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Polymerization of (E)-1,3-Pentadiene and (E)-2-Methyl-1,3-pentadiene with Neodymium Catalysts: Examination of the Factors that Affect the Stereoselectivity

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ABSTRACT: (E)-1,3-Pentadiene (EP) and (E)-2-methyl-1,3-pentadiene (2MP) were polymerized to cis-1,4 polymers with homogeneous and heterogeneous neodymium catalysts to examine the influence of the physical state of the catalyst on the polymerization stereoselectivity. Data on the polymerization of (E)-1,3-hexadiene (EH) are also reported. EP and EH gave cis-1,4 isotactic polymers both with the homogeneous and with the heterogeneous system, whereas 2MP gave an isotactic cis-1,4 polymer with the heterogeneous catalyst and a syndiotactic cis-1,4 polymer, never reported earlier, with the homogeneous one. For comparison, the results obtained with the soluble CpTiCl₃-based catalyst (Cp = cyclopentadienyl), which gives cis-1,4 isotactic poly(2MP), are examined. A tentative interpretation is given for the mechanism of the formation of the stereoregular polymers obtained and a complete NMR characterization of the cis-1,4-syndiotactic poly(2MP) is reported. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, 51, 3227–3232

KEYWORDS: neodymium catalysts; 1,3-diene stereospecific polymerization mechanism; stereoselectivity; stereospecific polymers; syndiotactic cis-1,4 poly(2-methyl-1,3-pentadiene)

INTRODUCTION Neodymium catalysts are well known to polymerize butadiene to cis-1,4 polymers. Various catalytic compositions have been proposed, but three-component catalyst systems of Nd carboxylate/chlorine donor (usually an Al alkyl halide)/Al(^{i}Bu)₃ or Al(^{i}Bu)₂H are the most important commercially.[1–12] The catalyst can be prepared by reacting first the Nd carboxylate with AlEt₂Cl or Al₂Et₃Cl₃ (Cl/Nd molar ratio, ca. 3) and then by adding Al(^{i}Bu)₃ to the suspension of Nd chloride. This system is generally considered as heterogeneous (**cat 1**). Recently, Nd systems completely soluble in toluene have been reported.[10–13] These can be obtained by modifying the addition order of the catalyst components, that is, by reacting first the Nd compound with Al(^{i}Bu)₃ or Al(^{i}Bu)₂H, then by adding, after some time of aging, AlEt₂Cl (**cat 2**).

In the previous articles, we examined the polymerization of some substituted 1,3-butadienes (e.g., isoprene, (E)-1,3-pentadiene [EP], 2,3-dimethylbutadiene, (E)-1,3-hexadiene [EH], and (E)-2-methyl-1,3-pentadiene [2MP]) with the insoluble Nd system (**cat 1**).[8,13] This catalyst gave cis-1,4 isotactic polymers from EP,[14] and EH,[15,16] whereas it gave a product consisting of a predominant cis-1,4 isotactic poly(2MP) from 2MP, along with a minor amount of a cis polymer with a different stereostructure, which was not fully characterized.[17]

We were interested in knowing if the physical state of the catalyst, soluble or insoluble, could have some influence on the stereoselective polymerization and, therefore, we have examined the polymerization of EP and 2MP with the homogenous Al^{i}Bu₃/Nd(OCOC₇H₁₅)₃/AlEt₂Cl catalyst (**cat 2**) and compared the results with those obtained with the heterogeneous AlEt₂Cl/Nd(OCOC₇H₁₅)₃/Al^{i}Bu₃ (**cat 1**). Moreover, we have also examined the polymerization of EH to compare its behavior with that of EP.

As the literature reports that the soluble system CpTiCl₃/MAO (MAO, methylaluminoxane) polymerizes 2MP to isotactic cis-1,4 polymer,[18,19] we have also taken into consideration this system, by examining similarities and differences with respect to the soluble Nd catalyst.

In this article, we are reporting on the polymerization of EP, EH, and 2MP with **cat 2** and comparing the results with those obtained with **cat 1** and the CpTiCl₃ catalyst. The factors that determine or influence the stereoselectivity with each of the above catalysts are discussed and an

interpretation of the mode of formation of the stereoregular polymers is reported.

EXPERIMENTAL

Chemicals

Manipulations of air- and/or moisture-sensitive materials were carried out under an inert atmosphere using a dual vacuum/nitrogen line and standard Schlenk-line techniques. Heptane (Baker product, >99% pure) was refluxed over Na for about 8 h, then distilled, and stored over molecular sieves under dry nitrogen. EP (Fluka, ≥96% pure), 2MP (Fluka, >98% pure), and 1,3-hexadiene (Aldrich, 95% pure, mixture of (Z) and (E) isomers) were refluxed over calcium hydride for about 3 h, then distilled trap-to-trap, and stored under dry nitrogen. Diethylaluminum chloride $AlEt_2Cl$ (Fluka, 97% pure), triisobutylaluminum $Al(^iBu)_3$ (Aldrich), and $Nd(O-COC_7H_{15})_3$ (Strem Chemicals) were used as received.

Neodymium Catalyst Preparation

Heterogeneous (cat 1)

A heptane solution (10 mL) of $Nd(OCOC_7H_{15})_3$ (5×10^{-4} mol) was introduced in a 50-mL dried flask containing 13.95 mL of heptane. $AlEt_2Cl$ (0.2 mL; 1.5×10^{-3} mol) was then slowly dropped; a white suspension was rapidly formed, which was kept under vigorous stirring for about 30 min. $Al(^iBu)_3$ (3.75 mL; 1.5×10^{-2} mol) was then added; the resulting suspension was cooled at -30 °C and kept at this temperature in a refrigerator for a few days, after that it was used for the polymerization runs.

Homogeneous (cat 2)

A heptane solution (10 mL) of $Nd(OCOC_7H_{15})_3$ (5×10^{-4} mol) was introduced in a 50-mL dried flask containing 13.95 mL of heptane. $Al(^iBu)_3$ (3.75 mL; 1.5×10^{-2} mol) was added and the resulting solution was kept under stirring at room temperature for 5 days. $AlEt_2Cl$ (0.2 mL; 1.5×10^{-3} mol) was then added; the resulting homogeneous solution was cooled at -30 °C and kept at this temperature in a refrigerator for 2–3 days, after that it was used for the polymerization runs.

Polymerization Procedure

A standard procedure is reported. Monomer (2 mL) was introduced into a 25-mL dried glass reactor, then heptane was added, and the solution so obtained was brought to the desired polymerization temperature. The catalyst solution (or suspension) was finally added. Polymerizations were stopped with methanol containing a small amount of hydrochloric acid; the precipitated polymers were collected by filtration, repeatedly washed with fresh methanol, and then dried in vacuum at room temperature to constant weight.

Fractionation of cis-1,4 poly(2MP)

In brief, 0.911 g of the crude polymer obtained with **cat 1** was extracted with the following boiling solvents: diethylether (70 mL, 16 h) and benzene (70 mL, 20 h). The soluble fractions were concentrated and the dissolved polymers coagulated with methanol, repeatedly washed with fresh methanol, and finally dried in vacuum at room temperature with the insoluble part as well.

Polymer Characterization

Differential scanning calorimetry (DSC) scans were carried out on Perkin-Elmer Pyris 1 instrument. Typically, about 5 mg of polymer was analyzed in each run, whereas the scan speed was 20 °C/min under dinitrogen atmosphere. The wide-angle X-ray diffraction data were obtained at 20 °C using a Siemens D-500 diffractometer equipped with a Siemens FK 60-10 2000W tube (Cu Kα radiation, $\lambda = 0.154$ nm). The operating voltage and current were 40 kV and 40 mA, respectively. The data were collected from $2\theta = 5$ to $35°$ at $2\theta = 0.05°$ intervals. The molecular weight averages (M_w) and the polydispersity index (M_w/M_n) were obtained by a GPCV 2000 system (from Waters) using two online detectors: a differential viscometer and a refractometer. The experimental conditions consisted of two PLgel Mixed C columns, toluene as mobile phase, 0.8 mL/min of flow rate, and 80 °C of temperature. The calibration of the GPC system was constructed by 18 narrow M_w/M_n polystyrene standards with the molar mass ranging from 162 to $3.3 \cdot 10^6$ g/mol. ^{13}C and ^1H NMR measurements were carried out on Bruker Avance 400 spectrometer. The spectra were obtained in $C_2D_2Cl_4$ at 103 °C (hexamethyldisiloxane, HMDS, as internal standard) or in $CDCl_3$ at room temperature (tetramethylsilane, TMS, as internal standard). The concentration of polymer solutions was about 10 wt %. The polymer microstructures were determined on the basis of the procedures reported in the previously published literature.[17,20] The syndiotactic content in the poly(2MP)s obtained with Nd catalysts, both homogeneous and heterogeneous, can be evaluated from the ^1H NMR spectra or from the ^{13}C NMR spectra by the following equation:

$$\text{syndio} \% = A_{sy}/(A_{sy} + A_{iso})$$

In the ^1H NMR spectra, A_{sy} is the integrated area of the peak at 4.92 ppm and A_{iso} is the integrated area of the peak at 4.86 ppm, assigned to the olefinic proton. In the ^{13}C NMR spectra, A_{sy} is the integrated area of the peak at 28.90 ppm and A_{iso} is the integrated area of the peak at 29.10 ppm, assigned to the CH aliphatic carbon.

RESULTS AND DISCUSSION

Polymerization with Nd Heterogeneous System

Some results obtained in the polymerization of EP and EH with the heterogeneous Nd catalyst (**cat 1**) are summarized in Table 1. This catalyst gave a poly(EP) consisting of about 90% cis-1,4 units at 20 °C, the other units being 1,2; a polymer with a cis content of about 94% was obtained at -20 °C. Similar results were obtained from EH. ^{13}C NMR data indicate that poly(EP) and poly(EH) have an isotactic structure (Fig. 1 and Table 2).

The polymerization of 2MP is much slower than that of EP and EH. This may be owing to the fact that 2MP is not linear, as are EP and EH, but may also be owing to impurities present in the monomer, which always affect polymerization rate and polymer yield. The polymer from 2MP was found to consist of a mixture of cis-1,4 macromolecular chains having different tacticities. In fact, in the ^{13}C NMR spectrum [Fig. 1(c)] some

TABLE 1 Polymerization of 1,3-Dienes with Heterogeneous (**cat 1**) and Homogeneous (**cat 2**) Neodymium Catalysts[a]

Catalyst	Monomer[b]	Time (h)	Conv. (%)	cis-1,4 (%)	[m][c] (%)	[r][d] (%)	T_m[e] (°C)	M_w (×10⁴)[f] (g/mol)
1	EP	1.5	65.7	90	≥99		42.4	135
	EH	4	47.2	~95	≥99		80.0	107
	2MP	216	43.5	99	51	49	158.5	ns[g]
2	EP	1	50.4	~90	≥99		40.3	133
	EH	2	61.3	95	≥99		78.5	95
	2MP	240	34.5	~99		~90		65

[a] Polymerization conditions: heptane, total volume 16 mL; monomer, 2 mL; Nd, 4×10^{-5} mol; temperature, 20 °C; cat 1 = AlEt$_2$Cl/Nd(OCOC$_7$H$_{15}$)$_3$/Al^{i}Bu$_3$; cat 2 = Al^{i}Bu$_3$/Nd(OCOC$_7$H$_{15}$)$_3$/AlEt$_2$Cl.
[b] EP, (E)-1,3-pentadiene; EH, 1,3-hexadiene; 2MP, (E)-2-methyl-1,3-pentadiene.
[c] Percentage of isotactic dyads, determined by ^{13}C NMR.

[d] Percentage of syndiotactic dyads, determined by ^{13}C NMR.
[e] T_m, melting temperature by DSC.
[f] M_w, molecular weight by SEC.
[g] Not soluble.

multiplicity was observed for each carbon signal, suggesting the presence of sequences having different stereoregularities.

To check this hypothesis, the crude poly(2MP) was fractionated by extraction with different boiling solvents (Table 3). The fraction soluble in diethyl ether consisted predominantly of syndiotactic cis-1,4 polymer [Fig. 1(d)], the benzene-soluble fraction was a mixture of iso- and syndiotactic cis-1,4 macromolecules, whereas the residue to benzene extraction

was found to consist of isotactic cis-1,4 polymer [Fig. 1(e)]. The NMR characterization of the different fractions is described in the following sections.

Polymerization with Nd Homogeneous System
Some results obtained with the homogeneous Nd system (**cat 2**) are summarized in Table 1. EP and EH give isotactic cis-1,4 polymers, practically identical with those obtained with the heterogeneous system [Fig. 1(a,b)], whereas 2MP
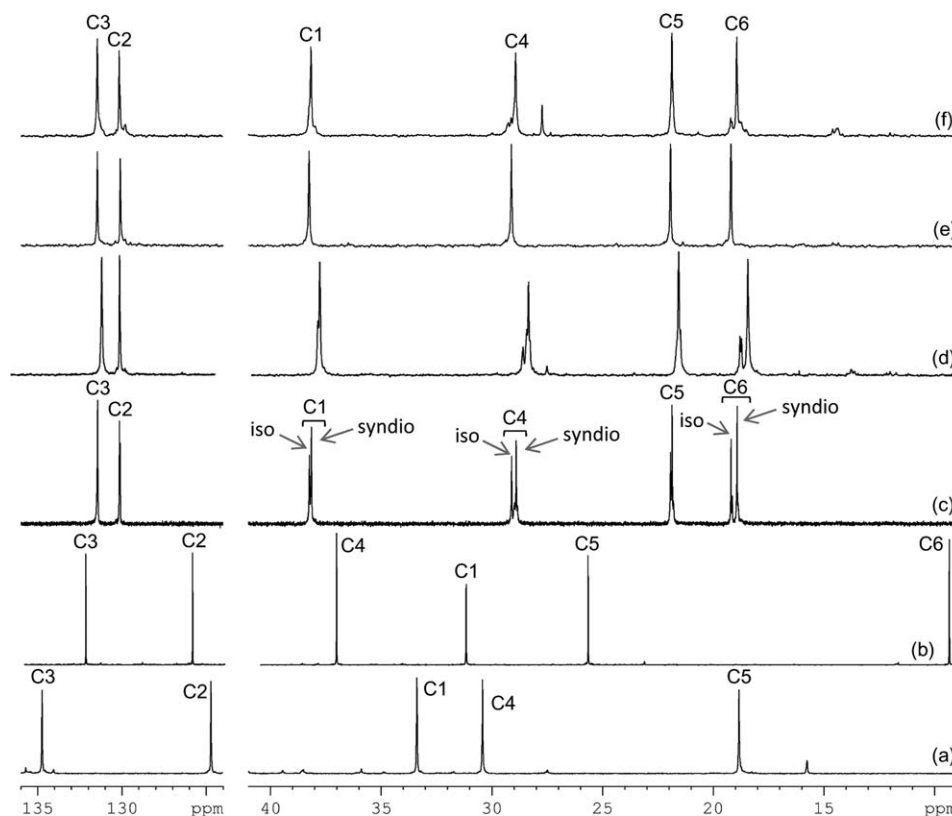

FIGURE 1 ^{13}C NMR spectra (C$_2$D$_2$Cl$_4$; 103 °C; HMDS as internal standard; spectrum of (d) obtained in CDCl$_3$, 25 °C, TMS as internal standard) of (a) cis-1,4 poly(EP), (b) cis-1,4 poly(EH), (c) cis-1,4 poly(2MP) (crude polymer); (d) cis-1,4 poly(2MP) (diethylether soluble fraction), and (e) cis-1,4 poly(2MP) (residue to the solvent fractionation) obtained with cat 1; (f) cis-1,4 poly(2MP) obtained with cat 2.

TABLE 2 Chemical Shifts (C$_2$D$_2$Cl$_4$, 103 °C, HMDS as internal standard) of the Polymers Obtained with Neodymium Catalysts

Polymer		δ (ppm)					
		C1	C2	C3	C4	C5	C6
(structure)	Isotactic cis-1,4 poly(EP)	33.38	124.73	134.72	30.42	18.84	
(structure)	Isotactic cis-1,4 poly(EH)	31.67	126.15	133.04	37.57	26.13	9.68
(structure)	Isotactic cis-1,4 poly(2MP)	38.24	130.09	131.45	29.10	21.93	19.19
	Syndiotactic cis-1,4 poly(2MP)	38.15	130.14	131.45	28.90	21.86	18.93

gives a syndiotactic cis-1,4 polymer [Fig. 1(f)]. The formation of a syndiotactic poly(2MP) with the soluble system suggests that cat 1, generally considered as a heterogeneous system, is most probably a mixture of homogeneous and heterogeneous catalytic species.

Mechanism of Stereocontrol

With regard to the mechanism of the formation of the Nd polymers, we must say that it is difficult to give an interpretation of the results obtained with the heterogeneous system because of the poor information we generally have on the nature of the catalytic species. We restrict, therefore, our analysis to the results obtained with the soluble catalyst. An interpretation of the results obtained in this study is possible, taking into account the schemes published in our previous articles about the formation of stereoregular polymers from 1,3-dienes.[21]

It is now generally accepted that with catalysts that give cis-1,4 polymers the growing chain is anti-η^3-bonded to the transition metal of the catalyst, whereas the incoming monomer is cis-η^4 coordinated. Although EP and 2MP can give, in principle, two types of allylic units (Fig. 3), they actually give units a and c only (Fig. 3). This assumption is based on the fact that in polymerizations with transition metal catalysts

TABLE 3 Results of the Fractionation of the cis-1,4 Poly(2MP) obtained with the Heterogeneous System AlEt$_2$Cl/Nd(OCOC$_7$H$_{15}$)$_3$/Al(^{i}Bu)$_3$ (**cat 1**)

Fraction	% by Weight	[η]^a (dL/g)	T_m^{b} (°C)	[r]/[m]^c Molar ratio
Diethylether soluble	18.6	0.3	147	70/30
Benzene soluble	59.6	0.9	160	58/42
Residue	21.8	–	168	5/95

^{a} Intrinsic viscosity, determined in toluene at 25 °C.
^{b} T_m, melting temperature by DSC.
^{c} [m], percentage of isotactic dyads; [r]; percentage of syndiotactic dyads, determined by ^{13}C NMR.

both EP and 2MP give only 1,4 and 1,2 units, whereas 3,4 units, which would contain a vinyl group [—C(Me)=CH(CH=CH$_2$)—] from EP and a vinylidene group [—C(Me)=CH(C(CH$_3$)=CH$_2$)—] from 2MP, have never been observed, to our knowledge.

A plausible interpretation of the stereoselectivity observed with the homogeneous system can be given on the basis of the schemes of Figure 4. The formation of iso- or syndiotactic cis-1,4 polymers depends on the orientation of the incoming monomer with respect to the last-inserted unit. In the presence of a generic ligand L (L = Cl, Cp, alkoxy group, phosphine, etc.), the new monomer can adopt a coordination as shown in Figure 4(a), giving rise to an exo–exo arrangement or as shown in Figure 4(b), giving rise to an exo–endo arrangement. As shown in the schemes of Figure 5, which report the same situations of Figure 4, observed from left to right, an exo–exo arrangement leads to a isotactic cis-1,4 polymer as shown by the fact that the new allylic unit has the same chirality with respect to the previous one [Fig. 5(a)]. On the other hand, an exo–endo situation leads to a
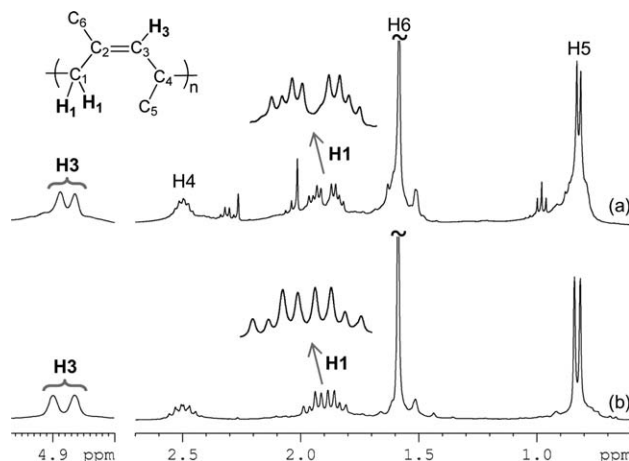

FIGURE 2 ^{1}H NMR spectra of (b) isotactic cis-1,4 poly(2MP) (residue to extraction) obtained with cat 1 and (a) syndiotactic cis-1,4 poly(2MP) obtained with cat 2.
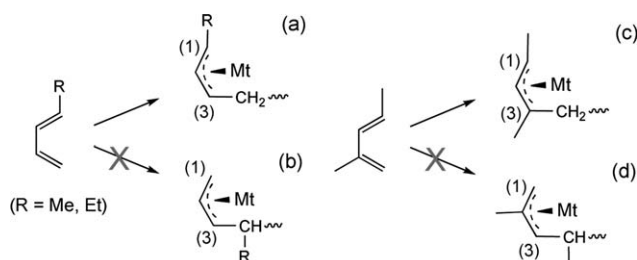
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FIGURE 3 η^3-Butenyl groups that can be obtained from EP (R = Me) and EH (R = Et) (a, b) and from 2MP (c, d) on insertion into the growing polymer chain (only the *anti* form is shown).

syndiotactic *cis*-1,4 polymer as shown by the fact that the new allylic unit has the opposite chirality with respect to the previous one [Fig. 5(b)]. The validity of these schemes is supported by the results obtained in the polymerization of various terminally substituted 1,3-dienes, including deuterated monomers as reported elsewhere.[21]

The different orientations of EP and 2MP with the soluble system likely depend on the presence of the methyl group in the 2MP monomer and in the allyl unit derived from it. In the case of EP and EH, the *exo–exo* arrangement as shown in Figure 5(a) is energetically favored, whereas in the case of 2MP the steric interaction between the methyl groups of the monomer and the allylic unit makes the *exo–endo* arrangement more favorable [Fig. 5(b)].

However, there are soluble catalysts, for example, CpTiCl$_3$/MAO, which give isotactic *cis*-1,4 polymers from 2MP.[18,19] This means that with this catalyst the new monomer and the allylic unit adopt an *exo–exo* arrangement, whereas they adopt, as seen, an *exo–endo* arrangement with the soluble Nd system. This likely depends on the different bulkiness of the L ligand in the two catalysts. In the case of the Nd catalyst, the ligand is a Cl atom, whose bulkiness is lower than that of the Cp group. As a consequence, in the polymerization of 2MP, the *exo–endo* arrangement is favored with the Nd catalyst, whereas the *exo–exo* one is favored with the Ti catalyst.

In conclusion, the results of this study indicate that the orientation of the *cis*-η^4-coordinated monomer with respect to the last-inserted unit is at least influenced by two factors: (i) the substituents on the internal carbon atoms of the monomer and of the allylic unit, and (ii) the identity of the L ligand.

NMR Characterization of cis-1,4 poly(2MP)

In a previous article from our laboratories,[17] we reported a preliminary ^{13}C NMR investigation of the isotactic *cis*-1,4 poly(2MP) whose structure was confirmed by X-ray analysis.[22] Here, we show a detailed ^{13}C and ^{1}H NMR characterization of the isotactic *cis*-1,4 poly(2MP) and compare the spectra with those of the syndiotactic *cis*-1,4 poly(2MP).

^{13}C NMR Spectra

In Figure 1, the ^{13}C NMR spectra of the crude poly(2MP), obtained with the heterogeneous system AlEt$_2$Cl/Nd(O-COC$_7$H$_{15}$)$_3$/Al(^{i}Bu)$_3$ (**cat 1**) [Fig. 1(c)], the diethylether

soluble fraction [Fig. 1(d)], and the residue [Fig. 1(e)], and the crude poly(2MP) obtained with the homogenous catalyst (**cat 2**) are shown. The differences between the spectra of the isotactic and syndiotactic *cis*-1,4 poly(2MP) are evident from the spectra of Figure 1(c) and the data summarized in Table 2.

^{1}H NMR Spectra

In Figure 2, the ^{1}H NMR spectra of the syndiotactic and isotactic *cis*-1,4 poly(2MP) [Fig. 2(a,b)] are shown. Specifically, in the spectra of the polymer obtained with the heterogeneous Nd catalyst [Fig. 2(b)], the two methylene protons, around 1.9 ppm, are practically isochronous which is typical of a *cis*-1,4 isotactic structure as already observed in the case of poly(EP)[14] and poly(EH).[15] In the ^{1}H NMR spectrum of *cis*-1,4 poly(2MP) obtained with the homogeneous system Al(^{i}Bu)$_3$/Nd(OCOC$_7$H$_{15}$)$_3$/AlEt$_2$Cl [Fig. 2(a)], the methylene protons are anisochronous, as indicated by the presence of two different signals for the two methylene protons. This fact, as already observed in the case of other *cis*-1,4 syndiotactic polymers (e.g., poly(EP), poly(EH), and poly(3-methyl-1,3-pentadiene),[23] is indicative of a syndiotactic structure. The syndiotacticity of the *cis*-1,4 poly(2MP) obtained with the homogeneous Nd system is also evidenced by the multiplicity of the olefin proton signal in the ^{1}H NMR spectra. In the ^{1}H NMR spectrum of the isotactic polymer (residue to the extraction of the polymer obtained with the heterogeneous Nd system; Fig. 2(b)) one doublet (4.86 and 4.89 ppm) is observed; in the ^{1}H NMR spectrum of the poly(2MP) obtained with the heterogeneous Nd system (crude polymer; spectrum not shown) two doublets superimposed having practically the same intensity (4.86 and 4.89 ppm; 4.89 and 4.92 ppm) are observed; one doublet (at 4.89 and 4.92 ppm) is finally observed in the ^{1}H NMR spectrum of the *cis*-1,4 poly(2MP) obtained with the homogeneous Nd system (Fig. 2(a)).

CONCLUSIONS

Using the homogeneous Nd catalyst, we have obtained a new polymer, *cis*-1,4 syndiotactic poly(2MP); the *cis*-1,4 isotactic poly(2MP) had been already obtained with the heterogeneous Nd system.

We have given a plausible interpretation for the formation, with the same catalyst (homogeneous Nd system), of *cis*-1,4 isotactic poly(EP) and *cis*-1,4 syndiotactic poly(2MP). The stereoselectivity depends on the coordination mode of the
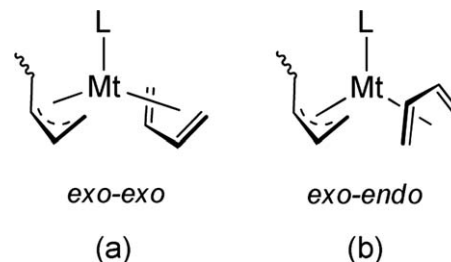

FIGURE 4 Possible orientations of the incoming monomer with respect to the last inserted unit. L is a generic anionic ligand.
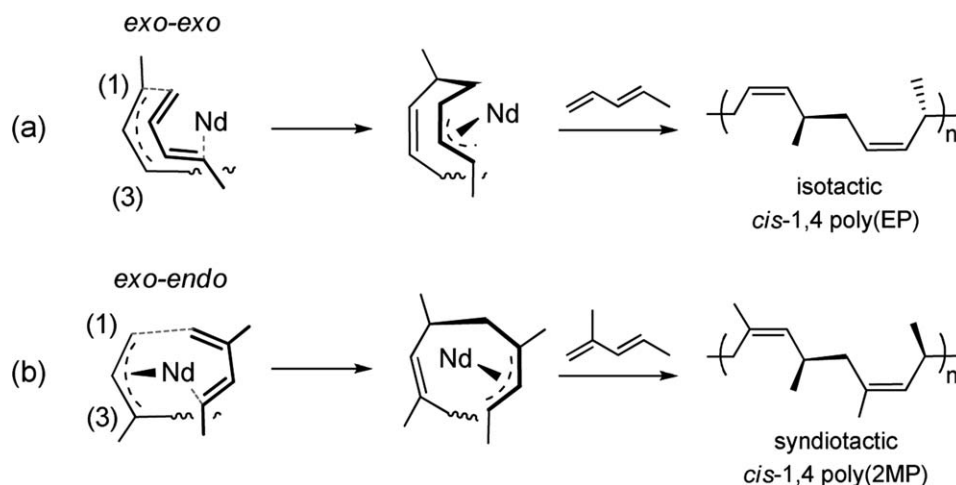
FIGURE 5 Scheme of the formation mode of (a) isotactic *cis*-1,4 poly(EP) and (b) syndiotactic *cis*-1,4 poly(2MP). It should be noted that in (a) and (b) the last polymerized unit is below the plane of the figure, the incoming monomer is above, and the Nd is on the plane.

new monomer with respect to the last inserted unit. In the case of 2MP, the steric interaction between the Me groups bonded to C2 of the monomer and of the last inserted unit favors the formation of an *exo–endo* situation, which leads to a syndiotactic polymer. Such a steric interaction does not exist with EP, and this favors the *exo–exo* situation for this monomer.

The formation of a *cis*-1,4 syndiotactic poly(2MP) with the soluble Nd system and of a *cis*-1,4 isotactic poly(2MP) with the soluble CpTiCl$_3$ system put in evidence the importance of the ligand nature with regard to the polymerization stereoselectivity. The coordination mode of the new monomer is very sensitive to the identity of the ligand (L). If L is a small group (e.g., Cl) an *exo–endo* situation is possible, but not if L is a bulky group (e.g., Cp). In conclusion, the presence of substituents at C2 in the monomer and the identity of the ligand are important factors for determining the orientation of the new monomer with respect to the last inserted unit, and hence the stereoselectivity, with soluble catalysts.

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