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Synthesis and Characterization of Isotactic 1,2-Poly(*E*-3-methyl-1,3-pentadiene). Some Remarks about the Influence of Monomer Structure on Polymerization Stereoselectivity

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ABSTRACT: 3-Methyl-1,3-pentadiene (mixture of *E* and *Z* isomers) was polymerized with the systems $CoCl_2(PRPh_2)_2$−MAO (R = methyl, ethyl *n*-propyl, isopropyl, cyclohexyl), obtaining crystalline, essentially isotactic 1,2-poly(*E*-3-methyl-1,3-pentadiene)s, as indicated by IR and NMR (^1H and ^{13}C in solution) analyses. The isotactic content was found to depend on the type of catalyst used (i.e., type of phosphine ligand bonded to the cobalt atom), increasing with decreasing the bulkiness of the phosphine ligand. The same cobalt systems were also used to polymerize 1,3-pentadiene and 1,3-hexadiene, obtaining polymers having the same 1,2 structure, but an opposite tacticity (syndiotactic instead of isotactic). The role played by the monomer structure in determining the polymerization stereoselectivity is discussed.

Introduction

We have recently reported on the synthesis and characterization of some cobalt phosphine complexes of the type $CoCl_2(PRPh_2)_2$ (R = methyl, ethyl, *n*-propyl, isopropyl, cyclohexyl).[1] These complexes, in combination with methylaluminoxane (MAO), were found to be highly active and stereoselective for the 1,2 polymerization of butadiene (1,2 content ≥80%). Specifically, 1,2-polybutadienes having different tacticity (predominantly syndiotactic or isotactic) were obtained depending on the type of cobalt complex used, permitting us to highlight the influence of catalyst structure (i.e., type of ligand bonded to the cobalt atom) on the polymerization stereoselectivity.[1b]

The system $CoCl_2(P^iPrPh_2)_2$−MAO was also used in the polymerization of 1,3-pentadiene and 1,3-hexadiene,[1a] allowing us to obtain highly stereoregular polymers: syndiotactic 1,2-poly(*E*-1,3-pentadiene)[2] and syndiotactic 1,2-poly(*E*-1,3-hexadiene).[3] The 1,2 content of these polymers was about 99%, while, as mentioned above, the 1,2 content of the polybutadiene obtained with the same system was about 80%. This result permitted us to put in evidence the influence of monomer structure on polymerization chemoselectivity, already observed in the polymerization of 1,3-dienes with $CpTiCl_3$−MAO.[4]

Keeping on with this investigation about the stereospecific polymerization of substituted butadienes with transition metal catalysts,[5] initiated long ago, and aimed at obtaining (i) new experimental data for improving our knowledge on the diene polymerization mechanism with transition metal catalysts and (ii) novel 1,3-diene stereoregular polymers in order to establish correlations between polymer structure and polymer properties, we have now examined the polymerization of 3-methyl-1,3-pentadiene with the systems $CoCl_2(PRPh_2)_2$−MAO. The polymers obtained have an essentially isotactic *E*-1,2 structure on the basis of the IR and NMR characterizations. The isotactic content was found to depend on the type of catalyst used (i.e., type of phosphine ligand bonded to the cobalt atom). Specifically, the polymers obtained with the catalyst systems having minimally hindered ligands (e.g., $PMePh_2$, $PEtPh_2$, P^nPrPh_2) were found to be highly crystalline and highly isotactic.

Isotactic 1,2-poly(*E*-3-methyl-1,3-pentadiene) is a novel polymer, never reported before. In the case of 3-methyl-1,3-pentadiene (3MP), 12 different stereoregular polymers can be obtained in principle, depending on the type of monomeric enchainment (Figure 1): *cis*-1,4 iso- and syndiotactic poly(3MP), *trans*-1,4 iso- and syndiotactic poly(3MP), 1,2 iso- and syndiotactic poly(*E*-3MP), 1,2 iso- and syndiotactic poly(*E*-3MP), 3,4 iso- (*erythro* and *threo*) and syndiotactic (*erythro* and *threo*) poly(3MP). Until now, only three stereoregular poly(3MP) have been described in the literature: *cis*-1,4 isotactic obtained with neodymium catalysts,[6] *cis*-1,4 syndiotactic obtained with cobalt or nickel catalysts,[6a,7] and 1,2 syndiotactic poly(*E*-3MP) obtained with iron catalysts.[8]

Furthermore, isotactic 1,2-poly(*E*-3-methyl-1,3-pentadiene) is one of the very few examples of crystalline isotactic 1,2-polydienes described in the literature, the other ones being isotactic 1,2-polybutadiene[9] and isotactic 1,2-poly(4-methyl-1,3-pentadiene),[10] reported several years ago by Porri, and isotactic 3,4-polyisoprene, recently described by Hou.[11]

The results obtained were also quite interesting from a mechanistic point of view. They permitted in fact, as mentioned above, to confirm some aspects of the diene polymerization mechanism such as the influence of monomer structure on the polymerization chemoselectivity[4,5] and the influence of catalyst structure on polymerization stereoselectivity,[1b,5,12] but, above all, they allowed us to clearly point out the relevant role played by the monomer structure in determining the polymerization

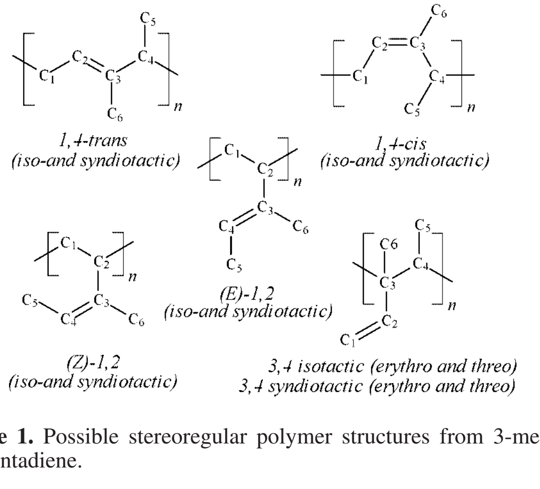

Figure 1. Possible stereoregular polymer structures from 3-methyl-1,3-pentadiene.

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Table 1. Polymerization of 1,3-Dienes with the Systems $CoCl_2(PRPh_2)_2$−MAO (R = Methyl, Ethyl, *n*-Propyl, Isopropyl, Cyclohexyl)[a]

run	monomer	Co complex	time (min)	conv (%)	1,2[b] (%)	rr[c] (%)	mm[c] (%)	M_w[d] (g mol^{-1})	M_w/M_n[d]	mp[e] (°C)
1	3MP	$CoCl_2(PCyPh_2)_2$	7200	78.3	~99		≥60	66 600	1.5	
2	3MP	$CoCl_2(P^iPrPh_2)_2$	7200	79.1	~99		≥60	62 000	1.6	79
3	3MP	$CoCl_2(P^nPrPh_2)_2$	7200	78.0	~99		≥90	81 000	1.2	96, 120
4	3MP	$CoCl_2(PEtPh_2)_2$	7200	80.0	~99		≥90	83 000	1.3	102, 123
5	3MP	$CoCl_2(PMePh_2)_2$	7200	78.7	~99		≥90	89 000	1.2	109, 132
6	EP	$CoCl_2(PCyPh_2)_2$	180	72.0	~99	75		250 000	1.8	127
7	EP	$CoCl_2(P^iPrPh_2)_2$	180	78.0	~99	72		220 000	1.7	129
8	EP	$CoCl_2(P^nPrPh_2)_2$	30	97.2	~99	45		101 000	1.4	
9	EP	$CoCl_2(PEtPh_2)_2$	30	96.1	~99	42		97 000	1.4	
10	EP	$CoCl_2(PMePh_2)_2$	30	100	~99	24		103 000	1.6	
11	H	$CoCl_2(PP^iPrPh_2)_2$	300	49.9	~99	63		65 000	1.9	101
12	H	$CoCl_2(P^nPrPh_2)_2$	300	50.4	~99	38		57 000	1.7	

[a] Polymerization conditions: monomer, 2 mL; toluene, total volume 16 mL; Co, 1×10^{-5} mol; MAO, Al/Co = 100; +20 °C. 3MP = 3-methyl-1,3-pentadiene; EP = *E*-1,3-pentadiene; H = 1,3-hexadiene. [b] Percentage of 1,2 units, determined by NMR analysis. [c] Triads molar ratio, determined by NMR analysis; complementary percentages are mainly due to *mr* triads. [d] Molecular weight and molecular weight distribution, determined by GPC analysis. [e] Melting point, determined by DSC analysis.

stereoselectivity. We have in fact also polymerized 1,3-pentadiene and 1,3-hexadiene with the same cobalt systems, obtaining polymers characterized by the same 1,2 structure, but a different tacticity, syndiotactic instead of isotactic.

Experimental Section

Materials. $CoCl_2(PRPh_2)_2$ (R = methyl, ethyl, *n*-propyl, isopropyl, cyclohexyl) were prepared as reported in the literature.[1] Methylaluminoxane (MAO) (Crompton, 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. 3-Methyl-1,3-pentadiene (Aldrich, 99% pure, mixture of (*E*) and (*Z*) isomers; *E*:*Z* molar ratio, 80:20, determined in our laboratory), *E*-1,3-pentadiene (Aldrich, 99% pure), and 1,3-hexadiene (Aldrich, 99% pure, mixture of (*E*) and (*Z*) isomers, *E*:*Z* molar ratio, 50:50, determined by gas chromatography (GC) in our laboratory[8b]) were refluxed for ca. 2 h over CaH_2, then distilled trap-to-trap, and stored at −25 °C under dry nitrogen.

Polymerization. The polymerization described in Table 1, run 3, is reported as a standard procedure. Toluene (total volume, 16 mL), (*E*+*Z*)-3-methyl-1,3-pentadiene (2 mL, 1.46 g), MAO (1.26 mL of toluene solution, 2×10^{-3} mol), and $CoCl_2(P^nPrPh_2)_2$ (2×10^{-5} mol, as toluene solution) were introduced in this order in a 25 mL dried flask. All operations were carried out under dry nitrogen. The polymerization was terminated with methanol containing a little amount of hydrochloric acid; the polymer was coagulated and repeatedly washed with fresh methanol and finally dried in vacuum overnight at room temperature.

The other polymerization runs shown in Table 1, using different monomers and different catalyst systems, were carried out in a similar way.

In the polymerizations of 3-methyl-1,3-pentadiene, the monomer mixture composition during the polymerization reaction was evaluated from GC analyses of polymer solution samples taken at different polymerization times. The GC analyses were performed on a Hewlett-Packard 6890 Plus instrument equipped with a flame ionization detector. The oven was set at 25 °C for 10 min and then heated at 150 °C at a rate of 5 °C/min. A fused silica capillary column Supelco SPB-5, 30 m × 0.32 mm i.d., with a film thickness of 0.25 μm, was used as a separation column.

Polymer Characterization. The infrared spectra were recorded on a Bruker IFS 48 instrument; the polymer spectra were obtained by using polymer films on KBr disks. The films were obtained by deposition from polymer solutions in hot benzene.

Differential scanning calorimetry (DSC) scans were carried out on a Perkin-Elmer Pyris 1 instrument. Typically, ca. 5 mg of polymer was analyzed in each run, with scan rate of 20 °C/min, under a nitrogen atmosphere.

^{13}C and ^1H NMR measurements were carried out on a Bruker Avance 400 instrument. 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 %. The HMBC (heteronuclear multiple bond correlation) experiment[13] was carried out with a delay of 100 ms for the evolution of long-range couplings and a delay of 3.4 ms for creation of the antiphase magnetization (corresponding to a $^1J_{CH} = 146$ Hz, peculiar of olefinic heteronuclear one bond coupling constants). The INADEQUATE (incredible natural abundance double quantum transfer experiment) 2D experiment[14] was acquired applying a standard Bruker inadqf procedure. A $\pi/2$ pulse of 14.3 μs was applied with a repetition time of 5.0 s. Spectral carbon width: 14 619 Hz; matrix size 1024 × 128 data; number of scans 512 with 16 DS; ^1J (C,C) 70 Hz, corresponding to a delay of 3.5 ms. The 2D data were processed in a magnitude mode and were zero-filled before Fourier transformation.

The molecular weight averages and the molecular weight distribution were obtained by a Waters GPCV 2000 system 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 temperature. The calibration of the GPC system was constructed by polystyrene standards with the molar mass ranging from 162 to 3.3×10^6 g/mol.

The wide-angle X-ray diffraction (WAXD) 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 5 to 35 2θ° at 0.05 2θ° intervals.

Results and Discussion

The results of the polymerization of 3-methyl-1,3-pentadiene (3MP) with the systems $CoCl_2(PRPh_2)_2$−MAO (R = methyl, ethyl, *n*-propyl, isopropyl, cyclohexyl) are shown in Table 1. The polymers obtained are in general crystalline, and the crystallinity degree seems to decrease with increasing the bulkiness of the phosphine ligand in the catalyst systems used for their preparation (Figure 2). This experimental evidence is confirmed by the DSC investigation (Figure 3). No melting point was detected for the polymer obtained with $CoCl_2(PCyPh_2)_2$−MAO, while endothermic events were observed for the other polymers (Figure 3) in the temperature range 60−140 °C. Particularly, the polymer obtained with $CoCl_2(PMePh_2)_2$−MAO shows two endothermic peaks at 109 and 132 °C (Figure 3d). Two endothermic peaks, even if characterized by a different enthalpy ratio, are also detectable in the case of the polymers obtained with $CoCl_2(PEtPh_2)_2$−MAO (102 and 123 °C; Figure 3c) and $CoCl_2(P^nPrPh_2)_2$−MAO (96 and 120 °C; Figure 3b). The DSC thermogram of the poly(3MP) obtained with $CoCl_2(P^iPrPh_2)_2$−MAO (Figure 3a) exhibits a single endothermic transition centered at 79 °C and characterized by a low heat of fusion.

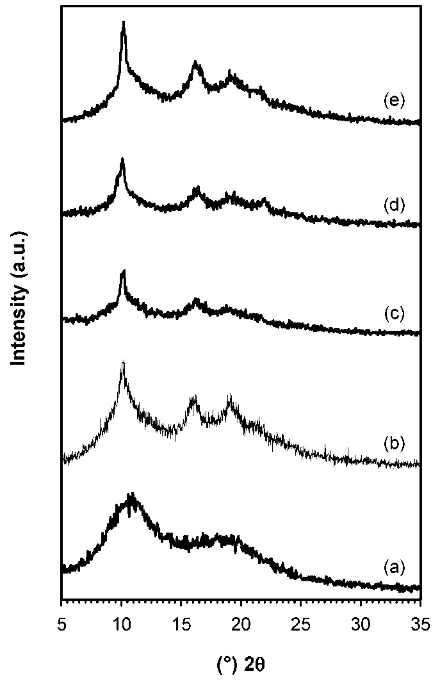


Figure 2. X-ray powder spectra of the poly(3-methyl-1,3-pentadiene)s obtained with (a) $CoCl_2(PCyPh_2)_2$−MAO, (b) $CoCl_2(P^{i}PrPh_2)_2$−MAO, (c) $CoCl_2(P^{n}PrPh_2)_2$−MAO, (d) $CoCl_2(PEtPh_2)_2$−MAO, and (e) $CoCl_2(PMePh_2)_2$−MAO.

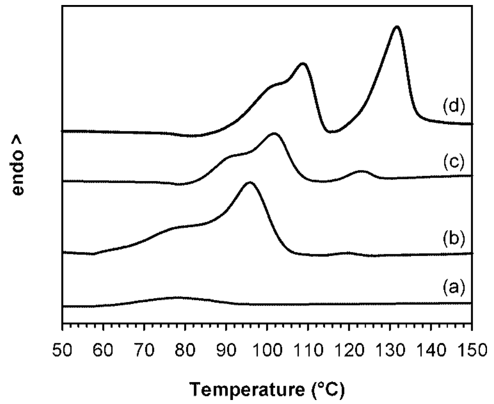


Figure 3. DSC curves of the poly(3-methyl-1,3-pentadiene)s obtained with (a) $CoCl_2(P^{i}PrPh_2)_2$−MAO, (b) $CoCl_2(P^{n}PrPh_2)_2$−MAO, (c) $CoCl_2(PEtPh_2)_2$−MAO, and (d) $CoCl_2(PMePh_2)_2$−MAO.

The presence of more than one endothermic peak in the DSC diagrams could be explained by the existence of different dimensional distribution of the crystals or different crystalline structures in the polymers under investigation. On this particular point we are actually investigating: work is in progress in order to determine the X-ray crystalline structure of the polymer, even if it is in part thwarted by the difficulty of obtaining suitable polymer fibers.

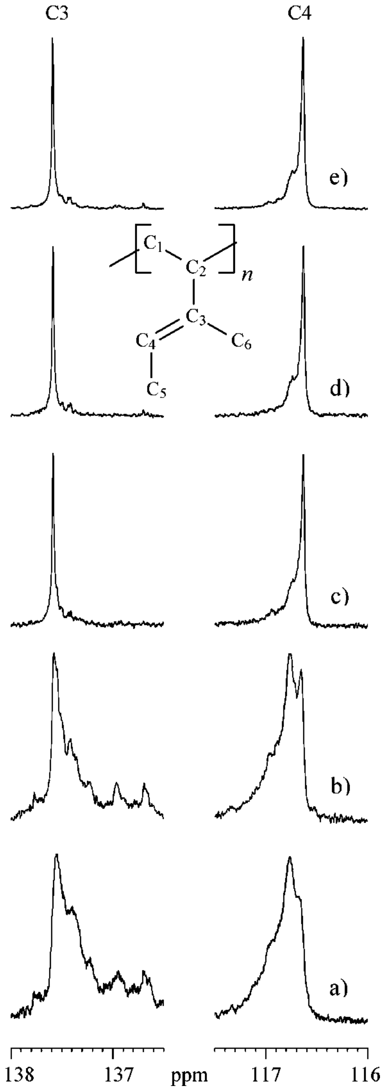


Figure 4. ^{13}C NMR spectra (olefinic region) of the poly(3-methyl-1,3-pentadiene)s obtained with (a) $CoCl_2(PCyPh_2)_2$−MAO, (b) $CoCl_2$-$(P^{i}PrPh_2)_2$−MAO, (c) $CoCl_2(P^{n}PrPh_2)_2$−MAO, (d) $CoCl_2(PEtPh_2)_2$−MAO, and (e) $CoCl_2(PMePh_2)$−MAO.

The different crystallinity degree and melting points exhibited by the various poly(3-methyl-1,3-pentadiene)s can be accounted for with a different stereoregularity degree of the polymers, as indicated by their ^{13}C NMR spectra (Figure 4; only the olefinic region is shown). The spectra of the polymers obtained with $CoCl_2(PMePh_2)_2$, $CoCl_2(PEtPh_2)_2$, and $CoCl_2(P^{n}PrPh_2)_2$ are quite similar (Figure 4, parts e, d, and c, respectively): two rather sharp signals, corresponding to the two olefinic carbons of the monomeric unit, can be observed. The situation is different in the case of the spectra of the polymers obtained with $CoCl_2(PCyPh_2)_2$ (Figure 4a) and $CoCl_2(P^{i}PrPh_2)_2$ (Figure 4b). Additional peaks are observed for each carbon signal, confirming the presence of some stereoirregularities.

In order to determine the microstructure of the polymers obtained, the polymer from $CoCl_2(P^{n}PrPh_2)_2$−MAO (Table 1, run 3) was fully characterized by IR and NMR (^{1}H and ^{13}C in solution). The IR spectrum is reported in Figure 5. The absence of any band at 911 cm^{-1} allows us to exclude the 3,4 structure for the polymer,[15] while the comparison of this spectrum with those of the previously reported *cis*-1,4-iso- and syndiotactic polymers[6] allows us to exclude these types of structures. A strong band is instead observed at 822 cm^{-1}, which is likely consistent with a 1,2 structure.[8] The 1,2 structure is also supported by the results of the detailed NMR studies carried out on the polymer.

The complete ^{1}H NMR spectrum (Figure 6) assignment was straightforward: methyl protons H6 (intensity 3) at 1.34 ppm, singlet; methyl protons H5 (intensity 3) at 1.46 ppm, doublet since coupled with the adjacent olefin proton; anisochronous methylene protons H1 (intensity 2) at 1.08 ppm, multiplet due to the coupling with the two adjacent H2's and with their own geminal protons; methine proton H2 (intensity 1) at 1.76 ppm, multiplet due to the coupling with H1's; finally, olefin proton H4 (intensity 1) at 5.0 ppm, multiplet due to the direct coupling with the H5′s and long-range couplings with H6's and H2.

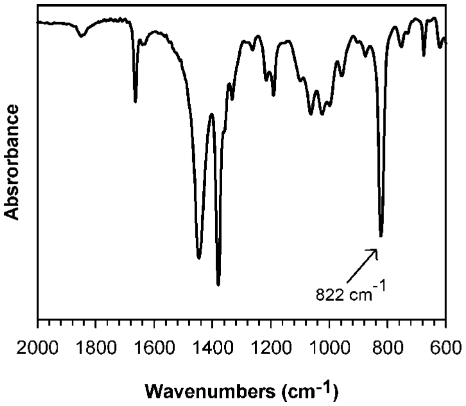


Figure 5. FT-IR spectrum of the poly(3-methyl-1,3-pentadiene) obtained with $CoCl_2(P^nPrPh_2)_2$−MAO.

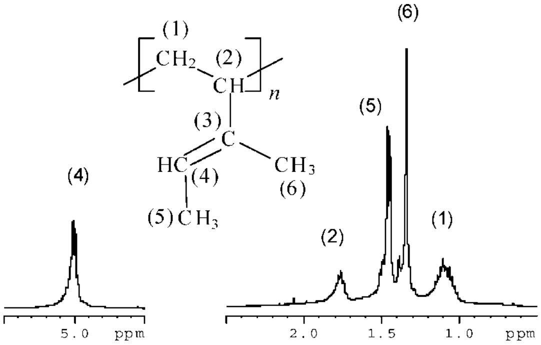


Figure 6. ^1H NMR spectrum of the poly(3-methyl-1,3-pentadiene) obtained with $CoCl_2(P^nPrPh_2)_2$−MAO.

The ^{13}C NMR spectrum of the polymer obtained with $CoCl_2(P^nPrPh_2)_2$−MAO is shown in Figure 7. The spectrum was assigned on the basis of the chemical shift values and of the multiplicity in the proton coupled spectrum (Figure 8).

The presence of a disubstituted alkene carbon (C3, at 137.60 ppm) excludes the 3,4 structure, as already suggested by the IR spectrum, but it is still consistent with 1,2 and 1,4 structures (see Figure 1). It was likewise possible to discriminate between a 1,4 and a 1,2 structure on the basis of the HMBC (Figure 9) and INADEQUATE (Figure 10) spectra. In a 1,4 structure (see Figure 1) H5 protons should have two three bond correlations with C3 (olefinic carbon) and C1 (aliphatic carbon) and H6 protons again two three-bond correlations with C2 (olefinic carbon) and C4 (aliphatic carbon). On the contrary, in a 1,2 structure (see Figure 1) H5 protons should have only one three-bond correlation with C3 (olefinic carbon) and H6 two three-bond correlations with C2 (aliphatic carbon) and C4 (olefinic carbon). In the HMBC spectrum (Figure 9) H5 protons exhibit only one three-bond correlation with C3. The absence of any correlation between H5 and aliphatic carbons is thus consistent with a 1,2 structure of the polymer under investigation, in good agreement with the IR indication.

The 1,2 structure is also supported by the INADEQUATE spectrum (Figure 10), showing that the C6 and C5 carbons are correlated to the adjacent olefinic carbons C3 and C4, respectively. In a 1,2 structure, in fact, both methyl groups are bonded to olefinic carbons, while in a 1,4 structure one of the two methyl groups is bonded to an aliphatic carbon (see Figure 1).

The two methyl signals at 10.14 and 11.04 ppm were distinguished on the basis of their different multiplicity as well: a quartet ($^1J_{CH3} = 125.07$ Hz) of double doublets ($^3J_{C-C=CH(4)} = 7.81$ Hz and $^3J_{C-C-CH(2)} = 4.65$ Hz) the former, i.e. C6, and a quartet ($^1J_{CH3} = 125.06$ Hz) of doublets ($^2J_{C\text{-}CH=} = 4.5$ Hz) the latter, i.e. C5.

Moreover, the experimental chemical shifts observed in the ^{13}C NMR spectrum are very close to the theoretical ones calculated from the spectrum of 1,2-polybutadiene by applying the addition rules,[16] thus confirming once again a 1,2 structure for the poly(3MP) under investigation.

Once established that the polymer under investigation had a 1,2 structure, it remained to be determined the configuration of the double bond in the side chain (*E* or *Z*) and the polymer tacticity (iso- or syndiotactic).

Concerning the double-bond configuration, we tried to determine it by considering the carbon−proton NMR coupling constant $^3J_{CH3-C=CH}$. In Table 2 the values of various coupling constants relative to some model compounds[17] and some other 1,2 (3,4) polymers[18] are shown. Interestingly, it can be observed that the $^3J_{CH3-C=CH}$ are strongly affected by the number of substituents on the double bond, the $^3J_{trans}$ varying in the range 8.4−11.3 Hz and the $^3J_{cis}$ in the range 6.6−7.4 Hz. The value of 7.8 Hz found for the polymer under investigation unfortunately does not permit discrimination between *E* and *Z* configuration; nevertheless, it is not in contrast with an *E* configuration which we were able to assign on the basis of the following experimental evidence.

The monomer used, as reported in the experimental part, is a mixture of (*E*) and (*Z*) isomers; the molar ratio of the two isomers, as determined by GC analysis, is about 80/20, the *E*-isomer being the more abundant one. We have monitored the polymerization reaction by analyzing the polymerization solution at different polymerization times by GC (Figure 11). We have found that only the (*E*) isomer is consumed while the (*Z*) isomer is not incorporated in the polymer chain and can be quantitatively recovered at the end of the polymerization by a trap-to-trap distillation. This evidence is confirmed by the fact that the monomer conversion, in many other polymerization runs we have carried out, even after long polymerization time, is never higher than 80%. Furthermore, the *E* configuration of the side-chain double bond is supported by the following experimental evidence; in the polymerization of 1,3-hexadiene (mixture of *E* and *Z* isomers) with $CoCl_2(P^iPrPh_2)_2$−MAO,[3] only the *E* isomer is polymerized and the side chain double bond exhibits exclusively an *E* configuration.

Concerning the polymer tacticity, the analysis of the ^1H NMR spectrum (Figure 6) permitted us to assign to the polymer an isotactic structure. It has been reported in the literature that in the ^1H NMR spectrum the signal corresponding to the methylene protons in position (1) is a triplet in a syndiotactic polymer[19] while two different doublet of triplets are observed in the case of an isotactic polymer;[10b] the two methylene protons are in fact isochronous in a syndiotactic structure, while they are anisochronous in an isotactic structure. In the spectrum of Figure 6 the signal at 1.08 ppm, corresponding to the methylene protons, is a multiplet, likely originating from the superimposition of two different doublet of triplets, consistent with an isotactic structure.

We mentioned above that the polymers from $CoCl_2(P^iPrPh_2)_2$−MAO and $CoCl_2(PCyPh_2)_2$−MAO were characterized by a lower stereoregularity than those from $CoCl_2(P^nPrPh_2)_2$−MAO, $CoCl_2(PEtPh_2)_2$−MAO, and $CoCl_2(PMePh_2)_2$−MAO, and this was particularly evident from the olefinic region of their ^{13}C NMR spectra (Figure 4). Indeed, it can be observed that practically only the signals corresponding to the *mmmm* pentad (116.63 ppm for C4 and 137.58 ppm for C3) are detectable in the spectra of the polymers obtained with $CoCl_2(PRPh_2)_2$−MAO being R = methyl, ethyl, or *n*-propyl (Figure 4c−e), while some peak broadenings, likely due to the presence of some stereodefects (maybe *rmmm* and *rmmr* pentads and pentads centered on *mr* triads), are observed in the spectra of the polymers obtained with $CoCl_2(PRPh_2)_2$−MAO being R

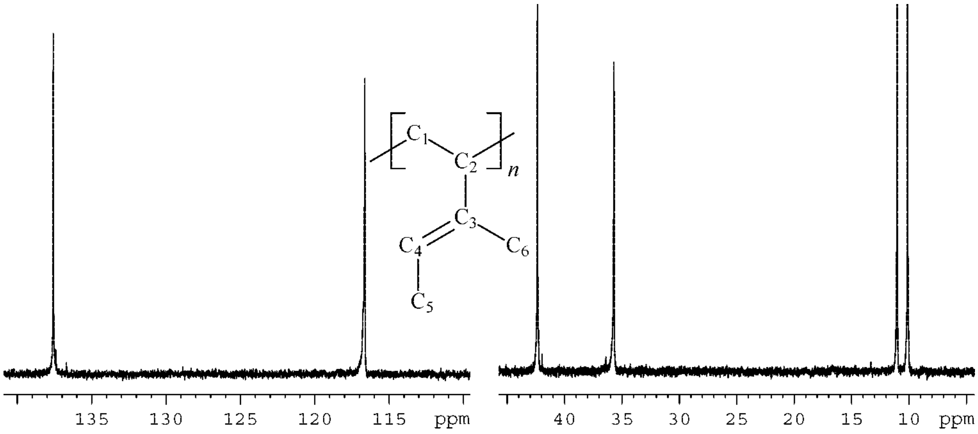


Figure 7. ^{13}C NMR spectrum of the poly(3-methyl-1,3-pentadiene) obtained with $CoCl_2(P^nPrPh_2)_2$−MAO.

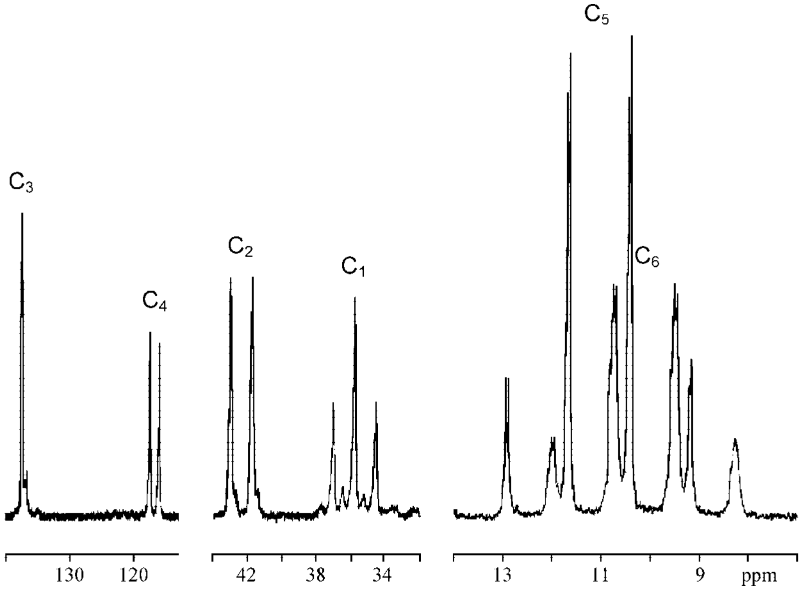


Figure 8. Proton coupled ^{13}C NMR spectrum of the poly(3-methyl-1,3-pentadiene) obtained with $CoCl_2(P^nPrPh_2)_2$−MAO.

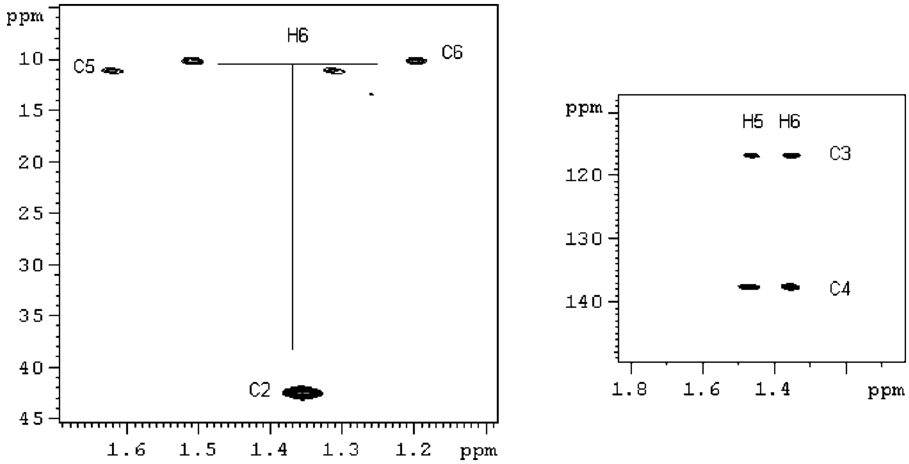


Figure 9. HMBC spectrum of the poly(3-methyl-1,3-pentadiene) obtained with $CoCl_2(P^nPrPh_2)_2$−MAO.

= isopropyl or cyclohexyl (Figure 4a,b). The presence of *rr* triads (and of the pentads centered on these triads, i.e., *mrrm, mrrr*, and *rrrr* pentads) can be excluded by comparing the spectra of Figure 4 with the ^{13}C NMR spectrum of syndiotactic 1,2 poly(*E*-3MP) obtained with iron systems, in which signals corresponding to *rrrr* sequences are found at 135.55 ppm for C3 and 117.70 ppm for C4.[8b]

Influence of Monomer Structure on Polymerization Stereoselectivity. We have shown that the catalyst systems $CoCl_2(PRPh_2)_2$−MAO give from 3-methyl-1,3-pentadiene 1,2 polymers with an essentially isotactic structure; the isotactic index, expressed as percentage of *mm* triads, was found to depend on the type of catalyst used, decreasing with increasing the steric bulkiness of the phosphine ligand coordinated to the

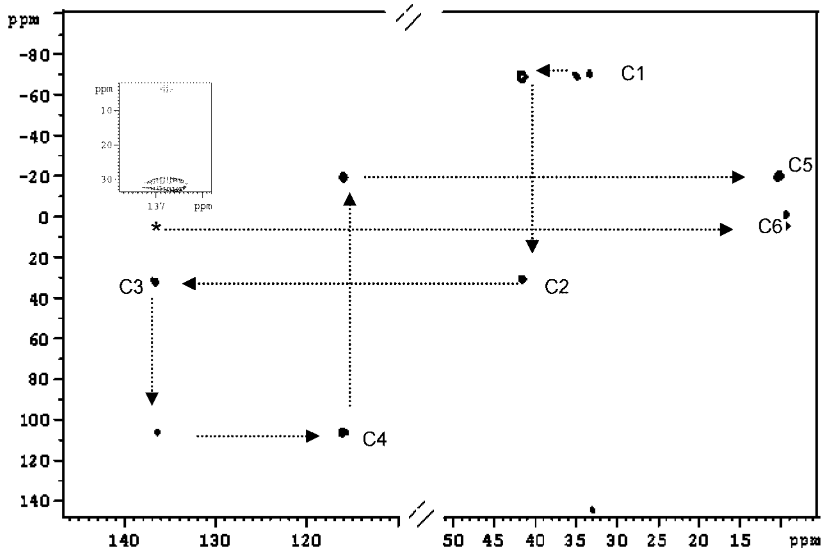
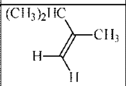
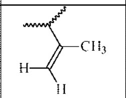
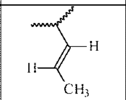
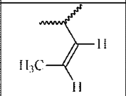
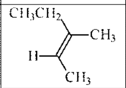
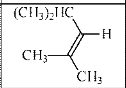
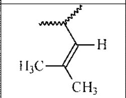
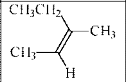
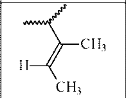


Figure 10. INADEQUATE spectrum of poly(3-methyl-1,3-pentadiene) obtained with $CoCl_2(P^nPrPh_2)_2$−MAO. The box shows C_3−C_6 and C_3−C_2 correlations, indicated by astericks, with a level increment multiplied by a factor of 2.

Table 2. $^3J_{CH3-C=CH}$ Coupling Constants for Some Model Compounds and 1,2 (3,4) Polymers

Compound	Structure	Type of coupling constant (values in Hz)		Ref.
		$J^{trans}_{CH3,H}$	$J^{cis}_{CH3,H}$	
2,3-Dimethyl-butene		11.3	6.9	17)
Syndiotactic 3,4 poly(2-methyl-1,3-butadiene)		11.3	6.6	18)
Syndiotactic 1,2 Poly(*E*-1,3-pentadiene)			6.8	18)
Syndiotactic 1,2 Poly(*Z*-1,3-pentadiene)		9.7		18)
3-Methyl-*trans*-2-pentene		8.6		17)
2,4-Dimethyl-2-pentene		8.4	7.5	17)
Syndiotactic 1,2 Poly(4-methyl-1,3-pentadiene)		8.4	7.5	18)
3-Methyl-*cis*-2-pentene			7.4	17)
Isotactic 1,2 Poly(*E*-3-methyl-1,3-pentadiene)		7.8		this paper

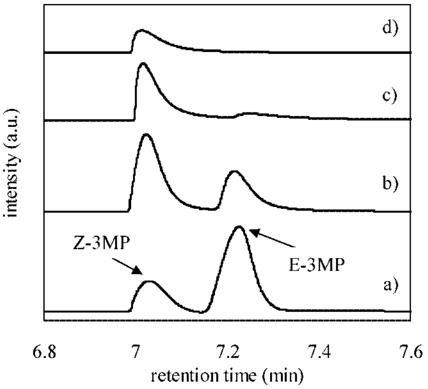


Figure 11. GC chromatograms of the polymerization solution (a) at the beginning of the polymerization, (b) after 48 h, (c) after 96 h, and (d) after 120 h.

cobalt atom. The same cobalt systems were also used in the polymerization of 1,3-pentadiene and 1,3-hexadiene; essentially 1,2 polymers were obtained also from these monomers, but the polymer tacticity was found to be syndiotactic instead of isotactic. In particular, $CoCl_2(PRPh_2)_2$−MAO (R = Me, Et, ^{n}Pr), giving the "most isotactic" poly(3-methyl-1,3-pentadiene)s, gave the "less syndiotactic" poly(1,3-pentadiene)s and poly(1,3-hexadiene)s; vice versa, $CoCl_2(P^iPrPh_2)_2$−MAO and $CoCl_2(PCyPh_2)_2$−MAO, giving the "less isotactic" poly(3-methyl-1,3-pentadiene)s, gave the "most syndiotactic" poly(1,3-pentadiene)s and poly(1,3-hexadiene)s.

Detailed results concerning the polymerization of 1,3-pentadiene and 1,3-hexadiene are shown in Table 1 and can be summarized as follows.

(i) The systems $CoCl_2(PRPh_2)_2$−MAO gave from (*E*)-1,3-pentadiene *trans*-1,2 polymers having a predominantly syndiotactic structure. The syndiotacticity degree (expressed as percentage of syndiotactic triads *rr*) was found to be dependent on the type of phosphorus ligand bonded to the metal, being around 72−75% in polymers obtained with the catalytic systems $CoCl_2(PCyPh_2)_2$−MAO and $CoCl_2(P^iPrPh_2)_2$−MAO[2] (Table 1, runs 6 and 7) and much lower (24−45%) with the other systems (Table 1, runs 8−10). This fact is clearly evident from the ^{13}C NMR spectra (olefinic region) of the different polypentadienes (Figure 12). The peaks at 122.01, 121.92, and 121.84 ppm (C4 signals), corresponding to the *mrrm*, *mrrr*, and *rrrr* pentads, respectively,[2] are largely predominant (specifically the signals at 121.92 and 121.84 ppm) in the ^{13}C NMR spectra of the polymers obtained with $CoCl_2(PCyPh_2)_2$−MAO and $CoCl_2(P^iPrPh_2)_2$−MAO (Figure 12a,b, respectively), while their intensities are comparable with those of the peaks corresponding to the other pentads centered on the *mr* triads (121.68, 121.64, 121.54, and 121.46 ppm) (Figure 12c−e). The various signals were assigned on the basis of the attribution already reported in the literature for 1,2-polybutadienes[20] and confirmed by

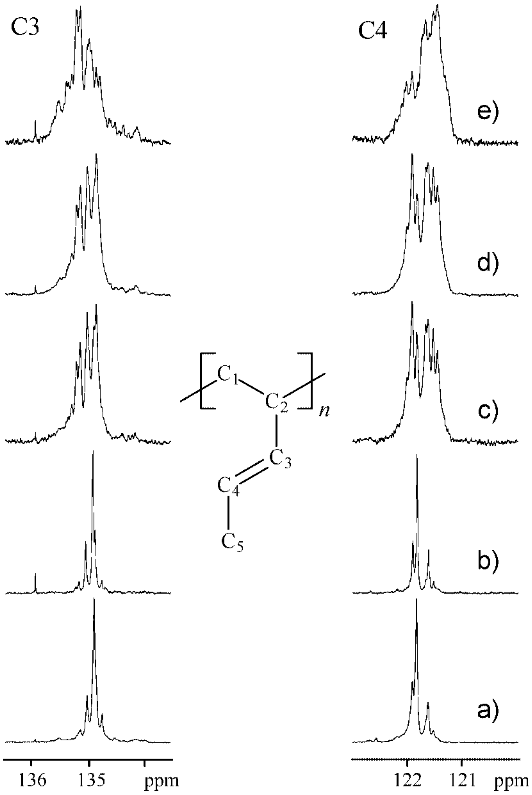


Figure 12. ^{13}C NMR spectra (olefinic region) of the poly(1,3-pentadiene)s obtained with (a) $CoCl_2(PCyPh_2)_2$−MAO, (b) $CoCl_2(P^iPrPh_2)_2$−MAO, (c) $CoCl_2(P^nPrPh_2)_2$−MAO, (d) $CoCl_2(PEtPh_2)_2$−MAO, and (e) $CoCl_2(PMePh_2)_2$−MAO.

applying the additive rules by Brouwer and Stothers[16] to the spectra of 1,2-polybutadienes. The melting points of the 1,2-polypentadienes obtained with $CoCl_2(PCyPh_2)_2$−MAO and $CoCl_2(P^iPrPh_2)_2$−MAO (Table 1, runs 6 and 7) are around 130 °C, while the molecular weights are about 200 000 g mol^{-1}.

(ii) The results obtained in the polymerization of 1,3-hexadiene were very similar to those reported above for the polymerization of (E)-1,3-pentadiene. For this reason we reported in Table 1 only the data concerning the polymerization of 1,3-hexadiene with the catalyst system $CoCl_2(P^iPrPh_2)_2$−MAO, giving a crystalline syndiotactic *trans*-1,2 polymer ([*rr*] = 63%) (Table 1, run 11),[3] and with the system $CoCl_2(P^nPrPh_2)_2$−MAO, giving a less stereoregular polymer ([*rr*] = 38%) (Table 1, run 12). The ^{13}C NMR spectra (olefinic region) of the two polymers are shown in Figure 13. It can be observed that peaks at 132.03 and 132.13 ppm, corresponding to the *rrrr* and *mrrr* pentads, are largely predominant in the polymer from $CoCl_2(P^iPrPh_2)_2$−MAO; in the spectrum of the polymer obtained with $CoCl_2(P^nPrPh_2)_2$−MAO (Figure 13b) the intensity of the same peaks is instead comparable with that of the peak at 132.26 ppm, corresponding to the *mrrm* pentad, and of the peaks centered on *mr* triads (around 131.4 ppm). Again the different peaks, as indicated above for polypentadiene, were assigned on the basis of the attribution already reported in the literature in the case of 1,2-polybutadienes[20] and confirmed by applying the Brouwer and Stothers approach.[3,16] The molecular weights of the poly(1,3-hexadiene)s is around 60 000 g mol^{-1}, lower than those of polypentadienes. The melting point of the polymer obtained with $CoCl_2(P^iPrPh_2)_2$−MAO is about 101 °C.

The above results have some mechanistic implications and suggest the following observations.

(i) It has been reported in previous papers that the type of catalyst, specifically the presence of a ligand on the metal and its nature, may have a strong influence on stereoselectivity.[1b,12b,c] According to the diene polymerization mechanism,[5] when a bulky ligand is bonded to the metal, the favored incoming monomer−butadienyl group orientation is the *exo*−*exo* one; with this type of orientation, a 1,2 syndiotactic polymer is formed if the new monomer reacts at C3 of the allylic unit. When the ligand is minimally hindered, the *exo*−*endo* orientation, giving rise to isotactic dyads, is also possible, and atactic sequences can be formed. The results reported in this paper concerning the polymerization of 1,3-pentadiene and 1,3-hexadiene are in agreement with this proposed mechanism, confirming indeed its validity. The cobalt systems $CoCl_2(P^iPrPh_2)_2$−MAO and $CoCl_2(PCyPh_2)_2$−MAO, using bulky ligands, give highly syndiotactic polymers from *E*-1,3-pentadiene and 1,3-hexadiene, while the systems $CoCl_2(PMePh_2)_2$−MAO, $CoCl_2(PEtPh_2)_2$−MAO, and $CoCl_2(P^nPrPh_2)_2$−MAO, using less hindered ligands, give atactic polymers, with predominance of syndiotactic sequences, from the same monomers.

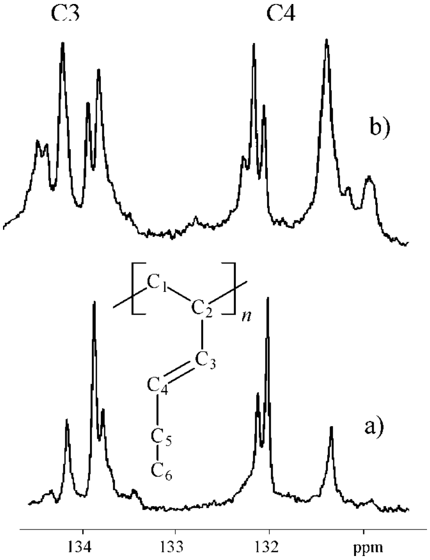
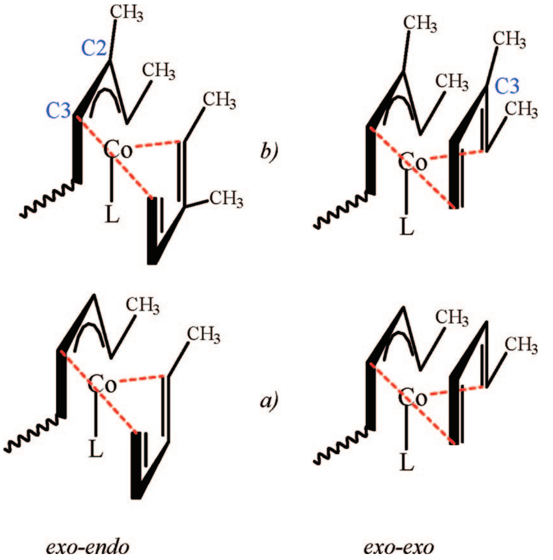


Figure 13. ^{13}C NMR spectra (olefinic region) of the poly(1,3-hexadiene)s obtained with (a) $CoCl_2(P^iPrPh_2)_2$−MAO and (b) $CoCl_2(P^nPrPh_2)_2$−MAO.

(ii) The most interesting result is however the following: using the same catalyst, polymers obtained from 3-methyl-1,3-pentadiene have an essentially isotactic structure (the isotactic degree depending on the type of catalysts, specifically increasing with decreasing the steric hindrance of the phosphine ligand bonded to the cobalt atom), while polymers from *E*-1,3-pentadiene and 1,3-hexadiene exhibit an essentially syndiotactic structure (again the syndiotactic degree depending on the type of catalyst, specifically increasing with increasing the steric hindrance of the phosphine ligand bonded to the cobalt atom). These results clearly indicate that the monomer structure too, and not only the catalyst structure, plays a relevant role in determining the polymerization stereoselectivity.

Upon the same polymerization catalyst, the formation of 1,2 syndiotactic polymers from *E*-1,3 pentadiene and 1,3-hexadiene, and of isotactic polymers from 3-methyl-1,3-pentadiene, can be explained, according to the diene polymerization mechanism,[5] by admitting that, in case of *E*-1,3-pentadiene (Figure 14a) and 1,3-hexadiene (not shown), the favorite incoming monomer−butadienyl group orientation is the *exo*−*exo* one, while in the case of 3-methyl-1,3-pentadiene (Figure 14b) the preferred orientation is the *exo*−*endo* one.

In fact, by insertion of the incoming monomer at C3 of the butadienyl group a 1,2 isotactic dyad is obtained in the case of



exo-endo *exo-exo*

Figure 14. Possible reciprocal orientation (*exo*−*exo* and *exo*−*endo*) of the 1,3-diene incoming monomer and the allylic group of the polymer growing chain in the polymerization of 1,3-pentadiene (a) and 3-methyl-1,3-pentadiene (b) with $CoCl_2(PRPh_2)_2$−MAO (R = methyl, ethyl, *n*-propyl, isopropyl, and cyclohexyl).

the *exo*−*endo* orientation, while a 1,2 syndiotactic dyad is obtained in the case of the *exo*−*exo* orientation. Most probably in the polymerization of internal substituted dienes such as 3-methyl-1,3-pentadiene, the steric hindrance due to the presence of a methyl on the C2 carbon of the butadienyl group and on the C3 carbon of the incoming monomer forces the two groups to assume an *exo*−*endo* orientation, even if this particular orientation is not the favorite one when a ligand (less or more hindered) is bonded to the metal.

In other words, there seem to be two factors governing the polymerization stereoselectivity: the catalyst structure and the monomer structure. When a bulky ligand (e.g., $PCyPh_2$, P^iPrPh_2) is coordinated to the cobalt atom and the incoming monomer is butadiene or a terminally substituted butadiene (e.g., 1,3-pentadiene, 1,3-hexadiene), the incoming monomer−allylic group *exo*−*exo* orientation seems to be the favored one, and highly 1,2 syndiotactic polymers are formed. When a minimally hindered ligand (e.g., $PMePh_2$, $PEtPh_2$, P^nPrPh_2) is bonded to the cobalt atom and the monomer is an internally substituted 1,3-butadiene (e.g., 3-methyl-1,3-pentadiene), the *exo*−*endo* orientation seems to be largely preferred, and highly 1,2 isotactic polymers are formed. For all the other combinations of the two above factors (e.g., bulky ligand and internally substituted monomer; minimally hindered ligand and terminally substituted monomer) atactic polymers, predominantly syndiotactic or predominantly isotactic, are formed, depending on the relative weight of the two factors.

The aforementioned hypotheses are supported by the results already obtained in the polymerization of butadiene and isoprene with $CrCl_2(dmpe)_2$−MAO (dmpe = 1,2-bis(dimethylphosphino)ethane)[12a] and in the polymerization of butadiene and 3-methyl-1,3-pentadiene with $FeEt_2(bipy)_2$−MAO (bipy = bipyridine).[8a]

The system $CrCl_2(dmpe)_2$−MAO gives a highly syndiotactic 1,2 polymer from butadiene but an atactic 3,4 polymer from isoprene (internally substituted butadiene). This experimental finding can be interpreted by assuming that in case of isoprene polymerization the ligand is not bulky enough to completely excel the effect of the monomer structure, which is in favor of an *exo*−*endo* orientation; both *exo*−*exo* and *exo*−*endo* orientations are possible, and atactic polymers are indeed formed.

The system $FeEt_2(bipy)_2$−MAO gives 1,2 syndiotactic polymers from both butadiene and 3-methyl-1,3-pentadiene. The interpretation given is that in the case of 3-methyl-1,3-pentadiene (internally susbstituted butadiene) the ligand bulkiness is such as to dominate the effect of the monomer structure, which would be in favor of an *exo*−*endo* orientation, and highly syndiotactic polymer is obtained also from 3-methyl-1,3-pentadiene.

Before concluding, a brief consideration: we always speak about *exo*−*exo* orientation, even if it has been reported by other authors,[21] on the basis of conformational and modeling calculations, that actually the energetically favored reciprocal orientation of the incoming monomer and of the butadienyl group should be the *endo*−*endo* one and not the *exo*−*exo*. From both the situations (*endo*−*endo* and *exo*−*exo*) 1,2 syndiotactic dyads are formed by insertion of the incoming monomer at the C3 of the butadienyl group; nevertheless, in this particular case, we prefer to represent the catalytic site with incoming monomer and butadienyl group *exo*−*exo* oriented because this is the situation found in the crystal structures of the but-2-enylbuta-1,3-diene cobalt complexes $(PPh_3)Co(\eta^4\text{-}C_4H_6)(\eta^3\text{-}C_4H_7)$[22] and $(PCyPh_2)Co(\eta^4\text{-}C_4H_6)(\eta^3\text{-}C_4H_7)$.[18]

Conclusions

A crystalline 1,2 isotactic poly(*E*-3-methyl-1,3-pentadiene) was obtained for the first time by polymerizing 3-methyl-1,3-pentadiene with the systems $CoCl_2(PRPh_2)_2$−MAO (R = methyl, ethyl, or *n*-propyl). This polymer represents one of the few examples of 1,2 isotactic polydienes described in the literature; up to now only the synthesis and characterization of 1,2 isotactic polybutadiene[9] and 1,2 isotactic poly(4-methyl-1,3-pentadiene) were reported.[10]

The results obtained have also some mechanistic implication, since they allowed us to clearly point out for the first time the fundamental role played by monomer structure in determining the polymerization stereoselectivity. We have however also shown that the stereoregularity exhibited by a polymer is always the result of the monomer structure−catalyst structure combined effect.

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