IPPI

Polyolefins Journal, Vol. 1 No. 1 (2014) 43-60

REVIEW PAPER

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)

Received: 31 January 2013, Accepted: 8 June 2013

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

CONTENT

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

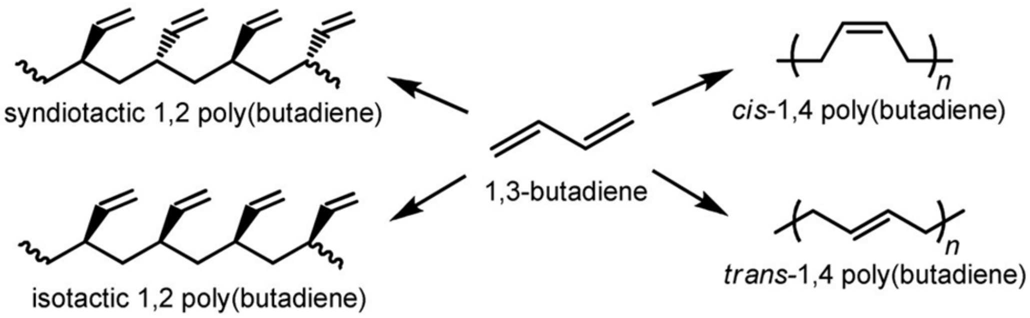


Figure 1. Stereoregular polymers from 1,3-butadiene

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., $Al(iBu)_3$–TiI_4; $AlEt_3$–VCl_3; $Cr(acac)_3$–$AlEt_3$; $Co(acac)_2$–$AlEt_2Cl$–H_2O; $Co(acac)_3$–$AlEt_3$–H_2O–CS_2; $AlEt_3$–$Ni(octanoate)_2$–$BF_3 \times OEt_2$;$AlEt_2Cl$–$Nd(OCOC_7H_{15})_3$–$Al(iBu)_3$)[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 $TiCl_4$ or $TiCl_3$ 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., $CpTiCl_3$, Cp_2TiCl_2, $CpVCl_2$) [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 (η^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 c*is*-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°C, a crystallization temperature (T_c) around –25°C, and a glass transition temperature (T_g) below –100°C. It is produced with various catalysts based on Ti, Co, Ni and Nd, and its main use is in

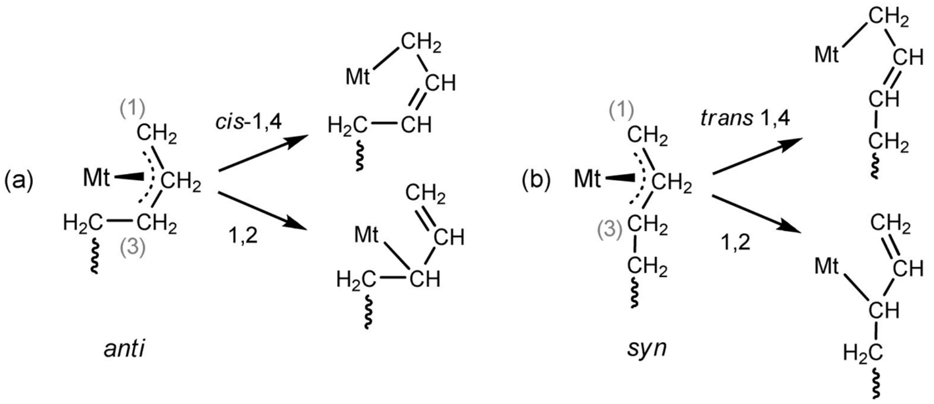


Figure 2. Formation of 1,4 vs 1,2 monomeric units from (a) anti and (b) syn Mt–η3−butenyl group

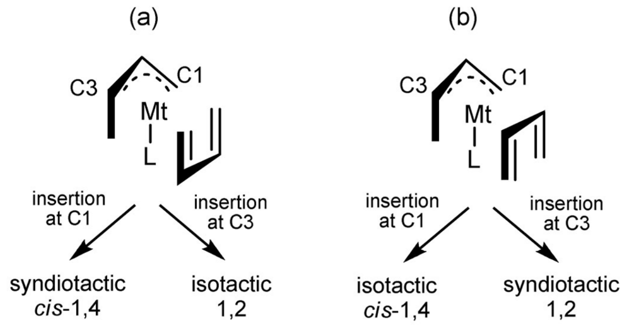


Figure 3. Possible orientations [(a) exo-endo and (b) exo-exo] of the new incoming monomer with respect to the last-inserted unit (L is a generic ligand) and formation of cis-1,4 and 1,2-polymers having a syndiotactic or an isotactic structure

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

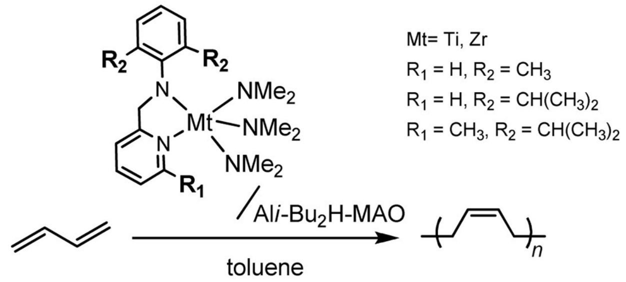


Figure 5. Butadiene polymerization by (anilidomethyl)pyridine Zr(IV) and Ti(IV) complexes with $Al(i\mathrm{Bu}_2H)$/MAO

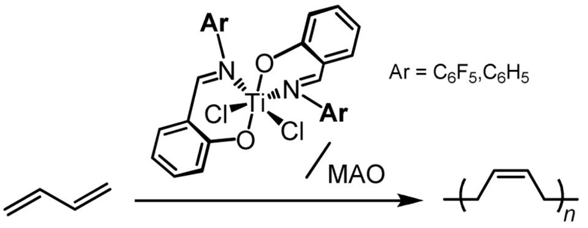


Figure 4. Butadiene polymerization by bis(phenoxy imino) $TiCl_2$–MAO catalyst

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(di ethylphosphino)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 $Al(i\mathrm{Bu}_2H)$/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 $Al(i\mathrm{Bu}_2H)$/MAO (Figure 5) [69]. Such new systems have provided exclusively *cis*-1, 4 poly(butadiene) (≥ 99.9%), at the

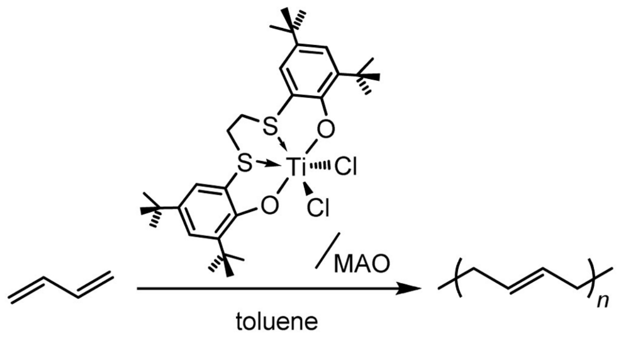


Figure 6. Butadiene polymerization by dichloro {1,4-dithiabutanediyl-2,2'-bis(4,6-di-tert-butylphenoxy)} titanium complex in combination with MAO

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_3×3THF–$AlEt_2Cl$ [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-*i*$Pr_2C_6H_3$)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.

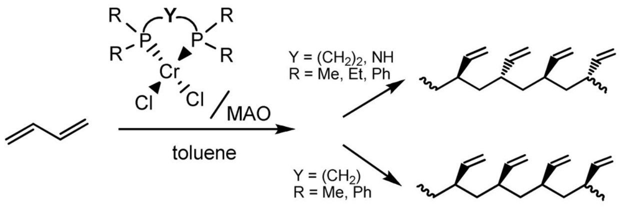


Figure 7. Butadiene polymerization by Cr(II) bidentate phosphine complexes with MAO

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)$_5$py, 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., $CrCl_2(dmpm)_2$–

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

Cr–complex	Polymerization$^{(a)}$		Polymer microstructure	
	Time (min)	Yield (%)	1,2$^{(b)}$(%)	rr/mr/mm$^{(c)}$
$CrCl_2(dmpm)_2$	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, 1×10^{-5} µmol; 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.

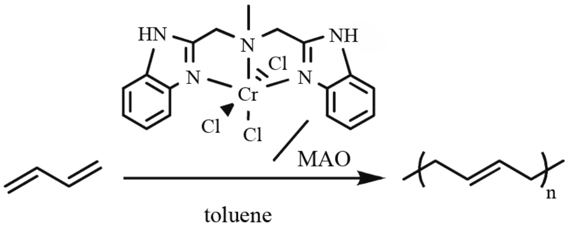


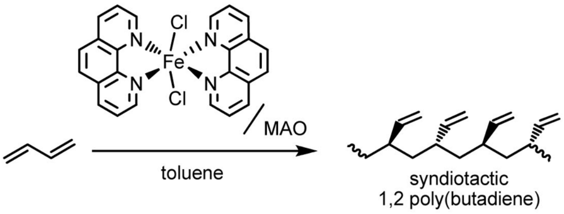
Figure 8. Butadiene polymerization with Cr(III) complex in combination with MAO

MAO; $CrCl_2$(dppm)–MAO; bis(dimethylphosphino) methane, dmpm; bis(diphenylphosphino) methane, dppm), while the use of catalysts with bulkier phosphines (e.g., $CrCl_2(dmpe)_2$–MAO; $CrCl_2(depe)_2$–MAO; $CrCl_2$(dppa)–MAO; 1,2-bis(dimethylphospino) 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 $Fe(acac)_3$, $Al(i Bu)_3$ 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.



T = 20 °C, 1,2 = 67.5 %, *rrrr* = 36.9 %
T = -40 °C, 1,2 = 83.2 %, *rrrr* = 42.5 %
T = -78 °C, 1,2 = 91.0 %, *rrrr* = 52.5 %

Figure 9. Butadiene polymerization with $(phen)_2FeCl_2$–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., $Al(i Bu)_3$, $AlEt_3$, 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 $Fe(2\text{-}EHA)_3/Al(i Bu)_3$/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 co-polymerization 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_2AlCl) 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)

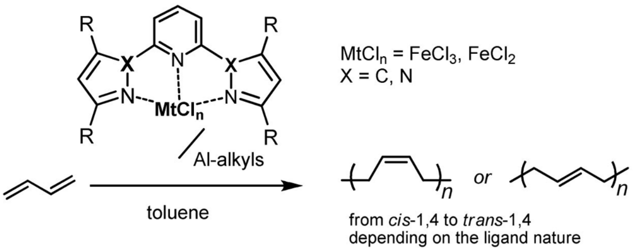


Figure 10. Butadiene polymerization with Fe(III) and Fe(II) complexes bearing *NNN* tridentate ligands

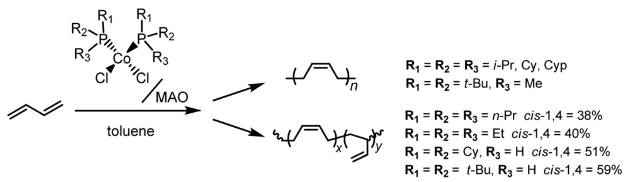


Figure 11. Butadiene polymerization with aliphatic phosphine Co(II) complexes and MAO

Table 2. Polymerization of butadiene with Co based catalysts

Catalyst	Poly(butadiene) microstructure	Reference
$Co(acac)_2$–$AlEt_2Cl$-H_2O	*cis*-1,4 (~97%)	[86]
$AlEt_2Cl$–$Co(acac)_2$–NMe_3 (or NEt_3)	*trans*-1,4 (~95%)	[87]
$CoCl_2$–MAO	*cis*-1,4 (~97%)	[51,88,89]
$CoCl_2$–MAOPPh$_3$	syndiotactic 1,2 (~85%)	[90-94]
$Co(acac)_3$–MAO	*cis*-1,4 (~97%)	[9]
$Co(acac)_3$–$AlEt_3$–H_2O	equibinary *cis*-1,4/1,2	[95]
$Co(acac)_3$–$AlEt_3$–H_2O–CS_2	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: $Co(acac)_2$-$AlEt_2Cl$-H_2O and $Co(acac)_3$-$AlEt_3$-H_2O-CS_2, 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 $CoCl_2$ 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^tBu_3, P^iPr_3), while polymers with a mixed *cis*-1,4/1,2 structure were obtained with aliphatic phosphines exhibiting lower steric hindrance (e.g., PEt_3, P^nPr_3) (Table 3 and Figure 11) [4, 5, 51, 103]. The use of catalysts based on Co complexes with aromatic phosphines ($PRPh_2$ and PR_2Ph; 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 ($CoCl_2[R_2P(CH_2)_nPR_2]$–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

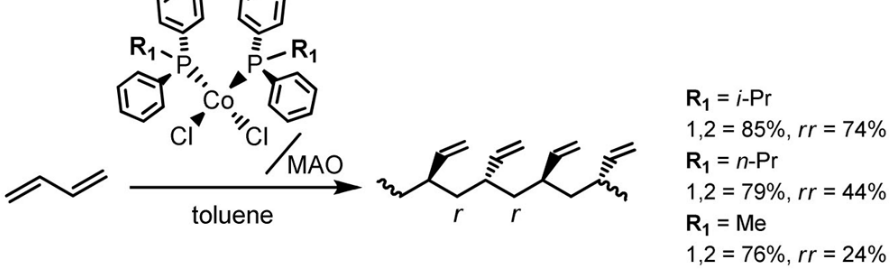


Figure 12. Butadiene polymerization with aromatic phosphine Co(II) complexes and MAO

Table 3. Polymerization of butadiene with catalysts based on phosphine Co(II)Cl_2 complexes

Co–complex	Polymerization[(a)]			Polymer microstructure[(b)]		
	Al/Co	time (min)	conversion (%)	cis-1,4 (%)	1,2 (%)	rr/mr/mm[(c)]
$CoCl_2$	1000	52	68.6	95.4	4.6	
$CoCl_2(PEt_3)_2$	1000	30	74.8	39.9	60.1	
$CoCl_2(P^{n}Pr_3)_2$	1000	35	85.5	38.2	61.8	
$CoCl_2(PCy_2H)_2$	1000	30	70.8	51.0	49.0	
$CoCl_2(P^{t}Bu_2H)_2$	1000	35	60.4	59.0	41.0	
$CoCl_2(P^{t}Bu_2Me)_2$	1000	40	59	94.0	6.0	
$CoCl_2(PCyp_3)_2$	1000	39	56.4	73.6	26.4	
$CoCl_2(PCy_3)_2$	1000	32	44.4	77.4	22.6	
$CoCl_2(P^{i}Pr_3)_2$	1000	20	57.4	94.5	5.5	
$CoCl_2(P^{t}Bu)_3$	1000	22	73.0	96.0	4.0	
$CoCl_2(PMePh_2)_2$	100	5	64.7	23.9	76.1	24/52/24
$CoCl_2(PEtPh_2)_2$	100	5	93.7	22.3	77.7	42/45/13
$CoCl_2(P^{n}PrPh_2)_2$	100	5	100	21.3	78.7	44/43/13
$CoCl_2(P^{i}PrPh_2)_2$	100	5	100	14.6	85.4	74/26/0
$CoCl_2(PCyPh_2)_2$	100	5	75.0	15.5	84.5	69/27/4
$CoCl_2(PMe_2Ph)_2$	100	5	39.8	27.0	73.0	15/51/34
$CoCl_2(PEt_2Ph)_2$	100	5	55.4	24.7	75.3	19/49/32
$CoCl_2(PCy_2Ph)_2$	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 × 10^{-5}; temperature, +20°C. (b) Determined by ^{1}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^{-1} was detected.(c) Molar ratio of 1,2 syndiotactic/atactic/isotactic triads, determined by ^{13}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].

Gibson et al. synthesized and characterized a series of bis(benzimidazole) Co(II)Cl_2 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

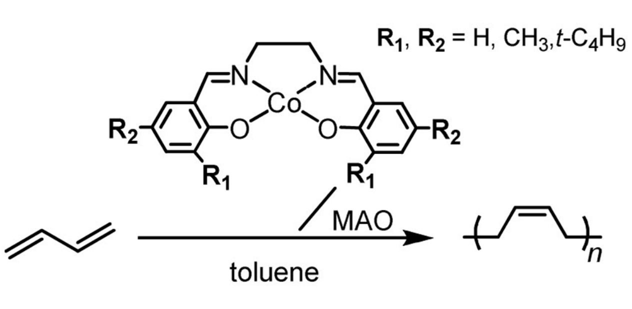


Figure 13. Butadiene polymerization with (salen) Co(II) complexes and MAO.

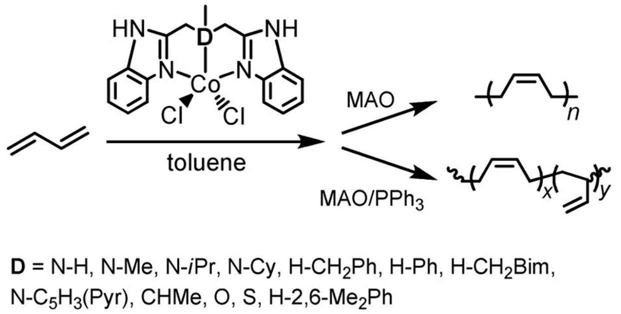


Figure 14. Butadiene polymerization by bis (benzimidazole) Co(II)Cl_2 complexes in combination with MAO and MAO/PPh_3

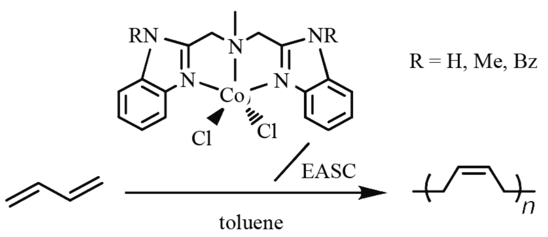


Figure 15. Butadiene polymerization by (dibenzimidazolyl) Co(II) Cl_2–EASC

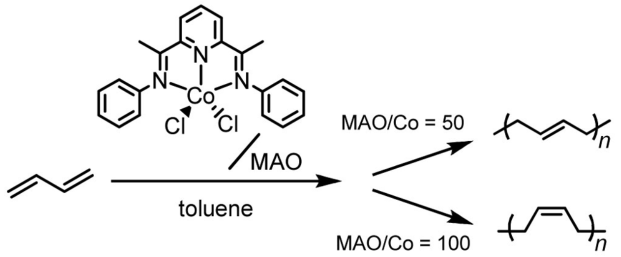


Figure 16. Butadiene polymerization by bis(imino)pyridyl Co(II) Cl_2–MAO

not affect the polymer microstructure. The addition of PPh_3 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 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 $[Py(Bm\text{-}R)_2]CoCl_2$ (Py=pyridyl; Bm= benzimidazolyl, R=H; Me; Bz) by combining tridentate 2,6-bis(benzimidazolyl)pyridine ligands with $CoCl_2$. 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

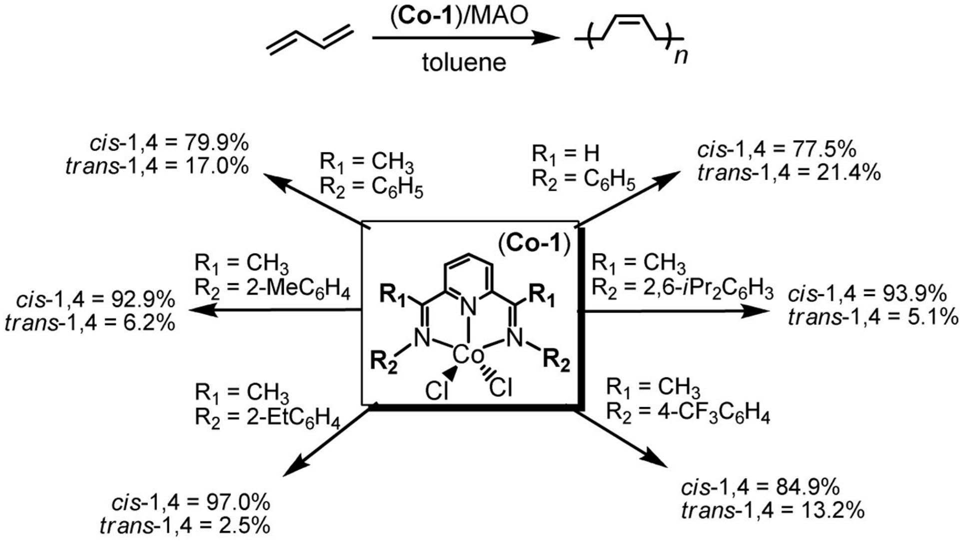


Figure 17. Synthesis of cis-1,4 poly(butadiene) by bis(imino) pyridyl-Co(II)Cl_2–MAO

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., $Ni(naph)_2$–$AlEt_2Cl$–H_2O, naph = naphthenate; $NiCp_2$–MAO; $Ni(acac)_2$–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 $AlEt_3$–$Ni(octanoate)_2$–$BF_3 \times OEt_2$ 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 acquo ligand was reported to be moderately active in the polymerization of 1,3-butadiene (*cis*-1,4, 92%) [122]. A dicationic Ni complex $[(dppf)Ni(MeCN)_4][BF_4]_2$ in combination with $AlEt_2Cl$ 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]. $Ni(bipy)Et_2$ cyclooligomerized butadiene to cyclo-dodecatriene [124].

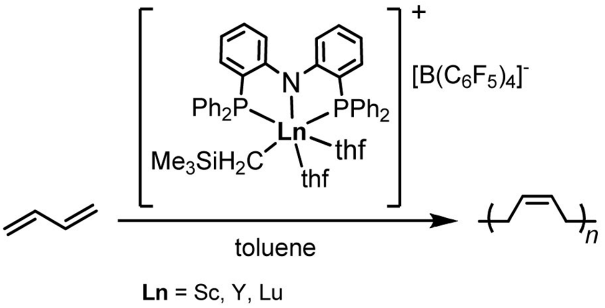


Figure 18. Butadiene polymerization by bis(phosphinophenyl) amido lanthanide complexes

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., $Nd(acac)_3$; Nd-2-ethyl-hexanoate, $Nd(OCOC_7H_{15})_3$) with a chlorine donor (e.g., $AlEt_2Cl$; $Al_2Et_3Cl_3$, *tert*-butyl chloride) and an aluminum alkyl (e.g., Al*i*Bu_3; Al*i*Bu_2H) [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 $AlEt_2Cl$–$Nd(OCOR)_3$–Al(*i*Bu)$_3$ (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 $[Ln(\eta^5\text{-}C_5Me_4SiMe_3)\{(\mu\text{-}Me)_2(AlMe_2)\}_2]$ (Ln = La, Nd) upon activation with $[Ph_3C]^+[BPh_4]^-$ and in presence of Al(*i*Bu)$_3$ 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

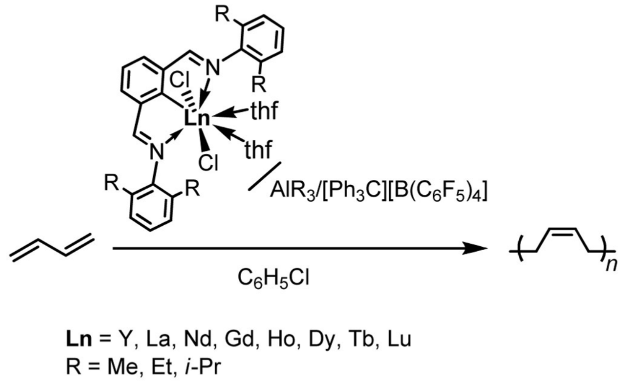


Figure 19. Butadiene polymerization by NCN–lanthanide complexes

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 = 1.05–1.13) 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 $[Ph_3C][B(C_6F_5)_4]$ [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 [(R = 2,6-iPr$_2$C$_6$H$_3$, 2,6-Et$_2$C$_6$H$_3$, 2,6-Me$_2$C$_6$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].

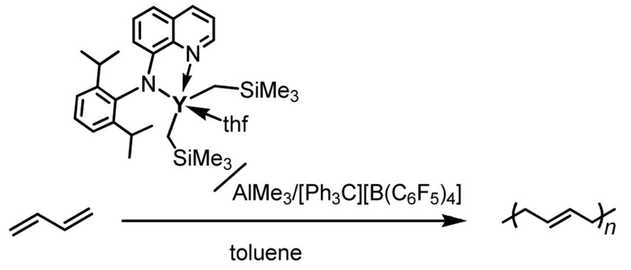


Figure 20. Butadiene polymerization by rare earth metal bis(alkyl)s complexes bearing a non-Cp quinolinyl aniline ligand, upon the activation by aluminium alkyls and organoborates

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 ≥ 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.

REFERENCES

1. Porri L, Giarrusso A (1989) Conjugated diene polymerization. In: Eastmond G, Ledwith A, Russo S, Sigwalt P (eds) Comprehensive polymer science. Pergamon, Oxford, 53-108
2. Thiele SKH, Wilson DR (2003) Alternate transition metal complex based diene polymerization. J Macromol Sci, Polym Rev C 43:581-628
3. Osakada K, Takeuchi D (2004) Coordination polymerization of dienes, allenes, and methylenecycloalkanes. Adv Polym Sci 171:137-194
4. Ricci G, Masi F, Boglia A, Sommazzi A, Ricci M (2007) In: Yamamoto K (ed) Advances in organometallic chemistry research. Nova Science, USA, 1-36
5. Ricci G, Sommazzi A, Masi F, Ricci M, Boglia A, Leone G (2010) Well-defined transition metal complexes with phosphorus and nitrogen ligands for 1,3-dienes polymerization. Coord Chem Rev 254:661-676
6. Friebe L, Nuyken O, Obrecht W (2006) Neodymium-based Ziegler/Natta catalysts and their application in diene polymerization. Adv Polym Sci 204:1-154
7. Sinn H, Bliemeister J, Clausnitzer D, Winter L, Zarncke O (1998) In: Kaminsky W, Sinn H (eds) Transition metals and organometallics as catalysts for olefin polymerization. Springer-Verlag, Berlin Heidelberg, New York, 257-268
8. Bliemeister J, Hagendorf W, Harder A, Heitmann B, Schimmel I, Schmedt E, Schnuchel W, Sinn H, Tikwe L, von Thiene N, Urlass K, Winter H, Zarncke O (1995) In: Fink G, Mülhaupt R, Brintzinger HH (eds) Ziegler catalysts. Springer-Verlag, Berlin Heidelberg, New York, 57-82
9. Ricci G, Italia S, Comitani C, Porri L (1991) Polymerization of conjugated dialkenes with transition metal catalysts. Influence of methylaluminoxane on catalyst activity and stereospecificity. Polym Commun 32:514-517
10. Ricci G, Italia S, Porri L (1994) Polymerization of 1,3-dienes with methylaluminoxane-triacetylacetonatovanadium. Macromol Chem Phys 195:1389-1397
11. Ricci G, Porri L (1997) Polymerization of 4-methyl-1,3-pentadiene with MAO/Ti(OnBu)$_4$. The influence of preparation/ageing temperature upon the stereospecificity of the catalyst. Polymer 38:4499-4503
12. Ricci G, Zetta L, Alberti E, Motta T, Canetti M, Bertini F (2007) Butadiene–isoprene copolymerization with V(acac)$_3$-MAO. Crystalline and amorphous trans-1,4 copolymers. J Polym Sci, Part A: Polym Chem 45:4635-4646
13. Zambelli A, Ammendola P, Proto A (1989) Synthesis of syndiotactic poly-1,2-(4-methyl-1, 3-pentadiene). Macromolecules 22:2126-2128
14. Oliva L, Longo P, Grassi A, Ammendola P, Pellecchia C (1990) Polymerization of 1, 3-alkadienes in the presence of Ni-and Ti-based catalytic systems containing methylalumoxane. Die Makromol Chem, Rapid Commun 11:519-524
15. Venditto V, De Rosa C, Guerra G, Napolitano R (1992) X-Ray diffraction, conformational analysis and stereoregularity of a crystalline poly (3-methyl-1,3-pentadiene). Polymer 33:3547-3551
16. Ricci G, Italia S, Giarrusso A, Porri L (1993) Polymerization of 1,3-dienes with the soluble catalyst system methylaluminoxanes-[CpTiCl$_3$]. Influence of monomer structure on polymerization stereospecificity. J Organomet Chem 451:67-72
17. Ricci G, Panagia A, Porri L (1996) Polymerization of 1,3-dienes with catalysts based on mono- and bis-cyclopentadienyl derivatives of vanadium. Polymer 37:363-365
18. Ricci G, Bosisio C, Porri L (1996) Polymerization of 1,3-butadiene, 4-methyl-1,3-pentadiene and styrene with catalyst systems based on biscyclopentadienyl derivatives of titanium. Macromol Chem, Rapid Commun 17:781-785
19. Porri L, Ricci G, Giarrusso A (1999) In: Kaminsky W (ed) Metal organic catalysts for synthesis and polymerization. Springer-Verlag, Berlin, Heidelberg, 519-530
20. Porri L, Giarrusso A, Ricci G (2000) In: Scheirs J, Kaminsky W (eds) Metallocene-based polyolefins. John Wiley, New York, 115-141
21. Longo P, Oliva P, Proto A, Zambelli A (1996) Low-temperature polymerization of some

conjugated diolefins in the presence of group 4 metal catalysts. Gazz Chim Ital 126:377-382

22. Ricci G, Italia S, Porri L (1994) Polymerization of (Z)-1, 3-pentadiene with $CpTiCl_3$/MAO. Effect of temperature on polymer structure and mechanistic implications. Macromolecules 27:868-869
23. Ricci G, Alberti E, Zetta L, Motta T, Bertini F, Mendichi R, Arosio P, Famulari A, Meille SV (2005) Synthesis, characterization and molecular conformation of syndiotactic 1,2 polypentadiene: the cis polymer. Macromolecules 38:8353-8361
24. Longo P, Guerra G, Grisi F, Pizzuti S, Zambelli A (1998) Chemoselective mechanism of (Z)-1,3-pentadiene polymerization in the presence of cyclopentadienyltitaniumtrichloride and methylaluminoxane. Macromol Chem Phys 199:149-154
25. Ricci G, Porri L (1997) Chemoselective mechanism of (Z)-1,3-pentadiene polymerization in the presence of cyclopentadienyltitaniumtrichloride and methylaluminoxane. Macromol Chem Phys 198:3647-3650
26. Johnson LK, Killian CM, Brookhart M (1995) New Pd (II)-and Ni (II)-based catalysts for polymerization of ethylene and. alpha.-olefins. J Am Chem Soc 117:6414-6415
27. Killian CM, Tempel DJ, Johnson LK, Brookhart M (1996) Living polymerization of α-olefins using niII-α-diiminecatalysts. Synthesis of new block polymers based on α-olefins. J Am Chem Soc 118:11664-11665
28. Killian CM, Johnson LK, Brookhart M (1997) Preparation of linear α-olefins using cationic nickel (II) α-diimine catalysts. Organometallics 16:2005-2007
29. Mecking S, Johnson LK, Wang L, Brookhart M (1998) Mechanistic studies of the palladium-catalyzed copolymerization of ethylene and α-olefins with methyl acrylate. J Am Chem Soc 120:888-899
30. Svejda SA, Johnson LK, Brookhart M (1999) Low-temperature spectroscopic observation of chain growth and migratory insertion barriers in (α-Diimine) Ni (II) olefin polymerization catalysts. J Am Chem Soc 121:10634-10635
31. Ittel SD, Johnson LK, Brookhart M (2000) Late-metal catalysts for ethylene homo- and copolymerization. Chem Rev 100:1169-1203
32. Gate DP, Svejda SA, Oñate E, Killian CM, Synthesis of branched polyethylene using (α-diimine) nickel (II) catalysts: influence of temperature, ethylene pressure, and ligand structure on polymer properties. Johnson LK, White PS, Brookhart M (2000) Macromolecules 33:2320-2324
33. Tempel DJ, Johnson LK, Huff PS, Brookhart M (2000) Mechanistic studies of Pd (II)-α-diimine-catalyzed olefin polymerizations. J Am Chem Soc 122:6686-6700
34. Shultz LH, Tempel DJ, Brookhart M (2001) Palladium (II) β-agostic alkyl cations and alkyl ethylene complexes:investigation of polymer chain isomerization mechanisms. J Am Chem Soc 123:11539-11555
35. Shultz LH, Brookhart M (2001) Measurement of the barrier to β-hydride elimination in a β-agostic palladium−ethyl complex: a model for the energetics of chain-walking in (α-diimine)PdR+ olefin polymerization catalysts. Organometallics 20:3975-3982
36. Leatherman MD, Svejda SA, Johnson LK, Brookhart M (2003) Mechanistic studies of nickel(II) alkyl agostic cations and alkyl ethylene complexes: investigations of chain propagation and isomerization in (α-diimine)Ni(II)-catalyzed ethylene polymerization. J Am Chem Soc 125:3068-3081
37. Mecking S (2001) Olefin polymerization by late transition metal complexes—a root of Ziegler catalysts gains new ground. Angew Chem Int Ed 40:534-540
38. Britovsek GJP, Gibson VC, Kimberley BS, Maddox PJ, McTavish SJ, Solan GA, White AJP, Williams DJ (1998) Novel olefin polymerization catalysts based on iron and cobalt. Chem Commun 7:849-850
39. Small BL, Brookhart M, Bennett AMA (1998) Highly active iron and cobalt catalysts for the polymerization of ethylene. J Am Chem Soc 120:4049-4050
40. Small BL, Brookhart M (1998) Iron-based catalysts with exceptionally high activities and selectivities for oligomerization of ethylene to linear α-olefins. J Am Chem Soc 120:7143-7144
41. Bennet AMA (1999) Novel, highly active iron and cobalt catalysts for olefin polymerization. Chem tech 29:24-28
42. Britovsek GJP, Bruce M, Gibson VC, Kimberley BS, Maddox PJ, Mastroianni S, McTavish SJ, Redshaw C, Solan GA, Stromberg S, White

AJP, Williams DJ (1999) Iron and cobalt ethylene polymerization catalysts bearing 2,6-bis (imino) pyridyl ligands: synthesis, structures, and polymerization studies. J Am Chem Soc 121:8728-8740

43. Britovsek GJP, Mastroianni S, Solan GA, Baugh SPD, Redshaw C, Gibson VC, White, AJP, Williams, AJP, Elsegood MRJ (2000) Oligomerisation of ethylene by bis (imino) pyridyliron and-cobalt complexes. Chem Eur J 6:2221-2231
44. Ricci G, Battistella M, Porri L (2001) Chemoselectivity and stereospecificity of chromium (II) catalysts for 1,3-diene polymerization. Macromolecules 34:5766-5769
45. Ricci G, Battistella M, Bertini F, Porri L (2002) 1,2 Syndiotactic polybutadiene of controlled crystallinity by butadiene-isoprene copolymerization with $CrCl_2(dmpe)_2$-MAO.Polym Bull 48:25-31
46. Bazzini C, Giarrusso A, Porri L (2002) Diethylbis (2,2′-bipyridine) iron/MAO. A very active and stereospecific catalyst for 1,3-diene polymerization. Macromol Rapid Commun 23:922-927
47. Ricci G, Morganti D, Sommazzi A, Santi R, Masi F (2003) Polymerization of 1,3-dienes with iron complexes based catalysts: influence of the ligand on catalyst activity and stereospecificity. J Mol Cat A: Chem 204/205:287-293
48. Bazzini C, Giarrusso A, Porri L, Pirozzi B, Napolitano R (2004) Synthesis and characterization of syndiotactic 3,4-polyisoprene prepared with diethylbis (2,2′-bipyridine) iron–MAO. Polymer 45:2871-2875
49. Pirozzi B, Napolitano R, Petraccone V, Esposito S (2004) Determination of the crystal structure of syndiotactic 3,4-poly(2-methyl-1,3-butadiene) by molecular mechanics and X-ray diffraction. Macromol Chem Phys 205:1343-1350
50. Ricci G, Forni A, Boglia A, Sonzogni M (2004) New chromium (II) bidentate phosphine complexes: synthesis, characterization, and behavior in the polymerization of 1,3-butadiene. Organometallics 23:3727-3732
51. Ricci G, Forni A, Boglia A, Motta T (2005) Synthesis, structure, and butadiene polymerization behavior of alkylphosphine cobalt (II) complexes. J Mol Cat A: Chem 226:235-241
52. Ricci G, Forni A, Boglia A, Motta T, Zannoni G, Canetti M, Bertini F (2005) Synthesis and X-ray structure of $CoCl_2(PiPrPh_2)_2$. A new highly active and stereospecific catalyst for 1,2 polymerization of conjugated dienes when used in association with MAO. Macromolecules 38:1064-1070
53. Ricci G, Forni A, Boglia A, Sommazzi A, Masi F (2005) Synthesis, structure and butadiene polymerization behavior of $CoCl_2(PR_xPh_{3-x})_2$ (R = methyl, ethyl, propyl, allyl, isopropyl, cyclohexyl; x = 1, 2). Influence of the phosphorous ligand on polymerization stereoselectivity. J Organomet Chem 690:1845-1854
54. Ricci G, Boglia A, Motta T (2007) Synthesis of new Cr(II) complexes with bidentate phosphine ligands and their behavior in the polymerization of butadiene: Influence of the phosphine bite angle on catalyst activity and stereoselectivity. J Mol Cat A: Chem 267:102-107
55. Ricci G, Boglia A, Boccia AC, Zetta L (2007) Chromium catalysts for butadiene and norbornene polymerization. Macromol Symp 260:172-178
56. Ricci G, Motta T, Boglia A, Alberti E, Zetta L, Bertini F, Arosio P, Famulari A, Meille SV (2005) Synthesis, characterization, and crystalline structure of syndiotactic 1,2-polypentadiene: the trans polymer. Macromolecules 38:8345-8352
57. Ricci G, Boglia A, Motta T, Bertini F, Boccia A.C, Zetta L, Alberti E, Famulari A, Arosio P, Meille SV (2007) Synthesis and structural characterization of syndiotactic trans-1,2 and cis-1,2-polyhexadienes. J Polym Sci, Part A: Polym Chem 45:5339-5353
58. Ricci G, Bertini F, Boccia AC, Zetta L, Alberti E, Pirozzi B, Giarrusso A, Porri L (2007) Synthesis and characterization of syndiotactic 1,2-poly (3-methyl-1,3-pentadiene). Macromolecules, 40:7238-7243
59. Pirozzi B, Napolitano R, Giusto G, Esposito S, Ricci G (2007) Determination of the crystal structure of syndiotactic 1,2-poly(E-3-methyl-1,3-pentadiene) by X-ray diffraction and molecular mechanics. Macromolecules 40:8962-8968
60. Ricci G, Leone G, Boglia A, Bertini F, Boccia AC, Zetta L (2009) 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. Macromolecules 48:3048-3056
61. Ricci G, Sommazzi A, Leone G, Boglia A, Masi F (2012) In: Ming Y C, Da-Xia Y (eds) Phosphorus:

Properties, Health effects and the Environment. Nova Science, USA, 53-94

62. Leone G, Boccia A C, Ricci G, Giarrusso A, Porri L (2013) Polymerization of (E)-1,3-pentadiene and (E)-2-methyl-1,3-pentadiene with neodymium catalysts. Examination of the factors that affect the stereoselectivity. J Polym Sci Part A: Polym Chem 51:3227-3232
63. Porri L (1981) In: Ciardelli F, Giusti P (eds) Structural order in polymers. Pergamon, Oxford, 51-62
64. Porri L, Giarrusso A, Ricci G (1991) Recent views on the mechanism of diolefin polymerization with transition metal initiator systems. Prog Polym Sci 16:405-441
65. Porri L, Giarrusso A, Ricci G (1991) The polymerization of conjugated dialkenes to isotactic and syndiotactic polymers. Effect of ligands on the stereospecificity. Makromol Chem, Macromol Symp 48/49:239-243
66. Porri L, Giarrusso A, Ricci G (1994) Mechanism of the steoreospecific polymerization of conjugated dienes: new insights and open questions. Polym Sci. 36:1421-1432
67. Porri L, Giarrusso A, Ricci G (2002) On the mechanism of formation of isotactic and syndiotactic polydiolefins. Macromol Symp 178:55-68
68. Lopez-Sanchez JA, Lamberti M, Pappalardo D, Pellecchia C (2003) Polymerization of conjugated dienes promoted by bis (phenoxyimino) titanium catalysts. Macromolecules 36:9260-9263
69. Annunziata L, Pragliola S, Pappalardo D, Tedesco C, Pellecchia C (2011) New (anilidomethyl) pyridine titanium (IV) and zirconium (IV) catalyst precursors for the highly chemo-and stereoselective cis-1, 4-polymerization of 1, 3-Butadiene. Macromolecules 44:1934-1941
70. Milione S, Cuomo C, Capacchione C, Zannoni C, Grassi A, Proto A (2007) Stereoselective polymerization of conjugated dienes and styrene-butadiene copolymerization promoted by octahedral titanium catalyst. Macromolecules 40:5638-5643
71. Natta G, Porri L, Corradini P, Morero D (1958) Polimerizzazioni stereospecifiche di diolefine coniugate. Nota I. Sintesi e struttura di polidiolefine a concatenamento 1,4-trans. Chim Ind 40: 362-371
72. Natta G, Porri L, Mazzei A (1959) Polimerizzazioni stereospecifiche di diolefine coniugate. Nota II Polimerizzazioni del butadiene con catalizzatori preparati da alluminio alchili e cloruri solubili di vanadio. Chim Ind 41:116122
73. Natta G, Porri L, Carbonaro A (1961) Stereospecificità di catalizzatori omogenei preparati da VCl_3 nella polimerizzazione di diolefine coniugate. Atti Accad Naz Lincei, Rend Cl Sci Fis Mat Nat 31(5):189-197
74. Porri L, Carbonaro A, Ciampelli F (1963) Copolymerization of 1,3-butadiene and 1,3-pentadiene with homogeneous $Al(C_2H_5)_2Cl$-vanadium compounds catalyst systems. I. Preparation and properties of the copolymers. Makromol Chem 61:90-103
75. Colamarco E, Milione S, Cuomo C, Grassi A (2004) Homo- and copolymerization of butadiene catalyzed by an bis(imino)pyridyl vanadium complex. Macromol Rapid Commun 25:450-454
76. Natta G, Porri L, Zanini G, Palvarini A (1959) Polimerizzazioni stereospecifiche di diolefine coniugate. Nota V. Preparazione e proprietà del polibutadiene 1,2 isotattico
77. Ricci G, Leone G, Masi F, Sommazzi A (2011) In: Salden MP (ed) Chromium: environmental, medical and material studies. Nova Science, USA, 121-140
78. Cariou R, Chirinos J, Gibson VC Jacobsen G, Tomov AK, Elsegood MRJ (2009) 1,3-Butadiene polymerization by bis(benzimidazolyl)amine metal complexes: remarkable microstructural control and a protocol for in-reactor blending of trans-1,4-, cis-1,4-, and cis-1,4-co-1,2-vinylpolybutadiene. Macromolecules 42:1443-1444
79. Yamamoto A, Shimizu T, Ikeda SM (1970) Polymerization of vinyl monomers by alkyl-iron and alkyl-cobalt complexes. Makromol Chem 136:297-302
80. Zhang ZY, Zhang HJ, Ma HM, Wu Y (1982) A novel iron catalyst for the polymerization of butadiene. J Mol Catal 17:65-76
81. Ricci G, Leone G, Masi F, Sommazzi A (2011) In: Phillips ES (ed) Ferrocenes: compounds, properties and applications. Nova Science, USA, 273-313
82. Gong D, Dong W, Hu J, Zhang X, Jiang L (2009) Living polymerization of 1,3-butadiene by a Ziegler-Natta type catalyst composed of iron(III) 2-ethylhexanoate, triisobutylaluminum and diethyl phosphate. Polymer 50:2826-2829

83. Gong D, Jia X, Wang B, Zhang X, Jiang L (2012) Synthesis, characterization, and butadiene polymerization of iron(III), iron(II) and cobalt(II) chlorides bearing 2,6-bis(2-benzimidazolyl) pyridyl or 2,6-bis(pyrazol)pyridine ligand. J Organomet Chem 702:10-18
84. Nobbs JD, Tomov Ak, Cariou R, Gibson VC, White AJP, Britovsek GJP (2012) Thio-pybox and thio-pheboxcomplexes of chromium, iron, cobalt and nickel and their application in ethylene and butadiene polymerisation catalysis. Dalton Trans 41:5949-5964
85. Ricci G, Leone G, Boglia A, Masi F, Sommazzi A (2011) Cobalt: Characteristics, compounds, and applications. Vidmar LJ (ed) Nova Science, USA, 39-81
86. Racanelli P, Porri L (1970) Cis-1,4-polybutadiene by cobalt catalysts. Some features of the catalysts prepared from alkyl aluminium compounds containing Al-O-Al Bonds. Eur Polym J 6:751-761
87. Cooper W, Eaves DE, Vaughan G (1966) Electron donors in diene polymerization. Adv Chem Ser 52:46-66
88. Deb Nath DC, Shiono T, Ikeda T (2002) Effects of halogen ligands on 1,3-butadiene polymerization with cobalt dihalides and methylaluminoxane. Macromol Chem Phys 203:1171-1177
89. Deb Nath DC, Shiono T, Ikeda T (2003) Polymerization of 1,3-butadiene by cobalt dichloride activated with various methylaluminoxanes. Appl Catal A-Gen 238:193-199
90. Takeushi M, Shiono T, Soga K (1992) Polymerization of 1,3-butadiene with the catalyst system composed of a cobalt compound and methylaluminoxane. Polym Int 29:209-212
91. Takeushi M, Shiono T, Soga K (1995) Polymerization of 1,3-butadiene with $MgCl_2$-supported cobalt catalysts activated by ordinary alkylaluminums. Polym Int 36:41-45
92. Takeushi M, Shiono T, Soga K (1995) Characterization of polybutadiene produced with $CoBr_2(PPh_3)_2$-based catalysts. Macromol Rapid Commun 16:373-378
93. Nath DCD, Shiono T, Ikeda T (2003) Additive effect of triphenylphosphine on the living polymerization of 1,3-butadiene with a cobalt dichloride-methylaluminoxane catalytic system. Macromol Chem Phys 204:2017-2022
94. Cai Z, Shinzawa M, Nakayama Y, Shiono T (2009) Synthesis of regioblock polybutadiene with $CoCl_2$-based catalyst via reversible coordination of lewis base. Macromolecules 42:7642-7643
95. Furukawa J, Haga K, Kobayashi E, Iseda Y, Yoshimoto T, Sakamoto K (1971) Cis-vinyl-1:1 Polymer of butadiene. Polym J 2:371-378
96. Ashitaka H, Isikawa H, Ueno H (1983) Syndiotactic 1,2-polybutadiene with Co-CS_2 catalyst system. I. Preparation, properties, and application of highly crystalline syndiotactic 1,2-polybutadiene. J Polym Sci, Part A: Polym Chem 21:1853-1860
97. Ashitaka H, Jinda K, Ueno H (1983) Syndiotactic 1,2-polybutadiene with Co-CS_2 catalyst system. II. Catalysts for stereospecific polymerization of butadiene to syndiotactic 1,2-polybutadiene. J Polym Sci, Part A: Polym Chem 21:1951-1972
98. Ashitaka H, Inaishi K, Ueno H (1983) Syndiotactic 1,2-polybutadiene with Co-CS_2catalyst system. III.^{1}H- and ^{13}C-NMR study of highly syndiotactic 1,2-polybutadiene. J Polym Sci, Part A: Polym Chem 21:1973-1988
99. Ashitaka H, Jinda K, Ueno H (1983) Syndiotactic 1,2-polybutadiene with Co-CS_2 catalyst system. IV. Mechanism of syndiotactic polymerization of butadiene with cobalt compounds–organoaluminum–CS_2. J Polym Sci, Part A: Polym Chem 21:1989-1995
100. Ricci G, Boglia A, Santi R, Sommazzi A, Masi F (2003) Procedimento per la preparazione di polibutadiene a contenuto variabile cis-1,4/1,2, Italian Patent MI03A 001807
101. Ricci G, Boglia A, Forni A, Santi R, Sommazzi A, Masi F (2003) Complessi fosfinici di cobalto e procedimento per la loro preparazione, Italian Patent MI 03A 001808
102. Ricci G, Boglia A, Santi R, Sommazzi A, Masi F (2003) Procedimento per la preparazione di polibutadiene ad alto contenuto in unità 1,2, Italian Patent MI03A 001809
103. Dierkes P, van Leeuwen PWNM (1999) The bite angle makes the difference: a practical ligand parameter for diphosphine ligands. J Chem Soc, Dalton Trans 1519-1530
104. van Leeuwen PWNM, Kamer CJ, Reek JNH, Dierkes P (2000) Ligand bite angle effects in metal-catalyzed C-C bond formation. Chem Rev 100:2741-2770
105. Freixa Z, van Leeuwen PWNM (2003) Bite angle effects in diphosphinemetal catalysts: steric or electronic? Dalton Trans 10:1890-1901

106. Tolman C (1977) Steric effects of phosphorus ligands in organometallic chemistry and homogeneous catalysis. Chem Rev 77:313-348
107. Kim JS, Ha CS, Kim II (2006) Highly stereospecific polymerization of 1,3-butadiene with cobalt(II) pyridylbis(imine) complexes. e-Polymer 27
108. Endo K, Kitagawa T, Nakatani K (2006) Effect of an alkyl substituted in salen ligands on 1,4-cis selectivity and molecular weight control in the polymerization of 1,3-butadiene with (salen) Co(II) complexes in combination with methylaluminoxane. J Polym Sci, Part A: Polym Chem 44:4088-4094
109. Cariou R, Chirinos JJ, Gibson VC, Jacobsen G, Tomov AK, Britovsek GJP, White AJP (2010) The effect of the central donor in bis(benzimidazole)-based cobalt catalysts for the selective cis-1,4 polymerisation of butadiene. Dalton Trans 39:9039-9045
110. Appukuttan V, Zhang L, Ha CS, Kim II (2009) Highly active and stereospecific polymerizations of 1,3-butadiene by using bis(benzimidazolyl) amine ligands derived Co(II) complexes in combination with ethylaluminumsesquichloride. Polymer 50:1150-1158
111. Gong D, Wang B, Bai C, Bi J, Wang F, Dong W, Zhang X, Jiang L (2009) Metal dependent control of cis-/trans-1,4 regioselectivity in 1,3-butadiene polymerization catalyzed by transition metal complexes supported by 2,6-bis[1-(iminophenyl) ethyl]pyridine. Polymer 50:6259-6264
112. Appukuttan V, Zhang L, Ha JY, Chandran D, Bahuleyan BK, Ha CS, Kim II (2010) Stereospecific polymerizations of 1,3-butadiene catalyzed by Co(II) complexes ligated by 2,6-bis(benzimidazolyl)pyridines. J Mol Cat A: Chem 325:84-90
113. Gong D, Wang B, Cai H, Zhang X, Jiang L (2011) Synthesis, characterization and butadiene polymerization studies of cobalt(II) complexes bearing bisiminopyridine ligand. J Organomet Chem 696:1584-1590
114. Sato H, Yagi Y (1992) Studies on nickel-containing Ziegler-type catalysts. I. New catalysts for high-cis-1,4 polybutadiene. Bull Chem Soc Jpn 65:1299-1302
115. Longo P, Grisi F, Proto A, Zambelli A (1998) New Ni(II) based catalysts active in the polymerization of olefins. Macromol Rapid Commun 19:31-34
116. Throckmorton MC, Saltman WM (1971), German Patent 2113527, (ChemAbstr 79, 67631, 1973)
117. Taube R, Gehrke J, Bohme P, Kottnitz J (1990) Komplexkatalyse XXXIV. Darstellung und charakterisierungkationischer η_3,η_2-Octa-2(E),7-dien-1-yl(ligand) nickel(II)-komplexe [Ni(C_8H_{13})L] X (X = PF6, BF_4; L = PIII-Ligand) alskatalysatoren der stereospezifischenbutadien polymerisation. J Organomet Chem 395:341-358
118. Sato H, Yasui S (1992) Studies on nickel-containing Ziegler-type catalysts. II. Low molecular weight (liquid) poly(diene)s with 1,4-microstructure. Bull Chem Soc Jpn 65:1307-1311
119. Sieler J, Kempe R, Wache S, Taube R (1993) Komplexkatalyse: XLI. Die Kristallstruktur des η_3,η_2-Octa-2(E),7-dien-1-yl-(triphenylphosphin) nickel(II)-tetrafluoroborats, ein beitragzur Klärung der Koordinationsverhältnisse in der kelkomplexkatalysierten butadien polymerisation. J Organomet Chem 455:241-246
120. Taube R, Maiwald S, Sommer C (2002) Highly active single-site catalysts for the 1,4-cis polymerization of butadiene from allylneodymium(III) chlorides and trialkylaluminiums – a contribution to the activation of tri(allyl)neodymium(III) and the further elucidation of the structure-activity relationship. Macromol Chem Phys 203:1029-1039
121. Kim JS, Chadran D, Park DW, Ha CS, Kim I (2007) Polymerization of 1,3-butadiene with nickel(II) alpha-diiminecomplexes combined with ethylaluminumsesquischloride. Stud Surf Sci Catal 172:525-526
122. Campora J, Ortiz de la Tabla L, Palma P, Alvarez E, Lahoz F, Mereiter K (2006) Synthesis and catalytic activity of cationic allylcomplexes of nickel stabilized by a single *N*-heterocyclic carbene ligand. Organometallics 25:3314-3316
123. Gerbase AE, de Souza RF, de Souza Vichi EJ, Vieira da Cunha F (1996) Stereoselective polymerization of butadiene by a new dicationic nickel complex. Angew Makromol Chem 239:33-41
124. Yamamoto A, Morifuji K, Ikeda S, Saito T, Uchida Y, Misono A (1965) Butadiene polymerization catalysts. Diethylbis(dipyridyl) iron and diethyldipyridyl nickel. J Am Chem Soc 87:4652-4653
125. Ai P, Chen L, Guo Y, Jie S, Li B (2012) Polymerization of 1,3-butadiene catalyzed by

cobalt(II) and nickel(II) complexes bearing imino- or amino-pyridylalcohol ligands in combination with ethylaluminumsesquichloride. J Organomet Chem 705:51-58

126. Cabassi F, Italia S, Ricci G, Porri L (1988) In: Quirk RP(ed) Transition metal catalyzed polymerizations. Cambridge Univ, MA, USA 655-670
127. Ricci G, Italia S, Cabassi F, Porri L (1987) Neodymium catalysts for 1,3-diene polymerization: influence of the preparation conditions on activity. Polym Commun 28:223-226
128. Wilson DJ, Jenkins DK (1992) Butadiene polymerisation using ternary neodymium-based catalyst systems. Polym Bull 27:407-411
129. Porri L, Ricci G, Shubin N (1998) Polymerization of 1,3-dienes with neodymium catalysts. Macromol Symp 128:53-61
130. Porri L, Ricci G, Giarrusso A, Shubin N, Lu Z (2000) In: Arjunan P, McGrath JC, Hanlon T (eds) ACS Symposium Series 749 - Olefin polymerization: emerging frontiers. Oxford University, USA, 15-30
131. Robert D, Spaniol TP, Okuda J (2008) Neutral and monocationic half-sandwich methyl rare-earth metal complexes: synthesis, structure, and 1,3-butadiene polymerization catalysis. Eur J Inorg Chem 2008:2801-2809
132. Wang D, Li S, Liu X, Gao W, Cui D (2008) Thiophene-NPN ligand supported rare-earth metal bis(alkyl) complexes. Synthesis and catalysis toward highly trans-1,4 selective polymerization of butadiene. Organometallics 27:6531-6538
133. Sugiyama H, Gambarotta S, Yap GPA, Wilson DR, Thiele SKH (2004) Preparation of an active neodymium catalyst for regioselective butadiene cis-polymerization supported by a dianionic modification of the 2,6-diiminopyridine ligand. Organometallics 23:5054-5061
134. Zhang L, Suzuki T, Luo Y, Nishiura M, Hou Z (2007) Cationic alkyl rare-earth metal complexes bearing an ancillary bis(phosphinophenyl) amidoligand: a catalytic system for living cis-1,4-polymerization and copolymerization of isoprene and butadiene. Angew Chem Int Ed 46:1909-1913
135. Gao W, Cui D (2008) Highly cis-1,4 selective polymerization of dienes with homogeneous Ziegler-Natta catalysts based on NCN-pincer rare earth metal dichloride precursors. J Am Chem Soc 130:4984-4991
136. Liu D, Cui D (2011) Highly trans-1,4 selective (co-)polymerization of butadiene and isoprene with quinolylanilido rare earth metal bis(alkyl) precursors. Dalton Trans 40:7755-7761
137. Pirozzi B, Napolitano R, Petraccone V, Esposito S (2004) Determination of the crystal structure of syndiotactic 3,4-poly(2-methyl-1,3-butadiene) by molecular mechanics and X-ray diffraction. Macromol Chem Phys 205:1343-1350
138. Zhang L, Luo Y, Hou Z (2005) Unprecedented isospecific 3,4-polymerization of isoprene by cationic rare earth metal alkyl species resulting from a binuclear precursor. J Am Chem Soc 127:14562-14563
139. Nakajima Y, Hou Z (2009) Rare-earth-metal/platinum heterobinuclear complexes containing reactive Ln-alkyl groups (Ln = Y, Lu): synthesis, structural characterization, and reactivity. Organometallics 28:6861-6870
140. Ricci G, Leone G, Boglia A, Boccia AC, Zetta L (2009) Cis-1,4-alt-3,4 polyisoprene: synthesis and characterization. Macromolecules 42:9263-9267
141. Ricci G, Motta T, Boglia A, Alberti E, Zetta L, Bertini F, Arosio P, Famulari A, Meille SV (2005) Synthesis, characterization, and crystalline structure of syndiotactic 1,2-polypentadiene: the trans polymer. Macromolecules 38:8345-8352
142. Ricci G, Boglia A, Motta T, Bertini F, Boccia AC, Zetta L, Alberti E, Famulari A, Arosio P, Meille SV (2007) Synthesis and structural characterization of syndiotactic trans-1,2 and cis-1,2 polyhexadienes. J Polym Sci, Part A: Polym Chem 45:5339-5353
143. Ricci G, Bertini F, Boccia AC, Zetta L, Alberti E, Pirozzi B, Giarrusso A, Porri L (2007) Synthesis and characterization of syndiotactic 1,2-poly(3-methyl-1,3-pentadiene).Macromolecules 40:7238-7243
144. Pirozzi B, Napolitano R, Giusto G, Esposito S, Ricci G (2007) Determination of the crystal structure of syndiotactic 1,2-poly(E-3-methyl-1,3-pentadiene) by X-ray diffraction and molecular mechanics. Macromolecules 40:8962-8968
145. Boccia AC, Leone G, Boglia A, Ricci G (2013) Novel stereoregular cis-1,4 and trans-1,2 poly(diene)s: synthesis, characterization, and mechanistic considerations. Polymer 54:3492-3503