 18;

Fig. 4b is ^1H NMR spectra of the samples of Examples 3, 6, 17 and 18;

Fig. 5a is ^1H NMR spectra of the samples of Examples 22-1 to 22-3;

Fig. 5b is ^1H NMR spectrum of the sample of Examples 22-7;

Fig. 6a - 6c are ^1H NMR spectra of the samples of Examples 23-4, 23-7 and 23-10;

Fig. 7a - 7c are ^1H NMR spectra of the samples of Examples 24-1, 24-3 and 24-4;

Fig. 7d is ^1H NMR spectrum of the sample of Example 24-5;

Fig. 8 is ^1H NMR spectrum of the sample of Example 25;

Fig. 9a is FT-IR spectrum of the sample of Example 26-2;

Fig. 9b is ^1H NMR spectrum of the sample of Example 26-2;

Fig. 10a is FT-IR spectrum of the sample of controlled trial of Example 6;

Fig. 10b is ^1H NMR spectrum of the sample of controlled trial of Example 6;

Fig. 10c is FT-IR spectrum of the sample of Example 27-1 with monomer n-butyl acrylate;

Fig. 10d is ^1H NMR spectrum of the sample of Example 27-1 with termonomer n-Butyl acrylate;

Fig. 10e is FT-IR spectrum of the sample of Example 27-2 with termonomer MMA;

Fig. 10f is ^1H NMR spectrum of the sample of Example 27-2 with termonomer MMA;

Fig. 10g is FT-IR spectrum of the sample of Example 27-3 with termonomer MAA;

5 Fig. 10h-10i are ^1H NMR spectra of the sample of Example 27-3 with termonomer MAA;

Fig. 10j is FT-IR spectrum of the sample of Example 27-4 with termonomer IA;

Fig. 10k-10l are ^1H NMR spectra of the sample of Example 27-4 with termonomer IA;

Fig. 10m is FT-IR spectrum of the sample of Example 27-5 with termonomer acrylamide;

10 Fig. 11a is FT-IR spectra of the samples of Examples 28-1 and 28-2 which are carried out for different reaction time;

the IR peak assignment is as follows:

2237 cm^{-1} , -CN;
970 cm^{-1} , Bd, trans-1,4;
920 cm^{-1} , Bd, vinyl;
15 722 cm^{-1} , Bd, cis-1,4

Fig. 11b is ^1H NMR spectrum of the sample of Example 28-4;

the ^1H NMR peak assignment is as follows:

5.2-5.8 ppm, Bd, 1,4-(-CH=CH-) and vinyl (-CH=CH₂);
4.9-5.2 ppm, Bd, vinyl (-CH=CH₂);
20 2.5-3.1 ppm, >CH-CN;
1.0-2.5 ppm, H on main chains

Fig. 12 is the FT-IR spectra and ^1H NMR spectra of S-NBR and hydrogenated S-NBR;

the IR peak assignment is as follows:

2237 cm^{-1} , -CN;
25 970 cm^{-1} , Bd, trans-1,4;
920 cm^{-1} , Bd, vinyl;
722 cm^{-1} , Bd, cis-1,4;
720 cm^{-1} , saturated -(CH₂)_n- units (n>4); and

the ^1H NMR (CDCl₃, δ ppm) peak assignment for NBR and HNBR is as follows:

30 5.38-5.55(CH₂CH=);
2.51(-CH(CN)-);
1.97-2.28(-CH₂CH=, -CH₂CH(CN) -);
1,26-1.57(-CH₂-);
0.88(-CH₃); and

35 Fig. 13 is the FT-IR spectra of S-NBR and hydrogenated S-NBR;

the IR peak assignment is as follows:

2237 cm^{-1} , -CN;
970 cm^{-1} , Bd, trans-1,4;
920 cm^{-1} , Bd, vinyl;
40 722 cm^{-1} , Bd, cis-1,4;
720 cm^{-1} , saturated -(CH₂)_n- units (n>4).

DETAILED DESCRIPTION OF THE INVENTION

As used throughout this specification, the term “nitrile rubber” is intended to have a broad meaning and is meant to encompass a copolymer having repeating units derived from at least one conjugated diene, at least one α,β -unsaturated nitrile and optionally further one or more copolymerizable monomers.

The conjugated diene may be any known diene, preferably a C_4 - C_6 conjugated diene. Preferred conjugated diene includes 1,3-butadiene, isoprene, 2,3-dimethylbutadiene, piperylene or mixtures thereof. More preferred C_4 - C_6 conjugated diene includes 1,3-butadiene, isoprene and mixtures thereof. The most preferred C_4 - C_6 conjugated diene is 1,3-butadiene.

The α,β -unsaturated nitriles may be any known α,β -unsaturated nitriles, preferably a (C_3 - C_5) α,β -unsaturated nitrile. Preferred (C_3 - C_5) α,β -unsaturated nitriles include acrylonitrile, methacrylonitrile, ethacrylonitrile or mixtures thereof. The most preferred (C_3 - C_5) α,β -unsaturated nitrile is acrylonitrile.

The present application provides the solution polymerization diene rubber polymer having a M_n in the range of less than 1000 to 300000 g/mol, a Mooney viscosity (ML 1+4@100 °C) of less than 1 to 30, and a polydispersity index of less than 5 and the hydrogenated diene rubber polymer having a M_n in the range of less than 1000 to 300000 g/mol, a Mooney viscosity (ML 1+4@100 °C) of 10 to 60, and a polydispersity index of less than 5.

For the purposes of this application, an embodiment of the invention provides a metal-containing catalyst system of the invention, which comprises (1) a metal-containing catalyst, (2) a co-catalyst, and optionally (3) an additive, for a solution polymerization process of diene and/or for hydrogenation of diene-containing polymers, wherein

(1) the metal-containing catalyst is selected from ML_nX_m , MX_m , $MX_m \cdot pH_2O$, $M(OC(O)R)_m$, or any combination thereof, wherein M represents a metal selected from Rh, Pd, Ru, Ir, Mo, Co,

Cu, Fe, or Ti, L is a group selected from $\begin{array}{c} R_1 \\ | \\ P \\ | \\ R_2 \\ | \\ R_3 \end{array}$, in which R_1 , R_2 , and R_3 may be same or different, and each R_1 , R_2 and R_3 is independently selected from H, C_1 - C_6 alkyl, C_5 - C_7 aryl or C_3 - C_6 cycloalkyl, substituted C_3 - C_6 cycloalkyl, substituted C_5 - C_7 aryl, with a proviso that R_1 , R_2 and R_3 are not all of H, X is a halogen, n is a integer of 1 to 5, p is a integer of 1 to 7, and m is equal to the valence of M;

(2) the co-catalyst is selected from a halide, an azo-compound, or a peroxide; and optionally

(3) the additive is selected from a group consisting of a primary amine (R_1-NH_2), a second

amine (R_1-NH-R_2), a tertiary amine ($N(R_1)(R_2)(R_3)$), $\begin{array}{c} R_1 \\ | \\ P \\ | \\ R_2 \\ | \\ R_3 \end{array}$, ascorbic acid, or an ammonium salt, or any combination thereof, in which R_1 , R_2 , and R_3 are defined as the above.

In a preferable embodiment, the metal-containing catalyst system of the invention, wherein

(1) in the metal-containing catalyst, M represents a metal selected from Rh, Pd, Ru, Ir or Mo,

preferably Rh, Pd, Ru, Ir, X is selected from Cl or Br, more preferably Cl; in $\begin{array}{c} \text{P} - \text{R}_1 \\ \quad \quad \text{R}_2 \\ \quad \quad \text{R}_3 \end{array}$, each R₁, R₂, and R₃ is independently selected from phenyl, C₃-C₆ cycloalkyl, substituted C₃-C₆ cycloalkyl, phenyl, substituted phenyl, preferably carboxy-substituted phenyl, sodium sulfonate-substituted

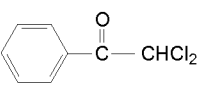
phenyl, more preferably PPh₃, phosphine tricyclohexyl (PCy₃), $\begin{array}{c} \text{O} \\ \parallel \\ \text{P} - \text{C}_6\text{H}_4 - \text{S} - \text{ONa} \\ \parallel \\ \text{O} \end{array}$,
 5 $\begin{array}{c} \text{COOH} \\ | \\ \text{P} - \text{C}_6\text{H}_4 \end{array}$,³, in which the sodium sulfonate group or carboxy group may be in ortho-, meta- or para-position of phenyl ring;

(2) in the co-catalyst, the halide is selected from $\begin{array}{c} \text{O} \\ \parallel \\ \text{R} - \text{C} - \text{CHX}_2 \end{array}$, $\begin{array}{c} \text{O} \\ \parallel \\ \text{R}_1 - \text{CH} - \text{C} - \text{OR}_2 \\ | \\ \text{X} \end{array}$,
 $\begin{array}{c} \text{X} \quad \text{O} \\ | \quad \parallel \\ \text{R}_1 - \text{C} - \text{C} - \text{OR}_2 \\ | \\ \text{X} \end{array}$, $\begin{array}{c} \text{X} \quad \text{O} \\ | \quad \parallel \\ \text{X} - \text{C} - \text{C} - \text{OR}_2 \\ | \\ \text{X} \end{array}$, $\begin{array}{c} \text{R} \\ | \\ \text{C}_6\text{H}_4 - \text{CH}_2 - \text{X} \end{array}$, $\begin{array}{c} \text{O} \\ \parallel \\ \text{R} - \text{C}_6\text{H}_4 - \text{S} - \text{Cl} \\ \parallel \\ \text{O} \end{array}$, CH₂Cl₂, CHCl₃, CCl₄,
 10 dichlorobenzene (DCB), trichlorobenzene (TCB), monobromobenzene (MBB), dibromobenzene (DBB), tribromobenzene (TBB), in which each of R, R₁, and R₂ is independently a C₁-C₆ alkyl or C₃-C₆ cycloalkyl, and R may be in ortho-, meta- or para-position of phenyl ring, and each X is independently defined as the above, the azo-compound is selected from 2,2'-
 azobisisobutylnitrile (AIBN), 2,2'-azobis-(2-methylbutylnitrile (AMBN), 2,2'-azobis-(2-
 15 methylbutylnitrile (AMBN), dimethyl 2,2'-azobis-(2-methylpropionate, 1-cyano-1-methylethylazofornamide, 1,1'-azobis(cyclohexane-1-carbonitrile (ACCN), 2,2'-azobis-(2-methylpropionamide) dihydrochloride (AIBA), or 4,4'-azobis-(4-cyanovaleric acid) (ACVA), and the peroxide is selected from tert-butylhydroperoxide, benzoyl peroxide (BPO) or cumyl peroxide; and optionally

(3) the additive is selected from a group consisting of ascorbic acid, methylamine, ethylamine, ethyldiamine, n-propylamine, iso-propylamine, propyldiamine, n-butylamine, iso-butylamine, butyldiamine, dibutylamine, dimethylamine, diethylamine, diiso-propylamine, t-butylamine, amylamines, cyclohexylamine, triethanolamine, trimethylamine, triethylamine, tri-n-propylamine, tri-n-butylamine, cycloheptylamine, cyclopentylamine, methyltri-n-

25 octylammonium chloride (MTOAC), $\begin{array}{c} \text{P} - \text{R}_1 \\ \quad \quad \text{R}_2 \\ \quad \quad \text{R}_3 \end{array}$, or any combination thereof, in which R₁, R₂, and R₃ are defined as the above.

In a preferable embodiment, the metal-containing catalyst system of the invention, wherein the metal-containing catalyst system is selected from:

a group consisting of (1) $MCl_m(PPh_3)_n$, (2) , 2,2-dichloroacetophenone (DCAP) or benzyl chloride, and optionally (3) PPh_3 ;

a group consisting of (1) MCl_m and/or $MX_m \cdot pH_2O$, (2) 2,2-dichloroacetophenone or benzyl chloride (BCL) and optionally (3) $P(Ph)_3$;

5 a group consisting of (1) $MCl_m(PPh_3)_n$, (2) $PhCH_2Cl$, and optionally (3) PPh_3 ;

a group consisting of (1) $(MCl_m(PPh_3)_n)$, (2) one of dichlorobenzene (DCB), trichlorobenzene (TCB), monobromobenzene (MBB), dibromobenzene (DBB), tribromobenzene (TBB), CH_2Cl_2 , $CHCl_3$, CCl_4 , and optionally (3) PPh_3 ;

a group consisting of (1) $MCl_m(PPh_3)_n$, (2) $Cl_3CCOOCH_2CH_3$ and (3) PPh_3 ;

10 a group consisting of (1) $MCl_m(PPh_3)_n$, (2) at least one of 2,2'-azobisisobutyronitrile (AIBN), 2,2'-azobis-(2-methylbutylnitrile (AMBN), 2,2'-azobis-(2-methylbutylnitrile (AMBN), dimethyl 2,2'-azobis-(2-methylpropionate, 1-cyano-1-methylethylazofornamide, 1,1'-azobis(cyclohexane-1-carbonitrile (ACCN), 2,2'-azobis-(2-methylpropionamide) dihydrochloride (AIBA), 4,4'-azobis-(4-cyanovaleric acid) (ACVA), and
15 optionally (3) PPh_3 ; or

a group consisting of (1) $M(OAc)_m$, (2) at least one of, CH_2Cl_2 , $CHCl_3$, CCl_4 , and optionally (3) $P(Ph)_3$;

wherein M is selected from Rh, Pd, Ru, Ir, Mo, preferably selected from Rh, Ru, Pd, and Ir, more preferably selected from Rh, Ru, and Pd, n is a integer of 3, p is a integer of 1 to 7, and m is equal to the valence of M.
20

In a more preferable embodiment, wherein the metal-containing catalyst system is selected from:

a group consisting of $RhCl(PPh_3)_3$, 2,2-dichloroacetophenone (DCAP), and optionally PPh_3 ;

a group consisting of $RhCl_3$ or $RhCl_3 \cdot 3H_2O$, 2,2-dichloroacetophenone and PPh_3 ;

a group consisting of $RhCl(PPh_3)_3$, $Cl_3CCOOCH_2CH_3$, and optionally PPh_3 ;

25 a group consisting of $RhCl_3$ or $RhCl_3 \cdot 3H_2O$, $Cl_3CCOOCH_2CH_3$ and PPh_3 ; a mixture comprising or consisting of $RhCl(PPh_3)_3$, $PhCH_2Cl$ and optionally PPh_3 ;

a group consisting of $RhCl_3$ or $RhCl_3 \cdot 3H_2O$, $PhCH_2Cl$ and PPh_3 ;

a group consisting of $PdCl_2$, 2,2-dichloroacetophenone and PPh_3 ;

a group consisting of $PdCl_2$, benzyl chloride and PPh_3 ;

30 a group consisting of $RhCl(PPh_3)_3$, at least one of CH_2Cl_2 , $CHCl_3$, CCl_4 and optionally PPh_3 ;

a group consisting of $RhCl_3$ or $RhCl_3 \cdot 3H_2O$, at least one of CH_2Cl_2 , $CHCl_3$, CCl_4 , and PPh_3 ;

a group consisting of $Pd(OAc)_2$, at least one of CH_2Cl_2 , $CHCl_3$, CCl_4 , and PPh_3 ; or

a group consisting of $RhCl(PPh_3)_3$, azobisisoheptonitrile (ABVN), and optionally PPh_3 .

In a further more preferable embodiment, the metal-containing catalyst system is selected from
35 the following compositions consisting of, by weight of,

$\text{RhCl}(\text{PPh}_3)_3 : \text{DCAP} : \text{PPh}_3 = 1 : 0.3-3.0 : 0-20;$

$\text{RhCl}_3 : \text{DCAP} : \text{PPh}_3 = 1 : 1.3-13 : 4.4-88;$

$\text{RhCl}_3 \cdot 3\text{H}_2\text{O} : \text{DCAP} : \text{PPh}_3 = 1 : 1.0-10 : 3.0-63;$

$\text{RhCl}(\text{PPh}_3)_3 : \text{Cl}_3\text{CCOOCH}_2\text{CH}_3 : \text{PPh}_3 = 1 : 0.3-3.0 : 0-20;$

5 $\text{RhCl}_3 : \text{Cl}_3\text{CCOOCH}_2\text{CH}_3 : \text{PPh}_3 = 1 : 1.3-3.9 : 4.4-88;$

$\text{RhCl}_3 \cdot 3\text{H}_2\text{O} : \text{Cl}_3\text{CCOOCH}_2\text{CH}_3 : \text{PPh}_3 = 1 : 1.0-10 : 3.0-63;$

$\text{RhCl}(\text{PPh}_3)_3 : \text{PhCH}_2\text{Cl} : \text{PPh}_3 = 1 : 0.05-2.0 : 0-20;$

$\text{RhCl}_3 : \text{PhCH}_2\text{Cl} : \text{PPh}_3 = 1 : 0.22-9.0 : 4.4-88;$

$\text{RhCl}_3 \cdot 3\text{H}_2\text{O} : \text{PhCH}_2\text{Cl} : \text{PPh}_3 = 1 : 0.2-7.0 : 3.0-63;$

10 $\text{PdCl}_2 : \text{DCAP} : \text{PPh}_3 = 1 : 0.3-3.0 : 0-20;$

$\text{RhCl}(\text{PPh}_3)_3 : \text{CCl}_4 : \text{PPh}_3 = 1 : 0.1-3 : 0-20;$

$\text{RhCl}_3 : \text{CCl}_4 : \text{PPh}_3 = 1 : 0.4-13 : 4.4-88;$

$\text{RhCl}_3 \cdot 3\text{H}_2\text{O} : \text{CCl}_4 : \text{PPh}_3 = 1 : 0.3-11 : 3.0-63;$

$\text{Pd}(\text{OAc})_2 : \text{CCl}_4 : \text{PPh}_3 = 1 : 10^{-4}-10^{-2} : 3.5-27; \text{ or}$

15 $\text{RhCl}(\text{PPh}_3)_3 : \text{ABVN} : \text{PPh}_3 = 0-1 : 1-10 : 2-20.$

In another more preferable embodiment, the metal-containing catalyst system is selected from the following compositions consisting of, by weight of,

$\text{RhCl}(\text{PPh}_3)_3 : \text{DCAP} : \text{PPh}_3 = 1 : 0.5-2.0 : 1-10;$

$\text{RhCl}_3 : \text{DCAP} : \text{PPh}_3 = 1 : 2.2-9.0 : 5.4-50;$

20 $\text{RhCl}_3 \cdot 3\text{H}_2\text{O} : \text{DCAP} : \text{PPh}_3 = 1 : 2.0-8 : 4.0-44;$

$\text{RhCl}(\text{PPh}_3)_3 : \text{Cl}_3\text{CCOOCH}_2\text{CH}_3 : \text{PPh}_3 = 1 : 0.5-2.0 : 1-10;$

$\text{RhCl}_3 : \text{Cl}_3\text{CCOOCH}_2\text{CH}_3 : \text{PPh}_3 = 1 : 2.2-9.0 : 5.4-50;$

$\text{RhCl}_3 \cdot 3\text{H}_2\text{O} : \text{Cl}_3\text{CCOOCH}_2\text{CH}_3 : \text{PPh}_3 = 1 : 2.0-8 : 4.0-44;$

$\text{RhCl}(\text{PPh}_3)_3 : \text{PhCH}_2\text{Cl} : \text{PPh}_3 = 1 : 0.08-1.5 : 1-10;$

25 $\text{RhCl}_3 : \text{PhCH}_2\text{Cl} : \text{PPh}_3 = 1 : 0.35-6.7 : 5.4-50;$

$\text{RhCl}_3 \cdot 3\text{H}_2\text{O} : \text{PhCH}_2\text{Cl} : \text{PPh}_3 = 1 : 0.3-6.0 : 4.0-44;$

$\text{PdCl}_2 : \text{DCAP} : \text{PPh}_3 = 1 : 0.5-2.0 : 1-10;$

$\text{RhCl}(\text{PPh}_3)_3 : \text{CCl}_4 : \text{PPh}_3 = 1 : 0.2-2 : 1-10;$

$\text{RhCl}_3 : \text{CCl}_4 : \text{PPh}_3 = 1 : 0.9-9 : 5.4-50;$

30 $\text{RhCl}_3 \cdot 3\text{H}_2\text{O} : \text{CCl}_4 : \text{PPh}_3 = 1 : 0.7-7 : 4.0-44;$

$\text{Pd}(\text{OAc})_2 : \text{CCl}_4 : \text{PPh}_3 = 1 : 5 \cdot 10^{-4}-5 \cdot 10^{-2} : 4.5-17; \text{ or}$

$\text{RhCl}(\text{PPh}_3)_3 : \text{ABVN} : \text{PPh}_3 = 0.2-0.5 : 0.5-2 : 0.5-4.$

In a yet more preferable embodiment, the additive is selected from the group consisting of ascorbic acid, methyltri-n-octylammonium chloride, n-propylamine, iso-propylamine, propyldiamine, n-butylamine, iso-butylamine, n-butylamine, dibutylamine, trimethylamine, triethylamine, tri-n-propylamine, tri-n-butylamine, or combination thereof.

5 In another embodiment, the invention provide a solution polymerization process of diene, comprising homopolymerization of diene or copolymerization of diene together with at least one of comonomers in the presence of at least one of the metal-containing catalyst system of the invention in at least one of organic solvents.

10 In a preferable embodiment, the diene is selected from any known diene, preferably selected from at least one of conjugated dienes, more preferably a C₄-C₆ conjugated diene, including 1,3-butadiene, isoprene, 2,3-dimethylbutadiene, piperylene or mixtures thereof, and most preferred 1,3-butadiene, isoprene or mixtures thereof.

15 In a more preferable embodiment, the at least one of comonomers are selected from at least one of α,β -unsaturated nitriles or styrene-based compounds, and preferably the at least one of α,β -unsaturated nitriles are selected from any known α,β -unsaturated nitriles, more preferably an α,β -unsaturated (C₃-C₅) nitrile including acrylonitrile, methacrylonitrile, ethylacrylonitrile or mixtures thereof, most preferred acrylonitrile; the styrene-based compounds are selected from styrene, α -methyl styrene or vinyl toluene. In another more preferable embodiment, the solution polymerization process of the invention, wherein the at least one of comonomers are selected from styrene.

20 In another more preferable embodiment, the at least one of comonomers further comprises monomers, including vinyl monomers, vinylidene monomers and α,β -unsaturated monomers, which is selected from at least one of (math)acrylic acid, any of (math)acrylic acid esters, any of (math)acrylic acid salts, any of olefin, and any of unsaturated carboxylic acid, preferably any of n-butyl (math)acrylate, i-butyl (math)acrylate, t-butyl (math)acrylate, ethylene, propylene, vinylidene monomers, methyl (math)acrylate, ethyl (math)acrylate, n-propyl (math)acrylate, i-propyl (math)acrylate, 2-ethylhexyl (math)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxy butyl (meth)acrylate, benzyl (meth)acrylate, cyclohexyl (meth)acrylate, phenyl (meth)acrylate, 2-aminoethyl (meth)acrylate, 2-dimethylaminoethyl (meth)acrylate, fumaric acid, maleic acid, and itaconic acid.

35 In another more preferable embodiment, the at least one of organic solvents are selected from any organic solvent which does not react with the catalyst or otherwise interfere with the reaction, preferably selected from benzene, toluene, cyclohexane, dimethyl sulfoxide (DMSO), ethylene carbonate (EC), tetrahydrofuran (THF), 1,4-dioxane, monochlorobenzene (MCB), dichlorobenzene (DCB), trichlorobenzene (TCB), monobromobenzene (MBB), dibromobenzene (DBB), tribromobenzene (TBB), methyl ethyl ketone (MEK), N,N-dimethyl formamide (DMF), N,N-dimethyl acetamide (DMAC), or the mixture thereof, more preferably selected from monochlorobenzene (MCB), methyl ethyl ketone (MEK), N,N-dimethyl formamide (DMF), or N,N-dimethyl acetamide (DMAC), further preferably selected from monochlorobenzene (MCB) and methyl ethyl ketone (MEK), most preferably monochlorobenzene (MCB).

In a yet more preferable embodiment, wherein the metal-containing catalyst system is selected from:

the group consisting of $\text{RhCl}(\text{PPh}_3)_3$: DCAP : PPh_3 , in which, by weight of, $\text{RhCl}(\text{PPh}_3)_3$: DCAP : $\text{PPh}_3 = 1 : 0.5-2.0 : 1-10$;

5 the group consisting of RhCl_3 : DCAP : PPh_3 , in which, by weight of, RhCl_3 : DCAP : $\text{PPh}_3 = 1 : 2.2-9.0 : 5.4-50$;

the group consisting of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$: DCAP : PPh_3 , in which, by weight of, $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$: DCAP : $\text{PPh}_3 = 1 : 2.0-8 : 4.0-44$;

10 the group consisting of PdCl_2 : DCAP : PPh_3 , in which, by weight of, PdCl_2 : DCAP : $\text{PPh}_3 = 1 : 0.5-2.0 : 1-10$;

the group consisting of $\text{Pd}(\text{OAc})_2$: CCl_4 : PPh_3 , in which, by weight of, $\text{Pd}(\text{OAc})_2$: CCl_4 : $\text{PPh}_3 = 1 : 5 \cdot 10^{-4} - 5 \cdot 10^{-2} : 3.5-27$;

the group consisting of $\text{RhCl}(\text{PPh}_3)_3$: PhCH_2Cl : PPh_3 , in which, by weight of, $\text{RhCl}(\text{PPh}_3)_3$: PhCH_2Cl : $\text{PPh}_3 = 1 : 0.08-1.5 : 1-10$;

15 the group consisting of RhCl_3 : PhCH_2Cl : PPh_3 , in which, by weight of, RhCl_3 : PhCH_2Cl : $\text{PPh}_3 = 1 : 0.35-6.7 : 5.4-50$; or

the group consisting of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$: PhCH_2Cl : PPh_3 , in which, by weight of, $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$: PhCH_2Cl : $\text{PPh}_3 = 1 : 0.3-6.0 : 4.0-44$.

20 In a still more preferable embodiment, the diene homopolymer or copolymer having a controlled Mn, from 1,000 to 300,000, with PDI from 1.0 to 5.0, preferably the controlled Mn, from 3,000 to 100,000, with PDI from 1.1 to 4.0, more preferably the controlled Mn, from 5,000 to 50,000, with PDI from 1.1 to 3.0, the ACN content in the diene homopolymer or copolymer from 0 to 65 wt%, or styrene content in the diene copolymer from 0 to 80, preferably the ACN content in the diene copolymer from 10 to 63 wt%, or styrene content in the diene copolymer from 20 to 80 wt%, more preferably the ACN content in the diene copolymer from 30 to 60 wt%, or styrene content in the diene copolymer from 20 to 70 wt%, based on the total weight of the diene homopolymer or copolymer.

30 In a further preferable embodiment, the polymerization is carried out with the feeding weight part of the diene is from about more than 0 to about less than 100, and the feeding weight part of the at least one of comonomers is from about less than 100 to about more than 0.

35 Particularly, the polymerization is carried out with the feeding weight part of α, β -unsaturated nitrile monomer is about 4 to about less than 96, or the feeding weight percent of the styrene and any of derivatives of styrene is from about less than 96 to about 4, preferably the feeding weight part of α, β -unsaturated nitrile monomer is about 4 to about less than 90, or the feeding weight percent of the styrene and any of derivatives of styrene is from about less than 96 to about 10.

More particularly, the polymerization is carried out at temperature of 10 °C - 160 °C for 5-200 hrs, preferably at temperature of 20 °C - 150 °C for 10-180 hrs, more preferably at temperature of 30 °C - 140 °C for 20-170 hrs, further preferably at temperature of 40 °C - 140 °C for 10-150

hrs, still preferably at temperature of 60 °C - 140 °C for 1-100 hrs, and the diene rubber polymers having.

5 In a further preferable embodiment, the solution polymerization process further comprises a step of removing the metal-containing catalyst, preferably by using ion-exchange resin as described in EP 2 072 532 A1, EP 2 072 533 A1, and CN101463096 A. Preferably, after copolymerization and/or hydrogenation reaction completing, the reaction mixture was taken out and treated with ion-exchange resin at 100 °C for 48 hours and then precipitated in cold methanol.

10 For the purposes of this application, nitrile rubbers (NBR) by solution polymerization are co- or terpolymers which contain repeating units of at least one conjugated diene, of at least one α,β -unsaturated nitrile and, if appropriate, of one or more copolymerizable monomers, and in which the C=C double bonds of the diene units incorporated into the polymer have been hydrogenated entirely or to some extent. The degree of hydrogenation of the diene units incorporated into the polymer is usually in the range from 50 to 100%, preferably in the range from 85 to 100% and particularly preferably in the range from 95 to 100%. The conjugated diene can be of any type. It is preferable to use C4-C6 conjugated dienes. Particular preference is given to 1,3-butadiene, isoprene, 2,3-dimethylbutadiene, piperylene or a mixture thereof. Particular preference is given to 1,3-butadiene and isoprene or a mixture thereof. 1,3-butadiene is very particularly preferred. The α,β -unsaturated nitrile used can comprise any known (α,β -unsaturated nitrile, and preference is given to C3-C5 α,β -unsaturated nitriles, such as acrylonitrile, methacrylonitrile, ethacrylonitrile or a mixture of these. Acrylonitrile is particularly preferred.

Particularly preferred hydrogenated nitrile rubber is provided by a hydrogenated copolymer based on the monomers acrylonitrile and 1,3-butadiene.

25 Alongside the conjugated diene and the α,β -unsaturated nitrile, it is also possible to use one or more other monomers known to the person skilled in the art, examples being α,β -unsaturated mono- or dicarboxylic acids, or their esters or amides. Preferred α,β -unsaturated mono- or dicarboxylic acids here are acrylic acid, methacrylic acid, fumaric acid, maleic acid, itaconic acid. Preferred esters used of the α,β -unsaturated carboxylic acids are their alkyl esters and alkoxyalkyl esters. Particularly preferred esters of the α,β -unsaturated carboxylic acids are methyl acrylate, ethyl acrylate, butyl acrylate, butyl methacrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate and octyl acrylate.

30 The proportions of conjugated diene and of α,β -unsaturated nitrile in the HNBR polymers to be used can vary widely. The proportion of the conjugated diene or of the entirety of the conjugated dienes is usually in the range from 40 to 90% by weight and preferably in the range from 55 to 75%, based on the entire polymer. The proportion of the α,β -unsaturated nitrile or of the entirety of the α,β -unsaturated nitriles is usually from 10 to 60% by weight, preferably from 25 to 45% by weight, based on the entire polymer. The proportions of the monomers in each case give a total of 100% by weight. The amounts that can be present of the additional monomers are from 0.1 to 40% by weight, preferably from 1 to 30% by weight, based on the entire polymer. In this case, corresponding proportions of the conjugated diene(s) and, respectively, of the α,β -unsaturated nitrile(s) are replaced via the proportions of the additional

monomers, and the proportions of all of the monomers here in each case give a total of 100% by weight.

The preparation of the nitrile rubbers via polymerization of the above mentioned monomers is well known to the person skilled in the art and is extensively described in the literature (Werner Hofmann, Nitrile Rubber, published by Division of Rubber Chemistry of the American Chemical Society, 1964; CX Zhang, JS Huo, et al, Acrylonitrile-Butadiene Rubber (Chief editor: XH Cao, Synthetic Rubber Technology Series, Part 4), published by China Petrochemical Press, 2010; C. S. Marvel, W. S. Anderson, Barbara H. Weil, et al., Industrial and Engineering Chemistry, 1955, 47 (2), 344-351; and Harold P. Brown, Industrial and Engineering Chemistry, 1955, 47 (5), 1006-1012).

The hydrogenation of the nitrile rubbers described above to give hydrogenated nitrile rubber (A) can take place in the manner known to the person skilled in the art. By way of example, a suitable method is reaction with hydrogen with use of homogeneous catalysts, e.g. the catalyst known as "Wilkinson" catalyst ($(PPh_3)_3RhCl$) or others. Processes for the hydrogenation of nitrile rubber are known. (see, for example, U.S. Pat. No. 3,700,637, DE-PS-2 539 132, EP-A-134 023, DE-A-35 41 689, DE-A-35 40 918, EP-A-298 386, DE-A-35 29 252, DE-A-34 33 392, U.S. Pat. No. 4,464,515 and U.S. Pat. No. 4,503,196).

Suitable catalysts and solvents for homogeneous-phase hydrogenation are described below and are also disclosed in DE-A-25 39 132 and EP-A-0 471 250.

Selective hydrogenation can be achieved, for example, in the presence of a rhodium-containing catalyst. metal-containing catalyst system, which comprises (1) a metal-containing catalyst, (2) a co-catalyst, and optionally (3) an additive, for a solution polymerization process of diene and/or for hydrogenation of diene-containing polymers, wherein the metal-containing catalyst is selected from ML_nX_m , MX_m , $MX_m \cdot pH_2O$, $M(OC(O)R)_m$, or any combination thereof, wherein M represents a metal selected from Rh, Pd, Ru, Ir, Mo, Co, Cu, Fe, or Ti, L is a group selected



from $\begin{array}{c} R_1 \\ | \\ P \\ | \\ R_2 \\ | \\ R_3 \end{array}$, in which R_1 , R_2 , and R_3 may be same or different, and each R_1 , R_2 and R_3 is independently selected from H, C_1 - C_6 alkyl, C_5 - C_7 aryl or C_3 - C_6 cycloalkyl, substituted C_3 - C_6 cycloalkyl, substituted C_5 - C_7 aryl, with a proviso that R_1 , R_2 and R_3 are not all of H, X is a halogen, n is a integer of 1 to 5, p is a integer of 1 to 7, and m is equal to the valence of M; the additive is selected from a group consisting of a primary amine (R_1-NH_2), a second amine (R_1-



$NH-R_2$), a tertiary amine ($N(R_1)(R_2)(R_3)$), ascorbic acid, or an ammonium salt, or any combination thereof, in which R_1 , R_2 , and R_3 are defined as the above.

Preferred catalysts are tris(triphenylphosphine)rhodium (I) chloride, tris(triphenylphosphine)rhodium (III) chloride and tris(dimethyl sulfoxide)rhodium (III) chloride, and also tetrakis(triphenylphosphine)rhodium hydride and the corresponding compounds in which the triphenylphosphine has been entirely or to some extent replaced by tricyclohexylphosphine. Small amounts of the catalyst can be used. A suitable amount is in the range from 0.01 to 1% by weight, preferably in the range from 0.03 to 0.5% by weight and particularly preferably in

the range from 0.1 to 0.3% by weight, based on the weight of the polymer.

It is usually advisable to use the catalyst together with a co-catalyst. Suitable co-catalysts are found by way of example in U.S. Pat. No. 4,631,315. Triphenylphosphine is preferred co-catalyst. The amounts used of the co-catalyst are preferably from 0.3 to 5% by weight, preferably in the range from 0.5 to 4% by weight, based on the weight of the nitrile rubber to be hydrogenated. The ratio by weight of the rhodium-containing catalysts to the co-catalyst is moreover preferably in the range from 1:3 to 1:55, preferably in the range from 1:5 to 1:45. A suitable method uses from 0.1 to 33 parts by weight of the co-catalyst, preferably from 0.5 to 20 parts by weight and very particularly preferably from 1 to 5 parts by weight, in particular more than 2 but less than 5 parts by weight, of co-catalyst, based on 100 parts by weight of the nitrile rubber to be hydrogenated.

The practical method for this hydrogenation is well known to the person skilled in the art from U.S. Pat. No. 6,683,136. In the usual method, the nitrile rubber to be hydrogenated is treated with hydrogen in a solvent such as toluene or monochlorobenzene at a temperature in the range from 100 to 150 °C and at a pressure in the range from 700 to 2 500 Psi for from 2 to 10 hrs.

For the purposes of this invention, hydrogenation is a reaction of the C=C double bonds present in the starting nitrile rubber, the extent of this reaction usually being at least 50%, preferably at least 75%, and particularly preferably at least 85%, based on the double bonds present in the starting nitrile rubber.

In the third embodiment, the invention provides a diene polymer, obtained by the solution polymerization, comprises in the range of from 40 to 85 weight part of repeating units derived from one or more dienes, in the range of from 0 to 70 weight part of repeating units derived from one or more α,β -unsaturated nitriles or styrene or any of derivatives of styrene, and in the range of from 0 to 40 weight part of repeating units derived from optional monomers other than α,β -unsaturated nitrile or styrene and any of derivatives of styrene.

In the fourth embodiment, the invention provides a use of the diene polymer obtained by the solution polymerization process of the invention in the hydrogenation in the present hydrogen and a catalyst of Rh, Ru, and/or Pd-based to obtain hydrogenated diene polymers

In a preferably embodiment, the metal-containing catalyst of Rh, Ru, and/or Pd-based is selected from a metal of Rh, Ru or Pd, or the metal-containing catalyst of Rh, Ru or Pd and PPh_3 of the invention.

In the fifth embodiment, the invention provides a one-pot process for synthesis of the hydrogenated diene polymers, comprising by directly introducing hydrogen into the reactor after the completion of solution polymerization of the invention and reacting at a desired temperature.

In a preferably embodiment, the desired temperature is from 60 to 200 °C and the hydrogenation reaction is carried out for 10 min to 20 hrs at a hydrogen pressure of 100-3000 Psi, preferably the desired temperature is from 80 to 180 °C and the reaction is carried out for 10 min to 10 hrs at a hydrogen pressure of 200-2000 Psi, more preferably the desired temperature is from 100 to 160 °C and the reaction is carried out for 30 min to 5 hrs at a hydrogen pressure of 300-1500 Psi,

further preferably the desired temperature is from 120 to 150 °C and the reaction is carried out for 30 min to 3 hrs at a hydrogen pressure of 500-1000 Psi.

5 In a more preferably embodiment, the one-pot process for synthesis of the hydrogenated diene polymers further comprises the step of removing the metal-containing catalyst, preferably by using ion-exchange resin as described in EP 2 072 532 A1, EP 2 072 533 A1, and CN101463096 A. Preferably, after copolymerization and/or hydrogenation reaction completing, the reaction mixture was taken out and treated with ion-exchange resin at 100 °C for 48 hours and then precipitated in cold methanol.

10 In the sixth embodiment, the invention provides a hydrogenated diene polymer, obtained by the one-pot process for the synthesis of the hydrogenated diene polymers of the invention.

In the seventh embodiment, the invention provides a process for hydrogenation of diene polymers, comprising a) solution homopolymerization of diene or copolymerization of diene together with at least one of comonomers in the presence of one of the metal-containing catalyst system of the invention in at least one of organic solvents to obtain diene rubber, b) directly
15 introducing hydrogen into the mixture of step a) after the completion of solution polymerization to obtain the hydrogenated diene-containing polymers.

In a preferably embodiment, the dienes are selected from any known diene, preferably selected from at least one of conjugated dienes and at least one of unconjugated dienes, more preferably a C₄-C₆ conjugated diene, including 1,3-butadiene, isoprene, 2,3-dimethylbutadiene, piperylene
20 or mixtures thereof, or a C₄-C₆ unconjugated diene, including 1,2-butadiene, and most preferred 1,3-butadiene, isoprene and mixtures thereof; the at least one of organic solvents are selected from any organic solvent which does not react with the catalyst or otherwise interfere with the reaction, preferably selected from benzene, toluene, cyclohexane, dimethyl sulfoxide (DMSO), ethylene carbonate (EC), tetrahydrofuran (THF), 1,4-dioxane, monochlorobenzene (MCB),
25 dichlorobenzene (DCB), trichlorobenzene (TCB), monobromobenzene (MBB), dibromobenzene (DBB), tribromobenzene (TBB), methyl ethyl ketone (MEK), N,N-dimethyl formamide (DMF), N,N-dimethyl acetamide (DMAC), or the mixture thereof, more preferably selected from monochlorobenzene (MCB), monobromobenzene (MBB), dichlorobenzene (DCB), methyl ethyl ketone (MEK), N,N-dimethyl formamide (DMF), or N,N-dimethyl acetamide (DMAC), further
30 preferably selected from monochlorobenzene (MCB) and methyl ethyl ketone (MEK), most preferably monochlorobenzene (MCB).

In a more preferably embodiment, the process for hydrogenation of diene polymers further comprises the step of removing the metal-containing catalyst, preferably by using ion-exchange resin. After hydrogenation reaction completing, the reaction mixture was taken out and treated
35 with ion-exchange resin at 100 °C for 48 hours and then precipitated in cold methanol.

In the eighth embodiment, the invention provides a process for hydrogenation of diene polymers, comprising:

- a) dissolving at least one diene polymer into at least one organic solvent in a autoclave reactor,
- b) adding at least one of the metal-containing catalyst system of the invention into the solution

obtained in step a),

c) introducing hydrogen into the autoclave reactor and heating the autoclave reactor up to a predetermined temperature for a predetermined time.

5 In a preferably embodiment, the at least one diene polymer is selected from one or more of BR NBR, SBR, preferably one or more of BR NBR, SBR obtained by solution polymerization, and the ACN content in the diene polymer from 0 to 65 wt%, or styrene content in the diene polymer from 0 to 80, preferably the ACN content in the diene polymer from 10 to 63 wt%, or styrene content in the diene polymer from 20 to 80 wt%, more preferably the ACN content in the diene polymer from 30 to 60 wt%, or styrene content in the diene polymer from 20 to 70
10 wt%, based on the total weight of the diene polymer.

The amount of at least one of the metal-containing catalyst system is from 0.000001 to 50 parts by weight based on 100 parts by weight the least one diene polymer, preferably from 0.00001 to 20 parts by weight, more preferably from 0.0001 to 10 parts by weight.

15 The at least one of organic solvents are selected from any organic solvent which does not react with the catalyst or otherwise interfere with the reaction, preferably selected from benzene, toluene, cyclohexane, dimethyl sulfoxide (DMSO), ethylene carbonate (EC), tetrahydrofuran (THF), 1,4-dioxane, monochlorobenzene (MCB), dichlorobenzene (DCB), trichlorobenzene (TCB), monobromobenzene (MBB), dibromobenzene (DBB), tribromobenzene (TBB), methyl ethyl ketone (MEK), N,N-dimethyl formamide (DMF), N,N-dimethyl acetamide (DMAC), or
20 the mixture thereof, more preferably selected from monochlorobenzene (MCB), monobromobenzene (MBB), dichlorobenzene (DCB), methyl ethyl ketone (MEK), N,N-dimethyl formamide (DMF), or N,N-dimethyl acetamide (DMAC), further preferably selected from monochlorobenzene (MCB) and methyl ethyl ketone (MEK), most preferably monochlorobenzene (MCB).

25 The predetermined temperature is from 80 to 180 °C and the predetermined time is from 10 min to 10 hrs at a hydrogen pressure of 200-2000 Psi, more preferably the predetermined temperature is from 100 to 160 °C and the predetermined time is from 30 min to 5 hrs at a hydrogen pressure of 300-1500 Psi, further preferably the predetermined temperature is from 120 to 150 °C and the predetermined time is from 30 min to 3 hrs at a hydrogen pressure of 500-
30 1000 Psi.

The diene polymer having a controlled Mn, from 1,000 to 300,000, with PDI from 1.0 to 5.0, preferably the controlled Mn, from 3,000 to 100,000, with PDI from 1.1 to 4.0, more preferably the controlled Mn, from 5,000 to 50,000, with PDI from 1.1 to 3.0.

35 In a more preferably embodiment, further comprises d) removing the metal-containing catalyst, preferably by using ion-exchange resin. The metal-containing catalyst may be removed as described in EP 2 072 532 A1, EP 2 072 533 A1, and CN101463096 A.

In the ninth embodiment, the invention provides a process for hydrogenation of diene polymers, comprising a) adding the solution homopolymerization of diene or copolymerization of diene obtained by the solution polymerization process of the invention, and optionally at least one of

organic solvents, b) directly introducing hydrogen into the mixture of step a) and heat up to a predetermined temperature to obtain the hydrogenated diene-containing polymers, wherein the at least one of organic solvents are selected from any organic solvent which does not react with the catalyst or otherwise interfere with the reaction, preferably selected from benzene, toluene, cyclohexane, dimethyl sulfoxide (DMSO), ethylene carbonate (EC), tetrahydrofuran (THF), 1,4-dioxane, monochlorobenzene (MCB), dichlorobenzene (DCB), trichlorobenzene (TCB), monobromobenzene (MBB), dibromobenzene (DBB), tribromobenzene (TBB), methyl ethyl ketone (MEK), N,N-dimethyl formamide (DMF), N,N-dimethyl acetamide (DMAC), or the mixture thereof, more preferably selected from monochlorobenzene (MCB), monobromobenzene (MBB), dichlorobenzene (DCB), methyl ethyl ketone (MEK), N,N-dimethyl formamide (DMF), or N,N-dimethyl acetamide (DMAC), further preferably selected from monochlorobenzene (MCB) and methyl ethyl ketone (MEK), most preferably monochlorobenzene (MCB).

In the tenth embodiment, the invention provides a hydrogenated diene rubber, obtained by the one-pot process for the synthesis of the hydrogenated diene-containing polymers of the invention.

In the eleventh embodiment, the invention provides a use of the catalyst system of the invention in the manufacture of diene polymer.

In the twelfth embodiment, the invention provides a use of the catalyst system of the invention in the manufacture of hydrogenated diene-containing polymer.

In the thirteenth embodiment, the invention provides a use of glass tube reactor and/or autoclave in the solution polymerization process of the invention or in the one-pot process for the synthesis of the hydrogenated diene polymers of the invention.

In the fourteenth embodiment, the invention provides a use of glass tube reactor and/or autoclave in process for the synthesis of the hydrogenated diene polymers of the invention.

The solution polymerization nitrile rubber which are used as starting material in the inventive process usually have a weight-average molecular weight M_w in the range from 200,000 to 1,000,000, preferably in the range from 200 000 to 400 000 and particularly preferably in the range from 200,000 to 300,000. They moreover have a polydispersity index $D = M_w/M_n$, where M_w is the weight-average molecular weight and M_n is the number-average molecular weight, in the range from 1.1 to 6.0, preferably in the range from 1.1 to 5.0 and in particular in the range from 1.1 to 4.0, more preferably in the range from 1.1 to 3.0, still more preferably in the range from 1.1 to 2.0.

In the case of a batchwise method, i.e. a batch procedure, operations are carried out in a stirred or non-stirred reactor.

The inventive solution polymerization process and/or hydrogenation processes can be carried out in any suitable solvent, which does not react with the catalyst or otherwise interfere with the reaction. The solvents used can comprise any solvents suitable for HNBR, examples being benzene, toluene, cyclohexane, dimethyl sulfoxide (DMSO), ethylene carbonate (EC),

5 tetrahydrofuran (THF), 1,4-dioxane, monochlorobenzene (MCB), dichlorobenzene (DCB), trichlorobenzene (TCB), monobromobenzene (MBB), dibromobenzene (DBB), tribromobenzene (TBB), methyl ethyl ketone (MEK), N,N-dimethyl formamide (DMF), or N,N-dimethyl acetamide (DMAC), and the mixture thereof. Monochlorobenzene (MCB), methyl ethyl ketone (MEK), N,N-dimethyl formamide (DMF), or N,N-dimethyl acetamide (DMAC) is preferred. Monochlorobenzene (MCB) and methyl ethyl ketone (MEK), N,N-dimethyl acetamide (DMAC) are more preferred.

10 The inventive process is usually carried out at a temperature in the range from 10 to 200 °C. It has been found that higher temperatures have a favorable effect on the polymerization reaction and/or hydrogenation reaction. The inventive process is therefore preferably carried out at temperatures in the range from 20 to 160 °C, more preferably at temperatures in the range from 60-150 °C.

15 The inventive solution polymerization process is usually carried out in a nature pressure of the monomers and the organic solvents, in the range from 10 to 100 Psi, preferably from 15 to 75 Psi. In the inventive hydrogenation process is usually carried out for 10 min to 20 hrs at a hydrogen pressure of 100-3000 Psi, preferably the desired temperature is from 80 to 180 °C and the reaction is carried out for 10 min to 10 hrs at a hydrogen pressure of 200-2000 Psi, more preferably the desired temperature is from 100 to 160 °C and the reaction is carried out for 30 min to 5 hrs at a hydrogen pressure of 300-1500 Psi, further preferably the desired temperature is from 120 to 150 °C and the reaction is carried out for 30 min to 3 hrs at a hydrogen pressure of 500-1000 Psi.

25 A feature of the solution polymerization rubbers and the hydrogenated nitrile rubbers obtained in the inventive process is particularly narrow molecular weight distribution and a correspondingly low value for the polydispersity index. The solution polymerization rubbers and the hydrogenated nitrile rubbers having this property profile were hitherto unknown and unobtainable.

30 The invention therefore provides a solution polymerization rubbers and a hydrogenated nitrile rubbers which have a polydispersity index less than or equal to 2, preferably less than 2, particularly preferably less than 1.9 and very particularly preferably less than 1.7. In particular, the polydispersity index is more than 1 and less than 2.0, and preferably more than 1 and less than 1.9.

35 The solution polymerization rubbers and a hydrogenated nitrile rubbers obtained in the inventive process have weight-average molecular weight Mw in the range from 30,000 to 250,000, preferably in the range from 30,000 to 150,000 and in particular preferably in the range from 30,000 to 100,000.

40 The Mooney viscosity of the solution polymerization rubbers and/or the hydrogenated nitrile rubbers obtained in the inventive processes (ML 1+4 @ 100 ° C.) is in the range from more than 0 to 50, preferably in the range from 1 to 40, more preferably in the range from 10 to 40. The Mooney viscosity is determined here to ASTM standard D1646.

The inventive solution polymerization rubbers and/or the hydrogenated nitrile rubbers having low molecular weight and narrow molecular weight distribution have very good processability.

5 The metal-containing catalyst may be removed after the polymerization and/or hydrogenation reaction completing by using ion-exchange resin as described in EP 2 072 532 A1, EP 2 072 533 A1, and CN101463096 A.

The concentration of monomers in the hydrogenated reaction mixture is not critical, but should be such that the reaction is not hampered if the mixture is too viscous to be stirred efficiently during reaction.

10 The invention is further illustrated but is not intended to be limited by the following examples in which all parts and percentages are by weight unless otherwise specified.

EXAMPLES

The following examples with the experimental conditions shown below illustrate the scope of the invention and are not intended to limit the same.

5 All polymerizations were performed under nitrogen. 1,3-Butadiene was purified by distilled from pressure bottle to glass bottle. Styrene and styrene derivatives, such as α -methyl styrene, vinyl toluene and acrylonitrile, were passed through active alumina column to remove the stabilizer prior to use. Triphenylphosphine (PPh_3) was recrystallized from ethanol. Other chemicals were used as received.

10 The glass tube containing a bar magnet and capped by a solid rubber stopper was purged of air, by a vacuum-nitrogen cycle repeated, before being added with the required amount of solvent, the monomers, and the catalyst system, respectively. All these liquids were introduced under nitrogen. The glass tubes were heated in a thermostated oil bath at a desired temperature, and the magnetic stirring was slowly maintained during the reaction. After the required reaction time, the samples were withdrawn from the tube. After reaction completing, the tube was
15 opened, and the reaction mixture was taken out and then precipitated in cold methanol. The polymer was filtered off and dried for 24 hours at 60 °C under vacuum. The reaction pressure was the vapor pressure of the monomers at the reaction temperature. The highest temperature used in these trials was limited to 80 °C due to safety reasons.

20 The metal-containing catalyst may be removed after the polymerization and/or hydrogenation reaction completing by using ion-exchange resin as described in EP 2 072 532 A1, EP 2 072 533 A1, CN101463096 A.

The Parr autoclave reactor was used for the copolymerization trials and/or hydrogenation trials in a bigger scale and at a higher temperature. After the required reaction time, the samples were withdrawn from the reactor. After copolymerization and/or hydrogenation reaction completing,
25 the reactor was opened, and the reaction mixture was taken out and treated with ion-exchange resin at 100 °C for 48 hours and then precipitated in cold methanol. The polymer was filtered off and dried for 24 hours at 60 °C under vacuum. The reaction pressure was the vapor pressure of the monomers or hydrogen at the reaction temperature. The temperature used in these trials may be at 10 °C to 200 °C, and usually at room temperature to 160 °C, i.e. hydrogenation
30 temperature.

The metal-containing catalyst may be removed after the polymerization and/or hydrogenation reaction completing by using ion-exchange rubber as described in EP 2 072 532 A1, EP 2 072 533 A1, CN101463096 A.

(a) Determination of the final polymerization conversion

35 The final polymerization conversion could be calculated by the gravimetric method using the initial total amount of monomers and the final amount of dried S-NBR.

(b) GPC, DSC, FT-IR and ^1H NMR Tests

The apparent molecular weight and the distribution were tested by a Waters GPC system equipping with a Waters 1515 high performance liquid chromatography pump, a Waters 717plus autosampler, a PLgel 10 μ m mixed B column and a Waters 2414 RI detector. The GPC test was carried out at 40 °C at 1 mL/min of flow rate with THF as the eluent, and the GPC column was calibrated with narrow PS standard samples.

T_g is the glass transition temperature of the polymer. T_g was measured with a Netzsch DSC 2014F1 Differential Scanning Calorimeter. The DSC test was conducted by: 1) firstly heated from -80 °C to 60 °C at a heating rate of 10 °C/min; 2) kept at 60 °C for 3 minutes and then cooled to -80 °C at a cooling rate of 20 °C/min; 3) kept at -80 °C for 3 minutes, then heated again to 60 °C at a heating rate of 10 °C/min. The T_g value was measured based on the second heating run.

FT-IR spectrum of obtained rubber was recorded on a Perkin Elmer spectrum 100 FT-IR spectrometer. The polymer samples were dissolved in MCB and then the solution was cast onto a KBr disk and dried to form a film for the IR test. The hydrogenation conversion is determined by the FT-IR analysis according to the ASTM (D 5670-95) method.

¹H NMR characterization was carried out on a Bruker AV500 machine using CDCl₃ or DMSO-*d*₆ as the solvent and TMS as the internal standard.

Examples 1-3

The glass tubes containing a bar magnet and capped by a solid rubber stopper were purged of air, by a vacuum-nitrogen cycle repeated three times, before being added with the required amount of solvent, the monomers, and the catalyst system, respectively. The required amount of the metal-containing catalyst system, RhCl(PPh₃)₃ (77 mg, 0.083 mmol), 2,2-dichloroacetophenone (DCAP) (93 mg, 69 μ L, 0.49 mmol), PPh₃ (154 mg, 0.59 mmol), organic solvent monochlorobenzene (MCB) (14.1 mL), 1,3-butadiene (Bd) (2.4 g, 44.4 mmol), acrylonitrile (ACN) (1.7 g, 32.1 mmol) were added into there glass tubes, respectively. All these liquids were introduced under nitrogen. The glass tubes were heated in a thermostated oil bath at temperature of 60 °C, and the magnetic stirring was slowly maintained during the reaction. After the required reaction time such as 17, 24 and 45 hrs, the tubes were opened respectively, and the reaction mixtures were taken out and treated with ion-exchange resin at 100 °C for 48 hours and then precipitated in cold methanol, respectively. The polymers were filtered off and dried for 24 hours at 60 °C under vacuum, respectively. The reaction pressure was the vapor pressure of the monomers at the reaction temperature. The results were summarized in Table 1.

Table 1

Example	Time (hrs)	Mn	Mw	PDI	Conv.
1	17	20528	43039	2.10	11.5%
2	24	34269	95605	2.79	13.7%
3	45	39060	121607	3.11	15.6%

Each tube: MCB, 14.1 mL; Bd, 2.4 g, 44.4 mmol; ACN, 1.7 g, 32.1 mmol; DCAP 93 mg, 69 μ L, 0.49 mmol; RhCl(PPh₃)₃, 77 mg, 0.083 mmol; PPh₃, 154 mg, 0.59 mmol; 60°C

The polymerization was not sensitive to water. The S-NBR rubber may be obtained after the polymerization reaction is carried out for about 10 min to 150 hrs.

Fig. 1 is the GPC curves of the samples of Examples 1-3, wherein numbers of 1-3 represent Examples 1-3 and range from right to left. It is seen that the apparent molecular weights of Examples 1-3 increased gradually with the increased reaction time. This suggests that the molecular weight of the polymer obtained by the solution polymerization process of diene according to the present invention may be controlled by adjusting the required reaction time.

Examples 4-6

The same catalyst system and monomers were used as in Examples 1-3, and the polymerization reaction was carried out under the same conditions as in Example 1 except that the reaction was carried out at the temperature of 80 °C for different time, such as 9.5hrs, 30hrs and 45hrs. The results were summarized in Table 2.

Table 2

Example	Time (hrs)	Mn	Mw	PDI	Conv.
4	9.5	30301	84701	2.80	8.9%
5	30	37433	95933	2.56	19.8%
6	45	45093	122623	2.72	28.5%

Each tube: MCB, 14.1 mL; Bd, 2.4 g, 44.4 mmol; ACN, 1.7 g, 32.1 mmol; DCAP 93 mg, 69 μ L, 0.49 mmol; RhCl(PPh₃)₃, 77 mg, 0.083 mmol; PPh₃, 154 mg, 0.59 mmol; 80°C

Similarly, the polymerization was not sensitive to water. The S-NBR rubber may also be obtained after the polymerization reaction is carried out for about 10 min to 150 hrs at a temperature of about 10 °C to about 160 °C.

Fig. 2 is the GPC curves of the samples of Examples 4-6, wherein numbers of 4-6 represent Examples 4-6 and range from right to left. It is seen that the apparent molecular weights of Examples 4-6 increased gradually with the increased reaction time. This also suggests that the molecular weight of the polymer obtained by the solution polymerization process of diene and/or at least one of comonomers according to the present invention may be controlled by adjusting the required reaction time. Meanwhile, the conversion of the reaction will increase if the polymerization reaction is carried out for a same time at a higher temperature.

Examples 7 - 16

The same catalyst system and monomers were used as in Examples 1-3, and the polymerization reaction was carried out under the same conditions as in Example 3 except that the reaction was carried out at the temperature of 80 °C for 45hrs, the feeding ratio of Bd and ACN by weight was changed, and all samples were withdrawn at 45hrs. The results were summarized in Tables 3-4.

Table 3

Example*	feeding			Mn	Mw	PDI	Conv.	T _g (°C)	obtained rubber		
	Bd/g	ACN/g	ACN%						1,4-Bd	1,2-Bd	ACN
7	0.37	3.73	91%	8277	13676	1.61	low	35.1	34.4%	3.4%	62.2%
8	0.78	3.32	81%	18278	37430	2.05	20.5%	18.1	41.2%	3.8%	55.0%
9	1.12	2.98	73%	32209	84591	2.63	23.9%	-2.7	53.4%	2.4%	44.2%
10	1.59	2.51	61%	43483	121692	2.80	28.6%	-13.7	54.0%	4.2%	41.8%
11	1.92	2.18	53%	46321	125464	2.71	30.7%	-17.4	55.1%	5.7%	39.2%
6	2.4	1.7	41%	45093	122623	2.72	28.5%	-23.7	57.1%	7.0%	35.9%
12	2.74	1.36	33%	39049	89646	2.30	28.9%	-32.7	57.2%	9.8%	33.0%
13	3.12	0.98	24%	27807	61603	2.22	30.2%	-49.7	60.4%	10.8%	28.8%
14	3.58	0.52	13%	26414	51926	1.97	30.8%	-53.3	66.2%	13.3%	20.5%
15	3.94	0.16	4%	13624	26232	1.93	21.2%	-71.6	74.7%	17.3%	8.0%
16	2.4	0	0%	6662	11860	1.78	6.8%	-81.2	80.2%	19.8%	0

*Each tube: DCAP 93 mg, 69 uL, 0.49 mmol; RhCl(PPh₃)₃, 77 mg, 0.083 mmol; PPh₃, 154 mg, 0.59 mmol ; MCB was added to reach the 20 mL of scale; 80°C, full time 45 hours; wherein 1,4-Bd represents the polymerization units of which polymerization occurs at 1,4-positions of Bd, and 1,2-Bd represents the polymerization units of which polymerization occurs at 1,2-positions of Bd.

Table 4

Example*	Temp. (°C)	Time (hrs)	Mn	Mw	PDI	Conv.	T _g (°C)
16*	80	119	6662	11860	1.78	6.8%	-81.2

* In this trial, 16.1 mL of MCB, 2.4 g of Bd, 93 mg of DCAP, 77 mg of RhCl(PPh₃)₃ and 154 mg of PPh₃ were served.

Similarly, the polymerization was not sensitive to water. Fig. 3a is Mn and PDI of the samples of Examples 6-15, Fig. 3b is conversions of the samples of Examples 6 and 8-15, Fig. 3c is FT-IR spectra of the samples of Examples 6-16, Fig. 3d is ¹HNMR spectra of the samples of Examples 6-16, Fig. 3e is ¹HNMR spectrum of the sample of Example 6 alone, and Fig. 3f is DBS curves of the samples of Examples 6-15.

In Figure 3e, the assignment of the peaks in ¹HNMR spectrum was listed as follows:

5.2-5.8 ppm, Bd, 1,4- ($-\underline{\text{CH}}=\underline{\text{CH}}-$) and vinyl ($-\underline{\text{CH}}=\underline{\text{CH}}_2$); 4.9-5.2 ppm, Bd, vinyl ($-\text{CH}=\underline{\text{CH}}_2$); 2.5-3.1 ppm, $>\underline{\text{CH}}-\text{CN}$; 1.0-2.5 ppm, $\underline{\text{H}}$ on main chains, wherein Bd, 1,4- (or 1,4-Bd) represents the polymerization units of which polymerization occurs at 1,4-positions of Bd, and vinyl (or 1,2-Bd) represents the polymerization units of which polymerization occurs at 1,2-positions of Bd. Please be advised that Bd, 1,4- (or 1,4-Bd) and vinyl (or 1,2-Bd) have the identical meaning herein after if no other specific definition.

It is seen that firstly Mn and PDI of the samples gradually increased with the feeding percent of ACN by weight of Examples 6-16 increasing, secondly the Mn and PDI of the Examples reached a top range when the feeding percent of ACN was from about 41wt% to 61wt%, and then the Mn and PDI of the Examples gradually reduced with the feeding percent of ACN further increasing. And, the conversions of the Examples were at a higher level from about

28.6wt% to 30.8wt% when the feeding percent of ACN was from about 13wt% to 61wt%. It is also seen that ACN content in the polymer obtained by the solution polymerization process of BD and ACN according to the present invention was from about 8.0wt% to about 62.2wt%.

As mentioned above, the solution polymerization process of BD and ACN according to the present invention may provide a S-NBR rubber with a super high level (more than 55wt%) of ACN. This super high level (more than 55wt%) of ACN in S-NBR rubber breaks through the limit of 55wt% of ACN content of the NBR rubber obtained by emulsion polymerization.

Due to the super high level (more than 55wt%) of ACN in S-NBR rubber according to the solution polymerization process of the present invention, it may provide excellent oil resistance than the NBR rubber obtained by routine emulsion polymerization.

Examples 17 - 18

The same catalyst system and monomers were used as in Example 1, and the polymerization reaction was carried out under the same conditions as in Example 1 except that the reaction was carried out at different temperature for different reaction time, and all samples were immediately withdrawn after the reaction time. The results were summarized in Table 5. The contents of 1,4-Bd, 1,2-Bd and ACN were the contents thereof polymerized into the S-NBR rubber.

Table 5

Example*	1,4-Bd	1,2-Bd	ACN	Temp. (°C)	Time (hrs)	Mn	Mw	PDI	Conv.
17	55.2%	5.5%	39.3%	30	136.5	24680	50551	2.05	17.8%
18	56.3%	5.5%	38.2%	40	47	25910	44126	1.70	10.6%
3	55.7%	7.2%	37.1%	60	45	39060	121607	3.11	15.6%
6	56.7%	7.1%	36.2%	80	45	45093	122623	2.72	28.5%

*Each tube: MCB, 14.1 mL; Bd, 2.4 g, 44.4 mmol; ACN, 1.7 g, 32.1 mmol; DCAP 93 mg, 69 μ L, 0.49 mmol; RhCl(PPh₃)₃, 77 mg, 0.083 mmol; PPh₃, 154 mg, 0.59 mmol; wherein 1,4-Bd represents the polymerization units of which polymerization occurs at 1,4-positions of Bd, and 1,2-Bd represents the polymerization units of which polymerization occurs at 1,2-positions of Bd.

Similarly, the polymerization was not sensitive to water. The S-NBR rubber may also be obtained after the polymerization reaction is carried out for about 10 min to 150 hrs at a temperature of about 10 °C to about 160 °C.

Fig. 4a is FT-IR spectra of the samples of Examples 3, 6, 17 and 18, and Fig. 4b is ¹HNMR spectra of the samples of Examples 3, 6, 17 and 18.

In Figure 4b, the assignment of the peaks in ¹HNMR spectrum was listed as follows:
 5.2-5.8 ppm, Bd, 1,4- ($-\underline{\text{CH}}=\underline{\text{CH}}-$) and vinyl ($-\underline{\text{CH}}=\underline{\text{CH}}_2$); 4.9-5.2 ppm, Bd, vinyl ($-\text{CH}=\underline{\text{CH}}_2$); 2.5-3.1 ppm, $>\underline{\text{CH}}-\text{CN}$; 1.0-2.5 ppm, $\underline{\text{H}}$ on main chains, wherein 1,4-Bd represents the polymerization units of which polymerization occurs at 1,4-positions of Bd, and 1,2-Bd represents the polymerization units of which polymerization occurs at 1,2-positions of Bd.

It indicates that the comonomer ACN may be copolymerized into S-NBR rubber at different

temperatures, and the conversion will reduce if the reaction is carried out at lower temperature for a same reaction time. If the reaction is carried out at lower temperature for a long reaction time, the conversion will increase as well. Polymerization temperature seemed to have slight effect on the ACN content.

5

Examples 19 - 21

The monomers were used as in Examples 1-3, the polymerization reaction was carried out under the same conditions as in Example 3, and all samples were immediately withdrawn after the reaction time 45hrs except that the catalyst system was different. In the catalyst system, the contents of $\text{RhCl}(\text{PPh}_3)_3$ and DCAP were the same as those in Example 1, and only the content of PPh_3 was different. The results were summarized in Table 6.

10

Table 6

Example*	PPh_3	Mn	Mw	PDI	Conv.	1,4-Bd	1,2-Bd	ACN
19	0 mg	52910	133422	2.52	9.2%	56.8%	6.4%	36.8%
20	77 mg	38779	118568	3.06	11.4%	56.8%	6.7%	36.5%
3	154 mg	39060	121607	3.11	15.6%	55.7%	7.2%	37.1%
21	616 mg	21986	43745	1.99	24.0%	56.7%	7.7%	35.6%

*Each tube: MCB, 14.1 mL; Bd, 2.4 g, 44.4 mmol; ACN, 1.7 g, 32.1 mmol; DCAP 93 mg, 69 μL , 0.49 mmol; $\text{RhCl}(\text{PPh}_3)_3$, 77 mg, 0.083 mmol; 0.59 mmol; 60°C, 45 hours; wherein 1,4-Bd represents the polymerization units of which polymerization occurs at 1,4-positions of Bd, and 1,2-Bd represents the polymerization units of which polymerization occurs at 1,2-positions of Bd.

15

Similarly, the polymerization was not sensitive to water. The S-NBR rubber may also be obtained after the polymerization reaction is carried out for about 10 min to 150 hrs at a temperature of about 10 °C to about 160 °C.

It indicates that the comonomer ACN may be copolymerized into S-NBR rubber at different contents of PPh_3 in the catalyst system. The conversion will reduce and the Mn and Mw will increase if the content of PPh_3 increases in the catalyst system. The contents of PPh_3 in the catalyst system seemed to have no effect on the ACN content in S-NBR rubber.

20

Examples 22-1 to 22-12

The monomers were used as in Examples 1-3, the polymerization reaction was carried out under the same conditions as in Example 3 or 6, and all samples were immediately withdrawn after the reaction time except that the additive in the catalyst system was different. The results were summarized in Tables 7-9.

25

In Examples 22-1, 22-1 and 22-3, the catalyst systems included $\text{RhCl}(\text{PPh}_3)_3$ of 77 mg, DCAP of 93 mg, PPh_3 of 154 mg, together with further additive of MTOAC, n-butylamine or dibutylamine. The results were summarized in Table 7.

30

Table 7

Example*	Additive	Temp (°C)	Time (hrs)	Mn	Mw	PDI	Conv.	T _g (°C)	1,4-Bd	1,2-Bd	ACN
6	-	80	45	45093	122623	2.72	28.5%	-23.7	57.1%	7.0%	35.9%
22-1	MTOAC, 0.1340g	80	45	34173	79948	2.34	36.7%	-25.8	55.1%	7.1%	37.8%

22-2	n-Butylamine 0.14g, 0.20mL	80	45	39617	96290	2.43	32.0%	-26.9	56.9%	6.9%	36.2%
22-3	Dibutylamine 0.25g, 0.33mL	80	45	28789	89499	3.11	38.3%	-26.1	55.5%	7.6%	36.9%

*Each tube: MCB, 14.1 mL; Bd, 2.4 g, 44.4 mmol; ACN, 1.7 g, 32.1 mmol; DCAP 93 mg, 69 μ L, 0.49 mmol; RhCl(PPh₃)₃, 77 mg, 0.083 mmol; PPh₃, 154 mg, 0.59 mmol; wherein 1,4-Bd represents the polymerization units of which polymerization occurs at 1,4-positions of Bd, and 1,2-Bd represents the polymerization units of which polymerization occurs at 1,2-positions of Bd; MTOAC: Methyltri-n-octylammonium chloride, Aliquat[®] 336.

- 5 The polymerization was not sensitive to water, and there no macro-gel occurred in all of the samples as well. The S-NBR rubber may also be obtained after the polymerization reaction is carried out for about 10 min to 150 hrs at a temperature of about 10 °C to about 160 °C.

10 Fig. 5a is ¹HNMR spectra of the samples of Examples 22-1, 22-2 and 22-3. It was seen that the conversions of the samples which used the catalyst system with further additive of MTOAC, n-butylamine or dibutylamine were at a higher level than that used the catalyst in Example 6, and the ACN contents in the polymer seemed to be slightly higher than that used the catalyst in Example 6.

Table 8

Example*	RhCl(PPh ₃) ₃ (mg)	PPh ₃ (mg)	VC (mg)	Temp. (°C)	Time (hrs)	Mn	Mw	PDI	Conv.
22-4	77	154	150	60	45	25033	46899	1.87	28.2%
22-5	77	154	75	60	45	33353	76682	2.30	23.9%
22-6	77	154	37	60	45	36352	92735	2.55	17.3%
3	77	154	0	60	45	39060	121607	3.11	15.6%
22-7	77	154	75	80	45	44411	101404	2.28	34.1%
22-8	39	77	75	80	45	76750	171458	2.23	24.3%
22-9	20	39	75	80	45	110233	219303	1.99	10.5%
22-10	5	10	75	80	45	150445	298148	1.98	6.5%
6	77	154	0	80	45	45093	122623	2.72	28.5%
22-11	39	77	0	80	45	79224	211426	2.67	16.8%
22-12	20	39	0	80	45	129960	261598	2.01	4.5%
22-13	77	0	75	80	45	71087	167190	2.35	19.3%

*MCB: 14.1 mL; Bd: 2.4 g; ACN: 1.7 g; DCAP: 93 mg.

- 15 In Examples 22-4 to 22-10, and 22-13, the catalyst systems included RhCl(PPh₃)₃, DCAP, optionally PPh₃, together with optionally further additive of Vitamine C. The results were summarized in Table 8. Fig. 5b is ¹HNMR spectrum of the sample of Example 22-7. The composition of the polymer of the sample of Example 22-7 was summarized in Table 9.

Table 9

Example	1,4-Bd	1,2-Bd	ACN
22-7	55.9%	7.3%	36.8%

- 20 Similarly, the polymerization was not sensitive to water. The S-NBR rubber may also be obtained after the polymerization reaction is carried out for about 10 min to 150 hrs at a temperature of about 10 °C to about 160 °C.

It is seen that the conversions of the samples, which used the catalyst system in Example 3 or 6 with further additive of Vitamine C, increase with the increasing contents of Vitamine C. In

addition, Vitamine C may be used replacing PPh₃ in the catalyst system in Example 3 or 6.

In addition, it is seen that the conversions of the samples, which used the catalyst system in Example 1, increase with the increasing contents of PPh₃ and/or RhCl(PPh₃)₃.

Examples 23-1 to 23-12

5 The monomers were used as in Examples 1-3, the polymerization reaction was carried out under the same conditions as in Example 3 or 6, and all samples were immediately withdrawn after the reaction time except that the co-catalyst in the catalyst system was different. The results were summarized in Tables 10 -12.

Table 10

Example*	Metal-containing catalyst/additive/co-catalyst		Temp. (°C)	Time (hrs)	Mn	Mw	PDI	Conv.
3	RhCl(PPh ₃) ₃ /PPh ₃ /DCAP	77mg/154mg/93mg	60	45	39060	121607	3.11	15.5%
6	RhCl(PPh ₃) ₃ /PPh ₃ /DCAP	77mg/154mg/93mg	80	45	45093	122623	2.72	28.4%
23-1	RhCl(PPh ₃) ₃ /PPh ₃ /PhCH ₂ Cl	77mg/154mg/8mg	60	45	112516	267388	2.38	4.7%
23-2	RhCl(PPh ₃) ₃ /PPh ₃ /PhCH ₂ Cl	77mg/154mg/16mg	60	45	101530	230253	2.27	6.2%
23-3	RhCl(PPh ₃) ₃ /PPh ₃ /PhCH ₂ Cl	77mg/154mg/31mg	60	45	94980	219271	2.31	6.7%
23-4	RhCl(PPh ₃) ₃ /PPh ₃ /PhCH ₂ Cl	77mg/154mg/62mg	60	45	79583	192148	2.41	8.9%
23-5	RhCl(PPh ₃) ₃ /PPh ₃ /PhCH ₂ Cl	77mg/154mg/62mg	80	45	92574	234803	2.54	16.6%
23-6	RhCl(PPh ₃) ₃ /PPh ₃ /CCl ₄	77mg/154mg/76mg	60	24	23745	78733	3.32	13.0%
23-7	RhCl(PPh ₃) ₃ /PPh ₃ /CCl ₄	77mg/154mg/76mg	60	45	30128	96079	3.19	17.9%
23-8	RhCl(PPh ₃) ₃ /PPh ₃ /CCl ₄	77mg/154mg/38mg	60	45	51737	158923	3.07	14.1%
23-9	RhCl(PPh ₃) ₃ /PPh ₃ /CCl ₄	77mg/154mg/19mg	60	45	85433	186189	2.18	12.3%
23-10	RhCl(PPh ₃) ₃ /PPh ₃ /Cl ₃ CCOOCH ₂ CH ₃	77mg/154mg/94mg	60	45	39718	130131	3.28	3.92%

*Each tube: MCB, 14.1 mL; Bd, 2.4 g, 44.4 mmol; ACN, 1.7 g, 32.1 mmol.

The polymerization was not sensitive to water, and there no macro-gel occurred in all of the samples as well. The S-NBR rubber may also be obtained after the polymerization reaction is carried out for about 10 min to 150 hrs at a temperature of about 10 °C to about 160 °C.

Fig. 6a - 6c are ¹HNMR spectra of the samples of Example 23-3, 23-7 and 23-10. The co-catalyst PhCH₂Cl, CCl₄, or Cl₃CCOOCH₂CH₃ may be used replacing DCAP in the catalyst system in Examples 1-3 or 4-6, and copolymer S-NBR may be obtained by using the co-catalyst PhCH₂Cl, CCl₄, or Cl₃CCOOCH₂CH₃ replacing DCAP in the catalyst system.

Table 11

Example*	RhCl(PPh ₃) ₃	PPh ₃	ABVN	Mn	Mw	PDI	Conv.	1,4-Bd	1,2-Bd	ACN
23-11	0	74 mg	53 mg	16729	68506	4.09	29.7%	54.8%	5.9%	39.3%
23-12	19 mg	74 mg	53 mg	15674	45086	2.88	30.5%	54.3%	5.2%	40.5%

*Each tube: MCB, 14.1 mL; Bd, 2.4 g, 44.4 mmol; ACN, 1.7 g, 32.1 mmol; 60°C, 45 hours.

Table 12

Example*	1,4-Bd	1,2-Bd	ACN
23-3	54.9%	6.1%	39.0%
23-7	55.1%	6.3%	38.6%
23-10	54.7%	6.3%	39.0%

*Each tube: MCB, 14.1 mL; Bd, 2.4 g, 44.4 mmol; ACN, 1.7 g, 32.1 mmol.

It was seen that the conversion of Example 23-11, which used the catalyst system with further additive of azobisisoheptonitrile (ABVN) without $\text{RhCl}(\text{PPh}_3)_3$, was the approximately same as that used the catalyst system with further additive of azobisisoheptonitrile (ABVN) and the metal catalyst of $\text{RhCl}(\text{PPh}_3)_3$ in Example 23-12, the content of ACN in Example 23-11 was slightly more than that in Example 23-12, and the PDI in Example 23-11 was much more than that in Example 23-12. It indicates that the metal catalyst of $\text{RhCl}(\text{PPh}_3)_3$ in the catalyst system may control the molecular weight distribution of the S-NBR rubber, and seems to have slightly effect on the content of ACN in the S-NBR rubber.

Examples 24-1 to 24-6

The monomers were used as in Example 1, the polymerization reaction was carried out under the same conditions as in Example 3 or 6, and all samples were immediately withdrawn after the reaction time except that the metal-containing catalyst in the catalyst system and the reaction time were different. The results were summarized in Tables 13 -14.

Table 13

Example*	Metal-containing catalyst/additive/ co-catalyst		Temp. (°C)	Time (hrs)	Mn	Mw	PDI	Conv.
24-1	$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/\text{PPh}_3/\text{DCAP}$	21mg/154mg/93mg	60	45	69220	171322	2.48	4.7%
24-2	$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/\text{PPh}_3/\text{DCAP}$	21mg/154mg/93mg	80	24	124604	258516	2.07	6.7%
24-3	$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/\text{PPh}_3/\text{DCAP}$	21mg/154mg/93mg	80	45	126445	267432	2.11	7.1%
24-4	$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/\text{PPh}_3/\text{CCl}_4$	21mg/154mg/76mg	60	45	115348	227889	1.98	8.6%
24-5	$\text{Pd}(\text{OAC})_2/\text{PPh}_3/\text{CCl}_4$	88mg/410mg/4uL	80	45	51007	137227	2.69	8.1%
24-6	$\text{Pd}(\text{OAC})_2/\text{PPh}_3/\text{CCl}_4$	44mg/205mg/2uL	80	45	72282	161727	2.24	4.8%

*Each tube: MCB, 14.1 mL; Bd, 2.4 g, 44.4 mmol; ACN, 1.7 g, 32.1 mmol.

Table 14

Example*	1,4-Bd	1,2-Bd	ACN
24-1	49.8%	7.0%	40.2%
24-3	55.4%	6.8%	37.8%
24-4	55.4%	6.1%	38.5%
24-5	55.6%	7.5%	36.9%

*Each tube: MCB, 14.1 mL; Bd, 2.4 g, 44.4 mmol; ACN, 1.7 g, 32.1 mmol.

In Examples 24-1 to 24-4, metal-containing catalyst $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ were used replacing $\text{RhCl}(\text{PPh}_3)_3$ in the catalyst system. In Example 24-4, co-catalyst CCl_4 was used replacing DCAP. Fig. 7a - 7c are ^1H NMR spectra of the samples of Examples 24-1, 24-3 and 24-4.

$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ may be reacted with PPh_3 to obtain $\text{RhCl}(\text{PPh}_3)_3$, and then copolymer S-NBR may be obtained by the solution polymerization in Examples 1-3 or 4-6. It indicates that the solution polymerization according to the present application is not sensitive to water. In addition, there no macro-gel occurred in all of the samples as well.

In Examples 24-5 to 24-6, metal-containing catalyst $\text{Pd}(\text{OAC})_2$ (palladium (II) acetate) was used replacing $\text{RhCl}(\text{PPh}_3)_3$ in the catalyst system. Fig. 7d is ^1H NMR spectrum of the sample of Example 24-5. The conversion and the PDI of the solution polymerization will increase with the amount of the catalyst system increasing when the reaction is carried out for the same time

at a same temperature.

Example 25

The catalyst system and monomers were used as in Example 1, the polymerization reaction was carried out under the same conditions as in Example 3, and all samples were immediately withdrawn after the reaction time except that the organic solvent was different. The results were summarized in Tables 15 -16.

Table 15

Example*	Metal-containing catalyst/additive/ co-catalyst	Temp. (°C)	Time (hrs)	Mn	Mw	PDI	Conv.	
25	RhCl(PPh ₃) ₃ /PPh ₃ / DCAP	77mg/154mg/ 93mg	60	45	18791	54822	2.92	5.3%

*This tube: MEK, 14.1 mL; Bd, 2.4 g, 44.4 mmol; ACN, 1.7 g, 32.1 mmol.

Table 16

Example*	1,4-Bd	1,2-Bd	ACN
25	53.1%	6.4%	40.4%

In Example 25, the organic solvent methyl ethyl ketone (MEK) was used replacing monochlorobenzene (MCB) in the polymerization reaction system. Fig. 8 is ¹HNMR spectrum of the sample of Example 25. Table 16 showed the composition of the S-NBR rubber obtained.

The other organic solvent, such as dimethyl sulfoxide (DMSO), N,N-dimethyl acetamide (DMAc) and N,N-dimethyl formamide (DMF) may be used in the solution polymerization of the present application as well.

Examples 26-1 to 26-2

The catalyst system and organic solvent were used as in Examples 1-3, the polymerization reaction was carried out under the same conditions as in Example 3 or 6, and all samples were immediately withdrawn after the reaction time except that the co-monomers were different. The results were summarized in Tables 17 - 18.

Table 17

Example*	Sample	Temp. (°C)	Mn	Mw	PDI	Conv.
26-1	29	60	11797	22713	1.93	2.6%
26-2	30	80	12000	30451	2.54	12.2%

*Each tube: MCB, 14.1 mL; Bd, 2.5 g, 46.2 mmol; Styrene, 1.7 g, 16.3 mmol; DCAP 93 mg, 69 uL, 0.49 mmol; RhCl(PPh₃)₃, 77 mg, 0.083 mmol; PPh₃, 154 mg, 0.59 mmol; 45 hours.

Table 18

Example 26-1					Example 26-2			
Item	Bd, 1,4-	Bd, vinyl	St	Total	Bd, 1,4-	Bd, vinyl	St	Total
Molar content	58.7%	11.7%	29.6%	100%	72.0%	14.7%	13.3%	100%
Mass content	46.1%	9.2%	44.7%	100%	64.1%	13.1%	22.8%	100%

Wherein Bd, 1,4- represents the polymerization units of which polymerization occurs at 1,4-positions of Bd, and Bd, vinyl represents the polymerization units of which polymerization occurs at 1,2-positions of Bd.

In Examples 26-1 to 26-2, the co-monomers butadiene (BD) and styrene (St) were used

replacing butadiene (BD) and acrylonitrile (ACN) in the polymerization reaction system. Fig. 9a is FT-IR spectrum of the sample of Example 26-2, and Fig. 9b is ¹HNMR spectrum of the sample of Example 26-2. Table 18 showed the composition of the S-SBR rubber obtained.

In Figure 9a the assignment of the peaks in FT-IR spectrum was listed as follows:

5 967 cm⁻¹, Bd, trans-1,4; 911 cm⁻¹, Bd, vinyl; 1452 cm⁻¹ and 699 cm⁻¹, phenyl ring wherein Bd, trans-1,4 represents the polymerization units of which polymerization occurs at 1,4-positions of Bd and is trans-polymerization, and Bd vinyl represents the polymerization units of which polymerization occurs at 1,2-positions of Bd.

In Figure 9b the assignment of the peaks in ¹HNMR spectrum was listed as follows:

10 6.9-7.1 ppm, H on phenyl rings; 5.0-5.6 ppm, H on 1,4-Bd units and 1,2-Bd units; 4.8-5.0 ppm, H on 1,2-Bd units.

The catalyst system of RhCl(PPh₃)₃/PPh₃/DCAP may catalyze the solution polymerization of Bd and St to afford S-SBR rubber. And, the content of styrene (St) in the S-SBR rubber increased when the polymerization reaction was carried out at a lower temperature.

15 Examples 27-1 to 27-5

The catalyst system and organic solvent were used as in Examples 1-3, the polymerization reaction was carried out under the same conditions as in Example 6, and all samples were immediately withdrawn after the reaction time except that the co-monomers included different termonomer. The results were summarized in Tables 19 - 24.

20 Table 19

Example*	Termonomer		Mn	Mw	PDI	Conv.	T _g (°C)	Incorporated
	Species	Amount						
6	Controlled trial	-	45093	122623	2.72	28.5%	-23.7	-
27-1	n-Butyl acrylate	4 mL	56882	152147	2.67	17.6%	-31.2	Yes
27-2	Methyl methacrylate	2 mL	62514	154048	2.46	23.1%	-14.4	Yes
27-3	Methacrylic acid	0.5 mL	n/a**	n/a**	n/a**	34.2%	-15.4	Yes
27-4	Itaconic acid	0.5 g	12622	24873	1.97	low	-21.2	Yes
27-5	Acrylamide	1 g	22923	50126	2.19	44.2%	-9.4	Yes

*Each tube: MCB, 14.1 mL; Bd, 2.4 g, 44.4 mmol; ACN, 1.7 g, 32.1 mmol; DCAP 93 mg, 69 uL, 0.49 mmol; RhCl(PPh₃)₃, 77 mg, 0.083 mmol; PPh₃, 154 mg, 0.59 mmol; 80°C, 45 hours; in which Controlled trial is the same as Example 6, and there is no termonomer.

**GPC system with DMF as eluent was needed. n/a = not available.

25 Table 20

Item*	ACN	Bd, 1,4-	Bd, vinyl	Total
Molar content	35.9%	57.1%	7.0%	100%
Mass content	35.5%	57.5%	7.0%	100%

* All the values were calculated through ¹H NMR spectrum.

Table 20 was the composition of the controlled trail of the sample of Example 6. Fig. 10a is FT-IR spectrum of the controlled trail of the sample of Example 6, and Fig. 10b is ¹HNMR spectrum of the controlled trail of the sample of Example 6.

30 In Figure 10a the assignment of the peaks in FT-IR spectrum was listed as follows:

2237 cm^{-1} , -CN; 970 cm^{-1} , Bd, trans-1,4; 920 cm^{-1} , Bd, vinyl; 722 cm^{-1} , Bd, cis-1,4.

In Figure 10b the assignment of the peaks in ^1H NMR spectrum was listed as follows:
5.2-5.8 ppm, Bd, 1,4- ($-\text{CH}=\text{CH}-$) and vinyl ($-\text{CH}=\text{CH}_2$); 4.9-5.2 ppm, Bd, vinyl ($-\text{CH}=\text{CH}_2$);
2.6 ppm, $>\text{CH}-\text{CN}$.

5

Table 21

Item	ACN	Bd, 1,4-	Bd, vinyl	n-BA	Total
Molar content	31.2%	49.6%	6.7%	12.5%	100%
Mass content	26.3%	42.5%	5.7%	25.5%	100%

Table 21 was the composition of the sample of Example 27-1 with termonomer n-butyl acrylate (n-BA). Fig. 10c is FT-IR spectrum of the sample of Example 27-1 with termonomer n-butyl acrylate, and Fig. 10d is ^1H NMR spectrum of the sample of Example 27-1 with termonomer n-Butyl acrylate.

10

In Figure 10c the assignment of the peaks in FT-IR spectrum was listed as follows:
1729 cm^{-1} , $>\text{C}=\text{O}$; 1164 cm^{-1} , $-\text{COOC}-$.

In Figure 10d the assignment of the peaks in ^1H NMR spectrum was listed as follows:
4.1 ppm, $-\text{COOCH}_2-$ of n-BA units; 0.8 ppm and 1.4 ppm, $-\text{CH}_2\text{CH}_3$ of n-BA units.

Table 22

Item	ACN	Bd, 1,4-	Bd, vinyl	MMA	Total
Molar content	27.7%	50.5%	5.7%	16.1%	100%
Mass content	24.0%	44.6%	5.0%	26.4%	100%

15

Table 22 was the composition of the sample of Example 27-2 with termonomer Methyl methacrylate (MMA). Fig. 10e is FT-IR spectrum of the sample of Example 27-2 with termonomer MMA, and Fig. 10f is ^1H NMR spectrum of the sample of Example 27-2 with termonomer MMA.

In Figure 10e the assignment of the peaks in FT-IR spectrum was 1729 cm^{-1} , $>\text{C}=\text{O}$.

20

In Figure 10f the assignment of the peaks in ^1H NMR spectrum was listed as follows:
3.7 ppm, $-\text{COOCH}_3$; 1.1 ppm, $-\text{CH}_3$ of MMA units.

Table 23

Item	ACN	Bd, 1,4-	Bd, vinyl	MAA	Total
Molar content	29.7%	54.8%	7.4%	8.1%	100%
Mass content	28.0%	52.6%	7.1%	12.3%	100%

25

Table 23 was the composition of the sample of Example 27-3 with termonomer methacrylic acid (MAA). Fig. 10g is FT-IR spectrum of the sample of Example 27-3 with termonomer MAA, and Fig. 10h-10i are ^1H NMR spectra of the sample of Example 27-3 with termonomer MAA.

In Figure 10g the assignment of the peaks in FT-IR spectrum was 1701 cm^{-1} , $-\text{COOH}$.

In Figures 10h-10i the assignment of the peaks in ^1H NMR spectrum was listed as follows:
1.0 ppm, $-\text{CH}_3$ on MAA units; 12.2 ppm, $-\text{COOH}$; 3.3 ppm, H_2O ; 2.5 ppm, DMSO.

Table 24

Item	ACN	Bd, 1,4-	Bd, vinyl	IA
Molar content	33.9%	58.1%	8.0%	undetermined*
Mass content	33.5%	58.5%	8.0%	

*The value of IA content could not be calculated through ^1H NMR spectrum.
Here the total content of ACN and Bd was deemed as 100%.

Table 24 was the composition of the sample of Example 27-4 with termonomer itaconic acid (IA). Fig. 10j is FT-IR spectrum of the sample of Example 27-4 with termonomer IA, and Fig. 10k-10l are ^1H NMR spectra of the sample of Example 27-4 with termonomer IA.

In Figure 10j the assignment of the peaks in FT-IR spectrum was 1701 cm^{-1} , $-\text{COOH}$.

In Figure 10k-10l the assignment of the peaks in ^1H NMR spectrum was listed as follows:
12.3 pm, $-\text{COOH}$; 3.3 ppm, H_2O ; 2.5 ppm, DMSO.

Fig. 10m is FT-IR spectrum of the sample of Example 27-5 with termonomer acrylamide. In Figure 10m the assignment of the peaks in FT-IR spectrum was listed as follows:
 1671 cm^{-1} , $>\text{C}=\text{O}$; $3100\text{-}3500\text{ cm}^{-1}$, $-\text{NH}_2$.

It was seen that termonomer acrylamide was copolymerized into the NBR polymer chains. Other termonomers, such as vinyl acetate, fumaric acid, and the like also may be solution copolymerized in the process according to the present invent.

Examples 28-1 to 28-4

A 600 mL Parr autoclave reactor was used for the copolymerization trials in a bigger scale. The experimental conditions and results are listed in Table 25, Figure 11a and Figure 11b.

Table 25

Example	Monomers			MCB (mL)	DCAP (g)	$\text{RhCl}(\text{PPh}_3)_3$ (g)	PPh_3 (g)
	ACN (g)	Bd (g)	ACN Content (%)				
28-1	36.5	52.7	41.0	240	1.26	0.62	1.3
28-2	36.5	52.7	41.0	240	1.26	0.62	1.3
28-3	54.7	79.1	34.2	180	1.26	0.62	0.62
28-4	35.6	79.5	31.0	180	0.32	0.62	0.62
28-5	54.8	79.1	41.0	180	0.15	0.31	0.31

Example	Temp (°C)	Time (hrs)	Mn	Mw	PDI	Conv.	Obtained NBR (g)	ML(1+4) 100 °C	Tg (°C)
28-1	60	17	74094	174515	2.35	low	n/a	n/a	-23.3
28-2	60	46	118956	250229	2.10	6%	5.3	n/a	-23.0
28-3	80	45	18696	29995	1.60	low	-	n/a	n/a
28-4	80	66	61841	120552	1.95	21.1%	24.4	1.9	-32.0

28-5	120	25	52308	100411	1.92	17%	22.9	4.6	-25.2
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Example	Composition of sample by ¹ HNMR analysis		
	1,4-Bd (%)	1,2-Bd (%)	ACN (%)
28-1	n/a	n/a	n/a
28-2	n/a	n/a	n/a
28-3	57.2	8.6	34.2
28-4	59.5	9.5	31.0
28-5	n/a	n/a	n/a

* n/a: not available

It is found that higher temperature is beneficial for obtaining higher polymerization conversion at shorter reaction time with lower catalyst concentration.

5 The polymerization reaction of BD with at least one co-monomer in organic solution may be carried out at a broader range of reaction temperature, from to 10 °C to the temperature used for hydrogenation, such as 160 °C. Preferably, the reaction may be carried out at room temperature to 150 °C, more preferably at 30 °C to 150 °C, further preferably at 60 °C to 150 °C, most preferably at 80 °C to 150 °C.

10 The polymerization is carried out at higher temperature to improve the productivity of the copolymerization with less catalyst.

The sample of Example 28-2 was hydrogenated continuously in one-pot in the autoclave reactor. The hydrogenation reaction conditions are listed in the following examples.

15 Fig. 11a is FT-IR spectra of the samples of Examples 28-1 and 28-2 which are carried out for different reaction time, and Fig. 11b is ¹HNMR spectrum of the sample of Example 28-4.

Example 29

The polymerization reaction was carried out in the autoclave reactor, and the reaction conditions and the results are listed in Table 26, and the sample was immediately withdrawn after the reaction time except that the co-monomers included termonomer n-butyl acrylate (n-BA).

20

Table 26

Example	Monomers			MCB (mL)	DCAP (g)	RhCl(PPh ₃) ₃ (g)	PPh ₃ (g)
	ACN (g)	Bd (g)	n-BA (G)				
29	54.8	79.1	117	150	0.32	0.62	0.62

Example	Temp (°C)	Time (hrs)	Mn	Mw	PDI	ML(1+4) 100 °C	Tg (°C)
29	80	45	135178	275657	2.04	47.8	-29.6

Example	Composition of sample by ¹ HNMR analysis			
	1,4-Bd (%)	1,2-Bd (%)	ACN (%)	n-BA
29 (molar ratio)	49.9	5.4	34.3	10.4
29 (weight ratio)	43.9	4.8	29.6	21.7

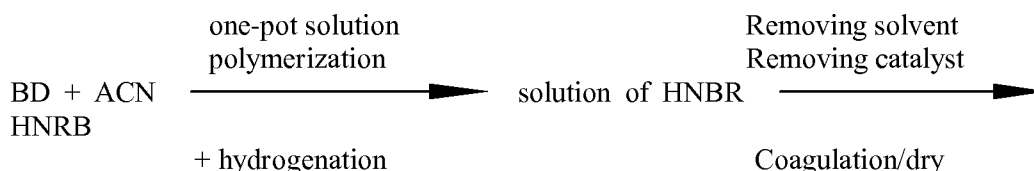
25 It is seen that the solution polymerization reaction of BD and ACN with termonomer may be

carried out in the autoclave reactor as well.

When n-BA (n-butyl acrylate) was used as the termonomer for the polymerization, higher molecular weight NBR was obtained at shorter time. Compared to the E-NBR product obtained by emulsion polymerization using n-BA as the termonomer, this S-NBR product has much narrower molecular weight distribution (PDI = 2.04).

Examples 30-1 to 30-7

The one-pot solution polymerization and hydrogenation process were carried out in 600 mL Parr autoclave reactor. After the solution polymerization completing, the excess monomers and/or DCAP were exhausted from the valve at polymerization temperature. And then, the valve was closed and the temperature was increased to hydrogenation temperature and hydrogen was injected into the autoclave reactor. The scheme of one-pot solution polymerization and hydrogenation (HD) process from butadiene and acrylonitrile to HNBR is listed out in scheme 1 as follows. The experimental conditions and results are shown in Table 27 and Figure 12.



Scheme 1 From butadiene and acrylonitrile to HNBR

15 Similarly, the one-pot solution polymerization and hydrogenation (HD) process from butadiene and acrylonitrile or other comonomer, such as styrene, and optionally termonomer to hydrogenated terpolymers, hydrogenated butadiene-styrene copolymers, or hydrogenated butadiene-styrene terpolymers may be synthesized as indicated in Scheme 1 by the different monomers as well.

20

Table 27

[illegible]

Example	Stage*	Mn	Mw	PDI	HD(%)	Obtained (g)	Mooney (1+4)@100	Tg (°C)	Gel
30-1	Polym.	n/a	n/a	n/a	n/a	n/a	n/a	n/a	No
30-2	HD	38,826	95,207	2.45	99	3.58	n/a	-20.3	No
30-3	Polym.	n/a	n/a	n/a	n/a	n/a	n/a	n/a	No
30-4	HD	39,978	89,457	2.36	99	3.36	n/a	n/a	No
30-5	Polym.	12,739	25,936	2.03	n/a	n/a	n/a	n/a	No
30-6		18,696	29,995	1.60	n/a	n/a	n/a	n/a	No
30-7	HD	19,677	35,136	1.78	86	24.5	<1	-28.5	No
30-8	Polym.	62744	199205	3.17	n/a	n/a	n/a	n/a	No
30-9	HD	66393	228608	3.44	94	93.3	73	-23.9	No

Composition by ¹ HNMR	1,4-Bd	1,2-Bd	ACN
30-5 (time 17 hrs)	56.0%	8.1%	35.9%
30-6 (time 45 hrs)	57.2%	8.6%	34.2%

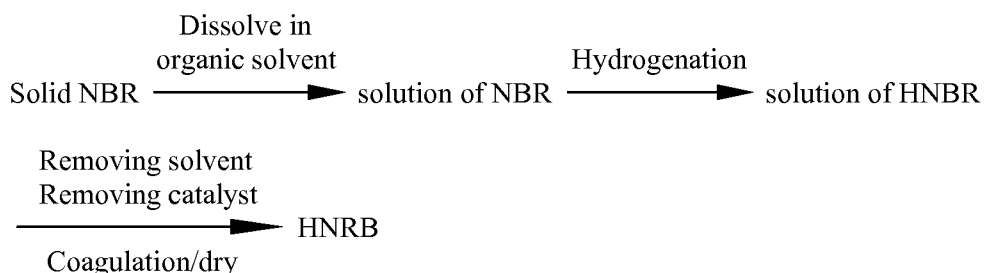
* There are two stages: polymerization (polym.) and hydrogenation (HD);
n/a: not available; No: there no gel occurred.

5 Fig.12 is the FT-IR spectra and ¹HNMR spectra of S-NBR and hydrogenated S-NBR. The assignments of FT-IR spectra and ¹HNMR spectra are listed in Fig. 12.

10 It is clear that the one-pot polymerization and hydrogenation was conducted successfully to produce HNBR directly from monomers. Therefore, the scheme of one-pot polymerization and hydrogenation is shorted great. That is, the catalyst system of the present invention is not only used as solution polymerization catalyst for BD and at least one comonomer, but also used as hydrogenation catalyst for the polymer obtained by solution polymerization.

Examples 31-1 to 31-4

15 The hydrogenation process for NBR polymer solid was carried out in 600 mL Parr autoclave reactor. The scheme of hydrogenation (HD) process from NBR solid to HNBR is listed out in scheme 2. The experimental conditions and results are shown in Tables 28-29 and Figure 13.



Scheme 2 From solid S-NBR to HNBR

20 Hydrogenation of S-NBR solid product was conducted in Example 31-1. S-NBR solid obtained from the sample in Example 28-4 was used for a hydrogenation trial in Example 31-1. S-NBR solid was dissolved into the organic solvent (such as MCB, MEK, DMAC, DEAC, particularly MCB). The solution mixture obtained was hydrogenated in the presence of the metal-containing catalyst and additive (such as RhCl(PPh₃)₃/PPh₃) of the metal catalyst system of the

present invention under desired hydrogen pressure, the experimental conditions and results are listed in Table 28 and Figure 13.

Table 28 Hydrogenation of S-NBR

Example	S-NBR (g)	MCB (mL)	RhCl(PPh ₃) ₃ (g)	PPh ₃ (g)	PH ₂ (Psi)	T (°C)	Time (hrs)
31-1	24.4	350	0.2	0.4	600	120	4

Example	Mn	Mw	PDI	HD (%)	Mooney	Tg (°C)	Gel formation
31-1	86,188	157,164	1.82	99	33	-23.4	No

5 Figure 13 is the FT-IR spectra of S-NBR and hydrogenated S-NBR. The assignments of FT-IR spectra and ¹HNMR spectra are listed in Fig. 13.

Furthermore, hydrogenation of commercial NBR was conducted in Example 31-2 in the presence of the metal-containing catalyst and additive (RhCl(PPh₃)₃/PPh₃) of the metal catalyst system of the present invention and organic solvent (such as MCB), and optionally co-catalyst
10 (such as DCAP) and monomer (such as ACN and/or Bd). The commercial NBR solid was dissolved into the organic solvent (such as MCB, MEK, DMAC, DEAC, particularly MCB). The solution mixture obtained was hydrogenated in the presence of the metal-containing catalyst and additive (such as RhCl(PPh₃)₃/PPh₃) of the metal catalyst system of the present invention under desired hydrogen pressure. The experimental conditions and results are listed
15 in Table 29.

Table 29 The hydrogenation of Krynac 3345F

Example	Krynac 3345F (g)	Adding other chemicals	Conversion (%)
31-2 (Control (using only commercial NBR))	3.6	None	97%
31-3 (Adding DCAP)	3.6	30.5 mg of DCAP	90%
31-3 (Adding ACN)	1.0	1 mL of ACN	89%
31-4 (Adding Bd)	1.0	5.5 g of Bd	85%

In each example: MCB, 170 mL; RhCl(PPh₃)₃, 15 mg, 0.016 mmol; PPh₃, 30 mg, 0.11 mmol; hydrogen pressure 600 psi, 120°C, 1 hour.

It was found that in the presence of small amount of monomers (such as ACN and/or Bd) or co-catalyst (such as DCAP), the hydrogenation could achieve high conversion, and even in the
20 presence of bigger amount of the Bd monomer (1 g NBR with 5.5 g of Bd) the NBR could still be hydrogenated. This result was the same as that in hydrogenation of the obtained S-NBR directly in a one-pot fashion one-pot fashion in the presence of monomer or optionally co-catalyst and/or additive residues.

25 The metal-containing catalyst may be removed by using ion-exchange resin as described in EP 2 072 532 A1, EP 2 072 533 A1, CN101463096 A. Particularly, after the copolymerization and/or hydrogenation reaction completing, the reaction mixture was taken out and treated with ion-exchange resin at 100 °C for 48 hours and then precipitated in cold methanol.

Conclusion

As mentioned above, the S-NBR process may simplify the HNBR production by directly providing NBR feedstock in solution form.

5 S-NBR (obtained by Controlled Radical Polymerization in solution) as feedstock and the one-pot process for HNBR production have the advantages to:

- 1) simplify the manufacturing process, and save time and cost in processing;
- 2) provide pure feedstocks and pure HNBR products;
- 3) provide HNBR with control molecular weight, and HNBR products with lower mooney viscosity without extra cost/process.

10 The results clearly show that under a broad variety of operating conditions it is possible to synthesize nitrile rubber polymers having controlled molecular weight and narrow molecular weight distribution in the presence of the catalyst of the metal-containing catalyst with suitable co-catalyst and optionally additive.

15 Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

WHAT IS CLAIMED IS:

1. A metal-containing catalyst system, which comprises (1) a metal-containing catalyst, (2) a co-catalyst, and optionally (3) an additive, for a solution polymerization process of diene and/or for hydrogenation of diene-containing polymers, wherein

5 (1) the metal-containing catalyst is selected from ML_nX_m , MX_m , $MX_m \cdot pH_2O$, $M(OC(O)R)_m$, or any combination thereof, wherein M represents a metal selected

from Rh, Pd, Ru, Ir, Mo, Co, Cu, Fe, or Ti, L is a group selected from , in which R_1 , R_2 , and R_3 may be same or different, and each R_1 , R_2 and R_3 is independently selected from H, C_1 - C_6 alkyl, C_5 - C_7 aryl or C_3 - C_6 cycloalkyl, substituted C_3 - C_6 cycloalkyl, substituted C_5 - C_7 aryl, with a proviso that R_1 , R_2 and R_3 are not all of H, X is a halogen, n is a integer of 1 to 5, p is a integer of 1 to 7, and m is equal to the valence of M;

(2) the co-catalyst is selected from a halide, an azo-compound, or a peroxide; and optionally

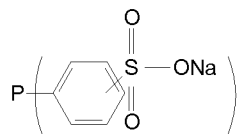
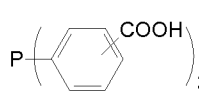
15 (3) the additive is selected from a group consisting of a primary amine (R_1-NH_2),

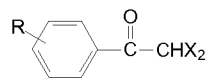
a second amine (R_1-NH-R_2), a tertiary amine ($N(R_1)(R_2)(R_3)$), , ascorbic acid, or an ammonium salt, or any combination thereof, in which R_1 , R_2 , and R_3 are defined as the above.

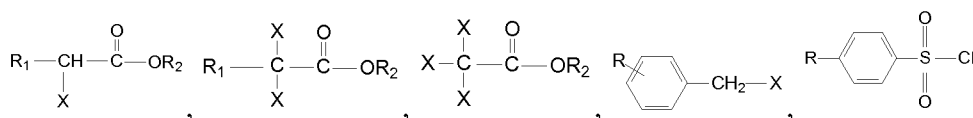
2. The metal-containing catalyst system of claim 1, wherein

20 (1) in the metal-containing catalyst, M represents a metal selected from Rh, Pd, Ru, Ir or Mo, preferably Rh, Pd, Ru, Ir, X is selected from Cl or Br, more preferably

Cl; in , each R_1 , R_2 , and R_3 is independently selected from phenyl, C_3 - C_6 cycloalkyl, substituted C_3 - C_6 cycloalkyl, phenyl, substituted phenyl, preferably carboxy-substituted phenyl, sodium sulfonate-substituted phenyl, more preferably

25 PPh_3 , phosphine tricyclohexyl (PCy_3), , , in which the sodium sulfonate group or carboxy group may be in ortho-, meta- or para-position of phenyl ring;

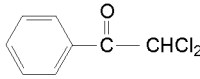
(2) in the co-catalyst, the halide is selected from ,



CH₂Cl₂, CHCl₃, CCl₄, in which each of R, R₁, and R₂ is independently a C₁-C₆ alkyl or C₃-C₆ cycloalkyl, and R group may be in ortho-, meta- or para-position of phenyl ring, and each X is independently defined as the above, the azo-compound is selected from 2,2'-azobisisobutylnitrile (AIBN), 2,2'-azobis-(2-methylbutylnitrile (AMBN), 2,2'-azobis-(2-methylbutylnitrile (AMBN), dimethyl 2,2'-azobis-(2-methylpropionate, 1-cyano-1-methylethylazofornamide, 1,1'-azobis(cyclohexane-1-carbonitrile (ACCN), 2,2'-azobis-(2-methylpropionamide)dihydrochloride (AIBA), or 4,4'-azobis-(4-cyanovaleric acid) (ACVA), and the peroxide is selected from tert-butylhydroperoxide, benzoyl peroxide (BPO) or cumyl peroxide; and optionally

(3) the additive is selected from a group consisting of ascorbic acid, methylamine, ethylamine, ethyldiamine, n-propylamine, iso-propylamine, propyldiamine, n-butylamine, iso-butylamine, butyldiamine, dibutylamine, dimethylamine, diethylamine, diiso-propylamine, t-butylamine, amylamines, cyclohexylamine, triethanolamine, trimethylamine, triethylamine, tri-n-propylamine, tri-n-butylamine, cycloheptylamine, cyclopentylamine, methyltri-n-octylammonium chloride (MTOAC), $\begin{array}{c} \text{P}-\text{R}_1 \\ | \\ \text{R}_2 \\ | \\ \text{R}_3 \end{array}$, or any combination thereof, in which R₁, R₂, and R₃ are defined as the above.

3. The metal-containing catalyst system in accordance with one or more of claims 1 - 2, wherein the metal-containing catalyst system is selected from:

a group consisting of (1) MCl_m(PPh₃)_n, (2) , 2,2-dichloroacetophenone (DCAP) or benzyl chloride, and optionally (3) PPh₃;

a group consisting of (1) MCl_m and/or MX_m·pH₂O, (2) 2,2-dichloroacetophenone or benzyl chloride (BCL) and optionally (3) P(Ph)₃;

a group consisting of (1) MCl_m(PPh₃)_n, (2) PhCH₂Cl, and optionally (3) PPh₃;

a group consisting of (1) (MCl_m(PPh₃)_n, (2) one of CH₂Cl₂, CHCl₃, CCl₄, and optionally (3) PPh₃;

a group consisting of (1) MCl_m(PPh₃)_n, (2) Cl₃CCOOCH₂CH₃ and (3) PPh₃;

a group consisting of (1) MCl_m(PPh₃)_n, (2) at least one of 2,2'-azobisisobutylnitrile (AIBN), 2,2'-azobis-(2-methylbutylnitrile (AMBN), 2,2'-azobis-(2-methylbutylnitrile (AMBN), dimethyl 2,2'-azobis-(2-methylpropionate, 1-cyano-1-methylethylazofornamide, 1,1'-azobis(cyclohexane-1-carbonitrile (ACCN), 2,2'-azobis-(2-methylpropionamide)dihydrochloride (AIBA), 4,4'-azobis-(4-cyanovaleric

acid) (ACVA), and optionally (3) PPh_3 ; or

a group consisting of (1) $\text{M}(\text{OAc})_m$, (2) at least one of CH_2Cl_2 , CHCl_3 , CCl_4 , and optionally (3) $\text{P}(\text{Ph})_3$;

wherein M is selected from Rh, Pd, Ru, Ir, Mo, preferably selected from Rh, Ru, Pd, and Ir, more preferably selected from Rh, Ru, and Pd, n is a integer of 3, p is a integer of 1 to 7, and m is equal to the valence of M.

4. The metal-containing catalyst system in accordance with one or more of claims 1 - 3, wherein the metal-containing catalyst system is selected from:

a group consisting of $\text{RhCl}(\text{PPh}_3)_3$, 2,2-dichloroacetophenone (DCAP), and optionally PPh_3 ;

a group consisting of RhCl_3 or $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, 2,2-dichloroacetophenone and PPh_3 ;

a group consisting of $\text{RhCl}(\text{PPh}_3)_3$, $\text{Cl}_3\text{CCOOCH}_2\text{CH}_3$, and optionally PPh_3 ;

a group consisting of RhCl_3 or $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, $\text{Cl}_3\text{CCOOCH}_2\text{CH}_3$ and PPh_3 ; a mixture comprising or consisting of $\text{RhCl}(\text{PPh}_3)_3$, PhCH_2Cl and optionally PPh_3 ;

a group consisting of RhCl_3 or $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, PhCH_2Cl and PPh_3 ;

a group consisting of PdCl_2 , 2,2-dichloroacetophenone and PPh_3 ;

a group consisting of PdCl_2 , benzyl chloride and PPh_3 ;

a group consisting of $\text{RhCl}(\text{PPh}_3)_3$, at least one of CH_2Cl_2 , CHCl_3 , CCl_4 and optionally PPh_3 ;

a group consisting of RhCl_3 or $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, at least one of CH_2Cl_2 , CHCl_3 , CCl_4 , and PPh_3 ;

a group consisting of $\text{Pd}(\text{OAc})_2$, at least one of CH_2Cl_2 , CHCl_3 , CCl_4 , and PPh_3 ;

or

a group consisting of $\text{RhCl}(\text{PPh}_3)_3$, azobisisoheptonitrile (ABVN), and optionally PPh_3 .

5. The metal-containing catalyst system in accordance with one or more of claims 1 - 4, wherein the metal-containing catalyst system is selected from the following compositions consisting of, by weight of,

$\text{RhCl}(\text{PPh}_3)_3$: DCAP : PPh_3 = 1 : 0.3-3.0 : 0-20;

RhCl_3 : DCAP : PPh_3 = 1 : 1.3-13 : 4.4-88;

$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$: DCAP : PPh_3 = 1 : 1.0-10 : 3.0-63;

$\text{RhCl}(\text{PPh}_3)_3$: $\text{Cl}_3\text{CCOOCH}_2\text{CH}_3$: PPh_3 = 1 : 0.3-3.0 : 0-20;

RhCl_3 : $\text{Cl}_3\text{CCOOCH}_2\text{CH}_3$: PPh_3 = 1 : 1.3-3.9 : 4.4-88;

$\text{RhCl}_3 \cdot 3\text{H}_2\text{O} : \text{Cl}_3\text{CCOOCH}_2\text{CH}_3 : \text{PPh}_3 = 1 : 1.0-10 : 3.0-63;$

$\text{RhCl}(\text{PPh}_3)_3 : \text{PhCH}_2\text{Cl} : \text{PPh}_3 = 1 : 0.05-2.0 : 0-20;$

$\text{RhCl}_3 : \text{PhCH}_2\text{Cl} : \text{PPh}_3 = 1 : 0.22-9.0 : 4.4-88;$

$\text{RhCl}_3 \cdot 3\text{H}_2\text{O} : \text{PhCH}_2\text{Cl} : \text{PPh}_3 = 1 : 0.2-7.0 : 3.0-63;$

5 $\text{PdCl}_2 : \text{DCAP} : \text{PPh}_3 = 1 : 0.3-3.0 : 0-20;$

$\text{RhCl}(\text{PPh}_3)_3 : \text{CCl}_4 : \text{PPh}_3 = 1 : 0.1-3 : 0-20;$

$\text{RhCl}_3 : \text{CCl}_4 : \text{PPh}_3 = 1 : 0.4-13 : 4.4-88;$

$\text{RhCl}_3 \cdot 3\text{H}_2\text{O} : \text{CCl}_4 : \text{PPh}_3 = 1 : 0.3-11 : 3.0-63;$

$\text{Pd}(\text{OAc})_2 : \text{CCl}_4 : \text{PPh}_3 = 1 : 10^{-4}-10^{-2} : 3.5-27; \text{ or}$

10 $\text{RhCl}(\text{PPh}_3)_3 : \text{ABVN} : \text{PPh}_3 = 0-1 : 1-10 : 2-20.$

6. The metal-containing catalyst system in accordance with one or more of claims 1- 5, wherein the metal-containing catalyst system is selected from the following compositions consisting of, by weight of,

$\text{RhCl}(\text{PPh}_3)_3 : \text{DCAP} : \text{PPh}_3 = 1 : 0.5-2.0 : 1-10;$

15 $\text{RhCl}_3 : \text{DCAP} : \text{PPh}_3 = 1 : 2.2-9.0 : 5.4-50;$

$\text{RhCl}_3 \cdot 3\text{H}_2\text{O} : \text{DCAP} : \text{PPh}_3 = 1 : 2.0-8 : 4.0-44;$

$\text{RhCl}(\text{PPh}_3)_3 : \text{Cl}_3\text{CCOOCH}_2\text{CH}_3 : \text{PPh}_3 = 1 : 0.5-2.0 : 1-10;$

$\text{RhCl}_3 : \text{Cl}_3\text{CCOOCH}_2\text{CH}_3 : \text{PPh}_3 = 1 : 2.2-9.0 : 5.4-50;$

$\text{RhCl}_3 \cdot 3\text{H}_2\text{O} : \text{Cl}_3\text{CCOOCH}_2\text{CH}_3 : \text{PPh}_3 = 1 : 2.0-8 : 4.0-44;$

20 $\text{RhCl}(\text{PPh}_3)_3 : \text{PhCH}_2\text{Cl} : \text{PPh}_3 = 1 : 0.08-1.5 : 1-10;$

$\text{RhCl}_3 : \text{PhCH}_2\text{Cl} : \text{PPh}_3 = 1 : 0.35-6.7 : 5.4-50;$

$\text{RhCl}_3 \cdot 3\text{H}_2\text{O} : \text{PhCH}_2\text{Cl} : \text{PPh}_3 = 1 : 0.3-6.0 : 4.0-44;$

$\text{PdCl}_2 : \text{DCAP} : \text{PPh}_3 = 1 : 0.5-2.0 : 1-10;$

$\text{RhCl}(\text{PPh}_3)_3 : \text{CCl}_4 : \text{PPh}_3 = 1 : 0.2-2 : 1-10;$

25 $\text{RhCl}_3 : \text{CCl}_4 : \text{PPh}_3 = 1 : 0.9-9 : 5.4-50;$

$\text{RhCl}_3 \cdot 3\text{H}_2\text{O} : \text{CCl}_4 : \text{PPh}_3 = 1 : 0.7-7 : 4.0-44;$

$\text{Pd}(\text{OAc})_2 : \text{CCl}_4 : \text{PPh}_3 = 1 : 5 \cdot 10^{-4}-5 \cdot 10^{-2} : 4.5-17; \text{ or}$

$\text{RhCl}(\text{PPh}_3)_3 : \text{ABVN} : \text{PPh}_3 = 0.2-0.5 : 0.5-2 : 0.5-4.$

7. The metal-containing catalyst system in accordance with one or more of claims 1- 6, wherein the additive is selected from the group consisting of ascorbic acid, methyltri-

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n-octylammonium chloride, n-propylamine, iso-propylamine, propyldiamine, n-butylamine, iso-butylamine, n-butylamine, dibutylamine, trimethylamine, triethylamine, tri-n-propylamine, tri-n-butylamine, or combination thereof.

- 5 8. A solution polymerization process of dienes, comprising homopolymerization of diene or copolymerization of diene together with at least one of comonomers in the presence of at least one of the metal-containing catalyst system in accordance with one or more of any of claims 1- 7 in at least one of organic solvents.
- 10 9. The solution polymerization process in accordance with claim 8, wherein the dienes are selected from any known diene, preferably selected from at least one of conjugated dienes, more preferably a C₄-C₆ conjugated diene, including 1,3-butadiene, isoprene, 2,3-dimethylbutadiene, piperylene or mixtures thereof, and most preferred 1,3-butadiene, isoprene or mixtures thereof.
- 15 10. The solution polymerization process in accordance with one or more of claims 8 - 9, wherein the at least one of comonomers are selected from at least one of α,β -unsaturated nitriles or styrene-based compounds, and preferably the at least one of α,β -unsaturated nitriles are selected from any known α,β -unsaturated nitriles, more preferably an α,β -unsaturated (C₃-C₅) nitrile including acrylonitrile, methacrylonitrile, ethylacrylonitrile or mixtures thereof, most preferred acrylonitrile; the styrene-based compounds are selected from styrene, α -methyl styrene or vinyl toluene.
- 20 11. The solution polymerization process in accordance with one or more of claims 8 - 10 wherein the at least one of comonomers are selected from styrene.
- 25 12. The solution polymerization process in accordance with one or more of claims 8-11, wherein the at least one of comonomers further comprises termonomers, including vinyl monomers, vinylidene monomers and α,β -unsaturated monomers, which is selected from at least one of (math)acrylic acid, any of (math)acrylic acid esters, any of (math)acrylic acid salts, any of olefin, and any of unsaturated carboxylic acid, preferably any of n-butyl (math)acrylate, i-butyl (math)acrylate, t-butyl (math)acrylate, ethylene, propylene, vinylidene monomers, methyl (math)acrylate, ethyl (math)acrylate, n-propyl (math)acrylate, i-propyl (math)acrylate, 2-ethylhexyl (math)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxy butyl (meth)acrylate, 30 benzyl (meth)acrylate, cyclohexyl (meth)acrylate, phenyl (meth)acrylate, 2-aminoethyl (meth)acrylate, 2-dimethylaminoethyl (meth)acrylate, fumaric acid, maleic acid, and itaconic acid.
- 35 13. The solution polymerization process in accordance with one or more of claims 8-12, wherein the at least one of organic solvents are selected from any organic solvent which does not react with the catalyst or otherwise interfere with the reaction,

preferably selected from benzene, toluene, cyclohexane, dimethyl sulfoxide (DMSO), ethylene carbonate (EC), tetrahydrofuran (THF), 1,4-dioxane monochlorobenzene (MCB), dichlorobenzene (DCB), trichlorobenzene (TCB), monobromobenzene (MBB), dibromobenzene (DBB), tribromobenzene (TBB), methyl ethyl ketone (MEK), N,N-dimethyl formamide (DMF), N,N-dimethyl acetamide (DMAC), or the mixture thereof, more preferably selected from monochlorobenzene (MCB), methyl ethyl ketone (MEK), N,N-dimethyl formamide (DMF), or N,N-dimethyl acetamide (DMAC), further preferably selected from monochlorobenzene (MCB) and methyl ethyl ketone (MEK), most preferably monochlorobenzene (MCB).

- 10 14. The solution polymerization process in accordance with one or more of claims 8-13, wherein the metal-containing catalyst system is selected from

the group consisting of $\text{RhCl}(\text{PPh}_3)_3$: DCAP : PPh_3 , in which, by weight of, $\text{RhCl}(\text{PPh}_3)_3$: DCAP : $\text{PPh}_3 = 1 : 0.5\text{-}2.0 : 1\text{-}10$;

15 the group consisting of RhCl_3 : DCAP : PPh_3 , in which, by weight of, RhCl_3 : DCAP : $\text{PPh}_3 = 1 : 2.2\text{-}9.0 : 5.4\text{-}50$;

the group consisting of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$: DCAP : PPh_3 , in which, by weight of, $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$: DCAP : $\text{PPh}_3 = 1 : 2.0\text{-}8 : 4.0\text{-}44$;

the group consisting of PdCl_2 : DCAP : PPh_3 , in which, by weight of, PdCl_2 : DCAP : $\text{PPh}_3 = 1 : 0.5\text{-}2.0 : 1\text{-}10$;

20 the group consisting of $\text{Pd}(\text{OAc})_2$: CCl_4 : PPh_3 , in which, by weight of, $\text{Pd}(\text{OAc})_2$: CCl_4 : $\text{PPh}_3 = 1 : 5 \times 10^{-4}\text{-}5 \times 10^{-2} : 3.5\text{-}27$;

the group consisting of $\text{RhCl}(\text{PPh}_3)_3$: PhCH_2Cl : PPh_3 , in which, by weight of, $\text{RhCl}(\text{PPh}_3)_3$: PhCH_2Cl : $\text{PPh}_3 = 1 : 0.08\text{-}1.5 : 1\text{-}10$;

25 the group consisting of RhCl_3 : PhCH_2Cl : PPh_3 , in which, by weight of, RhCl_3 : PhCH_2Cl : $\text{PPh}_3 = 1 : 0.35\text{-}6.7 : 5.4\text{-}50$; or

the group consisting of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$: PhCH_2Cl : PPh_3 , in which, by weight of, $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$: PhCH_2Cl : $\text{PPh}_3 = 1 : 0.3\text{-}6.0 : 4.0\text{-}44$.

15. The solution polymerization process in accordance with one or more of claims 8-14, wherein the diene homopolymer or copolymer having a controlled Mn, from 1,000 to 300,000, with PDI from 1.0 to 5.0, preferably the controlled Mn, from 3,000 to 100,000, with PDI from 1.1 to 4.0, more preferably the controlled Mn, from 5,000 to 50,000, with PDI from 1.1 to 3.0, the ACN content in the diene homopolymer or copolymer from 0 to 65 wt%, or styrene content in the diene copolymer from 0 to 80, preferably the ACN content in the diene copolymer from 10 to 63 wt%, or styrene content in the diene copolymer from 20 to 80 wt%, more preferably the ACN content in the diene copolymer from 30 to 60 wt%, or styrene content in the diene copolymer

from 20 to 70 wt%, based on the total weight of the diene homopolymer or copolymer.

16. The solution polymerization process in accordance with one or more of claims 8-15, wherein the polymerization is carried out with the feeding weight part of the diene is from about more than 0 to about less than 100, and the feeding weight part of the at least one of comonomers is from about less than 100 to about more than 0.
17. The solution polymerization process in accordance with one or more of claims 8-16, wherein the polymerization is carried out with the feeding weight part of α,β -unsaturated nitrile monomer is about 4 to about less than 96, or the feeding weight percent of the styrene and any of derivatives of styrene is from about less than 96 to about 4, preferably the feeding weight part of α,β -unsaturated nitrile monomer is about 4 to about less than 90, or the feeding weight percent of the styrene and any of derivatives of styrene is from about less than 96 to about 10.
18. The solution polymerization process in accordance with one or more of claims 8-17, wherein the polymerization is carried out at temperature of 10 °C - 160 °C for 5-200 hrs, preferably at temperature of 20 °C - 150 °C for 10-180 hrs, more preferably at temperature of 30 °C - 140 °C for 20-170 hrs, further preferably at temperature of 40 °C - 140 °C for 10-150 hrs, still preferably at temperature of 60 °C - 140 °C for 1-100 hrs, and the diene rubber polymers having.
19. The solution polymerization process in accordance with one or more of claims 8-18, further comprises a step of removing the metal-containing catalyst, preferably by using ion-exchange resin.
20. A diene polymer, obtained by the solution polymerization, comprises in the range of from 40 to 85 weight part of repeating units derived from one or more dienes, in the range of from 0 to 70 weight part of repeating units derived from one or more α,β -unsaturated nitriles or styrene or any of derivatives of styrene, and in the range of from 0 to 40 weight part of repeating units derived from optional termonomers other than α,β -unsaturated nitrile or styrene and any of derivatives of styrene.
21. A use of the diene polymer obtained by the solution polymerization process in accordance with one or more of claims 8-19 in the hydrogenation in the present hydrogen and a catalyst of Rh, Ru, and/or Pd-based to obtain hydrogenated diene polymers.
22. The use of claim 21, the metal-containing catalyst of Rh, Ru, and/or Pd-based is selected from metal of Rh, Ru or Pd, or the metal-containing catalyst of Rh, Ru or Pd defined in one or more of claims 1-7 and PPh_3 .
23. A one-pot process for synthesis of the hydrogenated diene polymers, comprising by

directly introducing hydrogen into the reactor after the completion of solution polymerization in accordance with one or more of claims 8-19 and reacting at a desired temperature.

24. The one-pot process for synthesis of the hydrogenated diene polymers in accordance with claim 23, wherein the desired temperature is from 60 to 200 °C and the hydrogenation reaction is carried out for 10 min to 20 hrs at a hydrogen pressure of 100-3000 Psi, preferably the desired temperature is from 80 to 180 °C and the reaction is carried out for 10 min to 10 hrs at a hydrogen pressure of 200-2000 Psi, more preferably the desired temperature is from 100 to 160 °C and the reaction is carried out for 30 min to 5 hrs at a hydrogen pressure of 300-1500 Psi, further preferably the desired temperature is from 120 to 150 °C and the reaction is carried out for 30 min to 3 hrs at a hydrogen pressure of 500-1000 Psi.
25. The one-pot process for synthesis of the hydrogenated diene polymers in accordance with one or more of claim 23 and 24, further comprises the step of removing the metal-containing catalyst, preferably by using ion-exchange resin.
26. A hydrogenated diene polymer, obtained by the one-pot process for the synthesis of the hydrogenated diene polymers in accordance with one or more of claim 23 - 25.
27. A process for hydrogenation of diene polymers, comprising a) solution homopolymerization of diene or copolymerization of diene together with at least one of comonomers in the presence of one of the metal-containing catalyst system in accordance with one or more of any of claims 1- 7 in at least one of organic solvents to obtain diene rubber, b) directly introducing hydrogen into the mixture of step a) after the completion of solution polymerization to obtain the hydrogenated diene-containing polymers.
28. The process for hydrogenation of diene polymers in accordance with claim 27, wherein the diene is selected from any known diene, preferably selected from at least one of conjugated dienes and at least one of unconjugated dienes, more preferably a C₄-C₆ conjugated diene, including 1,3-butadiene, isoprene, 2,3-dimethylbutadiene, piperylene or mixtures thereof, or a C₄-C₆ unconjugated diene, including 1,2-butadiene, and most preferred 1,3-butadiene, isoprene and mixtures thereof; the at least one of organic solvents are selected from any organic solvent which does not react with the catalyst or otherwise interfere with the reaction, preferably selected from benzene, toluene, cyclohexane, dimethyl sulfoxide (DMSO), ethylene carbonate (EC), tetrahydrofuran (THF), 1,4-dioxane, monochlorobenzene (MCB), dichlorobenzene (DCB), trichlorobenzene (TCB), monobromobenzene (MBB), dibromobenzene (DBB), tribromobenzene (TBB), methyl ethyl ketone (MEK), N,N-dimethyl formamide (DMF), N,N-dimethyl acetamide (DMAC), or the mixture

thereof, more preferably selected from monochlorobenzene (MCB), monobromobenzene (MBB), dichlorobenzene (DCB), methyl ethyl ketone (MEK), N,N-dimethyl formamide (DMF), or N,N-dimethyl acetamide (DMAC), further preferably selected from monochlorobenzene (MCB) and methyl ethyl ketone (MEK), most preferably monochlorobenzene (MCB).

29. The process for hydrogenation of diene polymers in accordance with one or more of claims 27-28, further comprises the step of removing the metal-containing catalyst, preferably by using ion-exchange resin.

30. A process for hydrogenation of diene polymers, comprising:

a) dissolving at least one diene polymer into at least one organic solvent in a autoclave reactor,

b) adding at least one of the metal-containing catalyst system in accordance with one or more of any of claims 1- 7 into the solution obtained in step a),

c) introducing hydrogen into the autoclave reactor and heating the autoclave reactor up to a predetermined temperature for a predetermined time.

31. The process for hydrogenation of diene polymers in accordance with claim 30, wherein

the at least one diene polymer is selected from one or more of BR NBR, SBR, preferably one or more of BR NBR, SBR obtained by solution polymerization, and the ACN content in the diene polymer from 0 to 65 wt%, or styrene content in the diene polymer from 0 to 80, preferably the ACN content in the diene polymer from 10 to 63 wt%, or styrene content in the diene polymer from 20 to 80 wt%, more preferably the ACN content in the diene polymer from 30 to 60 wt%, or styrene content in the diene polymer from 20 to 70 wt%, based on the total weight of the diene polymer;

the amount of at least one of the metal-containing catalyst system is from 0.000001 to 50 parts by weight based on 100 parts by weight the least one diene polymer, preferably from 0.00001 to 20 parts by weight, more preferably from 0.0001 to 10 parts by weight;

the at least one of organic solvents are selected from any organic solvent which does not react with the catalyst or otherwise interfere with the reaction, preferably selected from benzene, toluene, cyclohexane, dimethyl sulfoxide (DMSO), ethylene carbonate (EC), tetrahydrofuran (THF), 1,4-dioxane, monochlorobenzene (MCB), dichlorobenzene (DCB), trichlorobenzene (TCB), monobromobenzene (MBB), dibromobenzene (DBB), tribromobenzene (TBB), methyl ethyl ketone (MEK), N,N-dimethyl formamide (DMF), N,N-dimethyl acetamide (DMAC), or the mixture

thereof, more preferably selected from monochlorobenzene (MCB), monobromobenzene (MBB), dichlorobenzene (DCB), methyl ethyl ketone (MEK), N,N-dimethyl formamide (DMF), or N,N-dimethyl acetamide (DMAC), further preferably selected from monochlorobenzene (MCB) and methyl ethyl ketone (MEK), most preferably monochlorobenzene (MCB);

the predetermined temperature is from 80 to 180 °C and the predetermined time is from 10 min to 10 hrs at a hydrogen pressure of 200-2000 Psi, more preferably the predetermined temperature is from 100 to 160 °C and the predetermined time is from 30 min to 5 hrs at a hydrogen pressure of 300-1500 Psi, further preferably the predetermined temperature is from 120 to 150 °C and the predetermined time is from 30 min to 3 hrs at a hydrogen pressure of 500-1000 Psi; and

the diene polymer having a controlled Mn, from 1,000 to 300,000, with PDI from 1.0 to 5.0, preferably the controlled Mn, from 3,000 to 100,000, with PDI from 1.1 to 4.0, more preferably the controlled Mn, from 5,000 to 50,000, with PDI from 1.1 to 3.0.

32. The process for hydrogenation of diene polymers in accordance with one or more of claims 30-31, further comprises d) removing the metal-containing catalyst, preferably by using ion-exchange resin.
33. A process for hydrogenation of diene polymers, comprising a) adding the solution homopolymerization of diene or copolymerization of diene obtained by the solution polymerization process in accordance with one or more of claims 8-19, and optionally at least one of organic solvents, b) directly introducing hydrogen into the mixture of step a) and heat up to a predetermined temperature to obtain the hydrogenated diene-containing polymers, wherein the at least one of organic solvents are selected from any organic solvent which does not react with the catalyst or otherwise interfere with the reaction, preferably selected from benzene, toluene, cyclohexane, dimethyl sulfoxide (DMSO), ethylene carbonate (EC), tetrahydrofuran (THF), 1,4-dioxane, monochlorobenzene (MCB), dichlorobenzene (DCB), trichlorobenzene (TCB), monobromobenzene (MBB), dibromobenzene (DBB), tribromobenzene (TBB), methyl ethyl ketone (MEK), N,N-dimethyl formamide (DMF), N,N-dimethyl acetamide (DMAC), or the mixture thereof, more preferably selected from monochlorobenzene (MCB), monobromobenzene (MBB), dichlorobenzene (DCB), methyl ethyl ketone (MEK), N,N-dimethyl formamide (DMF), or N,N-dimethyl acetamide (DMAC), further preferably selected from monochlorobenzene (MCB) and methyl ethyl ketone (MEK), most preferably monochlorobenzene (MCB).
34. A hydrogenated diene rubber, obtained by the one-pot process for the synthesis of the hydrogenated diene-containing polymers in accordance with one or more of claims 27 - 29 or claims 30 - 33.

35. Use of the catalyst system in accordance with one or more of any of claims 1- 7 in the manufacture of diene polymer.
36. Use of the catalyst system in accordance with one or more of any of claims 1- 7 in the manufacture of hydrogenated diene-containing polymer.
- 5 37. Use of glass tube reactor and/or autoclave in the solution polymerization process in accordance with one or more of claims 8-19 or in the one-pot process for the synthesis of the hydrogenated diene polymers in accordance with one or more of claims 23-25 or in the process for the hydrogenation of diene polymers in accordance with one or more of claims 27-33.

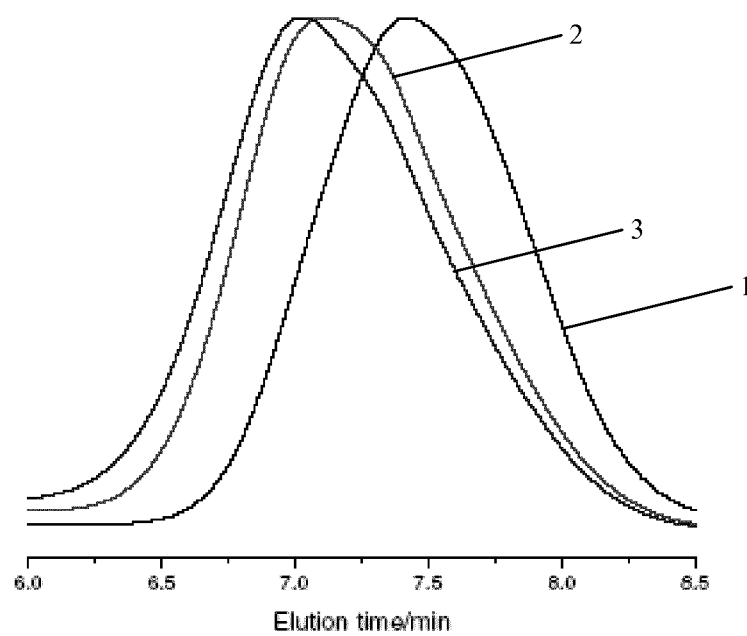


Fig. 1

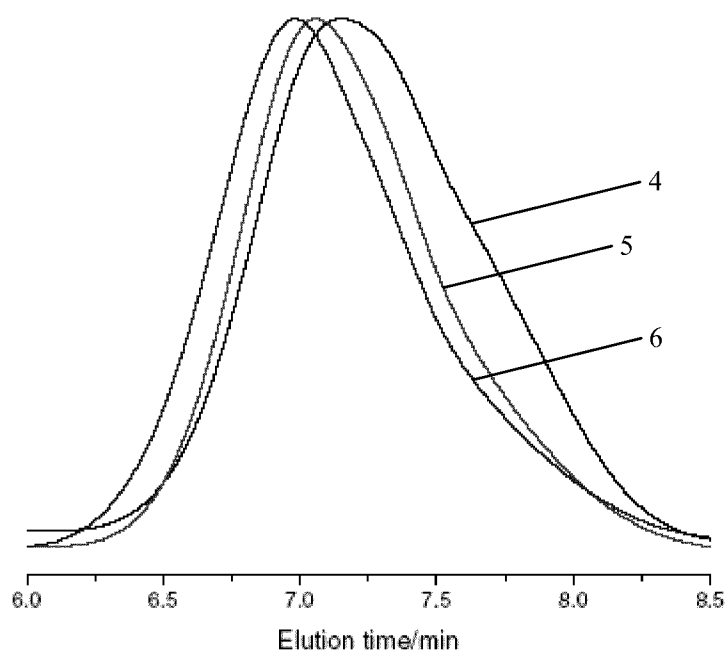


Fig. 2

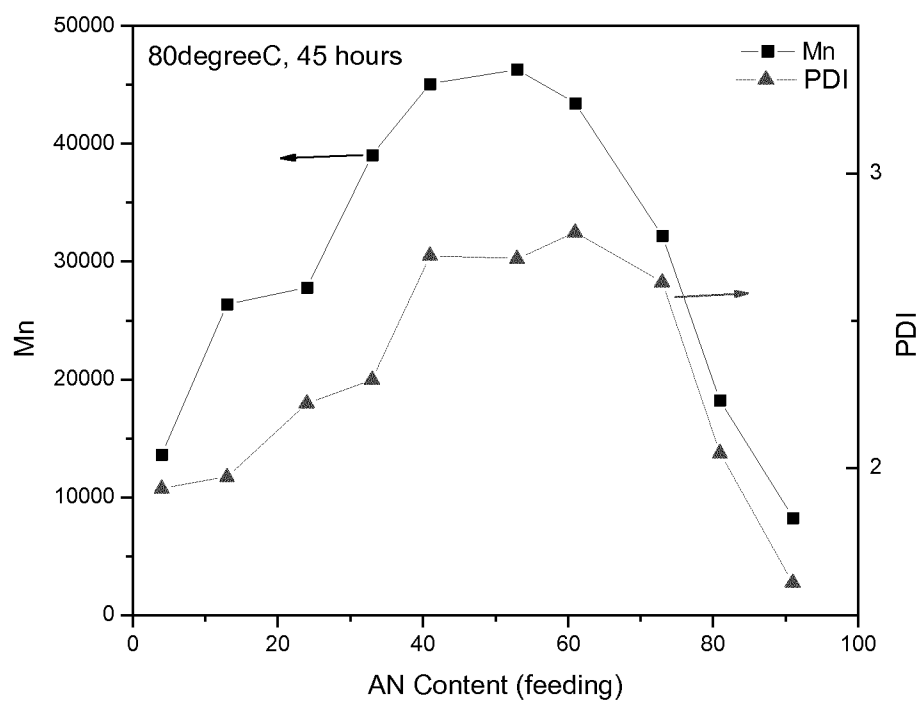


Fig. 3a

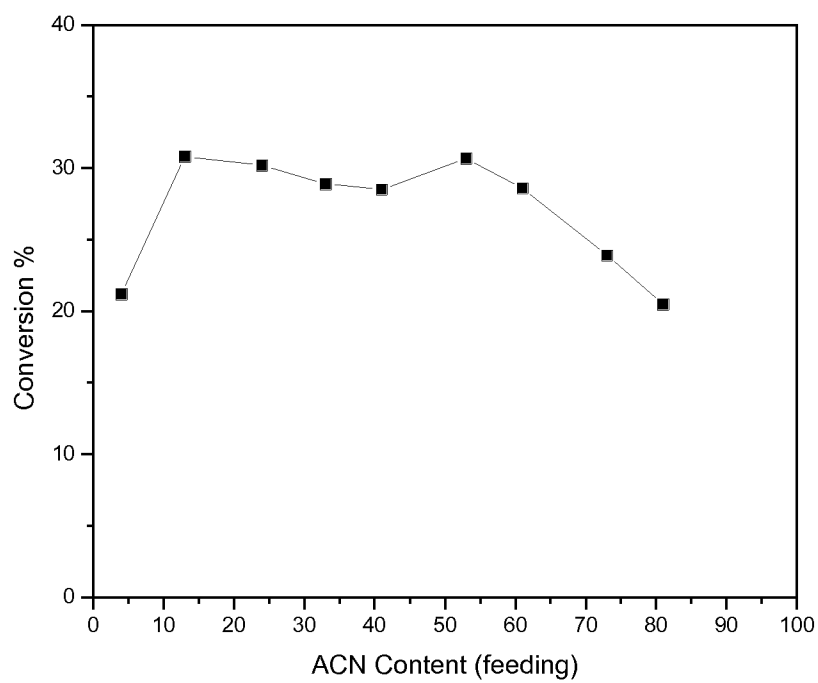


Fig. 3b

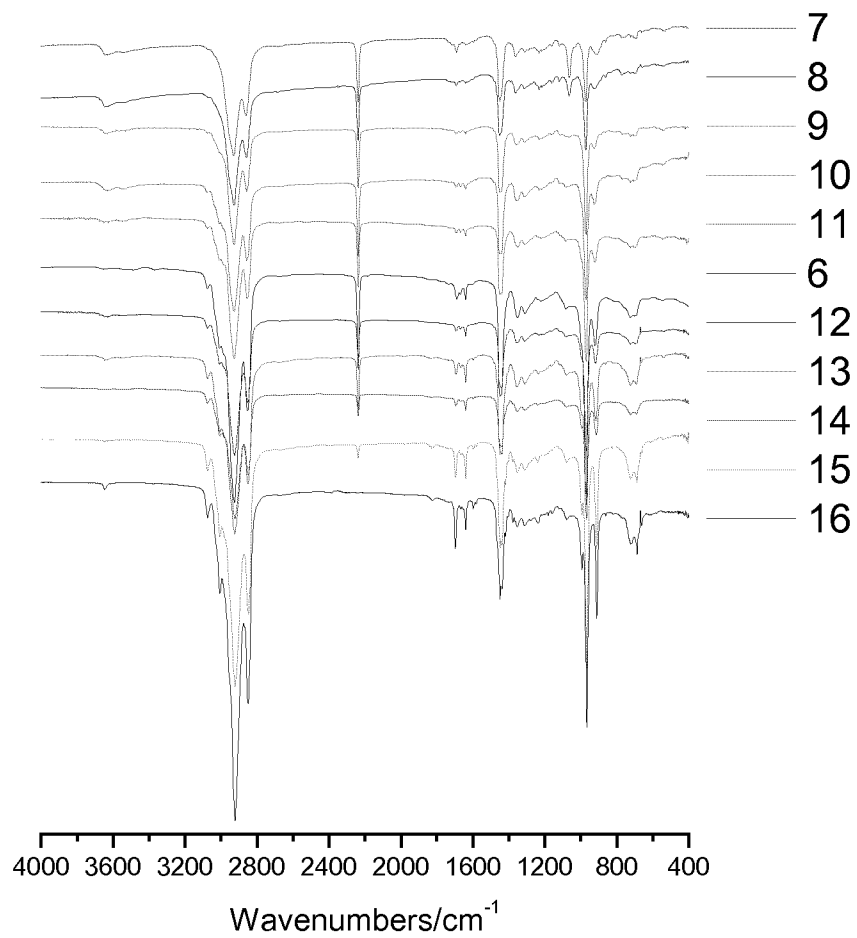


Fig. 3c

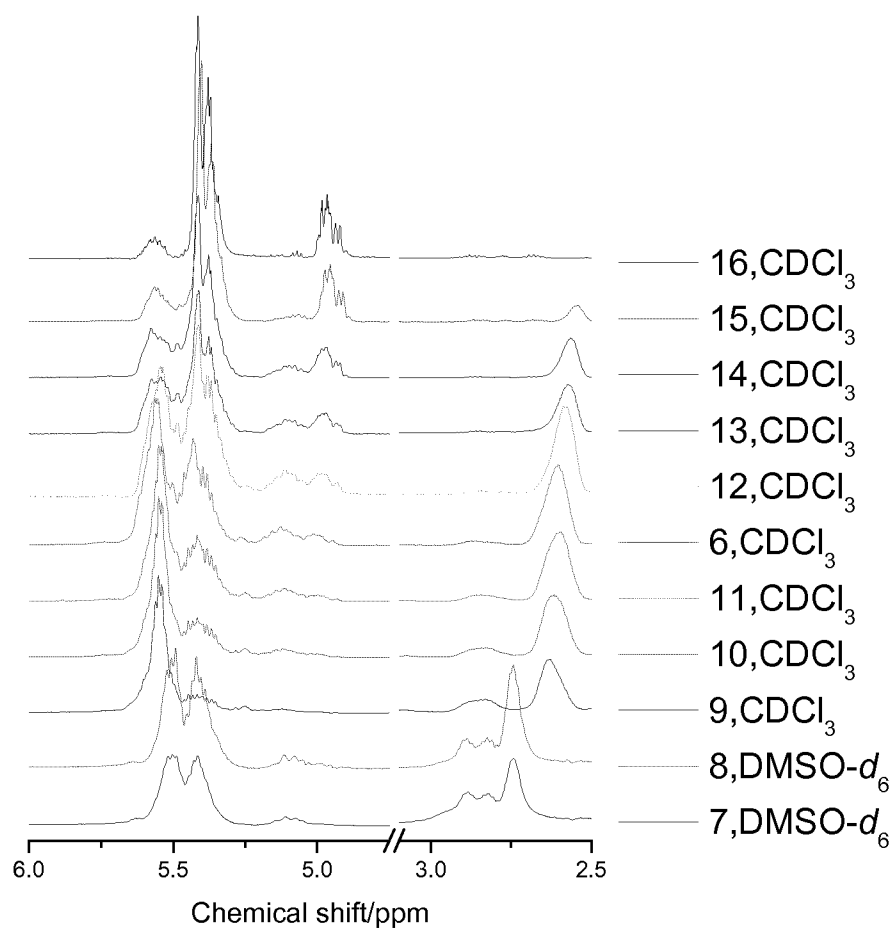


Fig. 3d

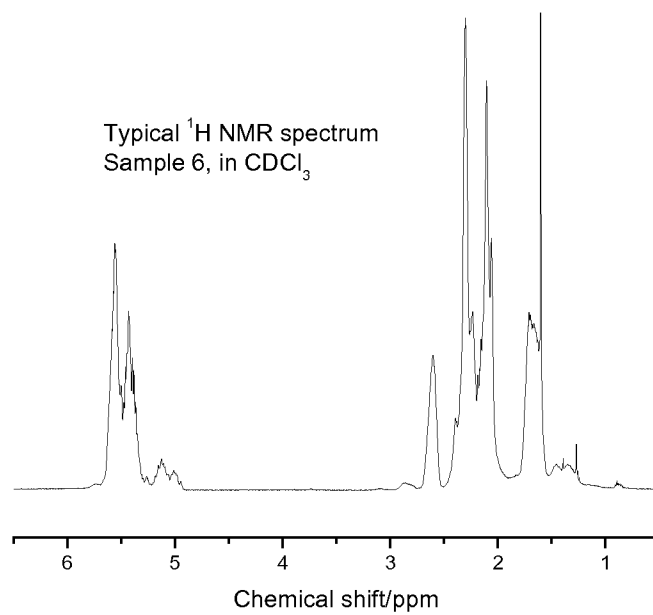


Fig. 3e

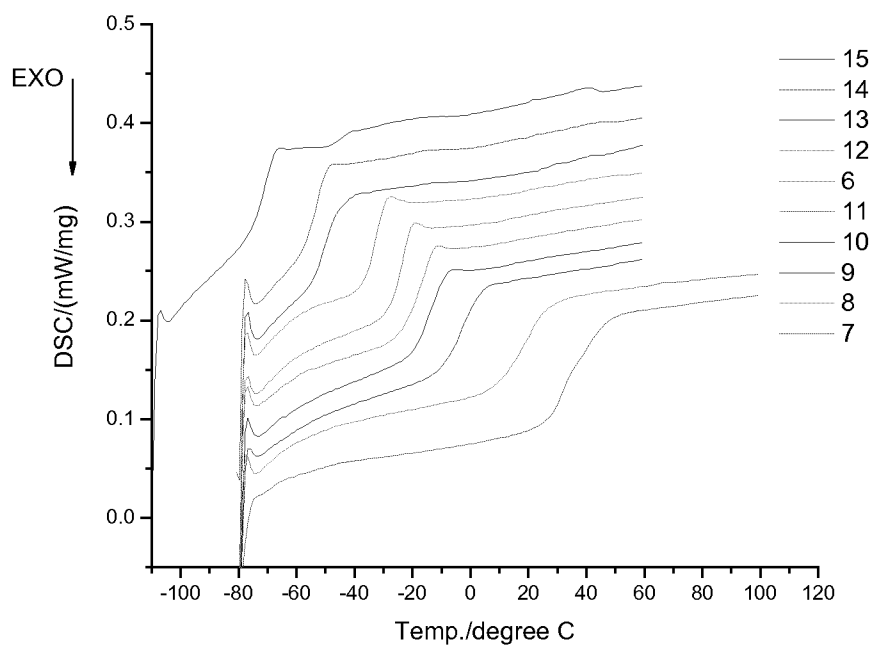


Fig. 3f

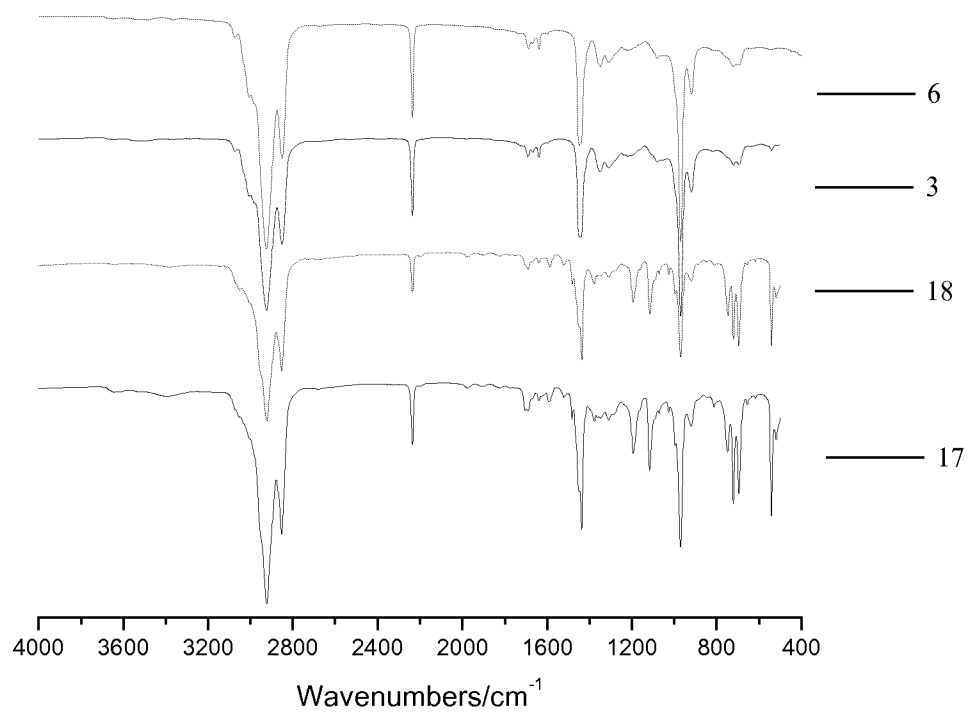


Fig. 4a

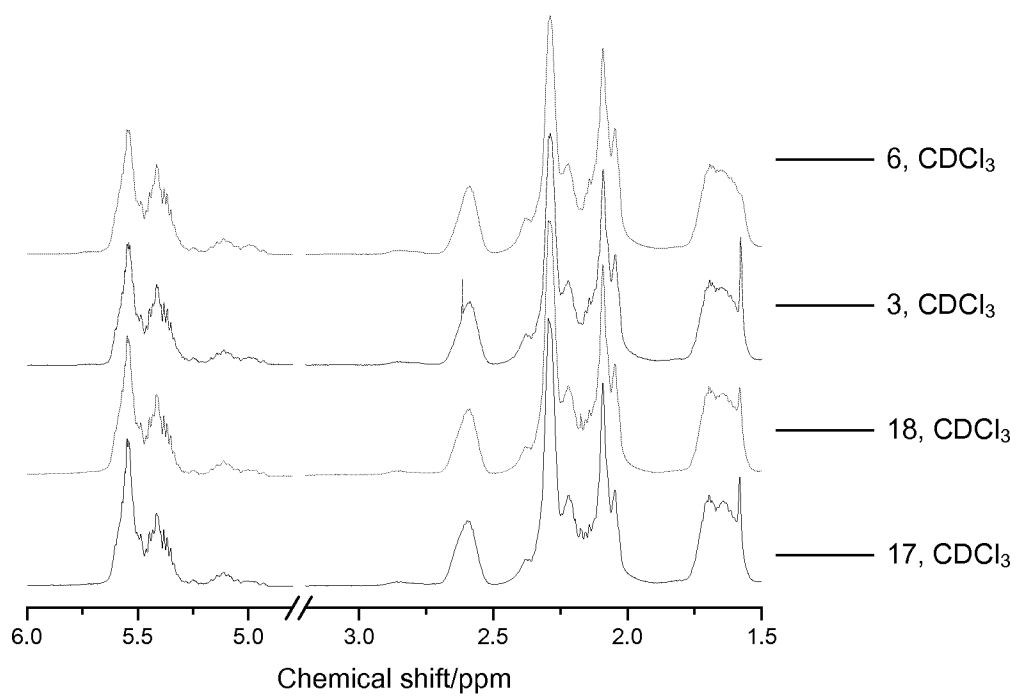


Fig. 4b

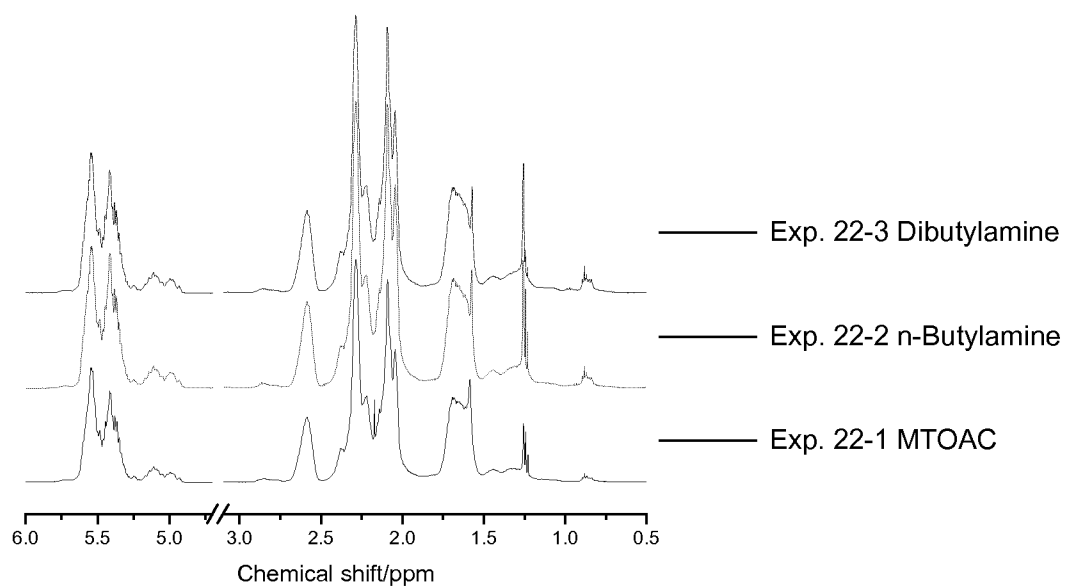


Fig. 5a

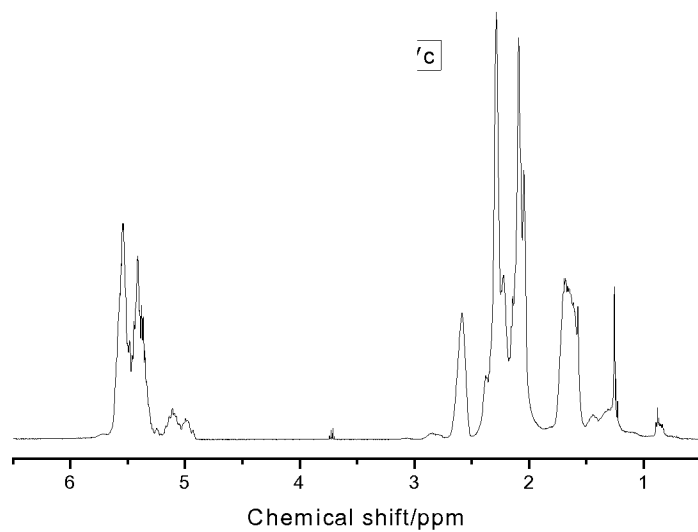


Fig. 5b

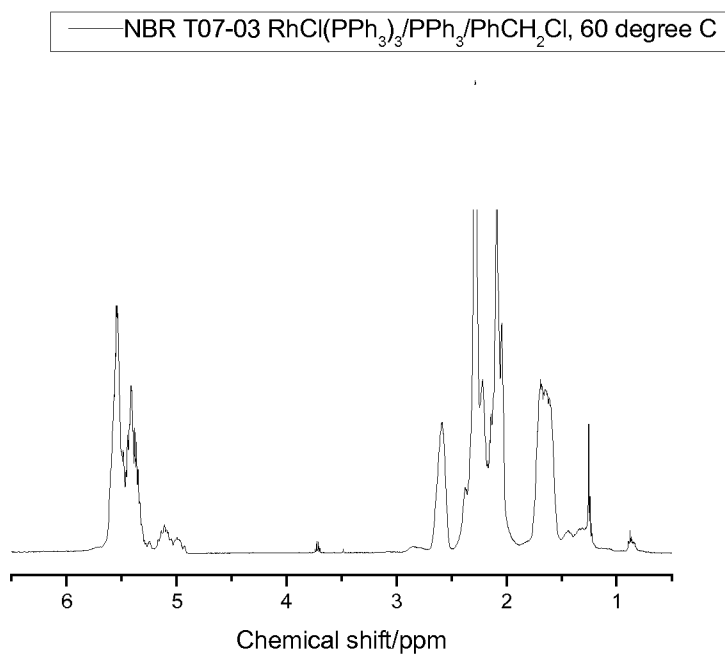


Fig. 6a

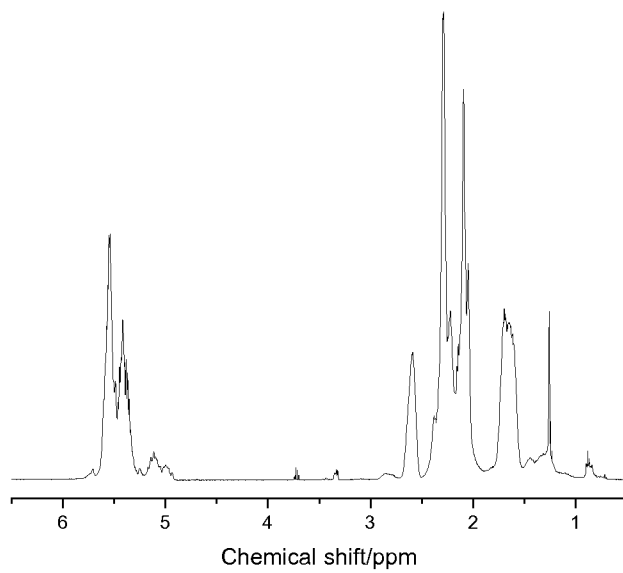


Fig. 6b

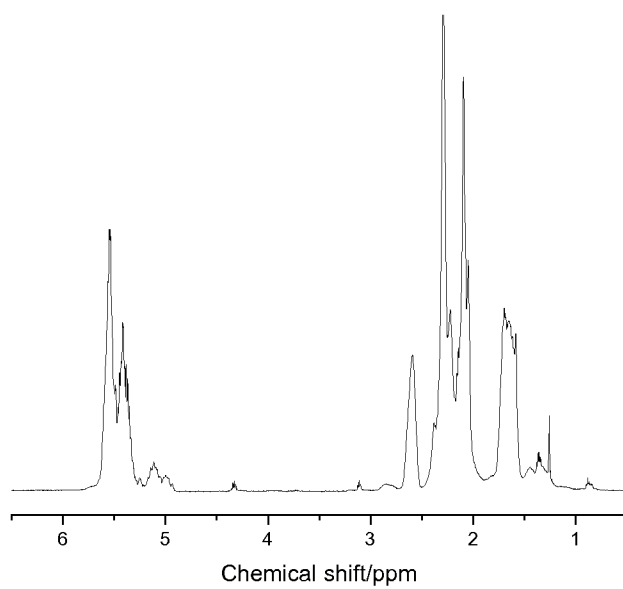


Fig. 6c

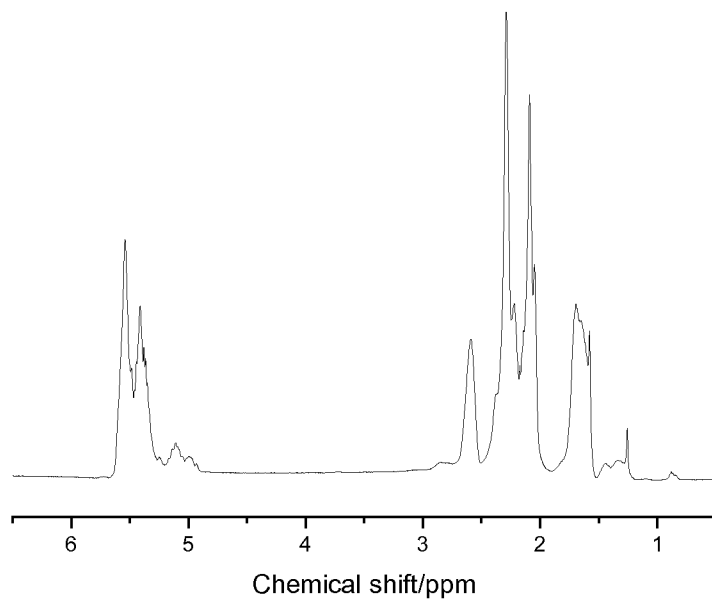


Fig. 7a

NBR T10-14 $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ / PPh_3 / DCAP 80 degree C

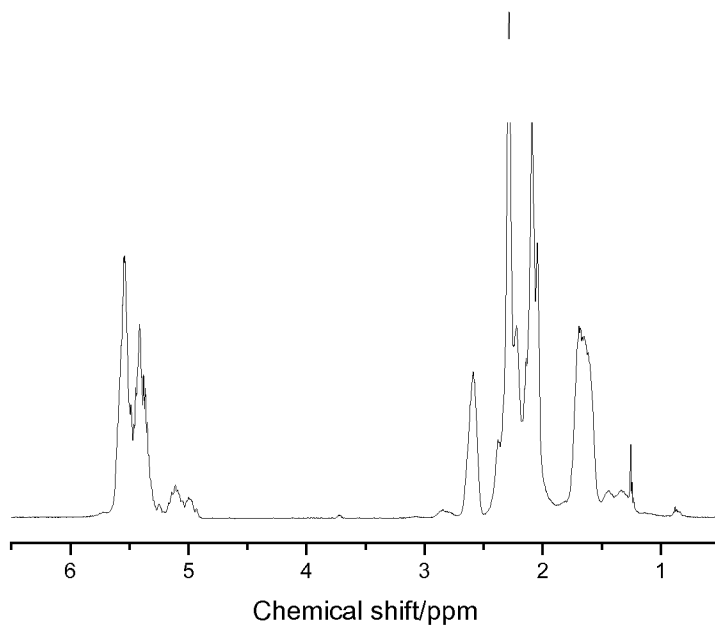


Fig. 7b

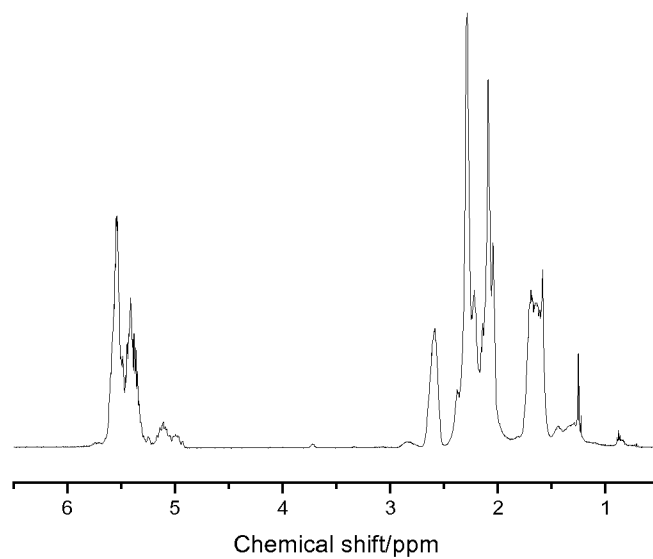


Fig. 7c

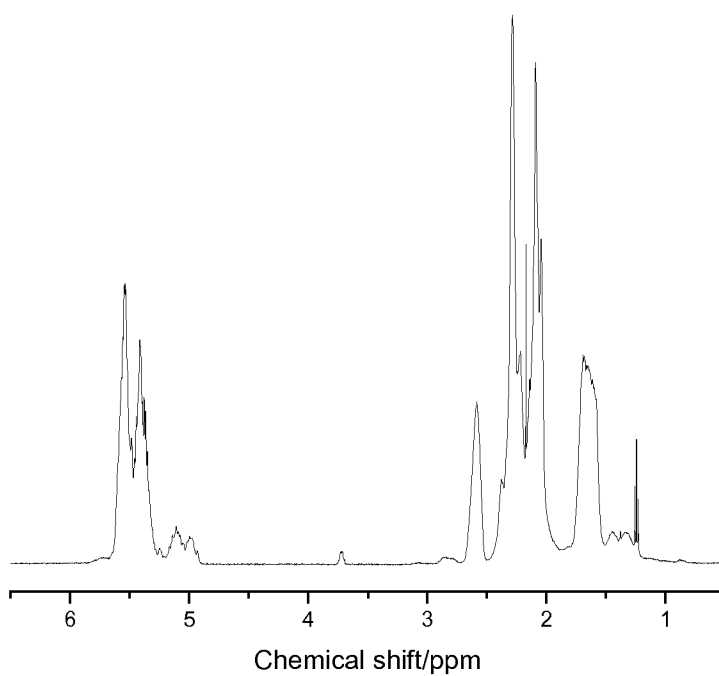


Fig. 7d

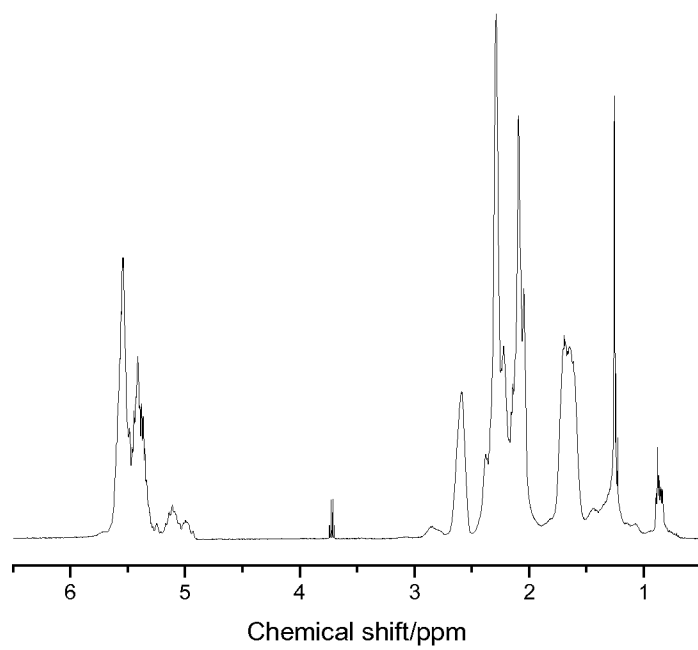


Fig. 8

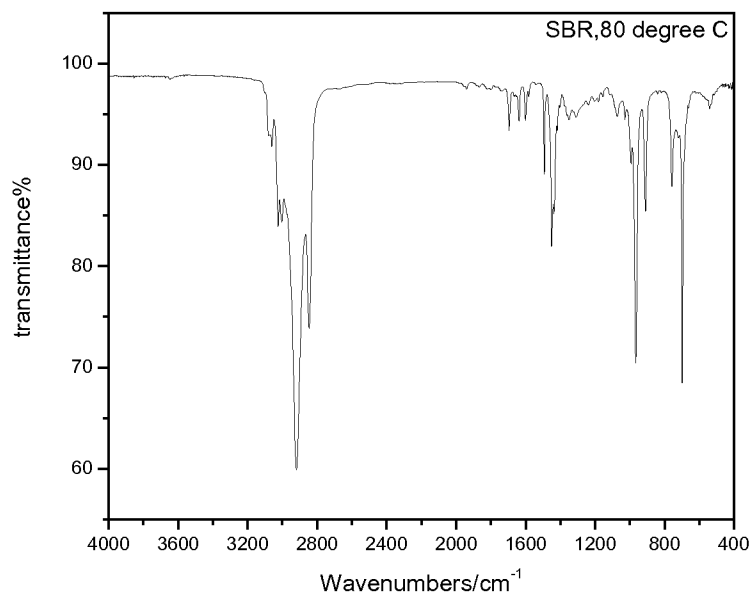


Fig. 9a

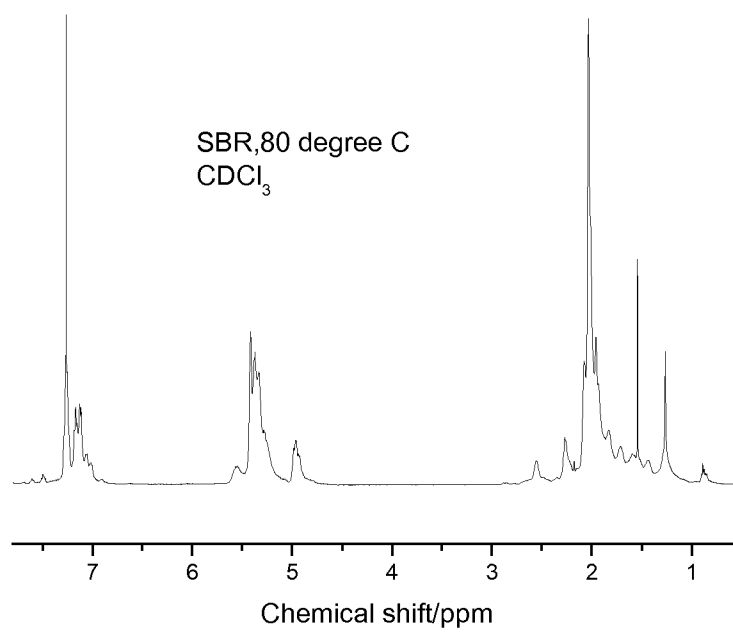


Fig. 9b

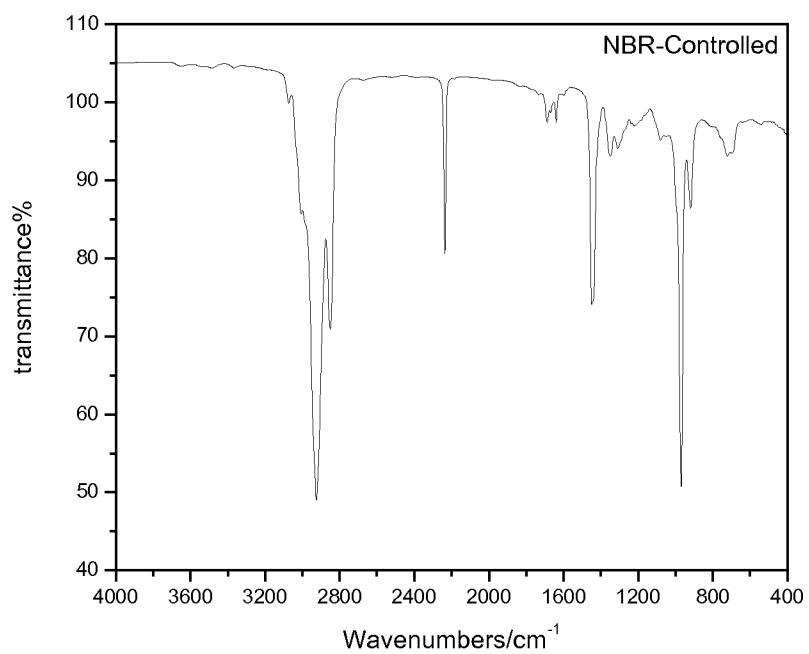


Fig. 10a

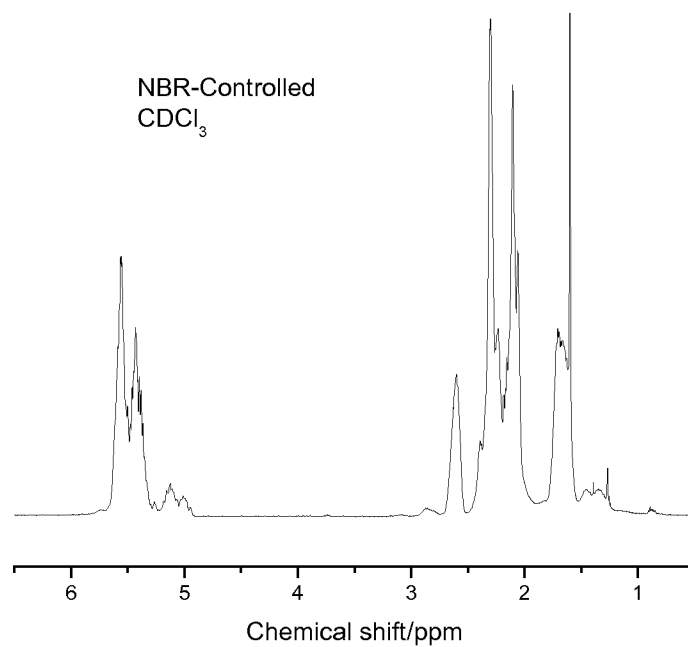


Fig. 10b

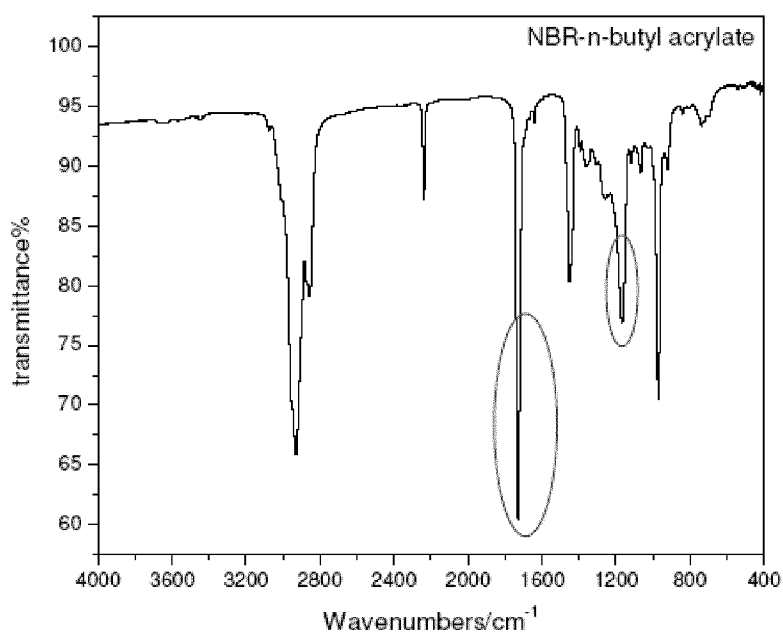


Fig. 10c

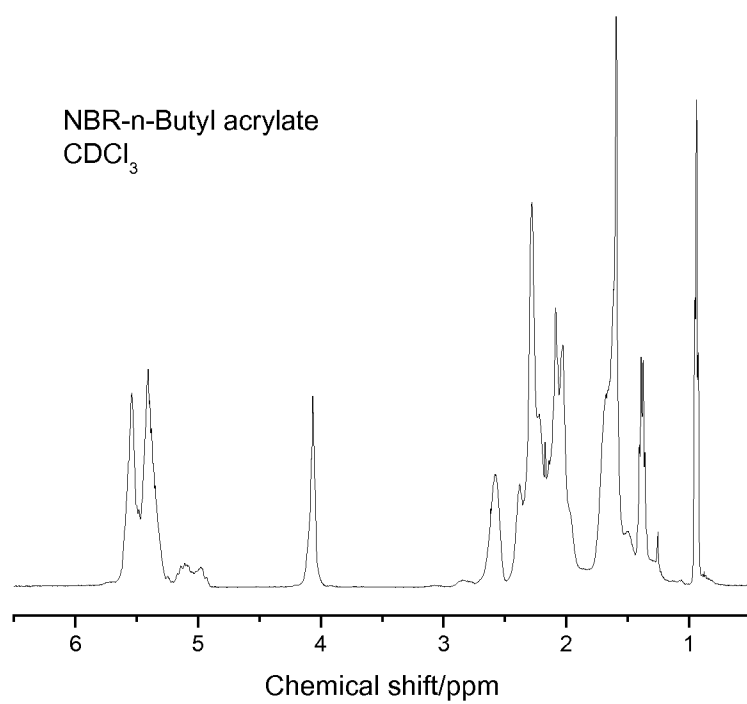


Fig. 10d

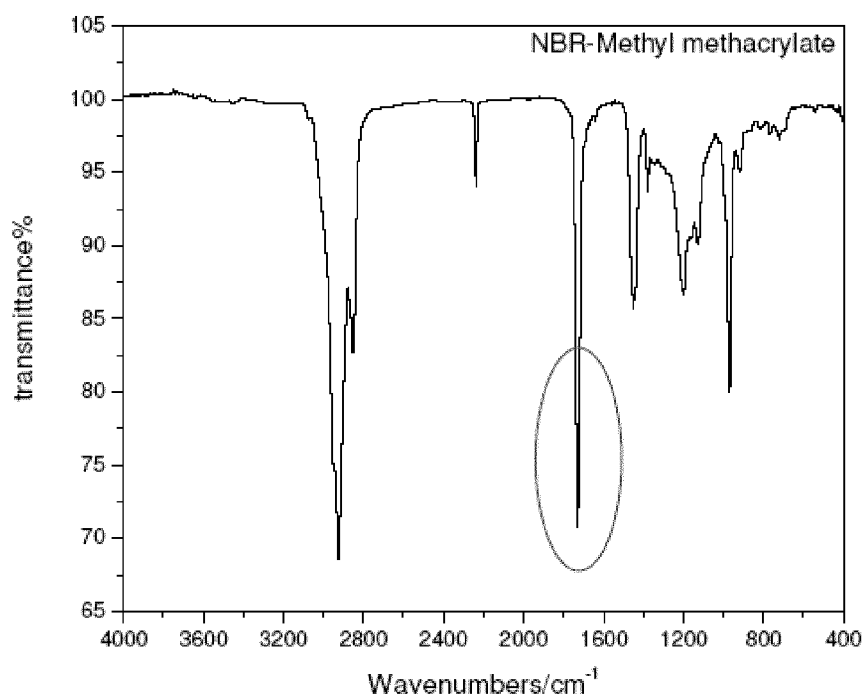


Fig. 10e

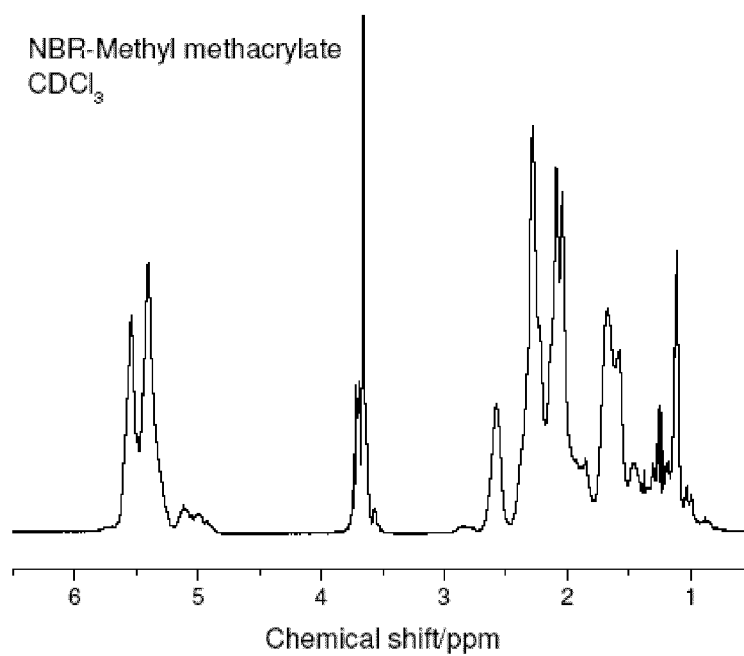


Fig. 10f

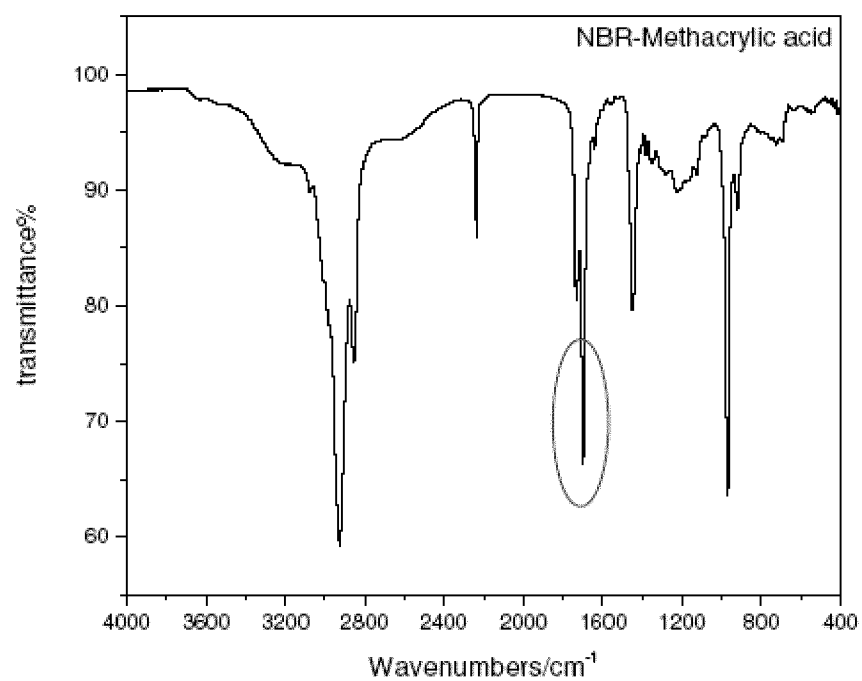


Fig. 10g

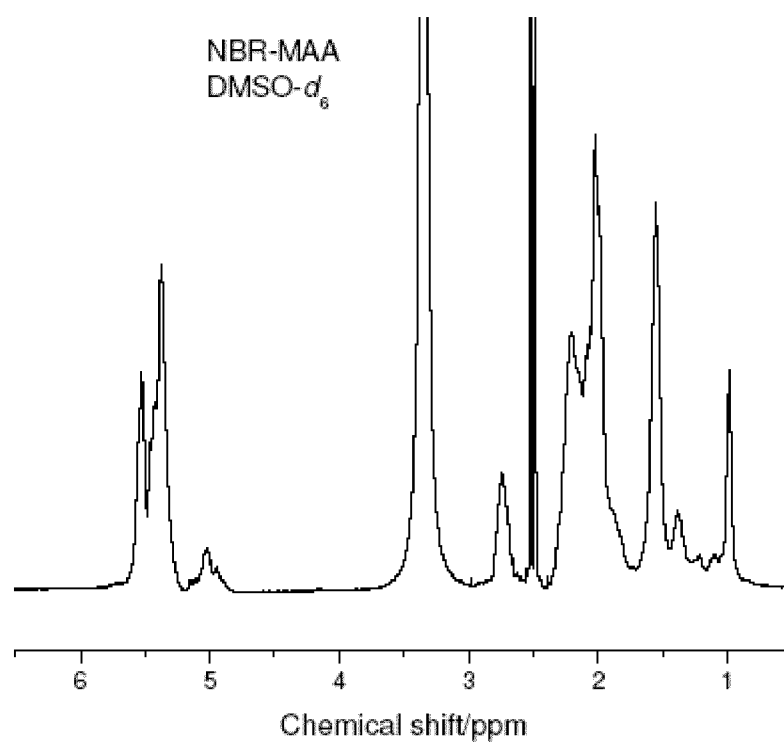


Fig. 10h

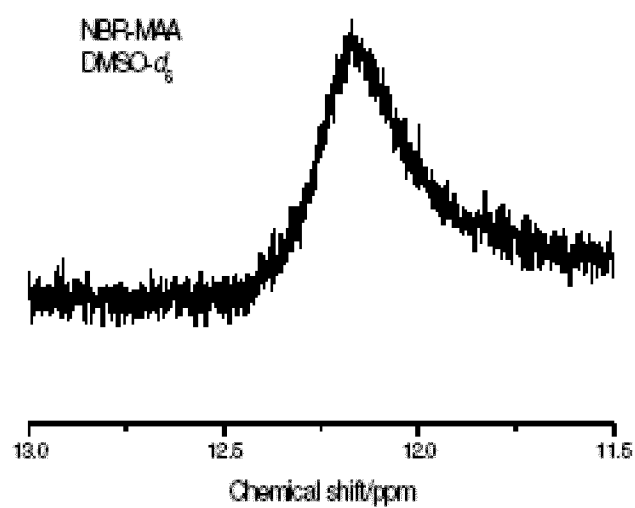


Fig. 10i

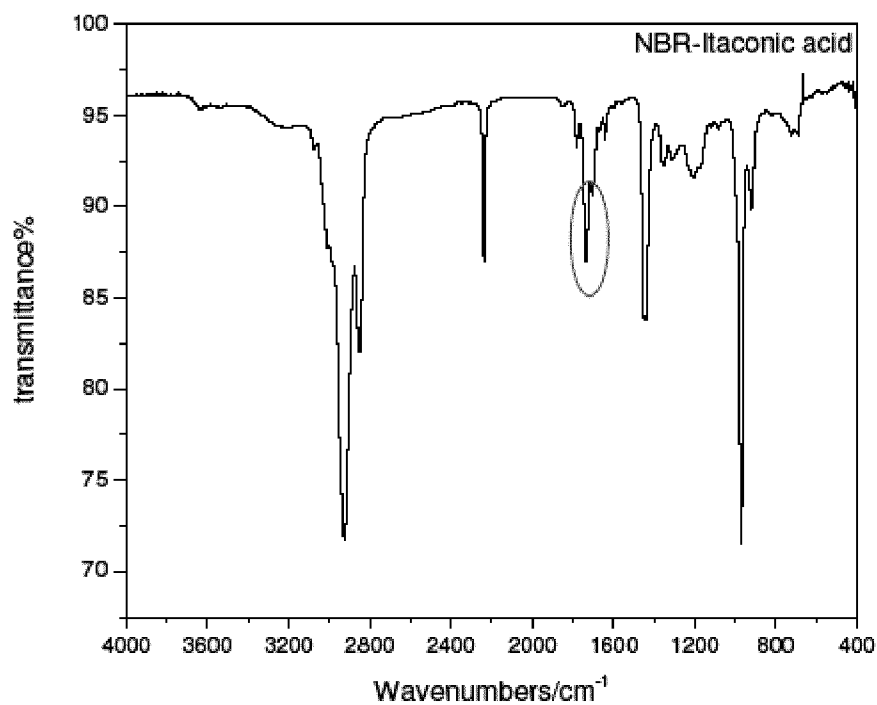


Fig. 10j

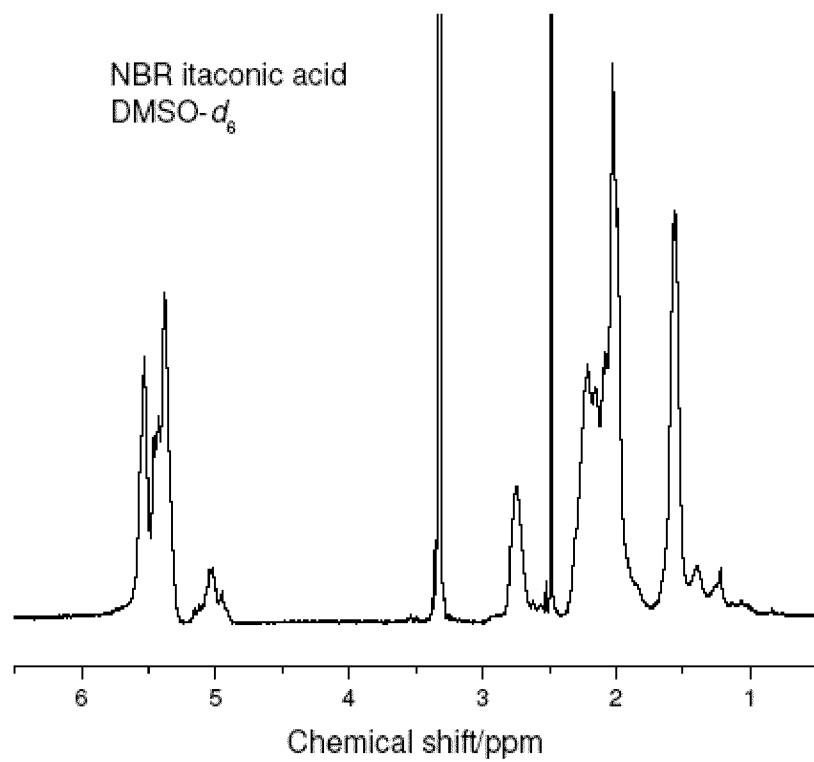


Fig. 10k

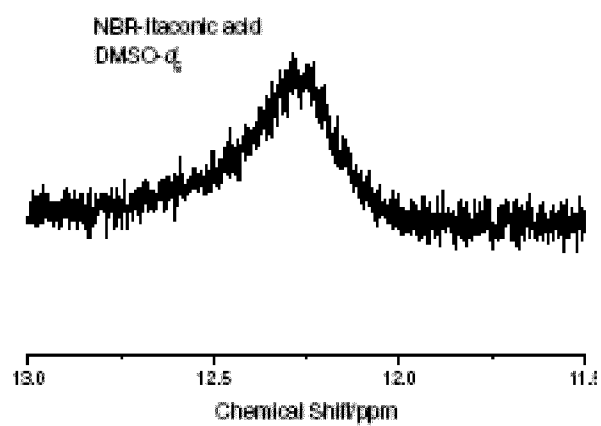


Fig. 10l

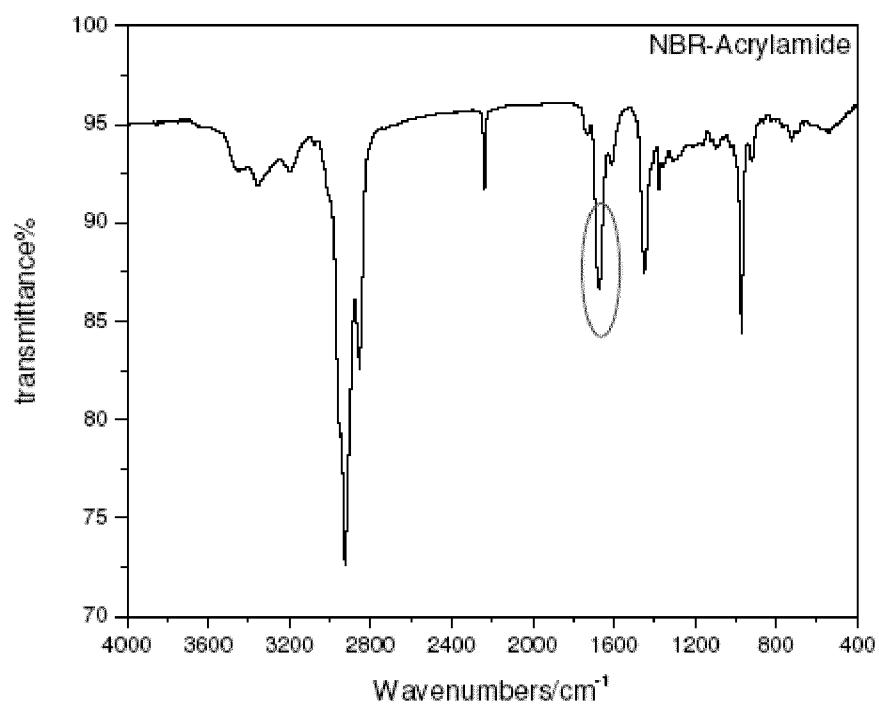


Fig. 10m

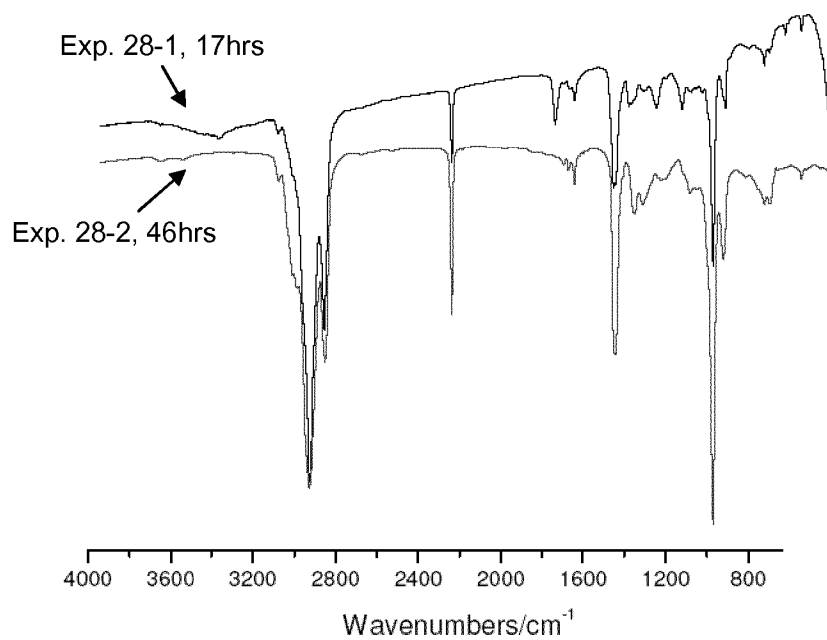


Fig. 11a

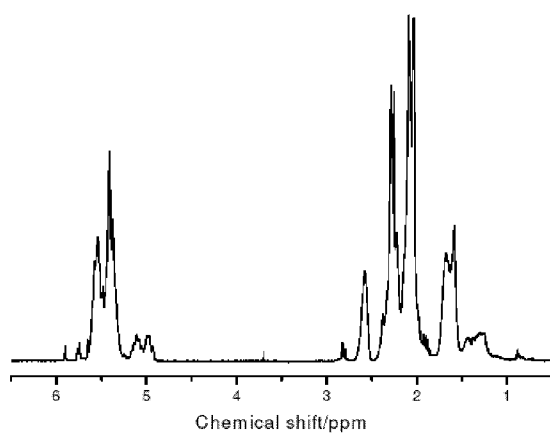


Fig. 11b

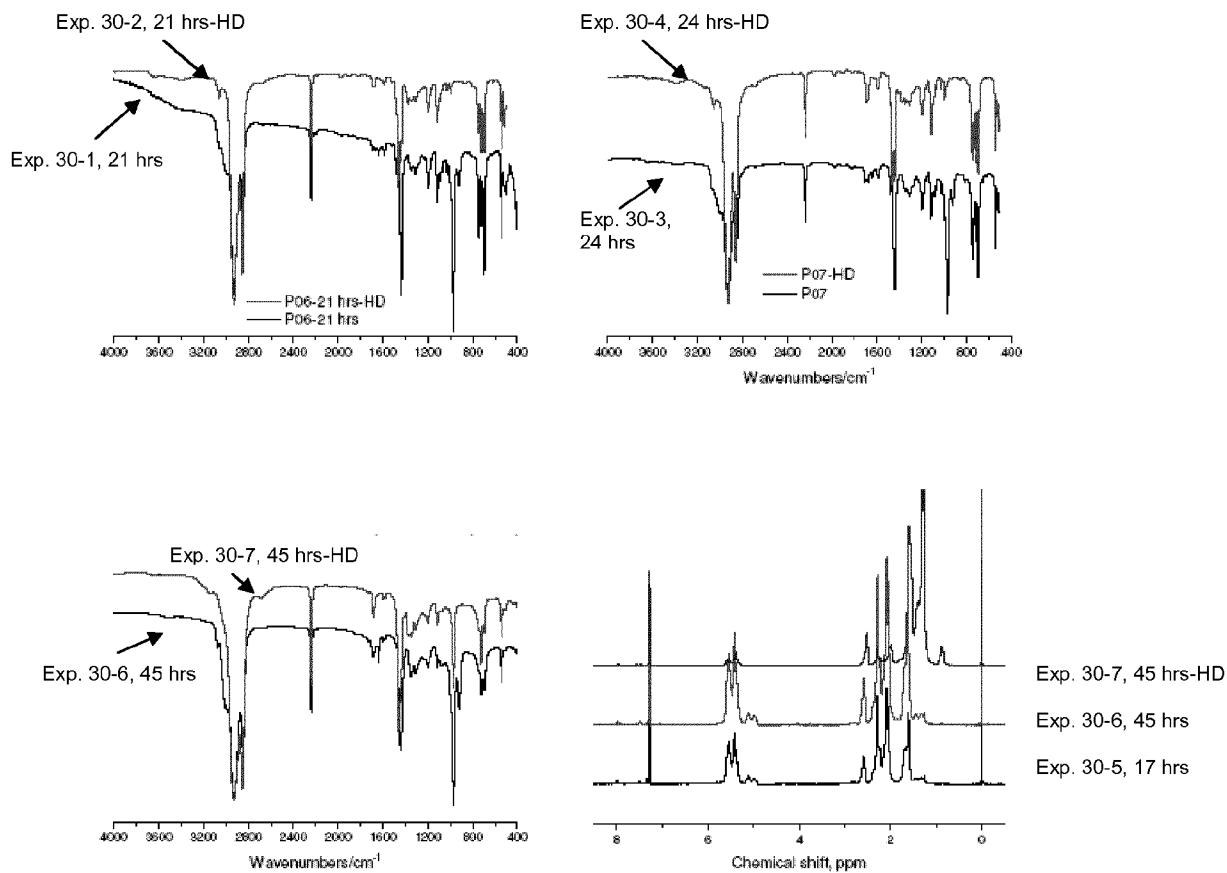


Fig. 12

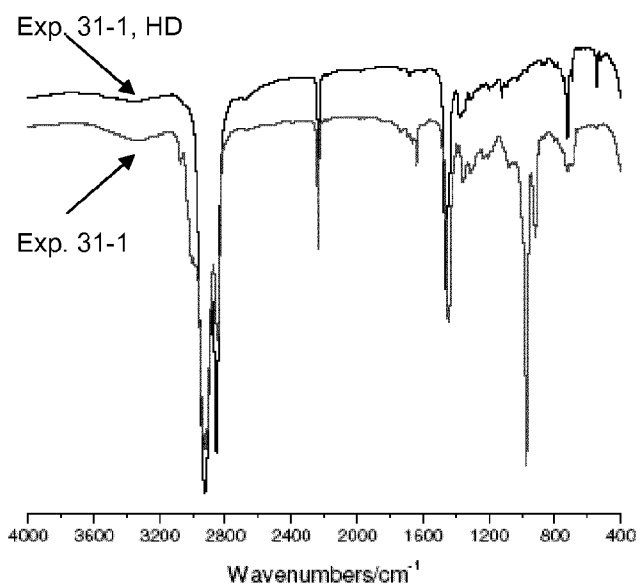


Fig. 13

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/062167

A. CLASSIFICATION OF SUBJECT MATTER

INV. B01J31/24 B01J31/22 B01J31/30 B01J31/34 B01J31/38
B01J31/02 B01J31/04

ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B01J

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

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

EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SAVAMOTO: "Design for Initiators for living radical polymerization of methyl methacrylate mediated by ruthenium (II) complex", TETRAHEDRON, vol. 53, no. 45, 1 January 1997 (1997-01-01), pages 15445-15457, XP002680163, compounds 1-13 scheme 3 ----- -/--	1-3,7



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

18 July 2012

Date of mailing of the international search report

24/10/2012

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Klaes, Daphne

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	MOINEAU: "Controlled radical polymerization of methyl methacrylate initiated by alkyl halide in the presence of the Wilkinson catalyst", MACROMOLECULES, vol. 31, 1 January 1998 (1998-01-01), pages 542-544, XP002680164, figures 1,2; table 3 -----	1-7
X	SAWAMOTO: "Star-shaped polymers by metal-catalysed living radical polymerization. 1. Design of Ru(II)-based systems and divinyl linking agents", MACROMOLECULES, vol. 34, 15 December 2000 (2000-12-15), pages 215-221, XP002680165, scheme 1 -----	1-3,7
X	SAWAMOTO: "Iron (II) chloride complex for living radical polymerization of methyl methacrylate", MACROMOLECULES, vol. 30, no. 16, 11 August 1997 (1997-08-11), pages 4507-4510, XP002680166, equation 1 -----	1-3,7
X	SAWAMOTO: "Living cationic and radical polymerizations via reversible activation of carbon-halogen bonds", POLYMER REPRINTS, vol. 36, no. 1, 1 January 1995 (1995-01-01), pages 539-540, XP009161203, ISSN: 0032-3939 scheme 3 -----	1-3,7
X	SAWAMOTO: "Controlled radical polymerization of 2-hydroxyethyl methacrylate with a hydrophilic ruthenium complex and the synthesis of amphiphilic random and block copolymers with methyl methacrylate", JOURNAL OF POLYMER SCIENCE: PART A: POLYMER CHEMISTRY, vol. 40, 1 January 2002 (2002-01-01), pages 2055-2065, XP002680167, claim 1 abstract -----	1-3,7

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2012/062167

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 1, 7(all partially)
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-7(partially)

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-7(partially)

A metal-containing catalyst system, which comprises (1) a metal containing catalyst, (2) a co-catalyst, and optionally (3) an additive, wherein the metal-containing catalyst is ML_nX_m , wherein M represents a metal selected from Rh, Pd, Ru, Ir, Mo, Co, Cu, Fe or Ti ; L is $PR_1R_2R_3$ and X is halogen, and (2) the co-catalyst is a halide, and optionally (3) the additive is selected from a group consisting of a primary amine, a second amine, a tertiary amine, ascorbic acid or an ammonium salt.

2. claims: 1-7(partially)

A metal-containing catalyst system, which comprises (1) a metal containing catalyst, (2) a co-catalyst, and optionally (3) an additive, wherein the metal-containing catalyst is ML_nX_m , wherein M represents a metal selected from Rh, Pd, Ru, Ir, Mo, Co, Cu, Fe or Ti ; L is $PR_1R_2R_3$ and X is halogen, and (2) the co-catalyst is an azo compound, and optionally (3) the additive is selected from a group consisting of a primary amine, a second amine, a tertiary amine, ascorbic acid or an ammonium salt.

3. claims: 1, 2(partially)

A metal-containing catalyst system, which comprises (1) a metal containing catalyst, (2) a co-catalyst, and optionally (3) an additive, wherein the metal-containing catalyst is ML_nX_m , wherein M represents a metal selected from Rh, Pd, Ru, Ir, Mo, Co, Cu, Fe or Ti ; L is $PR_1R_2R_3$ and X is halogen, and (2) the co-catalyst is a peroxide, and optionally (3) the additive is selected from a group consisting of a primary amine, a second amine, a tertiary amine, ascorbic acid or an ammonium salt.

4. claims: 1-7(partially)

A metal-containing catalyst system, which comprises (1) a metal containing catalyst, (2) a co-catalyst, and optionally (3) an additive, wherein the metal-containing catalyst is MX_m or $MX_m.pH_2O$, wherein M represents a metal selected from Rh, Pd, Ru, Ir, Mo, Co, Cu, Fe or Ti and X is halogen, and (2) the co-catalyst is a halide, and optionally (3) the additive is selected from a group consisting of a primary amine, a second amine, a tertiary amine, ascorbic acid or an ammonium salt.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

5. claims: 1, 2, 7

A metal-containing catalyst system, which comprises (1) a metal containing catalyst, (2) a co-catalyst, and optionally (3) an additive, wherein the metal-containing catalyst is MX_m or $\text{MX}_m.\text{pH}_2\text{O}$, wherein M represents a metal selected from Rh, Pd, Ru, Ir, Mo, Co, Cu, Fe or Ti and X is halogen, and (2) the co-catalyst is an azo-compound, and optionally (3) the additive is selected from a group consisting of a primary amine, a second amine, a tertiary amine, ascorbic acid or an ammonium salt.

6. claims: 1, 2, 7(all partially)

A metal-containing catalyst system, which comprises (1) a metal containing catalyst, (2) a co-catalyst, and optionally (3) an additive, wherein the metal-containing catalyst is MX_m or $\text{MX}_m.\text{pH}_2\text{O}$, wherein M represents a metal selected from Rh, Pd, Ru, Ir, Mo, Co, Cu, Fe or Ti and X is halogen, and (2) the co-catalyst is a peroxide, and optionally (3) the additive is selected from a group consisting of a primary amine, a second amine, a tertiary amine, ascorbic acid or an ammonium salt.

7. claims: 1-7(partially)

A metal-containing catalyst system, which comprises (1) a metal containing catalyst, (2) a co-catalyst, and optionally (3) an additive, wherein the metal-containing catalyst is $\text{M}(\text{OC}(\text{O})\text{R})_m$, wherein M represents a metal selected from Rh, Pd, Ru, Ir, Mo, Co, Cu, Fe or Ti, and (2) the co-catalyst is a halide, and optionally (3) the additive is selected from a group consisting of a primary amine, a second amine, a tertiary amine, ascorbic acid or an ammonium salt.

8. claims: 1, 2, 7(all partially)

A metal-containing catalyst system, which comprises (1) a metal containing catalyst, (2) a co-catalyst, and optionally (3) an additive, wherein the metal-containing catalyst is $\text{M}(\text{OC}(\text{O})\text{R})_m$, wherein M represents a metal selected from Rh, Pd, Ru, Ir, Mo, Co, Cu, Fe or Ti, and (2) the co-catalyst is an azo-compound, and optionally (3) the additive is selected from a group consisting of a primary amine, a second amine, a tertiary amine, ascorbic acid or an ammonium salt.

9. claims: 1, 2, 7(all partially)

A metal-containing catalyst system, which comprises (1) a metal containing catalyst, (2) a co-catalyst, and optionally

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

(3) an additive, wherein the metal-containing catalyst is $M(OC(O)R)_m$, wherein M represents a metal selected from Rh, Pd, Ru, Ir, Mo, Co, Cu, Fe or Ti, and (2) the co-catalyst is a peroxide, and optionally (3) the additive is selected from a group consisting of a primary amine, a second amine, a tertiary amine, ascorbic acid or an ammonium salt.

10. claims: 8-19

A solution polymerization process of dienes

11. claim: 20

A diene polymer

12. claims: 21, 22

Use of the diene polymer in hydrogenation

13. claims: 23-25, 27-29, 33

One-pot process for solution polymerization and hydrogenation of dienes

14. claim: 26

Hydrogenated diene polymer

15. claims: 30-32

Process for the hydrogenation of a polydiene

16. claim: 35

Use of the catalyst system of claims 1-7 in the manufacture of a diene polymer

17. claim: 36

Use of the catalyst system of claims 1-7 in the manufacture of a hydrogenated diene polymer

18. claim: 37

Use of a glass tube reactor/and or autoclave in a solution polymerization process.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

19. claim: 34

A hydrogenated diene rubber

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 1, 7(all partially)

The present part of independent claim 1 relating to the first invention relates to an extremely large number of possible metal-containing catalysts. Support and disclosure for the co-catalyst (2), namely the halide in the sense of Article 6 and 5 PCT is to be found however for only a very small proportion of said component claimed, see p. 8, l. 8-13 and the examples. The non-compliance with the substantive provisions is to such an extent, that the search was performed taking into consideration the non-compliance in determining the extent of the search of claims 1 and 6 (PCT Guidelines 9.19 and 9.23). The search of claims 1 and 6 was restricted to those metal-containing catalysts which appear to be supported, i.e. to catalyst systems for which the halide co-catalyst (2) is defined as in claim 2.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.2), should the problems which led to the Article 17(2) declaration be overcome.