

# Recent advances in the polymerization of butadiene over the last decade

Giovanni Ricci, Giuseppe Leone

CNR - Istituto per lo Studio delle Macromolecole (ISMAC), via E. Bassini 15, I-20133 Milano (Italy)

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## ABSTRACT

The stereospecific polymerization of conjugated dienes began in 1954 with the first catalysts obtained by combining  $TiCl_4$  or  $TiCl_3$  with aluminum-alkyls, i.e. the catalytic systems previously employed for ethylene and propylene polymerizations. Subsequently, many other catalytic systems were obtained and examined by a combination of transition metal or lanthanide compounds with appropriate alkylating agents. With the advent of MAO as alkylating agent, at the beginning of the 1980s, new catalytic systems were introduced, in some cases much more active and stereospecific than those based on common aluminum-alkyls. Starting from the 2000s, in the wake of what happened in the case of mono-olefins, a new generation of catalysts based on complexes of transition metals and lanthanides with various ligands containing donor atoms such as P, N, O (e.g., phosphines, imines, imino-pyridines, cheto-imines) has been introduced. These systems have proved particularly active and able to provide polymers with controlled microstructure (i.e., *cis*-1,4; 1,2; mixed *cis*-1,4/1,2 with a variable 1,2 content) from several types of 1,3-dienes, permitting indeed to establish new correlations between the catalyst structure, the monomer structure and the polymer microstructure, and to improve our knowledge on the polymerization mechanism of 1,3-dienes. This paper provides an exhaustive overview of the latest developments in the field of stereospecific polymerization of 1,3-butadiene. **Polyolefins J (2014) 1:43-60**

**Keywords:** butadiene, catalysts, stereospecific polymerization, polybutadiene

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## INTRODUCTION

Butadiene is the main and most distinctive member of conjugated dienes; the unsaturated organic compounds characterized by the presence of two conjugated double bonds. Butadiene can produce polymers containing different types of monomeric units: *cis*-1,4; *trans*-1,4; 1,2 (Figure 1).

Butadiene can be polymerized with different polymerization methods: radical polymerization, anionic polymerization and stereospecific polymerization.

\* Corresponding Author - E-mail: giovanni.ricci@ismac.cnr.it

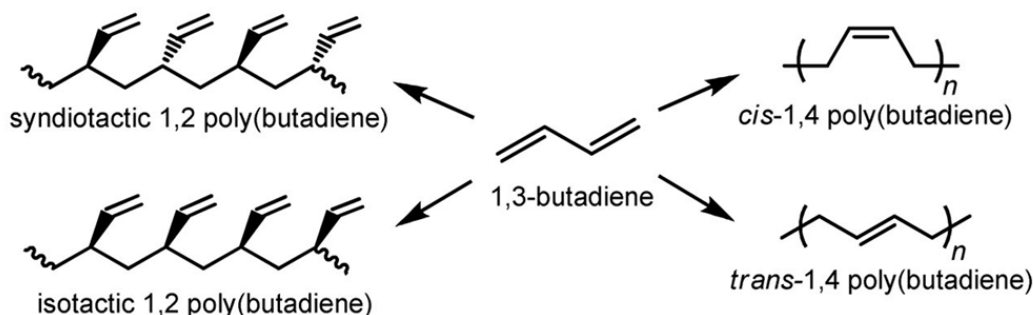


Figure 1. Stereoregular polymers from 1,3-butadiene

However, the stereoregular poly(butadiene)s (e.g., *cis*-1,4; *trans*-1,4; syndiotactic 1,2; isotactic 1,2) (Figure 1) can be obtained only through the stereospecific polymerization using various Ziegler-Natta catalysts based on a combination of transition metal and lanthanide compounds with different aluminum-alkyls (e.g.,  $\text{Al}(i\text{Bu})_3\text{-TiI}_4$ ;  $\text{AlEt}_3\text{-VCl}_3$ ;  $\text{Cr}(\text{acac})_3\text{-AlEt}_3$ ;  $\text{Co}(\text{acac})_2\text{-AlEt}_2\text{Cl-H}_2\text{O}$ ;  $\text{Co}(\text{acac})_3\text{-AlEt}_3\text{-H}_2\text{O-CS}_2$ ;  $\text{AlEt}_3\text{-Ni}(\text{octanoate})_2\text{-BF}_3 \times \text{OEt}_2$ ;  $\text{AlEt}_2\text{Cl-Nd}(\text{OCOC}_7\text{H}_{15})_3\text{-Al}(i\text{Bu})_3$ ) [1-6]. In fact, the stereospecific polymerization, differently from the other above given polymerization methods, is characterized by (i) high regioselectivity, i.e. it can give polymers having only one type of monomeric unit (1,4 or 1,2) and (ii) high stereoselectivity, i.e. it can give polymers with a very high configurational order when stereoisomeric sites are present on the monomeric unit (e.g., an internal double bond or an asymmetric carbon).

The stereospecific polymerization of conjugated dienes with catalysts based on transition metals began in 1954, immediately after the first results obtained for the polymerization of propylene [1]. The first generation of catalysts was obtained by a combination of  $\text{TiCl}_4$  or  $\text{TiCl}_3$  with aluminum-alkyls, i.e. catalytic systems previously employed for ethylene and propylene. At the beginning of the 1960s all the poly(butadiene) stereoisomers were already synthesized: *cis*-1,4; *trans*-1,4; syndiotactic 1,2; isotactic 1,2 (Figure 1). Subsequently, many other transition metals and lanthanide catalytic systems were proposed and examined [1, 2, 6]. Detailed information on catalysts and polymers can be found on some reviews already published on the subject [1-6].

With the advent of MAO as alkylating agent, at the beginning of the 1980s [7,8], new catalytic systems were introduced, in some cases much more active and

stereospecific than those based on common aluminum-alkyls [9-15]. In particular, MAO allowed the use of catalyst precursors such as cyclopentadienyl derivatives of transition metals (e.g.,  $\text{CpTiCl}_3$ ,  $\text{Cp}_2\text{TiCl}_2$ ,  $\text{CpVCl}_2$ ) [16-21], practically inactive in combination with the normal aluminum-alkyls, providing highly active and stereospecific catalytic systems, also capable of polymerizing monomers such as (*Z*)-1,3-pentadiene [22-24] and 4-methyl-1,3-pentadiene [16,19-21,25], which could not be polymerized with the common Ziegler-Natta catalysts.

Starting from the 2000s, in the wake of what happened in the case of mono-olefins [26-43], a new generation of catalysts emerged which was based on some complexes of transition metals and lanthanides with various ligands containing donor atoms such as P, N, O (e.g., phosphines, imines, imino-pyridines, cheto-imines) in combination with MAO. These systems have proved particularly active and able to provide polydienes with a controlled microstructure (i.e., *cis*-1,4; 1,2; mixed *cis*-1,4/1,2 with a variable 1,2 content) [44-55]. The same systems have also allowed to synthesize novel stereoregular poly(1,3-diene)s from different monomers such as isoprene, 1,3-pentadiene, 1,3-hexadiene, 3-methyl-1,3-pentadiene, 1,3-heptadiene, 1,3-octadiene, and 5-methyl-1,3-hexadiene [52, 56-62]. This has allowed to establish new correlations between the catalyst structure, the monomer structure and the polymer microstructure, allowing at the same time to improve our knowledge on the polymerization mechanism of conjugated dienes [1, 63-67]. On these new catalytic systems of the last decade we are reporting in the following, but before describing the various catalysts and for a better comprehension of the results obtained, it may be useful to recall some of the fundamental aspects of the conjugated dienes polymerization mechanism.

### Some remarks on the diene polymerization mechanism

The stereospecific polymerization of conjugated dienes, as it is well known, is an insertion polymerization, meaning that the polymer chain grows by monomer insertion into a metal-carbon bond between the growing chain and the transition metal of the catalytic complex [1]. The Mt–C bond is of allyl-type ( $\eta^3$ -allyl bond), and this particular feature is responsible, as explained below, for the great variety of polymer structures obtainable in the polymerization of 1,3-dienes. First of all, it is worthwhile to note that the Mt–allyl moiety is a chiral group [1, 63-67]. According to the polymerization mechanism proposed by Porri [1, 63-67], the allylic unit can exist in two forms (*anti* and *syn*), both exhibiting two reactive positions: C(1) and C(3). When the new entering monomer reacts at C(1), a 1,4 unit is formed (*cis*, when the allylic unit is in the *anti* form and *trans* when the allylic unit is in the *syn* form), whereas a 1,2 unit is obtained if the incoming monomer reacts at C(3) (Figure 2). Furthermore, the new monomer can orient in two different ways with respect to the allylic unit of the polymer growing chain, as in Figure 3a (*exo-endo*) or as in Figure 3b (*exo-exo*) (for simplicity we have reported only the case of the *anti* unit, but the same is also valid for *syn* unit). In a situation as in Figure 3a, *cis*-1,4 syndiotactic or 1,2 isotactic units are formed when the monomer reacts at C(1) or C(3), respectively; though in Figure 3b, we have instead the formation of *cis*-1,4 isotactic units when the monomer reacts at C(1), and of 1,2 syndiotactic units if the monomer reacts at C(3). Obviously, in case of butadiene and isoprene we cannot speak about isotactic and syndiotactic *cis*-1,4 polymers, but only about *cis*-1,4 polymers as there are no asymmetric

carbons in 1,4 unit; we can instead speak about isotactic and syndiotactic *cis*-1,4 polymers in case, for instance, of 1,3-pentadiene, because in this case an asymmetric carbon is present in 1,4 unit.

On the basis of the above polymerization mechanism, it is clearly evident how it is possible to obtain poly(butadiene)s having different structures simply varying the nature of the catalyst. For instance, when the catalyst structure is in favor of the insertion of the incoming monomer at C(1) of the allylic unit, 1,4 units are exclusively formed; if the catalyst structure is such to promote the insertion of the monomer at C(3) of the allylic unit and an *exo-exo* orientation of allylic unit and incoming monomer, a 1,2 syndiotactic poly(butadiene) is formed. Polymers with lower stereoregularity are instead obtained when, for instance, monomer insertions at C(1) or C(3) are both possible, or *exo-exo* and *exo-endo* orientations have comparable probability.

### POLYMERIZATION OF BUTADIENE

As cited above, four stereoregular poly(butadiene)s can be prepared through the stereospecific polymerization with transition metal and lanthanide-based catalysts: *cis*-1,4; *trans*-1,4; syndiotactic 1,2; isotactic 1,2 (Figure 1). Only *cis*-1,4 poly(butadiene) and syndiotactic 1,2 poly(butadiene) are polymers industrially produced and commercialized. High *cis*-1,4 poly(butadiene) is a polymer with a melting point ( $T_m$ ) of about  $-2^\circ\text{C}$ , a crystallization temperature ( $T_c$ ) around  $-25^\circ\text{C}$ , and a glass transition temperature ( $T_g$ ) below  $-100^\circ\text{C}$ . It is produced with various catalysts based on Ti, Co, Ni and Nd, and its main use is in

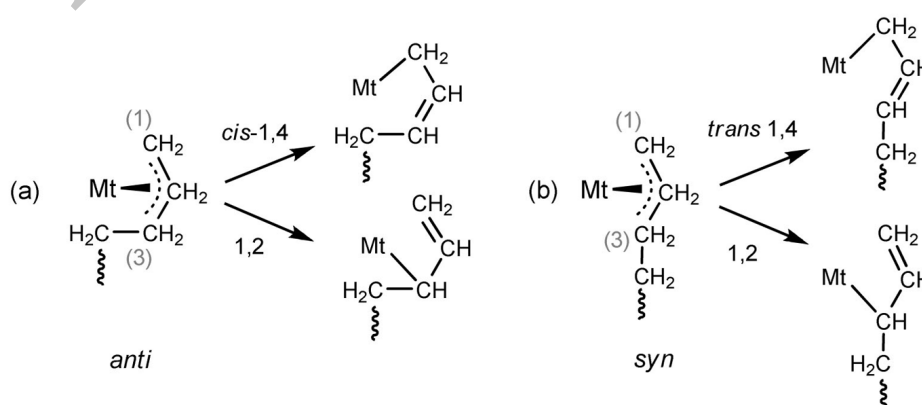
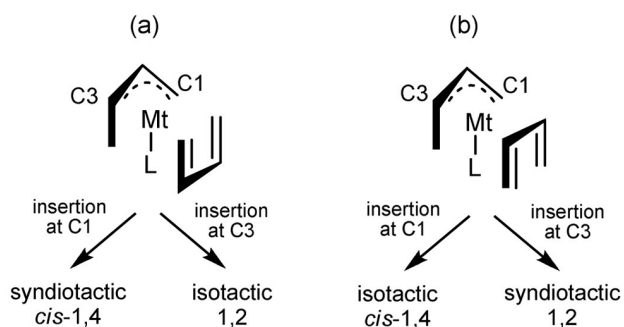


Figure 2. Formation of 1,4 vs 1,2 monomeric units from (a) *anti* and (b) *syn* Mt– $\eta^3$ –butenyl group



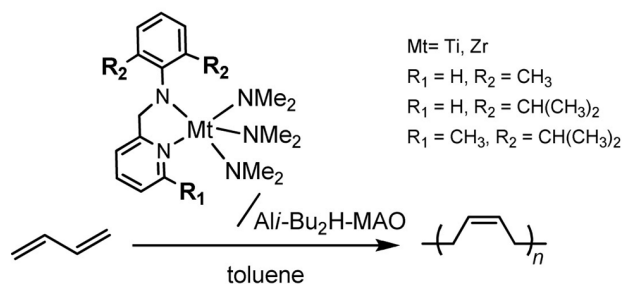
**Figure 3.** Possible orientations [(a) *exo*-*endo* and (b) *exo*-*exo*] of the new incoming monomer with respect to the last-inserted unit (L is a generic ligand) and formation of *cis*-1,4 and 1,2-polymers having a syndiotactic or an isotactic structure

the manufacture of passenger car and truck tires. Syndiotactic 1,2 poly(butadiene) is a crystalline polymer, with a  $T_m$  in the range 200–220°C, depending on its degree of syndiotacticity, with poor solubility characteristics. This stereoregular polymer is obtained with Co-based catalysts, and it is used to make transparent stretch films, tubes, hoses, shoe soles, and various sponges without plasticization and vulcanization. It can also be used to manufacture various rubber goods with vulcanization, vibration absorbing materials for automobiles, some injection-molded products, and plastic modifiers.

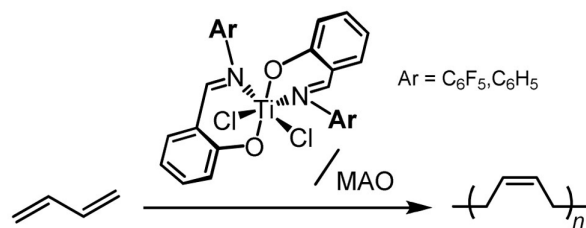
Let us now see the most recent developments made in the field of catalytic systems for the stereospecific polymerization of butadiene.

### Titanium and zirconium catalysts

Titanium catalysts were the first systems used for the synthesis of high-*cis* poly(butadiene) and have been the basis for commercial processes in Europe and USA. The systems were obtained by combining various types of  $AlR_3$  (mainly  $Al(iBu)_3$ ) with Ti compounds containing iodine (e.g.,  $TiI_4$ ,  $TiCl_2I_2$ ,  $TiCl_3I$ ), giving poly(butadiene)s with a *cis* content of about 95%,



**Figure 5.** Butadiene polymerization by (anilidomethyl)pyridine Zr(IV) and Ti(IV) complexes with  $Al(iBu_2H)/MAO$



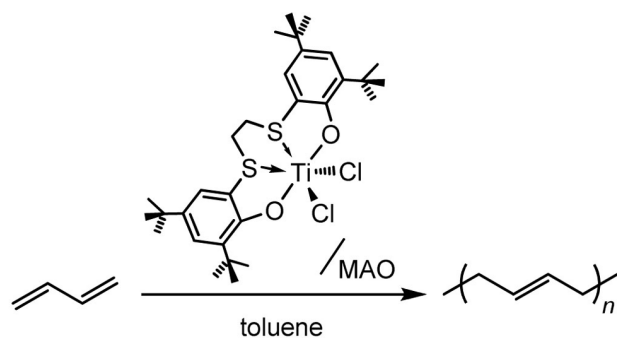
**Figure 4.** Butadiene polymerization by bis(phenoxy imino)  $TiCl_2$ -MAO catalyst

which is still industrially used, even if, actually, other systems with higher activity and stereospecificity (e.g.,  $Co(acac)_2-AlEt_2Cl-H_2O$ ;  $Co(acac)_3-AlEt_3-H_2O-CS_2$ ;  $AlEt_3-Ni(octanoate)_2-BF_3 \cdot OEt_2$ ;  $AlEt_2Cl-Nd(OCOC_7H_{15})_3-Al(iBu)_3$ ) are available.

Recently, catalysts based on some complexes of Ti(II) and Ti(IV) with bidentate dialkylphosphines (e.g.,  $TiCl_2(dmpe)_2$ ,  $dmpe=1,2$ -bis(dimethylphosphino)ethane;  $TiCl_4(dmpe)_2$ ;  $TiCl_4(depe)_2$ ,  $depe=1,2$ -bis(diethylphosphino)ethane) in combination with MAO were used in the polymerization of butadiene [5]; they were found to exhibit a rather low activity and stereospecificity, giving polymers with a mixed *cis*-1,4/1,2 structure. Most recently, it has been reported that the catalytic systems obtained by combining (i) a bis(phenoxyimino) $TiCl_2$  with MAO (Figure 4) [68] and (ii) an (anilidomethyl)pyridine Ti(IV) complex with  $Al(iBu_2H)/MAO$  (Figure 5) [69], are able to polymerize 1,3-butadiene to predominantly *cis*-1,4 polymers with a quite good activity.

Milione et al. reported the polymerization of butadiene using novel octahedral dichloro{1,4-dithiabutanediyl-2,2'-bis(4,6-di-*tert*-butylphenoxy)} Ti complex having a 1,4-dithiabutanediyl bridge. After activation with MAO, the catalyst resulted in *trans*-1,4 selective polymerization of butadiene with good activity (Figure 6). The polydispersity index ( $M_w/M_n$ ) was close to 2, consistent with a single-site catalyst [70].

Contrary to what occurred in the case of Ti, Zr-based catalysts have been less studied, mainly because they are found to be poorly active in the polymerization of conjugated dienes. Very recently, however, there has been a report on the polymerization of butadiene with catalysts obtained by combining (anilidomethyl)pyridine Zr(IV) complexes with  $Al(iBu_2H)/MAO$  (Figure 5) [69]. Such new systems have provided exclusively *cis*-1,4 poly(butadiene) ( $\geq 99.9\%$ ), at the



**Figure 6.** Butadiene polymerization by dichloro {1,4-dithiabutandiyl-2,2'-bis(4,6-di-tert-butylphenoxy)} titanium complex in combination with MAO

same time exhibiting a quite good catalytic activity.

### Vanadium catalysts

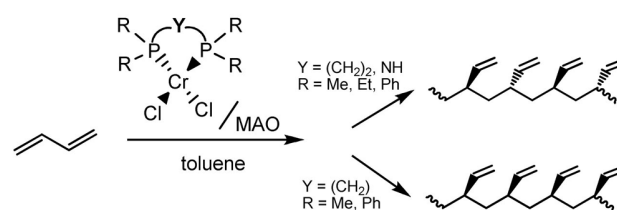
Vanadium catalysts are mainly known in the field of stereospecific diene polymerization for their ability to give highly *trans*-1,4 polymers, and by far they are the most important systems for preparing *trans*-1,4 poly(butadiene) [1]. Crystalline, highly stereoregular *trans*-1,4 poly(butadiene)s are in fact obtained with various V systems: the heterogeneous systems obtained by combination of a vanadium halide (e.g.,  $VCl_3$ ,  $VCl_4$ ) and an aluminum-alkyl (e.g.,  $AlEt_3$ ,  $AlEt_2Cl$ ) [71,72]; the soluble systems  $VCl_3 \times 3THF-AlEt_2Cl$  [73],  $V(acac)_3-AlEt_2Cl$  (*acac* = acetylacetonate) [74], and  $V(acac)_3-MAO$  [9,12].

In more recently, *trans*-1,4 poly(butadiene)s were predominantly obtained with novel catalysts obtained by combining a bis(imino)pyridyl V(III) complex [ $VCl_3\{2,6-bis[(2,6-iPr_2C_6H_3)NC(Me)]_2(C_5H_3N)\}$ ] with an alkylating agent ( $Al_2Et_3Cl_3$ ,  $AlEt_2Cl$ , MAO) [75]. The activity and stereospecificity of the catalyst were found to depend on the nature of cocatalyst employed.

**Table 1.** Polymerization of butadiene with Cr(II) catalysts

Cr-complex	Polymerization <sup>(a)</sup>		Polymer microstructure	
	Time (min)	Yield (%)	1,2 <sup>(b)</sup> (%)	rr/mr/mm <sup>(c)</sup>
$CrCl_2(dmpm)_2$	30	80.2	89	16/13/71
$CrCl_2(dmpe)_2$	60	39.5	95	83/17/0
$CrCl_2(depe)_2$	60	76.0	89	72/26/2
$CrCl_2(dppm)$	20	55.7	89	18/48/34
$CrCl_2(dppe)$	1020	15.3	88	61/34/5
$CrCl_2(dppa)$	5	37.5	90	66/30/4

(a) Polymerization conditions: butadiene, 2 mL; toluene, total volume 16 mL; MAO, Al/Cr = 1000; Cr,  $1 \times 10^{-6}$   $\mu$ mol; polymerization temperature, 20°C. (b) determined by NMR analysis; the remaining units are essentially *cis*-1,4. (c) molar ratio of 1,2 syndiotactic/atactic/isotactic triads, determined by  $^{13}C$  NMR analysis.

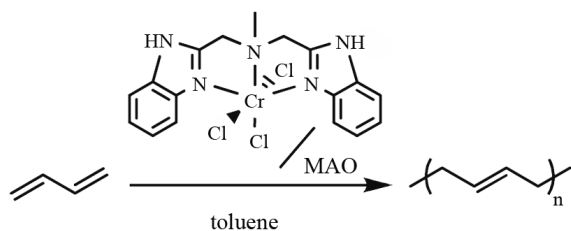


**Figure 7.** Butadiene polymerization by Cr(II) bidentate phosphine complexes with MAO

### Chromium catalysts

The Cr-based catalysts play an important role in the field of conjugated dienes polymerization being among the first systems capable of providing poly(butadiene) with a 1,2 structure [1-3,76]. For example, apparently soluble systems, obtained by combining a soluble Cr compound (e.g.,  $Cr(acac)_3$ ;  $Cr(CO)_3py$ , *py* = pyridine) with  $AlEt_3$ , produce 1,2-poly(butadiene) with an iso- or syndiotactic structure depending on the Al/Cr molar ratio (syndiotactic at low ratio, Al/Cr = 2-6; isotactic at high ratio, Al/Cr = 6-10) [76]. Significantly, confirming indeed the relevance of Cr catalysts in the field of butadiene polymerization, up to now the isotactic 1,2 poly(butadiene) has been obtained only with Cr-based catalysts.

In more recent years, new catalysts, more active and stereospecific, have been developed by combination of various Cr(II) complexes with bidentate phosphine ligands and MAO (Figure 7; Table 1) [44, 45, 50, 54, 55, 77]. These new systems have allowed to obtain 1,2 poly(butadiene)s with a 1,2 content up to 95%, having different tacticity, iso- or syndiotactic, depending on the type of phosphine coordinated to the Cr atom [44, 50, 54, 77]. In particular, isotactic polymers are mainly obtained with catalysts using sterically minimized hindered phosphines (e.g.,  $CrCl_2(dmpm)_2-$



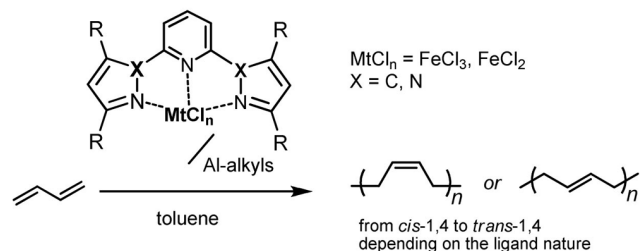
**Figure 8.** Butadiene polymerization with Cr(III) complex in combination with MAO

MAO; CrCl<sub>2</sub>(dppm)-MAO; bis(dimethylphosphino) methane, dmpm; bis(diphenylphosphino) methane, dppm), while the use of catalysts with bulkier phosphines (e.g., CrCl<sub>2</sub>(dmpe)<sub>2</sub>-MAO; CrCl<sub>2</sub>(depe)<sub>2</sub>-MAO; CrCl<sub>2</sub>(dppa)-MAO; 1,2-bis(dimethylphosphino) ethane, dmpe; 1,2-bis(diethylphosphino)ethane, depe; bis (diphenylphosphino)amine, dppa; 1,2-bis(diphenylphosphino)ethane, dppe) has made it possible to synthesize highly syndiotactic 1,2-poly(butadiene) (Table 1). The formation of 1,2-poly(butadiene)s of different types and degrees of tacticity (iso- and syndiotactic) upon the phosphine ligand may be interpreted on the basis of the diolefin polymerization mechanism previously proposed [1, 62-66] which indeed confirms its validity.

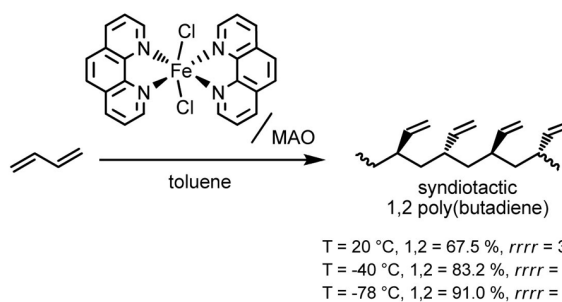
Most recently, catalysts based on Cr(III) complexes with tridentate nitrogen ligands have been reported to give essentially *trans*-1,4 polymers from butadiene (Figure 8) [78].

### Iron catalysts

Contrary to other transition metals such as Ti, V, Cr, Co, and Ni, Fe-based catalysts have not been extensively studied in the field of conjugated diolefin polymerization, but some systems obtained by mixing Fe(acac)<sub>3</sub>, Al(*i*Bu)<sub>3</sub> and 1,10-phenanthroline (phen) [79, 80] have provided a poly(butadiene) with a mixed *cis*-1,4/1,2 structure and a poly(isoprene) with an essentially 3,4 structure.

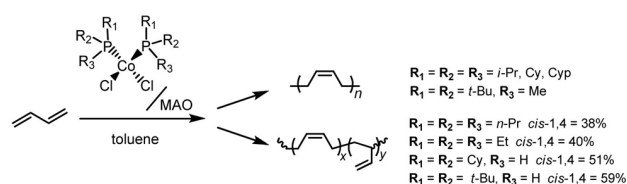


**Figure 10.** Butadiene polymerization with Fe(III) and Fe(II) complexes bearing *NNN* tridentate ligands



**Figure 9.** Butadiene polymerization with (phen)<sub>2</sub>FeCl<sub>2</sub>-MAO catalyst

Extremely active and stereospecific catalysts were recently obtained by combinations of some Fe(II) complexes with bidentate aromatic amines and aluminum-alkyls (e.g., Al(*i*Bu)<sub>3</sub>, AlEt<sub>3</sub>, MAO) (Figure 9) [46-48, 81]. These systems led essentially to formation of syndiotactic 1,2 poly(butadiene)s, in which the 1,2 content and the syndiotactic degree increased by lowering the polymerization temperature. Living characteristics of Fe(2-EHA)<sub>3</sub>/Al(*i*Bu)<sub>3</sub>/DEP catalyst (EHA = ethylhexanoate, DEP = diethyl phosphite) system have been found in the polymerization of 1,3-butadiene in hexane at 40°C by Zhang et al. [82]. These catalyst systems are found highly active which provide poly(butadiene) with a mixed 1,2/*cis*-1,4 structure. Feasible post-polymerization of 1,3-butadiene and block copolymerization of 1,3-butadiene and isoprene further supported the living nature of the polymerization. Very recently, Zhang et al. [83] synthesized a series of Fe(III) and Fe(II) complexes bearing neutral *N,N,N*-tridentate ligand. All the complexes were evaluated as pre-catalysts for the butadiene polymerization in combination with different aluminum alkyls (i.e., MAO, MMAO, Et<sub>2</sub>AlCl) in toluene at room temperature. Fe(III) and Fe(II) bearing the same ligand showed comparable catalytic performance. The catalytic activity and selectivity were found to be significantly influenced by the ligand structure, with the selectivity being tunable within a wide range from *cis*-1,4 to *trans*-1,4 (Figure 10). Analogous Fe(II)



**Figure 11.** Butadiene polymerization with aliphatic phosphine Co(II) complexes and MAO

**Table 2.** Polymerization of butadiene with Co based catalysts

Catalyst	Poly(butadiene) microstructure	Reference
Co(acac) <sub>2</sub> -AlEt <sub>2</sub> Cl-H <sub>2</sub> O	<i>cis</i> -1,4 (~97%)	[86]
AlEt <sub>2</sub> Cl-Co(acac) <sub>2</sub> -NMe <sub>3</sub> (or NEt <sub>3</sub> )	<i>trans</i> -1,4 (~95%)	[87]
CoCl <sub>2</sub> -MAO	<i>cis</i> -1,4 (~97%)	[51,88,89]
CoCl <sub>2</sub> -MAOPPh <sub>3</sub>	syndiotactic 1,2 (~85%)	[90-94]
Co(acac) <sub>3</sub> -MAO	<i>cis</i> -1,4 (~97%)	[9]
Co(acac) <sub>3</sub> -AlEt <sub>3</sub> -H <sub>2</sub> O	equibinary <i>cis</i> -1,4/1,2	[95]
Co(acac) <sub>3</sub> -AlEt <sub>3</sub> -H <sub>2</sub> O-CS <sub>2</sub>	syndiotactic 1,2	[96-99]

dibromide complexes with X = S were synthesized by Britovsek et al. [84], affording predominantly *cis*-1,4 polymer (73%) with moderate catalytic activity.

### Cobalt catalysts

Cobalt catalysts are probably the most versatile among the various catalytic systems based on transition metals for the polymerization of 1,3-dienes, since, by suitably varying the catalytic formulation, they exhibit high activity and stereospecificity in providing all the possible stereoisomers of poly(butadiene)[1-5, 85]. Table 2 shows some of the Co systems commonly used for the polymerization of butadiene: Co(acac)<sub>2</sub>-AlEt<sub>2</sub>Cl-H<sub>2</sub>O and Co(acac)<sub>3</sub>-AlEt<sub>3</sub>-H<sub>2</sub>O-CS<sub>2</sub>, in particular, still used for the industrial production of *cis*-1,4 poly(butadiene) and syndiotactic 1,2 poly(butadiene), respectively.

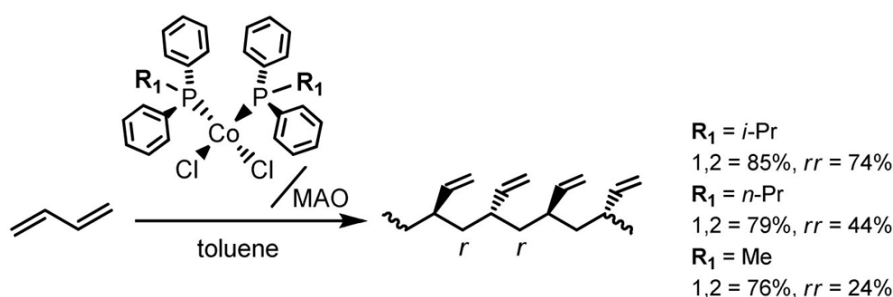
In recent years, new catalytic systems have been developed by combination of MAO with phosphine CoCl<sub>2</sub> complexes [4, 5, 51-53, 85, 100-102]. The peculiarity of such novel systems lies in their ability to allow the formation of poly(butadiene)s with controlled microstructures (*cis*-1,4; 1,2; and mixed structure *cis*-1,4/1,2) by simply varying the type of ligand coordinated to the Co atom. Poly(butadiene)s with extremely high *cis*-1,4 content were obtained using aliphatic bulky phosphines (e.g., P<sup>t</sup>Bu<sub>3</sub>, P<sup>i</sup>Pr<sub>3</sub>), while polymers with a mixed *cis*-1,4/1,2 structure were obtained with aliphatic phosphines exhibiting lower steric hindrance

(e.g., PEt<sub>3</sub>, P<sup>n</sup>Pr<sub>3</sub>) (Table 3 and Figure 11) [4, 5, 51, 103]. The use of catalysts based on Co complexes with aromatic phosphines (PRPh<sub>2</sub> and PR<sub>2</sub>Ph; R = alkyl or cycloalkyl group) resulted instead in the formation of essentially 1,2 poly(butadiene)s, with a degree of crystallinity and syndiotacticity depending on the type of phosphine ligand coordinated to the Co atom (Table 3 and Figure 12) [4, 5, 52, 53, 85, 102]. The formation of polymers with different structures by varying the type of ligand on the metal has been attributed to the steric hindrance of the ligand affecting the mutual orientation of the incoming monomer and of the butenyl group in the catalytic site; on the other hand, it is well known that steric and electronic properties of phosphines strongly depend on the nature of the substituents on the phosphorus atom [103-106].

High *cis*-1,4 polymers (around 95%) were also obtained with catalysts based on bidentate phosphine Co complexes (CoCl<sub>2</sub>[R<sub>2</sub>P(CH<sub>2</sub>)<sub>n</sub>PR<sub>2</sub>]-MAO; R = Me, Et, Ph; n = 1, 2), independent of the type of bidentate phosphine ligand bonded to the cobalt atom [4,5,100].

Most recently various catalysts based on Co complexes bearing nitrogen ligands, giving essentially *cis*-1,4 polymers from butadiene, have been described in the literature [107-113].

Kim et al. reported on the polymerization of 1,3-butadiene with catalysts based on Co(II) pyridyl bis(imino) complexes, bearing two methyl substituents in different positions on each imino-aryl group, and

**Figure 12.** Butadiene polymerization with aromatic phosphine Co(II) complexes and MAO

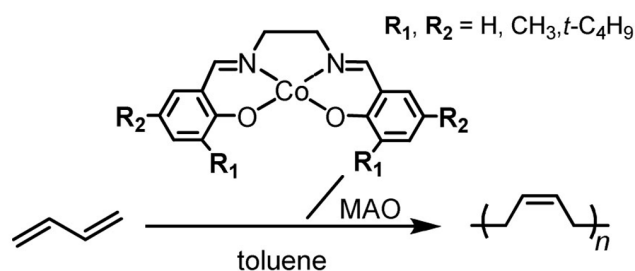
**Table 3.** Polymerization of butadiene with catalysts based on phosphine Co(II)Cl<sub>2</sub> complexes

Co-complex	Polymerization <sup>(a)</sup>			Polymer microstructure <sup>(b)</sup>		
	Al/Co	time (min)	conversion (%)	cis-1,4 (%)	1,2 (%)	rr/mr/mm <sup>(c)</sup>
CoCl <sub>2</sub>	1000	52	68.6	95.4	4.6	
CoCl <sub>2</sub> (PEt <sub>3</sub> ) <sub>2</sub>	1000	30	74.8	39.9	60.1	
CoCl <sub>2</sub> (P <sup>n</sup> Pr <sub>3</sub> ) <sub>2</sub>	1000	35	85.5	38.2	61.8	
CoCl <sub>2</sub> (PCy <sub>2</sub> H) <sub>2</sub>	1000	30	70.8	51.0	49.0	
CoCl <sub>2</sub> (P <sup>i</sup> Bu <sub>2</sub> H) <sub>2</sub>	1000	35	60.4	59.0	41.0	
CoCl <sub>2</sub> (P <sup>i</sup> Bu <sub>2</sub> Me) <sub>2</sub>	1000	40	59	94.0	6.0	
CoCl <sub>2</sub> (PCy <sub>3</sub> ) <sub>2</sub>	1000	39	56.4	73.6	26.4	
CoCl <sub>2</sub> (PCy <sub>3</sub> ) <sub>2</sub>	1000	32	44.4	77.4	22.6	
CoCl <sub>2</sub> (P <sup>n</sup> Pr <sub>3</sub> ) <sub>2</sub>	1000	20	57.4	94.5	5.5	
CoCl <sub>2</sub> (P <sup>i</sup> Bu) <sub>3</sub>	1000	22	73.0	96.0	4.0	
CoCl <sub>2</sub> (PMePh <sub>2</sub> ) <sub>2</sub>	100	5	64.7	23.9	76.1	24/52/24
CoCl <sub>2</sub> (PEtPh <sub>2</sub> ) <sub>2</sub>	100	5	93.7	22.3	77.7	42/45/13
CoCl <sub>2</sub> (P <sup>n</sup> PrPh <sub>2</sub> ) <sub>2</sub>	100	5	100	21.3	78.7	44/43/13
CoCl <sub>2</sub> (P <sup>i</sup> PrPh <sub>2</sub> ) <sub>2</sub>	100	5	100	14.6	85.4	74/26/0
CoCl <sub>2</sub> (PCyPh <sub>2</sub> ) <sub>2</sub>	100	5	75.0	15.5	84.5	69/27/4
CoCl <sub>2</sub> (PMe <sub>2</sub> Ph) <sub>2</sub>	100	5	39.8	27.0	73.0	15/51/34
CoCl <sub>2</sub> (PEt <sub>2</sub> Ph) <sub>2</sub>	100	5	55.4	24.7	75.3	19/49/32
CoCl <sub>2</sub> (PCy <sub>2</sub> Ph) <sub>2</sub>	100	5	55.1	20.6	79.4	44/41/15

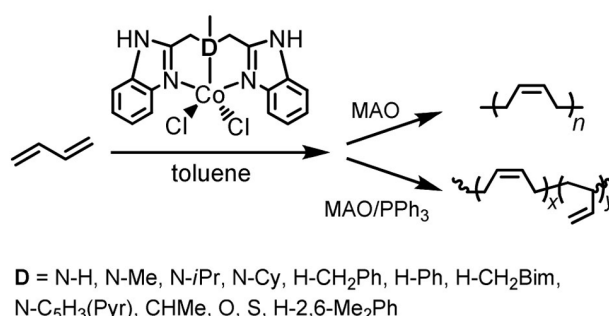
(a) Polymerization conditions: butadiene, 2 mL; toluene, 16 mL; MAO as alkylating agent (Al/Co molar ratio is reported); moles of Co,  $1 \times 10^{-5}$ ; temperature, +20°C. (b) Determined by <sup>1</sup>H NMR. *Trans*-1,4 units are almost negligible, as indicated by the fact that in the IR spectra of the polymers no band at 967 cm<sup>-1</sup> was detected. (c) Molar ratio of 1,2 syndiotactic/atactic/isotactic triads, determined by <sup>13</sup>C NMR analysis

ethylaluminum sesquichloride (EASC) as cocatalyst; these systems, and in particular those containing less hindered pyridyl bis(imino) ligands, were found to be very active, yielding high molecular weight polymers with a *cis*-1,4 content up to 96.4% [107].

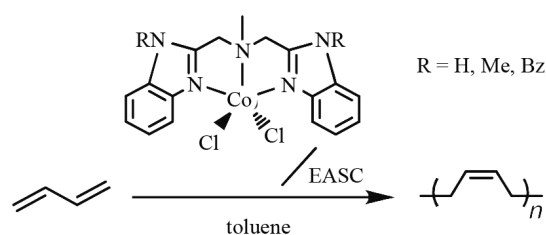
Catalysts exhibiting high activity and high *cis* selectivity (*cis*-1,4 content up to 96.9%) were obtained by combining (salen) Co(II) complexes with MAO (Figure 13). The activity was strongly affected by the ligand structure of the (salen)Co(II) complexes, while the selectivity was only slightly influenced [108].

**Figure 13.** Butadiene polymerization with (salen) Co(II) complexes and MAO.

Gibson et al. synthesized and characterized a series of bis(benzimidazole) Co(II)Cl<sub>2</sub> complexes containing different central donors. The nature of the central donor affects the binding of the ligand to the Co centre and determines the coordination geometry of the metal complexes. All complexes have been shown to catalyze the polymerization of butadiene, in combination with MAO, to give *cis*-1,4-poly(butadiene) with high selectivity. The nature of the central donor has a marked influence on the polymerization activity of the catalysts, but does

**Figure 14.** Butadiene polymerization by bis (benzimidazole) Co(II)Cl<sub>2</sub> complexes in combination with MAO and MAO/PPh<sub>3</sub>



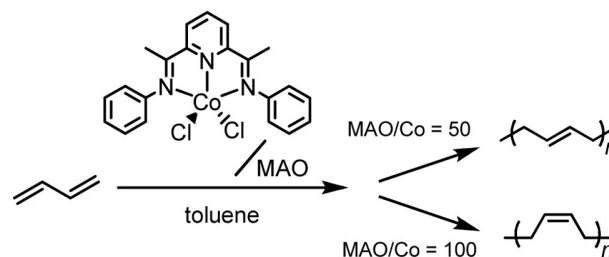


**Figure 15.** Butadiene polymerization by (dibenzimidazolyl) Co(II) Cl<sub>2</sub>-EASC

not affect the polymer microstructure. The addition of PPh<sub>3</sub> generally increases the polymerization activity and results in predominantly (60–70%) 1,2 poly(butadiene)(Figure 14) [78,109].

The synthesis and characterization of a series of Co(II) complexes supported on tridentate dibenzimidazolyl ligands and their use, in combination with EASC, for the polymerization of 1,3 butadiene, have been described by Kim [110]. Catalysts exhibiting high activity and yielding predominantly *cis*-1,4 polymers (up to 97%) were obtained (Figure 15).

Co(II) complexes supported by 2,6-bis[1-(iminophenyl) ethyl]pyridine were synthesized and characterized by Zhang et al. These complexes, in combination with MAO, have been involved in polymerization of butadiene (Figure 16) [111]. The catalytic activity and regioselectivity are strongly dependent on MAO/Co molar ratio. When the molar ratio of 50 is used, the polymer obtained has an essentially *trans*-1,4 structure (about 94.4%). Increases in MAO/Co molar ratio to 100 lead to a

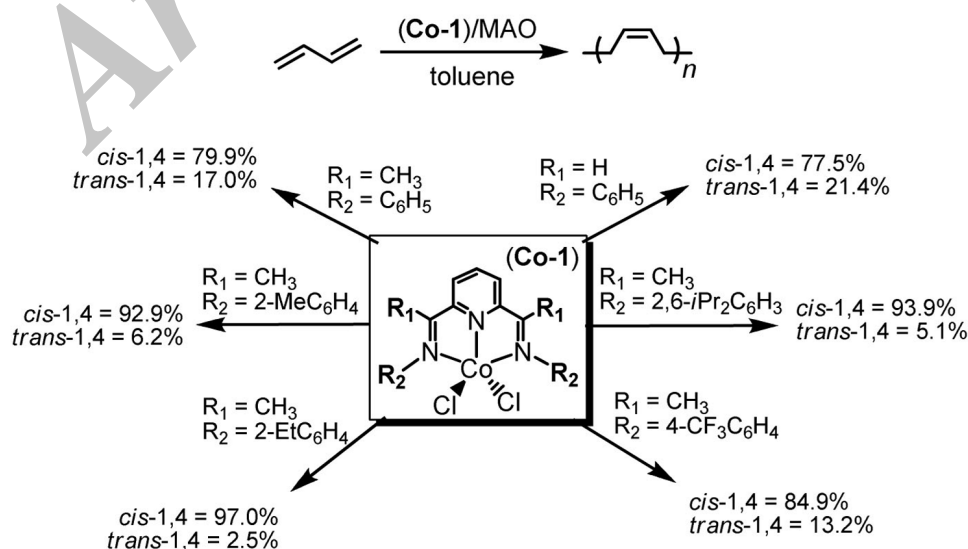


**Figure 16.** Butadiene polymerization by bis(imino)pyridyl Co(II) Cl<sub>2</sub>-MAO

dramatic increase of *cis*-1,4 selectivity, reaching 79.0%. This particular behavior may be attributed to the formation of two different types of active sites at different molar ratios, undergoing different polymerization mechanisms.

Kim et al. prepared a series of complexes of general formula [Py(Bm-R)<sub>2</sub>]CoCl<sub>2</sub> (Py=pyridyl; Bm=benzimidazolyl, R=H; Me; Bz) by combining tridentate 2,6-bis(benzimidazolyl)pyridine ligands with CoCl<sub>2</sub>. The Co(II) complexes exhibited high catalytic activity in the polymerization of 1,3-butadiene upon activation with aluminum-alkyls, yielding predominantly *cis*-1,4-poly(butadiene) with high molecular weight [112]. Choice of cocatalysts was found to be a key factor in determining the activity and polymer microstructure. EASC was found to be the most efficient one resulting in polymers with about 97% *cis*-1,4 content.

Zhang et al. prepared a series of 2,6-bis(imino)pyridyl Co(II) complexes which, in combination with MAO as cocatalyst, show a rather good activity in the polymerization of 1,3-butadiene, producing

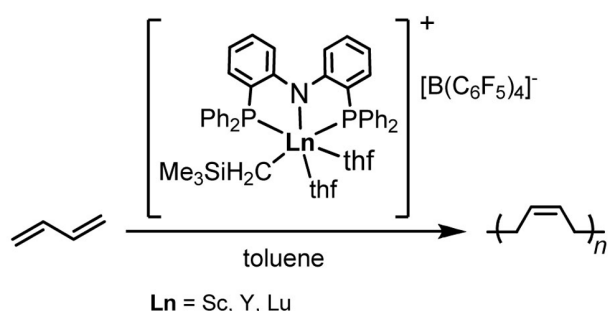


**Figure 17.** Synthesis of *cis*-1,4 poly(butadiene) by bis(imino)pyridyl-Co(II)Cl<sub>2</sub>-MAO

poly(butadiene)s with tunable *cis*-1,4 structure (in the range 77.5–97%) and controlled molecular weight and molecular weight distribution (Figure 17) [113].

### Nickel catalysts

A wide variety of Ni based catalysts (e.g., Ni(naph)<sub>2</sub>-AlEt<sub>2</sub>Cl-H<sub>2</sub>O, naph = naphthenate; NiCp<sub>2</sub>-MAO; Ni(acac)<sub>2</sub>-MAO) has been reported in the literature as active catalysts in the butadiene polymerization [1-3,14,114,115]. Some of them have activity and stereospecificity comparable with those of Co, and have become of industrial interest. Specifically, the catalyst system AlEt<sub>3</sub>-Ni(octanoate)<sub>2</sub>-BF<sub>3</sub>·OEt<sub>2</sub> is currently used for the industrial production of high *cis*-poly(butadiene) (*cis* content 96–97%) [1,116]. Several papers deal with the polymerization of butadiene with allyl Ni complexes [117-120]. A few papers have instead reported on the polymerization of butadiene with catalysts based on well defined nickel complexes with phosphorus and nitrogen ligands. Ni(II) based pyridylbis(imine) complexes combined with EASC showed good activity in butadiene polymerization affording *cis*-1,4-polymers up to about 95% [121]. A cationic allyl Ni complex stabilized by a single *N*-heterocyclic carbene ligand and a labile aquo ligand was reported to be moderately active in the polymerization of 1,3-butadiene (*cis*-1,4, 92%) [122]. A dicationic Ni complex [(dppf)Ni(MeCN)<sub>4</sub>][BF<sub>4</sub>]<sub>2</sub> in combination with AlEt<sub>2</sub>Cl exhibited high activity in the butadiene polymerization. The resulting poly(butadiene)s showed surprisingly high *cis*-1,4 content (> 80%) and only 2% of 1,2-units: it is known in fact that in the presence of phosphorus ligands the polymerization produces a polymer with high *trans*-1,4-units. The polymers obtained presented low molecular weights [123]. Ni(bipy)Et<sub>2</sub> cyclooligomerized butadiene to cyclo-dodecatriene [124].



**Figure 18.** Butadiene polymerization by bis(phosphinophenyl) amido lanthanide complexes

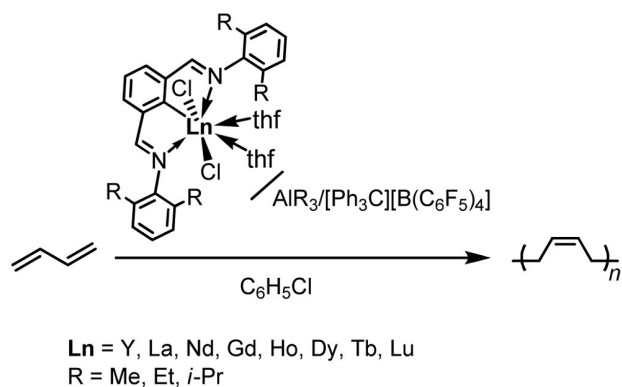
Only very recently, the synthesis of Ni(II) complexes bearing nitrogen based ligands, similar to those reported for Co(II), has been investigated. Jie et al. [125] synthesized a series of novel Ni(II) complexes supported by imino- or amino-pyridyl alcohol ligands. In comparison with the analogous Co-complexes, the Ni-complexes exhibited lower catalytic activity, *cis*-1,4 content, and molecular weight under the same polymerization conditions.

### Lanthanide catalysts

Lanthanide catalysts are known to be specific for the *cis* polymerization of 1,3-dienes, butadiene in particular [1-3,6]. Conventional lanthanide catalysts, Nd in particular, are typically obtained by reacting a Nd-compound (e.g., Nd(acac)<sub>3</sub>; Nd-2-ethyl-hexanoate, Nd(OCOC<sub>7</sub>H<sub>15</sub>)<sub>3</sub>) with a chlorine donor (e.g., AlEt<sub>2</sub>Cl; Al<sub>2</sub>Et<sub>3</sub>Cl<sub>3</sub>, *tert*-butyl chloride) and an aluminum alkyl (e.g., Al*i*Bu<sub>3</sub>; Al*i*Bu<sub>2</sub>H) [126-130]. Depending on the order of catalyst component addition, homogeneous or heterogeneous systems can be obtained; homogeneous if the Nd-compound is first reacted with the aluminum alkyl and then with the chlorine donor, heterogeneous if it is first reacted with the chlorine donor and then with the aluminum alkyl [130]. The ternary system AlEt<sub>2</sub>Cl-Nd(OCOR)<sub>3</sub>-Al(*i*Bu)<sub>3</sub> (R=alkyl group) is actually used for the commercial production of *cis* poly(butadiene). For detailed information on the lanthanide catalysts for the polymerization of 1,3-dienes the reading of the review recently published by Friebe et al. on “Advance Polymer Science” is strongly recommended [6].

More recently, catalysts based on cyclopentadienyl lanthanide complexes and lanthanide complexes with various nitrogen ligands, were used as catalyst precursors for the polymerization of butadiene. The half-sandwich bis(aluminate) complexes [Ln(η<sup>5</sup>-C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub>{(μ-Me)<sub>2</sub>(AlMe<sub>2</sub>)<sub>2</sub>}<sub>2</sub>] (Ln = La, Nd) upon activation with [Ph<sub>3</sub>C]<sup>+</sup>[BPh<sub>4</sub>]<sup>-</sup> and in presence of Al(*i*Bu)<sub>3</sub>, give active catalysts for the controlled 1,4-*trans* polymerization of 1,3-butadiene [131]. Cui et al. synthesized a series of new rare-earth metal bis(alkyl)s stabilized by NPN-type ligands which, upon activation with aluminum alkyls and borate, provided catalysts of medium activity, characterized by a *trans*-1,4 selectivity [132].

An active Nd catalysts for the *cis* polymerization of butadiene, supported by a dianionic modification of the 2,6-diiminopyridine ligand, was described by

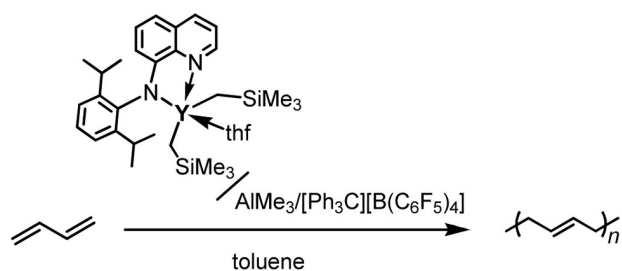


**Figure 19.** Butadiene polymerization by NCN-lanthanide complexes

Gambarotta [133].

A novel catalytic system, based on a cationic alkyl rare-earth metal species bearing an ancillary bis(phosphinophenyl)amido ligand, exhibiting an extremely high *cis* selectivity (99%) and excellent livingness ( $M_w/M_n = 1.05\text{--}1.13$ ) in the polymerization of 1,3-butadiene and isoprene, was reported by Hou et al. [134] (Figure 18).

Novel lanthanide catalysts, characterized by a very high *cis* selectivity in the polymerization of butadiene (*cis* content, 99.9%) and isoprene (*cis* content, 98.8%), were also obtained by Cui et al. by combining aryldiimine NCN-pincer ligated rare earth dichlorides with aluminum-alkyl and  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  [135] (Figure 19). On the other hand, high *trans*-1,4 selectivity was obtained by using rare earth metal complexes bearing *N*-R-quinolinyl-8-amino ligands [ $\text{R} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3, 2,6\text{-Et}_2\text{C}_6\text{H}_3, 2,6\text{-Me}_2\text{C}_6\text{H}_3$ ]. Specifically, these complexes, in combination with aluminum alkyls and organoborates, gave homogeneous ternary systems exhibiting good catalytic activity and *trans*-1,4 selectivity (*trans*-1,4 content of about 80%) in the polymerization of butadiene (Figure 20) [136].



**Figure 20.** Butadiene polymerization by rare earth metal bis(alkyl) complexes bearing a non-Cp quinolinyl aniline ligand, upon the activation by aluminium alkyls and organoborates

## CONCLUSION

As cited above, the polymerization of conjugated dienes with transition metals began in 1954, and at the beginning of the 1960s all the polybutadiene stereoisomers were already synthesized: since then much work has been done and several catalytic systems, more active and stereospecific, based on transition metals and lanthanides, have been developed [1-3].

A renewed interest in the study of catalysts for the polymerization of 1,3-dienes, butadiene and isoprene in particular, occurred with the introduction of catalysts based on several types of transition metal and lanthanide complexes with nitrogen, oxygen and phosphorus ligands. These novel catalysts permitted to obtain (i) a better control of the polymerization regio- and stereoselectivity, and (ii) a better regulation of the molecular weight and molecular weight distribution of the resulting polymers.

Poly(butadiene)s and poly(isoprene)s with higher *cis* content (99.9% and  $\geq 98\%$ , respectively) were prepared and considered important achievements from the industrial point of view, since (i) even a slight increase in the polymer *cis* content may lead to a great improvement in the elastic properties of the polymers, and (ii) the increased demand for synthetic polyisoprene due to the limited supply of natural rubber. Novel, highly stereoregular polymeric structures, which were not possible to prepare before, were also obtained from several types of 1,3-dienes: syndiotactic [48,137] and isotactic [138,139] 3,4 polyisoprene; *cis*-1,4-*alt*-3,4 polyisoprene [140]; syndiotactic *E*-1,2-poly(1,3-pentadiene) [141]; syndiotactic-*E*-1,2-poly(1,3-hexadiene) [42]; syndiotactic [143,144] and isotactic [60] *E*-1,2-poly(3-methyl-1,3-pentadiene); syndiotactic *E*-1,2-poly(5-methyl-1,3-hexadiene) [145]; syndiotactic *E*-1,2 poly(1,3-heptadiene) [145]; syndiotactic *E*-1,2-poly(1,3-octadiene) [145]. These polymers may not be industrially relevant, given the high cost of substituted butadienes, however they were quite interesting from a scientific perspective, since it has been possible to establish connections between the catalyst structure, monomer structure and polymer microstructure, thus obtaining information on the influence of catalyst and monomer structure on the polymerization regio- and stereoselectivity.

Based on what was reported above, it is clearly evident that the synthesis of novel transition metal

and lanthanide complexes and their use as catalyst components for the polymerization of 1,3-dienes, seem to pave the way for future studies.

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