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# Chromium Catalysts for Butadiene and Norbornene Polymerization

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**Summary:** A new class of chromium catalysts were obtained by combining bidentate phosphine chromium(II) complexes with methylaluminoxanes. These systems were found to be very active in the polymerization of butadiene giving 1,2 polymers having different tacticity (iso or syndio) depending on the type of phosphine bonded to the chromium atom. Moreover, they were also able to polymerize norbornene, giving crystalline all *exo*-enchained vinyl addition polymers, exhibiting a rather unusual structure in the field of olefin stereospecific polymerization, namely diheterotactic structure, characterized by regular sequences of (*mr*) atactic triads.

**Keywords:** 1,2 polybutadiene; chromium catalysts; diheterotactic polynorbornene; polymerisztion; stereoregular polymers

## Introduction

Chromium catalysts play a relevant role in the field of 1,3-butadiene polymerization, being among the first systems used for the preparation of 1,2 polybutadiene.[1] 1,2 Polybutadiene is a polymer of industrial interest, which can exist in three different isomeric forms: isotactic, syndiotactic and atactic. Specifically, the syndiotactic polymer is used in the production of films (packaging breathing items for fruits, vegetables and seafood), footwear soles, tubes and hoses; the atactic polymer is used in the rubber and tire industry.[2] The importance of chromium catalysts in the field of butadiene polymerization is pointed out by the fact that, up to now, 1,2 isotactic polybutadiene was obtained only with chromium systems. Cr(acac)$_3$-AlEt$_3$, for example, gave from butadiene 1,2 polymers having a syndiotactic or isotactic structure depending on the Al/Cr molar ratio used (syndiotactic with $\mathrm{Al/Cr} = 2–6$; isotactic with $\mathrm{Al/Cr} = 6–10$).[3] This system was however characterized by low activity (large amount of catalyst to obtain appreciable polymer yields) and low stereospecificity (only a small part of the crude polymer was crystalline). It has been found, however, that the active species in this system is a Cr(II) species.[4]

Starting from this evidence, in order to obtain more active and stereospecific catalysts, we prepared several new chromium(II) phosphine complexes by reacting CrCl$_2$(THF) with various bidentate phosphines.[5] The complexes thus obtained were characterized by IR spectroscopy and elemental analysis; for some of them single crystals were obtained and the crystal molecular structure determined.[5e] They were successively used in combination with methylaluminoxanes (MAO) for the polymerization of 1,3-butadiene. The resulting catalysts were found to be extremely active and stereospecific, giving essentially 1,2 polybutadienes, syndiotactic or isotactic depending on the type of phosphine bonded to the chromium atom.

The same systems were also tested in the polymerization of bicyclo[2,2,1]hept-2-ene, commonly known as norbornene, and also in this case they were found to be very active and stereospecific. Low molecular weight vinyl-type polynorbornenes were obtained, having a diheterotactic structure, characterized by a regular sequence of atactic *mr*

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triads. This type of structure is rather unusual for polyolefins and in general for polymers obtained through stereospecific polymerization.

It is well known that norbornene can be polymerized by three different catalytic routes: ring opening metathesis polymerization (ROMP), cationic and radical polymerization, and vinyl addition polymerization. ROMP polymerization [6] gives polymers containing double-bonds within the main chain, which have found applications as elastomers. Cationic and radical polymerizations give low molecular weight oligomers with 2,7-connectivity of the monomer.[7] Vinyl addition polymerization gives completely saturated polymers which retain the bicyclic structural unit.[8] Polynorbornenes produced in this way exhibit properties that make them suitable for optical and electronic applications.

Much work has been done to find catalysts for the vinyl polymerization of norbornene. Most of the work has been carried out with catalysts based on Ni compounds, nevertheless catalysts based on Ti, Zr, Cr, Co and Pd have also been investigated.[9] As concern chromium catalysts in particular, only three papers were reported in the literature. The papers by Heitz[10] regard the norbornene polymerization with $[CpCrMeCl]_2$-MAO (Cp = $C_5H_5$, $C_5Me_5$, Ind, Flu) systems leading to partially crystalline material, while the paper by Bochmann[11] reports on the polymerization of norbornene with catalysts based on chromium (II) allyl ($Cr[1,3\text{-}C_3H_5(SiMe_3)_2]_2$) and chromium (IV) alkyl ($Cr(CH_2SiMe_3)_4$) giving, respectively, insoluble vinyl-type and very low molecular weight polynorbornenes.

## Results and Discussion

The following chromium (II) phosphine complexes were used, in combination with MAO, for the polymerization of 1,3-butadiene and norbornene: $CrCl_2(dmpm)_2$, $CrCl_2(dmpe)_2$, $CrCl_2(depe)_2$, $CrCl_2(dppm)$, $CrCl_2(dppe)$, $CrCl_2(dppp)$ and $CrCl_2(dppa)$ [dmpm = bis(diphenylphosphino)methane; dmpe = 1,2-bis(dimethylphosphino)ethane; depe = 1,2-bis(diethylphosphino)ethane; dppm = bis(diphenylphosphino)methane; dppe = 1,2-bis(diphenylphosphino)ethane; dppp = 1,3-bis(diphenylphosphino)propane; dppa = bis(diphenylphosphino)amine]. All the above complexes have been prepared in our laboratory and a detailed description of their synthesis and characterization has already been reported.[5d–f]

### Polymerization of 1,3-Butadiene

The results obtained in the polymerization of 1,3-butadiene with the different chromium catalysts are reported in Table 1 and can be summarized as follows.

(1) All the systems give essentially 1,2 polymers from butadiene; the 1,2 content ranges from 80 to 95%, depending on the catalyst used (*i.e.* type of phosphine bonded to the chromium atom).
(2) The catalyst activity is in general quite good; high monomer conversions are reached in a relatively short polymerization time. Catalyst activity is higher for catalysts using less hindered phosphines (*e.g.* dmpm and dppm; only one $CH_2$ group bridging the two phosphorus atoms). The maximum activity is however exhibited by the $CrCl_2(dppa)$-MAO system; this is likely to be attributed to the presence of a potential donor nitrogen in the bridge between the two phosphorus atoms, in some way affecting the electronic properties of the complex.
(3) The most interesting result is however the following: depending on the phosphine ligand bonded to the chromium atom, prevalently isotactic or highly syndiotactic polymers are obtained, spanning from amorphous to highly crystalline polymers. This different behaviour is evident from the $^{13}C$ NMR spectra of the various polybutadienes (Figure 1). In general, essentially syndiotactic polymers are formed with catalysts having more hindered ligands (*e.g.* dmpe, depe, dppe,

***Table 1.***
Polymerization of 1,3-butadiene with chromium(II) catalysts.

| Run | Cr-complex | Polymerization[a)] | | | Polymer | | |
|---|---|---|---|---|---|---|---|
| | | time (min) | yield (%) | N[b)] ($\text{min}^{-1}$) | 1,2[c)] (molar %) | rr/mr/mm[d)] (molar ratio) | m.p.[e)] (°C) |
| 1 | $CrCl_2(dmpm)_2$ | 30 | 80.2 | 69 | 89 | 16/13/71 | — |
| 2 | $CrCl_2(dmpe)_2$ | 60 | 39.5 | 17 | 95 | 83/17/0 | 152 |
| 3 | $CrCl_2(depe)_2$ | 60 | 76.0 | 33 | 89 | 72/26/2 | 106 |
| 4 | $CrCl_2(dppm)$ | 20 | 55.7 | 72 | 89 | 18/48/34 | — |
| 5 | $CrCl_2(dppe)$ | 1020 | 15.3 | 0.4 | 88 | 61/34/5 | 95 |
| 6 | $CrCl_2(dppp)$ | 1440 | 17.6 | 0.3 | 80 | 64/32/4 | 100 |
| 7 | $CrCl_2(dppa)$ | 5 | 37.5 | 195 | 90 | 66/30/4 | 105 |

[a)] Polymerization conditions: butadiene, 2 mL; toluene, total volume 16 mL; MAO, Al/Cr = 1000; Cr, $1 \times 10^{-5}$ mol; temperature, +20 °C;
[b)] Moles of butadiene polymerized per mol of Cr per minute;
[c)] Determined by NMR analysis; the remaining units are essentially cis-1,4;
[d)] Molar ratio of 1,2 syndiotactic/atactic/isotactic triads, determined by $^{13}C$ NMR analysis;
[e)] Determined by DSC analysis.

dppp), [12] while prevalently isotactic polymers are obtained with low hindered ligands (*e.g.* dmpm and dppm) [12] (Figure 1). Again the behavior of the system using dppa, giving syndiotactic polymers, is anomalous, but in this case, as reported by van Leeuwen, [12b–d] the presence of a potential donor nitrogen atom, determining weak interaction with the metal center, may lead to an enlargement of the bite angle *(i.e.* its steric hindrance), thus explaining the formation of an essentially syndiotactic polymer.

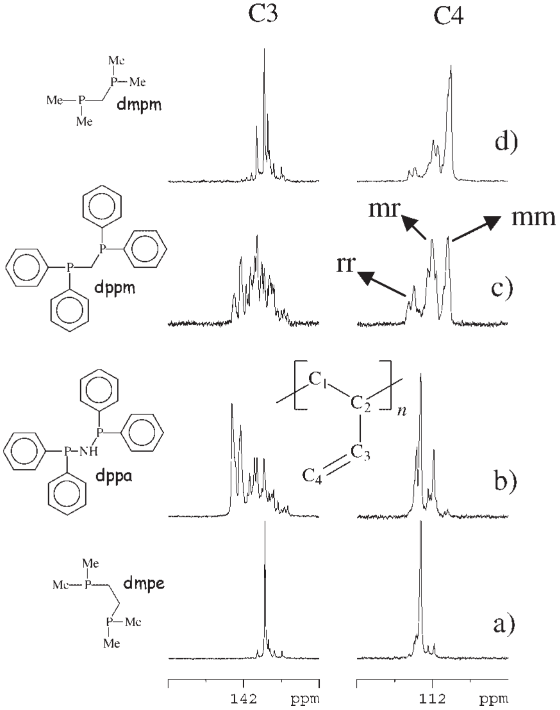

***Figure 1.***
$^{13}C$ NMR spectra (olefinic region; $C_2D_2Cl_4$ as solvent; HMDS as internal standard, 103 °C) of 1,2 polybutadienes obtained with a) $CrCl_2(dpme)_2$-MAO; b) $CrCl_2(dppa)$-MAO; c) $CrCl_2(dppm)$-MAO; d) $CrCl_2(dmpm)_2$-MAO.

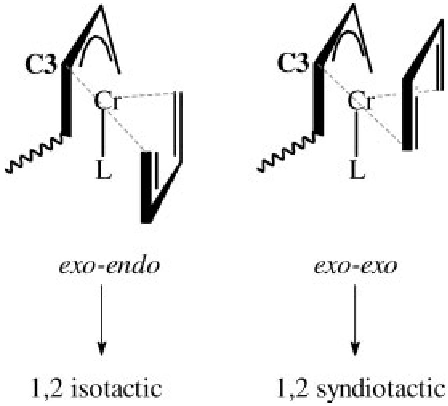

***Figure 2.***
Possible orientations of incoming diene monomer and butadienyl group in the polymerization of butadiene with chromium catalysts (L bidentate phosphine ligand).

The formation of isotactic or syndiotactic polymers depending on the type of phosphine on the metal atom can be interpreted on the basis of the diene polymerization mechanism proposed several years ago by Porri,[13] confirming indeed its validity. If we admit that the structure of the active site is that shown in Figure 2, with only one ligand bonded to the metal, the allylic group and the butadiene monomer can assume two different orientations: *exo-exo* and *exo-endo*. From both situations, by insertion of the monomer at C3 of the allylic group, 1,2 units are formed. However, from an *exo-exo* orientation a syndiotactic diad is formed, while from an *exo-endo* orientation an isotactic diad is obtained. In our case, when L is a sterically demanding ligand (*e.g.* dmpe, depe, dppe, dppp and dppa), the *exo-exo* orientation is much favored and syndiotactic polymers are obtained; when L is a low hindered ligand (*e.g.* dmpm, dppm) the *exo-endo* orientation is preferred and prevalently isotactic polymers are obtained. If the two orientations are equally probable, an atactic polymer may be formed.

## Polymerization of Norbornene

The results obtained in the polymerization of norbornene with catalysts obtained by combining various chromium(II) phosphine complexes with MAO are shown in Table 2.

All the polymers, independently on the catalyst used, are characterized by a rather low molecular weight, in the range 1000–3000 g × mol$^{-1}$, as indicated by the GPC analysis and by the resonances observed in the $^{13}$C NMR spectra (Figure 3a) at 15–16 ppm, due to methyl-end groups likely arising by norbornene insertion into Cr-Me bonds followed by rapid transfer to aluminium. The polymer molecular weight slightly increases with decreasing the polymerization temperature, meaning that the transfer reaction to the aluminium compound is less effective at low temperature. Moreover, in $^{1}$H NMR spectra (not reported) and in the $^{13}$C NMR spectra no signals are observed in the olefinic region (not reported), indicating that the polymers are fully saturated

***Table 2.***
Polymerization of norbornene with chromium(II) catalysts.

| Run | Cr-compound | Polymerization$^{a)}$ | | | Polymer | |
|---|---|---|---|---|---|---|
| | | time (min) | yield (%) | N$^{b)}$ (min$^{-1}$) | Mw$^{c)}$ (g × mol$^{-1}$) | T$_g$$^{d)}$ (°C) |
| 1 | $CrCl_2(dmpm)_2$ | 13 | 44.9 | 180 | 1270 | 126 |
| 2 | $CrCl_2(dmpe)_2$ | 60 | 25.3 | 22 | 1380 | 104 |
| 3 | $CrCl_2(depe)_2$ | 60 | 18.4 | 16 | 1155 | 102 |
| 4 | $CrCl_2(dppm)$ | 5 | 66.1 | 689 | 1490 | 140 |
| 5 | $CrCl_2(dppe)$ | 55 | 34.5 | 33 | 1425 | 99 |
| 6 | $CrCl_2(dppa)$ | 15 | 50.7 | 176 | 1305 | 88 |
| 7 | $CrCl_2(dppa)$ | 1320 | 54.8 | ∼1 | 2760 | 135 |

[a)] Polymerization conditions: norbornene, 2.45 g; toluene, total volume 16 mL MAO, Al/Cr = 1000; Cr, $5 \times 10^{-6}$ mol ($1 \times 10^{-5}$ in run 7); temperature, +20 °C (−30 °C in run 7);
[b)] Moles of norbornene polymerized per mol of Cr per minute;
[c)] Molecular weight, determined by GPC analysis;
[d)] Glass transition temperature, determined by DSC analysis.

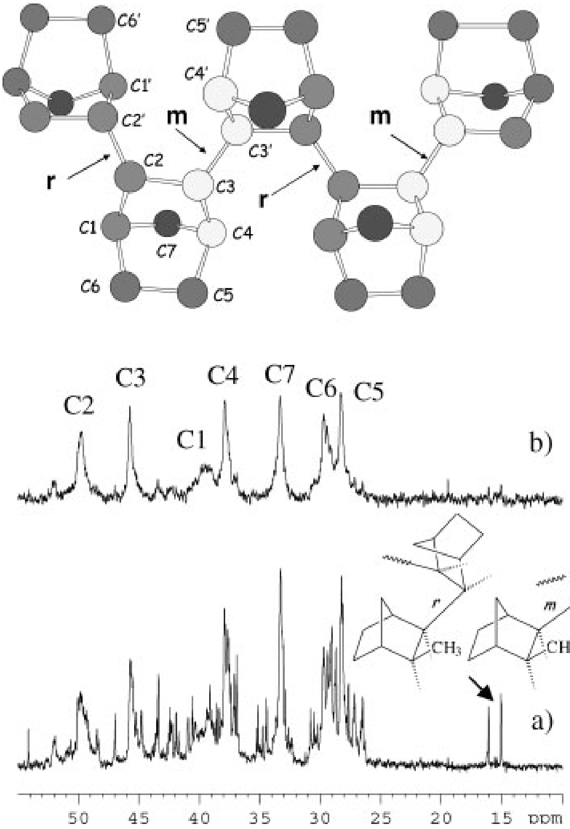

**Figure 3.**
$^{13}$C NMR spectra ($C_2D_2Cl_4$, HMDS as internal standard, 103 °C) of polynorbornene obtained with $CrCl_2$(dppa)-MAO at −30 °C. a) crude polymer; b) heptane insoluble fraction.

and are produced by vinyl addition polymerization; the absence of any signal at 20–24 ppm indicates instead that the polymer is all *exo*-enchained.[14]

It has been reported above that the type of phosphine bonded to the chromium atom has a strong influence on activity and stereospecificity in the polymerization of 1,3-butadiene. In case of norbornene polymerization, we only observe a strong effect on activity, and it is worthwhile that catalysts exhibiting the highest activity in the polymerization of butadiene ($CrCl_2(dmpm)_2$-MAO; $CrCl_2$(dppm)-MAO; $CrCl_2$(dppa)) are also the most active systems in the polymerization of norbornene.

Nothing can be said at the moment on a possible effect on stereoselectivity; the $^{13}$C NMR spectra of the various polymers obtained with the different systems are quite similar and, as shown in Figure 3a, rather complicated, due to the presence of low molecular weight macromolecules. Nevertheless, in order to get information on the polymer microstructure, we fractionated the polymers by extracting them with boiling heptane. Specifically, in the case of the polymer obtained with $CrCl_2$(dppa)-MAO at −30 °C, we were able to separate two different fractions. The heptane insoluble fraction (35% by weight), having a molecular weight (4300 $g \times mol^{-1}$) higher than the crude polymer, was deeply examined by NMR spectroscopy, and its $^{13}$C NMR spectrum is shown in Figure 3b.

Seven main peaks were observed at 28.3, 29.7, 33.3, 37.9, 39.6, 45. 7 and 49.8 ppm, which were assigned as indicated on the basis of DEPT experiments and accordingly to what reported in the literature.[15] The sharp highly symmetric resonances, particularly those at 29.7, 33.3, 37.9 and 45.7 ppm, are indicative of a stereoregular polymer. Moreover, the $^{13}$C NMR spectrum shows that each resonance, except for C7, splits into two peaks of a nearly equal area. On the basis of these features, a diheterotactic structure was assigned to this polymer. This configuration, in fact, imposes that in a triad the two bridging carbons C7 of the side units point respectively in the same and in the opposite direction with respect to the C7 of the central unit. As a consequence, adjacent C1s are in a gauche arrangement (r diad), while adjacent C4s are in trans arrangement (m diad) (Figure 3). Indeed, in agreement with that reported in the literature,[15] the resonances at 37.9 and 39.6 ppm were assigned to C4 and C1, respectively; these two signals are separated by 1.7 ppm and the lower peak is strongly broadened (covering about 4 ppm). The resonances at 49.8 and 45.7 ppm were assigned to C2 and C3, respectively; they are separated by around 4 ppm, suggesting that C3 is shielded by a $\gamma$-gauche effect. This spectral feature can be interpreted as follows: while in the *m* diad, in order to avoid steric interactions, the torsional angle C4-C3-C3′-C4′ can only be in the *trans* conformation, in the *r* diad the torsional angle C1-C2-C2′-C1′ can assume different values along the main chain, inducing variable $\gamma$-gauche effects on C1 and C1’, thus causing a 4 ppm range of values for their chemical shift. The same signal splitting and broadening have been previously observed in the $^{13}$C spectrum (not specifically assigned) of a polynorbornene described as containing low diisotacticity and most likely constituted by *mr* sequences with a small amount of *rr* sequences.[15c]

## Conclusion

A new class of chromium catalysts have been prepared and used in the polymerization of butadiene and norbornene. As regards butadiene polymerization, they resulted to be very active, exhibiting a catalyst activity comparable with that of the cobalt systems actually used for the industrial production of 1,2 polybutadiene. Furthermore, they permitted to prepare 1,2 polybutadienes having different tacticity (iso or syndio) by varying the phosphine ligand bonded to the chromium atom. This fact was also important from a mechanistic point of view, since it allowed us to point out some aspects of the diene polymerization mechanism, *e.g.* the influence of the catalysts structure on polymerization stereoselectivity.

As regards norbornene polymerization, the chromium systems were found to be extremely active, giving crystalline stereoregular polymers having diheterotactic structure. Only few example of polymers having such a structure are reported in the literature, [16] and, as far as we know, the polynorbornene here described represents the first example of diheterotactic polyolefin obtained by means of stereospecific polymerization. Work is in progress in order to determine the crystalline molecular structure of this novel stereoregular polymer.

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