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cis-1,4-*alt*-3,4 Polyisoprene: Synthesis and Characterization

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ABSTRACT: We recently reported on the synthesis and characterization of $CoCl_2(PRPh_2)_2$ (R = methyl, ethyl, *n*-propyl, isopropyl, and cyclohexyl). The catalyst systems obtained by combining the above complexes with methylaluminoxanes (MAO) were highly active in the polymerization of 1,3-dienes, giving 1,2 syndiotactic polymers from butadiene and terminally substituted butadienes (e.g., *E*-1,3-pentadiene and *E*-1,3-hexadiene) and 1,2 isotactic polymers from internally substituted 1,3-dienes such as *E*-3-methyl-1,3-pentadiene. We have now polymerized isoprene with the same cobalt catalysts, and unexpectedly the polymers obtained resulted to have an equibinary, alternating *cis*-1,4/3,4 structure, as indicated by the two-dimensional NMR data. A structure of this type is rather unusual in the field of diolefins stereospecific polymerization, and only few cases have been reported in the literature. An interpretation for the formation of such a polymer is proposed. The structure of *cis*-1,4-*alt*-3,4 polyisoprene, with alternating sequences of in-chain and side-chain double bonds, makes it of potential interest in view of a possible selective functionalization of the double bonds.

Introduction

The stereospecific polymerization of isoprene permitted to synthesize up to now the following highly stereoregular polymers: *cis*-1,4, *trans*-1,4, isotactic 3,4, and syndiotactic 3,4 (Figure 1).

High *cis*-1,4 polyisoprene, with a structure very close to that of natural rubber, can be obtained with titanium (e.g., AlR_3-TiCl_4, heptane as solvent)[1-3] or neodymium (e.g. $AlEt_2Cl-Nd(OCOC_7H_{15})_3-Al^iBu_3$, heptane as solvent)[2-13] based catalysts. High *trans*-1,4 polyisoprene, with a structure like that of natural gutta-percha, was obtained for the first time in 1955, using $AlEt_3-\alpha TiCl_3$ as catalyst in aliphatic solvent;[14] vanadium catalysts (e.g., AlR_3-VCl_3 in aliphatic solvent; $V(acac)_3-MAO$, toluene as solvent) too give polyisoprenes with a very high *trans*-1,4 content.[14-18] 3,4 Syndiotactic polyisoprene was recently obtained with iron catalysts (e.g., $FeEt_2(bipy)_2-MAO$, toluene as solvent),[19-23] while the isotactic isomer was reported by Hou.[24]

An atactic 3,4 polyisoprene was obtained with the system $CrCl_2(dmpe)_2-MAO$ in toluene as solvent,[25] while Cui et al. reported on the living polymerization of isoprene with rare earth catalysts to highly 3,4 polymer, having a predominantly syndiotactic structure.[26]

We have now polymerized isoprene with the systems $CoCl_2(PRPh_2)_2-MAO$ (R = methyl, ethyl, *n*-propyl, isopropyl, and cyclohexyl). These systems were highly active and stereospecific in the polymerization of butadiene, giving 1,2 polymers (1,2 content ≥85%) having a syndiotacticity degree depending on the phosphine ligand bonded to the metal.[27-29] Specifically, the systems $CoCl_2(P^iPrPh_2)_2-MAO$ and $CoCl_2(PCyPh_2)_2-MAO$ gave highly syndiotactic polymers, while the systems $CoCl_2(PMePh_2)_2-MAO$, $CoCl_2(PEtPh_2)_2-MAO$, and $CoCl_2(P^nPrPh_2)_2-MAO$ gave atactic polymers with predominance of syndiotactic sequences.[28,29]

Moreover, the same systems were also able to polymerize susbstituted butadienes[27,29,30] such as *E*-1,3-pentadiene, *E*-1,3-hexadiene, and *E*-3-methyl-1,3-pentadiene: crystalline highly syndiotactic 1,2 polymers were obtained from *E*-1,3-pentadiene[31] and *E*-1,3-hexadiene[32] with $CoCl_2(P^iPrPh_2)_2-MAO$, while highly isotactic 1,2 polymers were obtained from *E*-3-methyl-1,3-pentadiene with $CoCl_2(PRPh_2)_2-MAO$ (R = methyl, ethyl, *n*-propyl).[30]

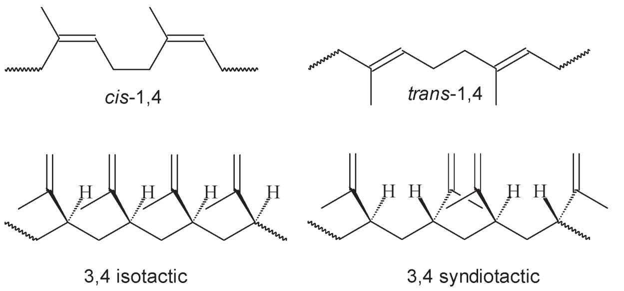

Figure 1. Stereoregular polyisoprenes until now synthesized.

In the polymerization of isoprene we did not obtain, as expected on the basis of the above results, a 3,4 polyisoprene, but surprisingly the polymers exhibited an equibinary *cis*-1,4-*alt*-3,4 structure. A structure of this type is rather unusual in the field of diolefins stereospecific polymerization, and only few cases have been reported in the literature.[33-35]

This paper reports on the synthesis and detailed NMR characterization of this particular polymer; some hypotheses on the mechanism of formation of such an unusual polymeric structure are also formulated.

Experimental Section

Materials. $CoCl_2(PRPh_2)_2$ (R = methyl, ethyl, *n*-propyl, isopropyl, cyclohexyl) were prepared as reported in the literature.[27,28] MAO (Aldrich, 10 wt % solution in toluene) was used as received without further purification. Toluene (Fluka, >99.5% pure) was refluxed over Na for ca. 8 h, then distilled, and stored over molecular sieves under dry nitrogen. Isoprene (Aldrich, ≥99% pure) was refluxed over CaH_2 for about 2 h, then distilled trap-to trap, stored under dry nitrogen, and kept at −20 °C.

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Table 1. Polymerization of Isoprene with Cobalt−Phosphine Complex Based Catalysts[a]

	Co compound		polymerization			polymer		
run	type	mol ($\times 10^5$)	time (min)	conv (%)	N^b (h^{-1})	M_w^c ($\times 10^3$)	MWD[d]	T_g^e (°C)
1	$CoCl_2(PMePh_2)_2$	3	60	89.0	593	171	2.2	−19.0
2	$CoCl_2(PEtPh_2)_2$	4	85	72.7	256	82	1.7	−18.5
3	$CoCl_2(P^nPrPh_2)_2$	4	96	90.3	282	85	1.6	−17.6
4	$CoCl_2(P^iPrPh_2)_2$	3	330	89.0	108	68	1.5	−18.7
5	$CoCl_2(PCyPh_2)_2$	4	357	79.9	67	60	1.5	−17.9
6	$CoCl_2(P^iPrPh_2)_2$	1	443	76.4	207	173	1.6	−18.5
7	$CoCl_2(P^iPrPh_2)_2$	1	2640	66.3	30	273	1.6	−18.7

[a] Polymerization conditions: toluene, total volume 16 mL; isoprene, 2 mL; MAO, Al/Co = 100 (in runs 1−5, commercial MAO as received was used; in runs 6 and 7, free-$AlMe_3$ MAO was used); 20 °C (0 °C in run 7). [b] Moles of isoprene polymerized per mol of Co per hour. [c] Number-average molecular weight, determined by GPC. [d] Molecular weight distribution (M_w/M_n), determined by GPC. [e] Glass transition temperature, determined by DSC. All the polymers reported in the table have a mixed *cis*-1,4/3,4 (50:50 molar ratio) structure.

Polymerization. Toluene (total volume, 16 mL), isoprene (2 mL, 1.36 g), and MAO (1.3 mL, 2×10^{-3} mol) were introduced in a 25 mL dried flask in this order. The obtained solution was brought at the desired polymerization temperature, and then $CoCl_2(PRPh_2)_2$ (2×10^{-5} mol, as 1 mg/mL toluene solution) was added. All operations were carried out under dry nitrogen. The polymerization was terminated with methanol containing a small amount of hydrochloric acid; the polymer was coagulated and repeatedly washed with fresh methanol and then dried in vacuum at room temperature.

Polymer Characterization. ^{13}C and ^1H NMR measurements were carried out on a Bruker Avance 400 spectrometer, operating at 400 MHz for ^1H and 100.58 MHz for ^{13}C. The spectra were obtained in $C_2D_2Cl_4$ at 103 °C (hexamethyldisiloxane, HMDS, as internal standard). The concentration of polymer solutions was about 10 wt %. ^{13}C conditions: 10 mm probe; 14.50 μs as 90° pulse, relaxation delay 18 s; acquisition time 1.87 s. Proton broadband decoupling was achieved with a 1D sequence using bi_waltz_16_32 power-gated decoupling.

The INADEQUATE 2D experiment (*i*ncredible *n*atural *a*bundance *d*ouble *qua*ntum *t*ransfer *e*xperiment)[36−39] was acquired by using the standard Bruker pulse sequence. The $^{13}C-^{13}C$ coupling constant was characteristic for the aliphatic region ^1J (C,C) 40 Hz, with the aim to determine the main carbon skeleton of the polymer, neglecting the olefinic region. The repetition time was 5 s long; matrix size 1024 × 256 data; DS 16; spectral width 16 025 Hz in F2 and 32 051 Hz in F1. The data were zero-filled before Fourier transformation and processed with a square sine-bell weighting function in both domains.

DSC scans were carried out on a Perkin-Elmer Pyris 1 instrument equipped with a liquid nitrogen subambient device. The sample, ca. 4 mg, was placed in a sealed aluminum pan, and the measurements were carried out using heating and cooling rates of 20 °C/min.

The molecular weight averages and the molecular weight distribution (MWD) were obtained by a Waters GPCV 2000 system using two online detectors: a differential viscosimeter and a refractometer. The experimental conditions consisted of two PLgel Mixed C columns, toluene as mobile phase, 0.8 mL/min flow rate, and 80 °C temperature. The calibration of the GPC system was carried out using 18 narrow MWD polystyrene standards with the molar mass ranging from 162 to 3.3×10^6 g/mol.

Results and Discussion

The catalyst systems $CoCl_2(PRPh_2)_2$−MAO (R = methyl, ethyl, *n*-propyl, isopropyl, cyclohexyl) give from isoprene amorphous polymers with a transition glass temperature (T_g) around −19 °C (Table 1). The polymerizations were carried out in toluene as solvent, for a better homogeneity of the system (cobalt complexes and methylaluminoxane are more soluble in aromatic than in aliphatic solvent), but the same results can be obtained by using heptane as solvent. The number-average molecular weight (M_w) seems to decrease with increasing the bulkiness of the phosphine ligand on the cobalt atom; it is 171 000 and 60 000 dL g^{-1} for the polymers obtained with $CoCl_2(PMePh_2)_2$−MAO and $CoCl_2(PCyPh_2)_2$−MAO, respectively. Higher polymer molecular weight can be obtained by using dry MAO instead of commercial MAO, likely because of the absence of free $AlMe_3$ acting as chain transfer agent, and by polymerizing isoprene at low temperature. The molecular weight distribution is rather narrow, in the range 1.5−1.7, indicating a pseudo-living single site nature of the catalyst. Catalyst activity is quite good, and it decreases with increasing the phosphine ligand steric hindrance.

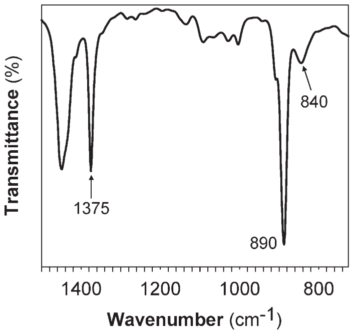


Figure 2. IR spectrum of the polyisoprene obtained with $CoCl_2(P^nPrPh_2)_2$−MAO (Table 1, run 3).

The IR spectra (Figure 2) of all the polyisoprenes prepared were registered in order to determine their microstructure. No band was observed at 911 cm^{-1}, indicating that no 1,2 units are present along the polymer chain; the two bands observed at about 840 and 890 cm^{-1} are instead indicative of the presence of 1,4 and 3,4 units, respectively. Furthermore, the presence of a band at 1375 cm^{-1} is in agreement with a *cis* nature of the 1,4 units, being the typical band of a *trans* 1,4 unit displayed at 1385 cm^{-1}.[40] A mixed *cis*-1,4/3,4 structure for the polymers under investigation was quite surprising, since, as told above, the systems $CoCl_2(PRPh_2)_2$−MAO gave essentially 1,2 polymers from butadiene, *E*-1,3-pentadiene, *E*-1,3-hexadiene, and *E*-3-methyl-1,3-pentadiene.[27−32]

The amount of *cis*-1,4 and 3,4 units, determined by ^1H NMR analysis (Figure 3),[41] resulted to be about 50:50 in all the polymers examined, suggesting an equibinary structure for the polyisoprenes obtained with $CoCl_2(PRPh_2)_2$−MAO catalysts.

The ^{13}C NMR spectrum of the polymer obtained with $CoCl_2(P^iPrPh_2)_2$−MAO (Table 1, run 4) is shown in Figure 4b. The DEPT experiment carried out on the same polymer (Figure 5), evidencing the presence of two olefinic quaternary carbons, confirms the absence of 1,2 units, in agreement with the IR indications.

In fact, as shown in Figure 6, only one quaternary olefinic carbon is present in a mixed *cis*-1,4/1,2 polymer (structures **I** and **II**) while two quaternary olefinic carbons are present in a mixed *cis*-1,4/3,4 polymer (structures **III** and **IV**).

The analysis of the ^{13}C NMR spectrum (Figure 4b) clearly indicates that the ^{13}C resonances values of the 10 main signals

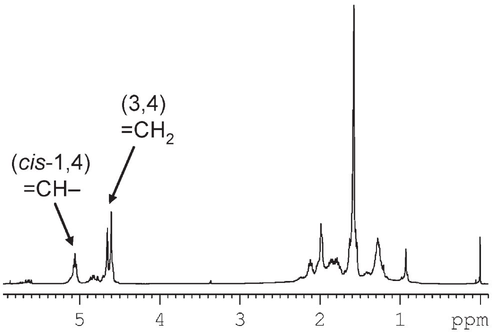


Figure 3. ^{1}H NMR spectrum of the polyisoprene obtained with $CoCl_2(PMePh_2)_2$−MAO (Table 1, run 1).

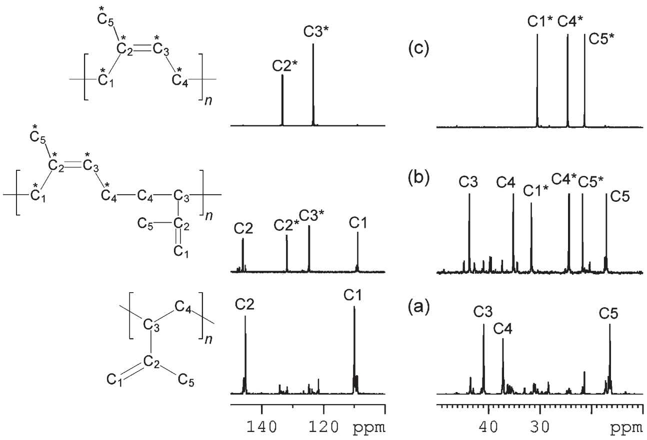


Figure 4. ^{13}C NMR spectra ($C_2D_2Cl_4$, HMDS as internal standard, 103 °C) of (a) 3,4 syndiotactic polyisoprene obtained with $FeCl_2(bipy)_2$−MAO;[20] (b) *cis*-1,4-*alt*-3,4 polyisoprene obtained with $CoCl_2(P^iPrPh_2)_2$−MAO (Table 1, run 4); (c) *cis*-1,4 polyisoprene obtained with $Nd(OCOC_7H_{15})_3$−$AlEt_2Cl$−$Al(^iBu)_3$.[2,3]

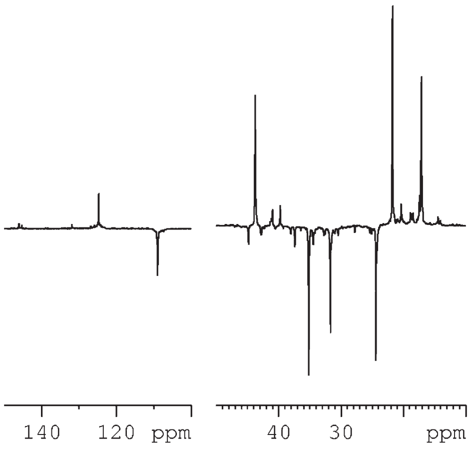


Figure 5. DEPT spectrum of the polyisoprene obtained with $CoCl_2(P^iPrPh_2)_2$−MAO (Table 1, run 4).

observed do not correspond to those of the signals observed in the ^{13}C NMR spectra of the *cis*-1,4 (Figure 4c) and 3,4 (Figure 4a) isoprene homopolymers. This experimental evidence suggests that *cis*-1,4 and 3,4 sequences are not present along the polymer chain and that the most probable structure is a *cis*-1,4-*alt*-3,4 structure. We may have in principle two different types of *cis*-1,4/3,4 enchainments (Figure 6, structures **III** and **IV**). To discriminate between them, an INADEQUATE experiment was carried out (Figure 7).

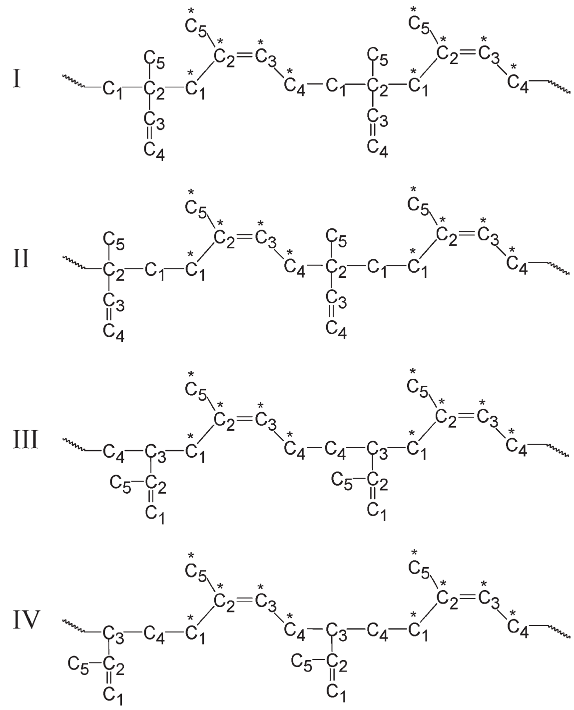


Figure 6. Possible enchainments in the equibinary *cis*-1,4-*alt*-1,2 (**I** and **II**) and *cis*-1,4-*alt*-3,4 (**III** and **IV**) polyisoprenes.

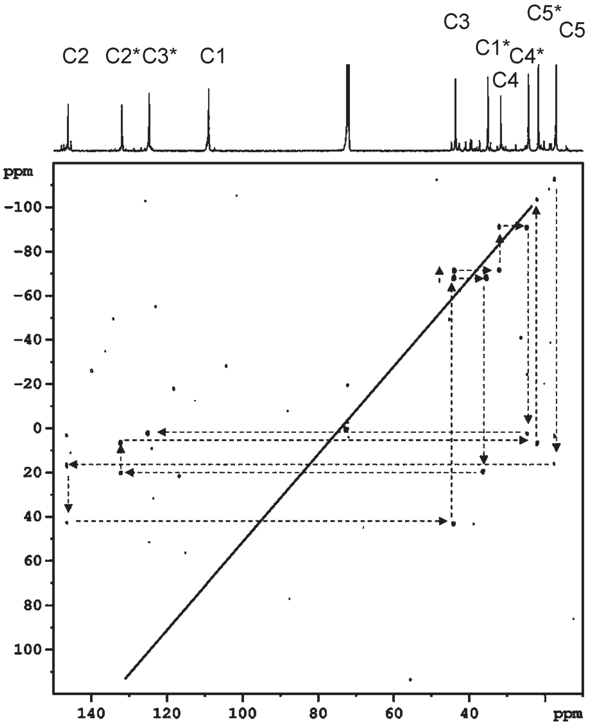


Figure 7. INADEQUATE spectrum of the polyisoprene obtained with $CoCl_2(P^iPrPh_2)_2$−MAO (Table 1, run 4).

Acquiring a 2D INADEQUATE experiment, based on the $^1J(^{13}C-^{13}C)$ homonuclear coupled spins, it is possible to detect the $^{13}C-^{13}C$ linkage in the investigated polymer. In general, the experiment is time-consuming and requires a large quantity of sample due to the very low sensitivity of the experiment because of the low natural abundance of the ^{13}C isotope, which is only 1.1%. Figure 7 evidences the 2D INADEQUATE spectrum of the polymer obtained with $CoCl_2(P^iPrPh_2)_2$−MAO (Table 1, run

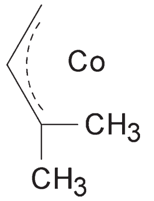


Figure 8. Allylic unit structure in the cobalt allyl complex $(\eta^4\text{-}C_5H_8)(\eta^3\text{-}C_5H_9)Co(PPh_3)$.

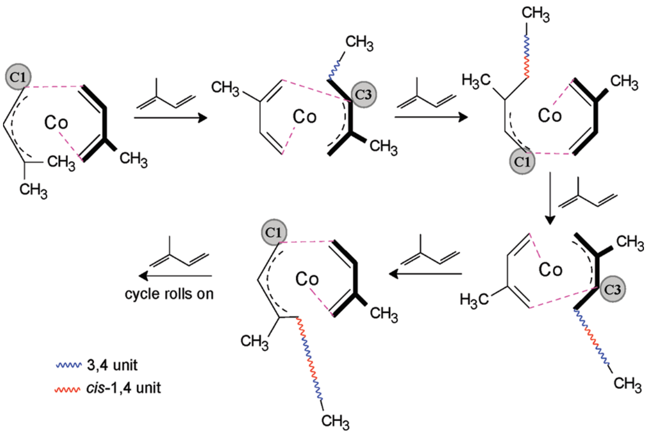
4); the corresponding ^{13}C spectrum is plotted on the top. The correlations, indicating the direct attachment of two ^{13}C atoms, can be identified by resonances along a horizontal line and equally spaced from the diagonal. The unknown structure can be determined from Figure 7, following the arrows representing the carbon atoms sequence. Two connections were lost during the experiment, the C2−C1 and C2*−C3*, due to the experimental $^1J(C,C)$ applied, which was characteristic for aliphatic carbons. This experiment permitted to exclude the structure **IV** of Figure 6, indicating that the *cis*-1,4 and 3,4 units are enchained as shown in structure **III** of Figure 6.

As cited above, the systems $CoCl_2(PRPh_2)_2$−MAO were also able to polymerize 1,3-pentadiene, 1,3-hexadiene, and 3-methyl-1,3-pentadiene.[27,30−32] They gave exclusively 1,2 polymers, having a predominantly isotactic or syndiotactic structure depending on the catalyst structure (i.e., type of ligand bonded to the cobalt atom), meaning that the type of ligand has some influence on the polymerization stereoselectivity. The same cobalt catalysts gave an equibinary *cis*-1,4-*alt*-3,4 polymer from isoprene, independently on the type of ligand coordinated to the cobalt atom, suggesting that the type of ligand, in this case, has no influence on the polymer microstructure and that the monomer structure is likely the main factor responsible for the formation of such an unusual polymer.

The mode of formation of the equibinary *cis*-1,4-*alt*-3,4 polyisoprene described in this paper is rather difficult to explain. Teyssie, who synthesized several years ago an analogous polyisoprene with cobalt catalysts obtained by reaction of cobalt halides with ethoxydiethylaluminum and of cobalt halides with phenylmagnesium bromide and alcohol, attributed the formation of such a polymer to a stereoregulation mechanism implying an alternating propagation mechanism on a nonsymmetrical transition-metal complex.[33,34] The formation of a polymer with alternated constitutional units, *cis*-1,4 and 3,4, could be also accounted for by admitting an alternated coordination and insertion of the isoprene monomer with a η^4 bond (for the *cis*-1,4 units) or with a η^2 bond (for the 3,4 units), according to the models proposed by Guerra et al.[42]

We could hypothesize however another possible mode of formation of the equibinary *cis*-1,4-*alt*-3,4 polyisoprene, based on the diene polymerization mechanism proposed by Porri several years ago.[2,43−49] If we consider that (i) according to this mechanism the growing chain is η^3-bonded to the metal atom and the diene monomer *cis*-η^4 coordinated to the metal atom; (ii) the allylic unit has two reactive sites, C1 and C3, and a *cis*-1,4 unit is formed by insertion of the incoming monomer at C1, while a 1,2 (3,4) unit is formed by insertion of the incoming monomer at C3; (iii) in the polymerization of internally substituted 1,3-dienes with $CoCl_2(PRPh_2)_2$−MAO the butenyl group−diene monomer reciprocal orientation *exo*−*endo* seems to be preferred with respect to the *exo*−*exo* one;[29,30] (iv) in the allylic cobalt complexes $(\eta^4\text{-}C_5H_8)(\eta^3\text{-}C_5H_9)Co(PPh_3)$[50,51] and $(\eta^4\text{-}C_5H_8)(\eta^3\text{-}C_5H_9)Co(PMePh_2)$[52] the structure of the allylic unit is that shown in Figure 8; and (v) 1,2 units are almost negligible in the polyisoprenes obtained with $CoCl_2(PRPh_2)_2$−MAO (R = methyl, ethyl, *n*-propyl, isopropyl, cyclohexyl), the formation of the *cis*-1,4-*alt*-3,4 polyisoprene could be described, as shown in Scheme 1. According to this scheme, we should obtain highly stereoregular polymers with a syndiotactic structure of the 3,4 units along the polymer chain, whereas, as cited above, the *cis*-1,4-*alt*-3,4 polyisoprenes obtained are amorphous. Some steric errors could occur during the polymerization process (e.g., *exo*−*exo* orientations of incoming isoprene monomer and butenyl group together with the predominantly *exo*−*endo* ones), leading to the introduction of stereodefects along the polymer chain. The lack of crystallinity, however, could also be due to some difficulties in the crystal packing of the macromolecules, apart from the presence of defects along the polymer chain.

Scheme 1. Possible Mode of Formation of *cis*-1,4-*alt*-3,4 Polyisoprene[a]



[a] Co is on the plane; structures in bold type above the plane; structures in normal type below the plane.

However, our proposed mechanism (Scheme 1), along with the other ones based on the work of Teyssie and Guerra, only show possible modes of formation of the equibinary *cis*-1,4-*alt*-3,4 polyisoprene but do not tell us which are the factors determining the type of coordination and insertion of isoprene molecules. Some further work is necessary in order to better clarify this problem, and for this purpose modeling and computational chemistry could be of great help.

Conclusion

Equibinary *cis*-1,4/3,4 polyisoprenes have been obtained by polymerizing isoprene with the cobalt systems $CoCl_2(PRPh_2)_2$−MAO (R = methyl, ethyl, *n*-propyl, isopropyl, cyclohexyl). A detailed NMR study of the polymers permitted to assign them an alternating *cis*-1,4-*alt*-3,4 structure. A structure of this type is rather unusual in the field of diolefins stereospecific polymerization, and only few cases have been reported in the literature. An interpretation for the formation of such a polymer is proposed.

Furthermore, this particular structure, with alternating sequences of in-chain and side-chain double bonds, makes this polymer of potential interest in view of a possible selective functionalization of the different double bonds; work on this point is still in progress.

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