

Polymerization of 1,3-Conjugated Dienes with Rare-Earth Metal Precursors

Zhichao Zhang, Dongmei Cui, Baoli Wang, Bo Liu, and Yi Yang

Abstract This chapter surveys the publications except patents related to *cis*-1,4-, *trans*-1,4-, 3,4-regio-, and stereoselective polymerizations of 1,3-conjugated dienes with rare-earth metal-based catalytic systems during the past decade from 1999 to 2009. The concerned catalyst systems are classified into the conventional Ziegler–Natta catalysts, the modified Ziegler–Natta catalysts, and the single-site cationic systems composed of lanthanocene and noncyclopentadienyl precursors, respectively. For the conventional Ziegler–Natta catalysts of the most promising industry applicable recipe, the multicomponents based on lanthanide carboxylate or phosphate or alkoxide precursors, research works concern mainly about optimizing the catalyst preparation and polymerization techniques. Special emphases are put on the factors that influence the catalyst homogeneity, catalytic activity and efficiency, as well as *cis*-1,4-selectivity. Meanwhile, tailor-made lanthanide aryloxide and amide complexes are designed and fully characterized to mimic the conventional Ziegler–Natta catalysts, anticipated to elucidate the key processes, alkylation and cationization, for generating the active species. Regarding to the single-site catalytic systems generally comprising well-defined complexes containing lanthanide–carbon bonds, investigations cover their versatile catalytic activity and efficiency, and the distinguished regio- and stereoselectivity for both polymerization of dienes and copolymerization of dienes with alkenes. The correlation between the sterics and electronics of ligands and the molecular structures of the complexes and their catalytic performances are highlighted. The isolation of the probable active species in these polymerization processes from the stoichiometric reactions of the precursors with activators will be presented.

Keywords: Diene polymerization · Metallocene · Rare-earth metals · Specific polymerization · Ziegler–Natta

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Abbreviations

Ar	Aryl
BD	Butadiene
BR	Polybutadiene rubber
Bu	Butyl
CN	Coordination number
cot	Cyclooctatetraene
Cp	Cyclopentadienyl
d	Day(s)
DIBAC	Diisobutylaluminum chloride
DIBAH	Diisobutylaluminum hydride
DMAC	Dimethylaluminum chloride
DME	Dimethoxyethane
DMPE	1,2-Bis(dimethylphosphino)ethane
DMSO	Dimethyl sulfoxide
EASC	Ethylaluminum sesquichloride
equiv	Equivalent(s)
Et	Ethyl
Flu	Fluorenyl
FTIR	Fourier transform infrared spectroscopy
h	Hour(s)
Hex	Hexyl
HIBAO	Hexaisobutylaluminoxane
ⁱ Bu	Isobutyl
Ind	Indenyl
IP	Isoprene
ⁱ Pr	Isopropyl
IR	Polyisoprene rubber
L	Liter(s)
Ln	Rare-earth metal (i.e., Sc, Y, La–Lu)
MAO	Methylaluminoxane
Me	Methyl

Mes	Mesityl
min	Minute(s)
MMA	Methyl methacrylate
MMAO	Modified methylaluminoxane
ND	Neodecanoate
NDH	Neodecanoic acid
NdP	Neodymium bis(2-ethylhexyl)phosphate
NdV	Neodymium versatate
NHC	<i>N</i> -heterocyclic carbene
NMR	Nuclear magnetic resonance
NR	Natural rubber
Oct	Octyl
Ph	Phenyl
Phen	1,10-Phenanthroline
Pr	Propyl
Py	Pyridine
RT	Room temperature
SBR	Styrene–butadiene rubbers
SEC	Size exclusion chromatography
TBP	Tributylphosphate
^t Bu	Tertbutyl
TEA	Triethylaluminum
THF	Tetrahydrofuran
TIBA	Triisobutylaluminum
TMA	Trimethylaluminum
TNHA	Tri(<i>n</i> -hexyl)aluminum
TNOA	Tri(<i>n</i> -octyl)aluminum
TON	Turnover number
VT	Variable temperature

1 Introduction

One of the everlasting topics in macromolecule chemistry is to prepare polymers with designated properties through precisely controlling the microstructures of polymer chains. Thus, polymerizations of 1,3-conjugated dienes have been one of the most important processes via which the simple C₄–C₅ monomers transfer into polymeric materials possessing *cis*-1,4, *trans*-1,4, *iso*-3,4 (or 1,2), *syndio*-3,4 (or 1,2), and *atactic*-3,4 (or 1,2) regularities and versatile properties and wide applications. For instance, the *cis*-1,4-regulated polybutadiene (BR) is high-performance rubber that can blend with other elastomers to make tyres, whilst polyisoprene (IR) when its *cis*-1,4-regularity is over 98% meanwhile has high molecular weight can be applied as an alternative to natural rubber (NR). The *trans*-1,4-regulated polydienes are usually employed as an important component of tires-sides and tread rubbers

as well as shape-memory elastomers, the crystallinity of which is governed by *trans*-1,4-content. The 3,4-(or 1,2-) polydienes have attracted an increasing attention for they can be used to prepare high-value-added rubbers or long-life “green” tires such as those with wet-skid resistance and low-rolling resistance. 3,4-(or 1,2-) Polybutadienes could be amorphous, semicrystalline and crystalline depending on both the 3,4-(or 1,2-) regiospecificity and the iso- or syndiotactic stereoregularity.

Although the 1,3-conjugated dienes could be polymerized via radical and anionic mechanisms, it was the discovery of the Ziegler–Natta catalysts at the middle of 1950s that started the era of coordination polymerizations, which exhibited overwhelming advantages on governing the regio- and stereoregularity to afford polymers with designed properties. Shortly after this event, patents on the use of Ziegler–Natta catalysts for the specific polymerizations of 1,3-conjugated dienes were filed, and Co- and Ti-based catalysts were employed to the large-scale industrial application. The Ziegler–Natta type catalyst systems based on lanthanide (Ln) elements came to the researchers’ eyesight in 1964 when the Chinese scientists Shen et al. [1] discovered the binary lanthanide trichlorides combined with aluminum alkyls to initiate the highly *cis*-1,4-selective polymerization of butadiene albeit with low activity. Meanwhile, patents concerning the lanthanide binary catalyst systems and the succedent lanthanide ternary catalyst systems were submitted by Union Carbide Corporation and Goodyear, respectively [2–5]. Since 1980s, research on lanthanide catalysis toward polymerization of dienes had experienced a renaissance and become booming, as their superior performance than the Co-, Ti-, and Ni-based systems with respect to the activity and selectivity, less-gel formation as well as providing polymers with outstanding properties [6, 7]. For instance, *cis*-1,4-polymerization of butadiene with a Ziegler–Natta neodymium system affords polybutadiene, showing excellent abrasion and cracking resistance, raw polymer strength, and high tensile strength of the vulcanizates. Moreover, the residue of the catalysts does not arouse the aging performances except the cerium complexes owing to the stable trivalent oxidation state of lanthanide ions. Therefore, lanthanide η^3 -allyls, the homogeneous Ziegler–Natta catalyst systems composed of lanthanide carboxylates, phosphates, or alkoxides and coactivators aluminum alkyls or aluminum alkyl chlorides, have been extensively investigated for their behaviors toward the *cis*-1,4-polymerization of dienes. Some research works relating butadiene polymerization were reviewed by Shen, Kuran, and Obsrecht [6–9], respectively. Meanwhile investigation of the mechanism of Ziegler–Natta catalysts and the molecular structure of the active species were carried out, emphases have been drawn on the interaction between the cocatalysts with the tailor-made and fully characterized lanthanide precursors, part of which was summarized by Anwender [10]. Recently, the single-site cationic catalysts based on lanthanocene, half-sandwich lanthanocene, and lanthanide precursors bearing noncyclopentadienyl (non-Cp) ligands, respectively, have gathered an upsurge in research interests [11–13]. These well-defined precursors have exhibited distinguished high *cis*-1,4-selectivity, well control on molecular weight and molecular weight distribution of the resultant polymers, which are strongly influenced by the sterics and electronics and framework of the ligands attached to the central metal ions. This will be discussed in detail in this contribution.

Regarding *trans*-1,4-selective polymerization of dienes, catalysts showing both high activity and *trans*-1,4-selectivity are rather limited, among which the widely explored systems are based on Ti, V, and Fe metals [14–19], those based on rare-earth metals [20, 21] emerged only recently, which will be highlighted. Similarly, the 3,4-selective polymerization of isoprene (the corresponding 1,2-polymerization of butadiene with lanthanide-based catalysts has been an unexplored area) has also received less attention. The efficient catalyst systems are scarce and restricted to the smaller transition metal-based complexes, and in few cases the 3,4-selectivity is over 90% [22–27]. The landmark constrain-geometry-configuration half-sandwich lanthanocenes, and the *C*₂ symmetric non-Cp-ligated rare-earth metal complexes exhibiting high 3,4-selectivity or even stereoselectivity for the polymerization of isoprene, were just reported, which will be particularized. The copolymerization of dienes with alkenes *etc* monomers, providing new structural materials or high-added-value rubbers, has been reported less and usually suffers from the lowered activity and decreased molecular weight as well as broadened molecular weight distribution because of different polymerization mechanisms. Moreover, the amount of alkenes or dienes inserted into the copolymer chain remains low which is generally concomitant with the formation of homopolymers. Some recent breakthroughs in this research area will be presented at the last part of this chapter.

2 *cis*-1,4-Polymerization of 1,3-Conjugated Dienes

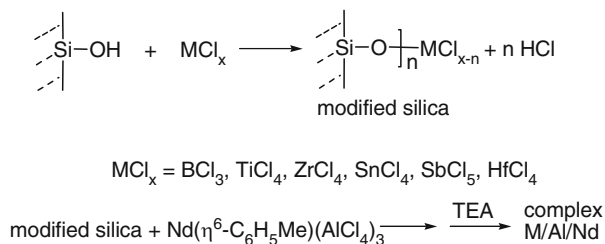
cis-1,4-Selective polymerization of diene is a very important process in the chemical industry to afford products among the most significant and widely used rubbers. It has been believed that a slight increase in the *cis*-1,4-regularity of the product leads to a great improvement in elastic properties [28–30]. A direct consequence of high *cis*-1,4-contents is strain-induced crystallization of raw rubbers as well as of the respective vulcanizates. As strain-induced crystallization beneficially influences the tack of raw rubbers as well as tensile strength and resistance of vulcanizates to abrasion and fatigue; therefore, the high *cis*-1,4-content makes Nd-BR particularly useful for tire applications [8].

2.1 Ziegler–Natta Rare-Earth Metal Precursors

2.1.1 Conventional Ziegler–Natta Rare-Earth Metal Precursors

The Ziegler–Natta rare-earth metal catalysts, mainly the binary systems $\text{LnCl}_3\text{--AlR}_3$ and the ternary systems $\text{LnL}_3\text{--AlR}_3\text{--HAlR}_2$ (or R_2AlX) (Ln = lanthanide including yttrium and scandium, L = carboxylate, phosphate, alkyl(aryl) oxide, allyl, X = halogen), have been the most simple to be prepared, economic, thermal

stable, and less sensitive to moisture and oxygen compared to those of metallocene catalysts. Meanwhile, they provide high *cis*-1,4-selectivity ($\sim 97\%$) and exhibit high activity at very low catalytic concentration. Therefore, Ziegler–Natta rare-earth metal catalysts have the most promising potentials for industry application. However, there still have problems, for instance, the *cis*-1,4-selectivity drops obviously when the polymerization is performed at a higher temperature such as within $60\text{--}80^\circ\text{C}$, which will reduce the tensile strength of the polymers especially polyisoprene. The other is the less controlled molecular weight and broad molecular weight distribution of the resultant polymers owing to the multisite nature of these systems and their inferior solubility in the industry-used medium cyclohexane or hexane. Moreover, the structures of the catalytic precursors and the active species need to be characterized, and the mechanisms are still not completely understood [6–10]. Therefore, many efforts have been paid to modify the Ziegler–Natta catalysts to settle these problems. To enhance the activity of the binary catalyst systems [31–35], the addition of electron donor ligands such as alcohols, tetrahydrofuran, pyridine, dimethyl sulfoxide, phosphates, and amines to the system have been widely employed which usually does not result in any decrease in stereospecificity [36–40]. Zhang reported that addition of long-chain alcohol could generate soluble binary system $\text{NdCl}_3 \cdot 3\text{EHOH}$ (2-ethylhexanol) in hexane, which in combination with AlEt_3 exhibited higher activity for isoprene polymerization as compared with the typical ternary catalysts $\text{NdCl}_3/3^i\text{PrOH}$ (isopropanol)/TEA(AlEt_3) and $\text{NdV}(\text{neodymium versate})/\text{DEAC}(\text{AlEt}_2\text{Cl})/\text{DIBA}(\text{Al}^i\text{Bu})_2\text{H}$). Moreover, the molecular weight of the resultant polyisoprene can be controlled by varying the Al-to-Nd ratio and polymerization temperature and time, showing some degree of living mode, and its microstructure featuring high *cis*-1,4-stereospecificity (ca. 96%) [41]. Jain described the new neodymium chloride tripentanol catalysts of the general formula $\text{NdCl}_3 \times 3\text{L}$ ($\text{L} = 1\text{-pentanol}, 2\text{-pentanol}, \text{and } 3\text{-pentanol}$) prepared by an alcohol interchange reaction between neodymium chloride and the alcohols. The systems were evaluated for the polymerization of butadiene in cyclohexane using TEA as cocatalyst, among which the combination of NdCl_3 and 2-pentanol has higher catalytic activity followed by 1-pentanol and 3-pentanol. The conversions were increased with increases in catalyst and cocatalyst concentrations and temperature, and decrease in intrinsic viscosity value. The microstructure was found to have a predominantly *cis*-1,4-structure (99%), which was marginally influenced by variation in cocatalyst concentration and temperature [42]. Boisson employed a soluble arene complex $\text{Nd}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{AlCl}_4)_3$, prepared by mixing NdCl_3 and AlCl_3 in toluene to react in situ with the Lewis-acid MCl_x -masked silica ($\text{MCl}_x = \text{BCl}_3, \text{AlCl}_3, \text{TiCl}_4, \text{ZrCl}_4, \text{SnCl}_4, \text{SbCl}_5, \text{HfCl}_4$) (Scheme 1). They found that the resultant supported system based on BCl_3 -modified silica was the most active for butadiene polymerization with an activity of $1,188 \text{ g}_{\text{polym.}}/(\text{g}_{\text{cata.}} \text{ h})$ allowing to polymerize butadiene at a very low neodymium concentration of around 10 ppm, and meanwhile the *cis*-1,4 insertion was superior by 99%. This supported catalyst also yielded high molecular weight polyisoprene with a high *cis*-1,4-content of 96.1% (Table 1) [43]. Masuda [44] synthesized directly neodymium isopropoxide $\text{Nd}(\text{O}^i\text{Pr})_3$ which activated by MAO alone exhibited high efficiency

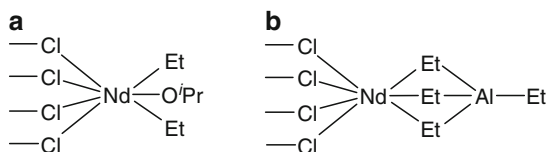
**Scheme 1** Synthesis of silica-supported catalysts**Table 1** Polymerization of butadiene with various heterogeneous catalysts [43]

Run	Complex (mg)	Time (min)	Yield (g)	TOF (h^{-1})	η_{inh} (dL g^{-1})	<i>cis</i> -1,4 (%)
1 ^a	Al/Nd1 (85)	60	1.1	13	3.12	>99
2 ^b	Al/Nd2 (85)	30	6.5	153	2.28	>99
3	Ti/Al/Nd (83)	15	11.1	535	2.20	>99
4	Zr/Al/Nd (71)	60	0.8	11	2.25	>99
5	B/Al/Nd (35)	15	10.4	1,188	2.15	>99
6 ^c	B/Al/Nd (30)	60	2.8	93	4.0	96.1
7	Sn/Al/Nd (77)	15	9.5	493	5.22	>99
8	Sb/Al/Nd (32)	30	4.0	250	4.39	>99
9	Hf/Al/Nd (108)	20	4.3	119	4.0	>99

^aAl/Nd1: silica/AlCl₃/NdCl₃^bAl/Nd2: (Al/Nd1)/AlEt₃^cPolymerization of isoprene: solvent: cyclohexane (120 mL), isoprene (15 mL), DIBAH (3 mmol L⁻¹), 60°C

for isoprene polymerization in heptane even at low [Al]/[Nd] ratios (ca. 30) to give polyisoprene that possessed moderate to high *cis*-1,4-stereoregularity (ca. 90%), high molecular weight ($M_n = 10^5$), and relatively narrow molecular weight distributions ($M_w/M_n = 1.9\text{--}2.8$) without a halogen source although it is generally essential for high activity and high *cis*-1,4-specificity of AlR₃-activated Nd catalysts [45–48]. However, the same catalyst with MMAO resulted in relatively low polymer yield and low molecular weight in toluene and cyclized polyisoprene in dichloromethane, which might be ascribed to the cationic active species derived from MMAO. Addition of chlorine sources (DEAC, *t*BuCl, Me₃SiCl) improved the *cis*-1,4-stereoregularity of polymer up to 95% even at a high temperature 60°C albeit sacrificing polymer yield [49]. When dimethylphenylammonium tetrakis(pentafluorophenyl)borate [HNMe₂Ph][B(C₆F₅)₄] and TIBA were applied as cocatalysts, the optimal catalyst composition was [Nd]/[borate]/[Al] = 1/1/30, which gave polyisoprene (>97% yield) with high molecular weight ($M_n \sim 2 \times 10^5$) and relatively narrow molecular weight distribution ($M_w/M_n \sim 2.0$) albeit a reduced *cis*-1,4-tacticity (~90%). If [Al]/[Nd] ratio was over 50 or [borate]/[Nd] ratio was not the exact 1, the resultant polymer had low *cis*-1,4-content or showed bimodal peaks in GPC accompanied by low yield, owing to the formation of multiple active species [50]. Boisson investigated the behavior of a new ternary system based

Fig. 1 Possible structures of active centers (a) and (b)



on an amide compound, $\text{Nd}\{\text{N}(\text{SiMe}_3)_2\}_3/\text{TIBA}/\text{DEAC}$ in the polymerization of butadiene [51], which was at least as efficient as the classical ternary systems [52, 53], and remained highly active at very low neodymium concentrations ($1.35 \times 10^6 \text{ g}/(\text{mol}_{\text{Nd}} \cdot \text{h})$). Unlike neodymium alkoxides, the $\text{Nd}\{\text{N}(\text{SiMe}_3)_2\}_3$ was well dispersed in solution and did not form clusters. As commonly reported for lanthanide salts with oxygenated ligands, the catalyst activity depended on the Al-to-Nd ratio. The highest conversion was observed for a ratio between 2 and 2.5; unfortunately, the GPC curves showed a bimodal distribution, indicating the existence of at least two different active centers as shown in Fig. 1. When the ratio increased from 2 to 5, the lowest molecular weight peak (active center **b**) became predominant accompanied by the low *cis*-1,4-stereoregularity. Therefore, the active center which gave the highest molecular weight polymer (active center **a**) was also probably the most stereospecific.

In the meantime, many research works focused on optimizing the composition of the conventional homogeneous ternary Ziegler–Natta catalyst as well as the polymerization conditions. Coutinho et al. investigated a system composed of NdV, *tert*-butyl chloride, and diisobutylaluminum hydride (DIBAH) for butadiene polymerization. They found that increase of the monomer concentration shifted the activity curves to lower polymerization temperatures, meaning that the same activity obtained at higher polymerization temperatures, when higher monomer concentrations were used, can be attained at lower temperatures. This was in consistent with the performance of catalyst systems based on lanthanides with which the reaction rate presented a first-order dependence on the monomer concentration [54]. In contrast, the polymer microstructure was slightly influenced by the monomer concentration in the range of reaction temperature studied; however, a tendency of increasing the *cis*-1,4-unit content with the decrease of monomer concentration was indeed observed. This behavior may be attributed to a lower reaction medium viscosity, which provided higher monomer molecules mobility, thus favoring their complexation to the catalyst sites in appropriate configuration [55]. Obsrecht et al. [56] reported that solvents such as *n*-hexane, *tert*-butylbenzene (TBB), and toluene exerted distinct influence on the polymerization of butadiene by using NdV/DIBAH/EASC (ethylaluminum sesquichloride). From the polymerization kinetics that polymerization rates decreased in the order: *n*-hexane > TBB > toluene there was evidence of competitive coordination between aromatic solvents and butadiene to activate Nd-sites supported by Porri's view [57]. In addition, the conversion-time plot for the polymerization in toluene deviated from the first-order dependency, indicating the presence of the irreversible transfer of benzyl-H-atoms from toluene to active allyl-anionic polymer chains. The evolution of molecular weight distributions with monomer

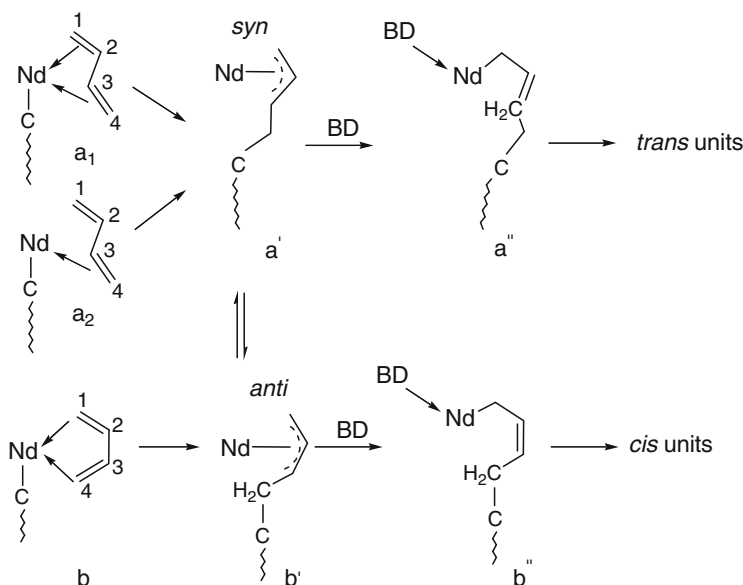
conversion suggested two active catalyst species present in all three solvents. One of these two species was highly reactive (“hot”) and short-lived. This species generated polybutadiene with high molecular weight. The second species had a low reactivity and lived the entire course of the polymerization. In *n*-hexane, the “hot” short-lived species was present only at the start of the polymerization, whereas in TBB and toluene, the “hot” short-lived species became evident at monomer conversion 10% and was constantly (re)generated. However, their finding – that *cis*-1,4-contents determined at final monomer conversion, 94.0% (*n*-hexane), 96.0% (toluene), and 98.0% (TBB) were higher in aromatic solvents than in *n*-hexane – was in contradiction with most other available studies in this field. Coutinho [58] also found that the aliphatic solvents, hexane, cyclohexane, and their mixtures behaved differently toward the NdV/DIBAH/*t*BuCl-catalyzed butadiene polymerization. Cyclohexane had a solubility parameter (δ) higher than that of hexane and near of polybutadiene. As a consequence with the increase of cyclohexane proportion in the reaction medium, *cis*-1,4-content of the produced polybutadiene increased from 98.2 to 99.1%; however, the molecular weight (M_n from 1.9×10^5 to 0.44×10^5) reduced owing to its higher solvating power, that is, providing more active sites. This supposition was supported by the progressive increase on the molecular weight distribution (from 3.3 to 5.0) as the cyclohexane content increases in the polymerization solvent (Table 2).

Addition of electron donor compounds to binary systems significantly increased the solubility and the consequent higher activity, whereas, addition of which to ternary systems provoked a decrease in *cis*-1,4-units and an increase in *trans*-1,4-units [59,60]. This could be explained by Scheme 2 The *trans*-1,4-units are formed via route a_1 or $a_2 \rightarrow a' \rightarrow a''$; meanwhile, the *cis*-1,4-units are formed via route $b \rightarrow b' \rightarrow b''$. Therefore, when electron donors such as amines or ethers (TMEDA or THF) are added to the catalyst system, they are able to occupy a coordination site, forcing the new incoming monomer molecule to coordinate with only one double bond, resulting in *trans*-1,4-repeating units via route a_2 [61].

For multicomponent catalyst systems, the activation degree of the precursor, namely the aging time, influenced the catalytic performances obviously. The catalyst activity increased for a long ageing time, but the stereoselectivity of active catalyst sites seemed not to be affected by aging conditions. Moreover, increase of aging temperature led to a significant drop on polymerization reaction rate [62]. The alkylaluminum played a significant role on governing the

Table 2 Influence of solvent nature on the microstructure of polybutadiene produced by NdV/DIBAH/*t*BuCl [58]

Composition (% v/v)		PB microstructure (%)			M_n ($\times 10^5$)	M_w ($\times 10^5$)	PDI	Activity (g PB)
Hexane	Cyclohexane	<i>cis</i> -1,4	<i>trans</i> -1,4	1,2-vinyl				
100	0	98.2	1.3	0.5	1.10	3.68	3.3	30
80	20	98.3	1.2	0.5	1.02	4.11	4.0	29
50	50	98.4	1.1	0.5	0.84	3.73	4.4	30
20	80	98.9	0.5	0.6	0.57	2.89	5.1	30
0	100	99.1	0.4	0.5	0.44	2.23	5.1	29



Scheme 2 Regularity of polybutadiene influenced by the coordination mode of butadiene to the metal center

Table 3 Influence of alkylaluminum compounds on the microstructure and molecular weight of polybutadiene afforded by NdV/*t*BuCl [63]

Run	Al cocat.	Microstructure (%)			$M_w (\times 10^5)$	PDI
		<i>trans</i> -1,4	1,2-vinyl	<i>cis</i> -1,4		
1	DIBAH	0.86	0.39	98.74	4.30	3.54
2	TIBA	1.13	0.65	98.22	7.34	2.82
3	TNHA	1.67	0.68	97.65	8.97	2.55
4	TNOA	1.61	0.79	97.60	10.52	2.54

catalytic performances. Coutinho reported when the long-chain aluminum compounds such as tri(*i*-butyl)aluminum (TIBA), tri(*n*-hexyl)aluminum (TNHA), and tri(*n*-octyl)aluminum (TNOA) were employed, the isolated polybutadiene had the highest molecular weight; however, those with the highest contents of *cis*-1,4-units and the lowest molecular weight were produced when DIBAH was employed. The order observed for catalyst activity obtained with the different types of aluminum compounds was: TNOA > TNHA > TIBA > DIBAH (Table 3) [63]. This might be because the organoaluminum compound changed the kinetic heterogeneity of active sites as reported by Monakov [64]. The heterogeneity of the investigated catalytic systems was shown in the existence of four types of active centers. They were formed at the beginning of the polymerization process and produced macromolecules with lengths that were definite for each type of active center. The nature of the organoaluminum compound greatly influenced the kinetic activity

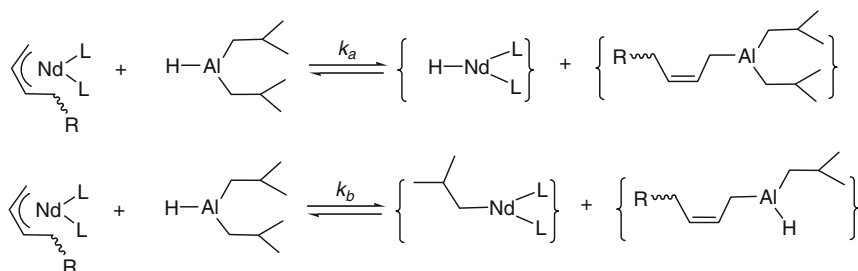
of the polymerization centers. Thus, the difference in the distributions of kinetic activity and the behavior of active centers of the catalytic system with TEA and the similarity of the behavior of the systems with TIBA, TNHA, and TNOA can be explained by inclination toward association of TEA because of its short carbon chain [63,64]. Besides as a cocatalyst to activate the lanthanide precursors, the role of aluminum compounds can act as a chain transfer agent to adjust the molecular weight, which was soundly investigated by Obsrecht with NdV/DIBAH/EASC. At low monomer conversions, the molecular weight distribution was distinctly bimodal at the initial process; with the increase of monomer conversion the position of the high molecular weight peak remained constant, while the position of the low molecular weight peak shifted toward lower retention times (high molecular weight). For the highest monomer conversion (=82.5%), the two peaks more or less overlapped resulting in apparently unimodal albeit broad distribution. The system in fact proceeded in a living mode as the molecular weight increased linearly with conversion. However, in contrast to the classical living polymerization, each Nd center generated more than one polymer chain, and the numbers ranged from 2.3 to 15.4 with increasing the $[DIBAH]/[Nd]$ ratio (Table 4). This indicated that aluminum was involved in the generation of polymer chains via chain transfer from Nd onto Al during the course of the polymerization. As Al species attached to isobutyl groups or hydrogen were inert toward the polymerization of butadiene, the chain transfer should be reversible and the polymer chains attached to Al would be back-transferred to Nd and reactivated. Thus, Al with attached polymer chains can be treated as a dormant species. As the molecular weight distributions did not broaden with monomer conversion, it had to be concluded that the reversible transfer of polymer chains between Nd and Al was fast in relation to the speed of polymerization (Scheme 3) [65].

Table 4 Number ($p_{exp.}$) of chains generated by one Nd species of NdV/DIBAH/EASC system at different n_{DIBAH}/n_{Nd} ratios [65]

n_{DIBAH}/n_{Nd}	10	20	30	50
$\overline{DP}n_{theo.}^a$	9,250	9,250	9,250	9,250
$\overline{DP}n_{exp.}^b$	4,020	1,970	1,100	600
$p_{exp.}$	2.3	4.7	8.4	15.4

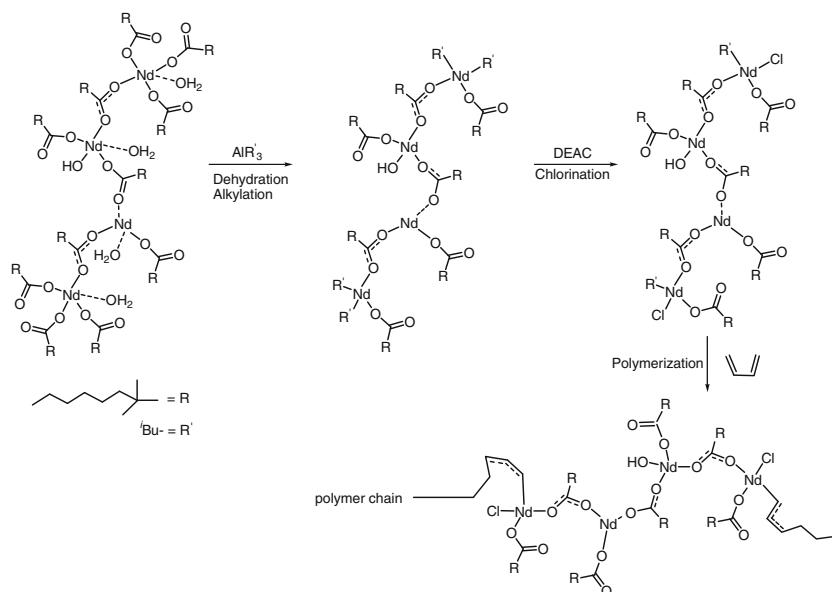
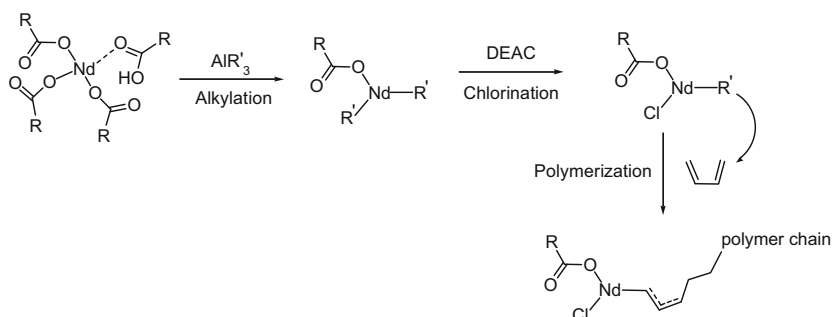
^aFor $x = 1$ (100% conversion) and 1 chain per Nd ($p = 1$)

^bFor $x = 1$ (100% conversion)



Scheme 3 Interchange of alkyl between Nd and Al

TIBA was used to compare with DIBAH. Within a broad range of Al-to-Nd ratios for both aluminum compounds, the features of a living polymerization with a reversible exchange of the living polybutadienyl chains between neodymium (Nd) and aluminum were observed differentiating at the equilibrium position for TIBA and DIBAH. For instance at the same molar loadings, DIBAH resulted in polybutadiene with molecular weights which were one eighth of those obtained in the presence of TIBA. This was explained by a more facile substitution of a hydride moiety from DIBAH than an isobutyl group from either DIBAH or TIBA by a living polybutadienyl chain, indicating that DIBAH was eight times more effective in molecular weight control than TIBA [66]. The molecular weight control could be also achieved by addition of diethyl zinc (ZnEt_2) to the ternary catalyst system of NdV/DIBAH/EASC, which had a negligible impact on polymerization rates. In addition to the reduction of molecular weight, ZnEt_2 also reduced the polydispersity (PDI) but unfortunately led to a decrease of the *cis*-1,4-content [67]. Fixing the cocatalysts to DIBAH and EASC, the catalyst system based on NdV (Cl-to-Nd ratio of 2 and H-to-Nd ratio of 30) was found highest polymerization activity for the polymerization of butadiene, whilst that comprising NdA catalyst system was less active as compared with NdV and NdP (neodymium bis(2-ethylhexyl)phosphate) systems [68]. When SiCl_4 was used as a chloride source to replace EASC, at the optimum concentration ratio of NdV/ SiCl_4 /DIBAH = 1:1:25, *cis*-1,4-contents were consistently high (about 97%) for all polymerizations [69]. The effects of the concentrations of cocatalysts and water and versatic acid were reported by Quirk. Using in situ catalyst activation, the optimum concentration ratios of NdV/EASC/DIBAH = 1:1:25 at a catalyst concentration of 0.11 mmol Nd/100 g BD was established and used to determine the influence of water and excess versatic acid on polymerization performance. It was found that unless $[\text{H}_2\text{O}]/[\text{Nd}] = 0.11$, higher and lower amounts of water as well as excess versatic acid above $[\text{versatic acid}]/[\text{Nd}] = 0.22$ resulted in lower conversions, broader molecular weight distributions, and higher molecular weights. In contrast, the *cis*-1,4-contents of the polybutadiene were consistently high (ca. 98%) and independent of the water content and excess acid level [70]. The role of the carboxylic acid in the Ziegler–Natta catalyst systems was elucidated by Kwag, when they studied the system $\text{Nd}(\text{neodecanoate})_3(\text{ND})/\text{DEAC}/\text{TIBA}$ that was ultra-highly *cis*-1,4-selective for the polymerization of butadiene but very low active with unknown reason. By means of MALDI–TOF mass spectroscopic analysis, they found that ND was a mixture of various oligomeric and hydrated compounds (Scheme 4). The hydrated oligomeric structure would considerably lower the catalytic activity. To prove this, they designed a $\text{ND} \cdot \text{NDH}$ (neodecanoic acid) catalyst which was prepared through a ligand-exchange method and identified as monomeric structure, satisfying eight-coordination nature and did not contain water, bases, and salts (Scheme 5). In the polymerization of 1,3-butadiene, NDH showed a very high activity of $2.5 \times 10^6 \text{ g}/(\text{mol}_{\text{Nd}} \text{ h})$ and produced polybutadiene with over 98% *cis*-1,4-content without gel [71]. The microstructure of polybutadiene was controlled by chain transfer with $\text{ND} \cdot \text{NDH}$, catalyst composition, and phosphine compounds. With increase in Nd concentration, increase in branch and decrease in cold flow were observed (Table 5). Addition of phosphine additives helped to

**Scheme 4** The mechanism of catalyst activation and chain propagation of ND**Scheme 5** The mechanism of catalyst activation and chain propagation of NDH**Table 5** Polymerization of 1,3-butadiene by Nd(neodecanoate)₃ (neodecanoic acid)/DEAC/TIBA and the analysis of microstructure and cold flow [72]

Run	Cat. ratio ^a	Nd conc. ($\times 10^{-4}$ mol)	Conv. ^b (%)	cis (%)	ML (1+4, 100°C)	C/F^c (mg min ⁻¹)	M_w ($\times 10^4$)	PDI
1	1/95/2/2.5	0.4	90	98.7	45.2	5.5	59.2	2.55
2	1/30/13/2.5	0.6	91	98.5	44.0	3.6	57.1	2.65
3	1/12/8/2.5	1.0	93	97.5	44.3	1.8	54.8	2.88
4	1/12/10/2.5	1.1	97	97.5	47.6	1.9	59.5	2.97
5	1/15/5/2.5	1.3	100	96.8	41.0	1.3	61.7	3.32
6	1/95/2/2.5	0.4	55	94.5	65.6	2.1	95.6	4.25

^aCat. Ratio = Nd/TIBA/DIBAL/DIAE^b2 h^c C/F = cold flow

enhance the *cis*-1,4-selectivity, for instance, when *tris*(*para*-fluorophenyl) phosphine was used polybutadiene with over 99% *cis*-1,4-content was produced, which was in contrast to the previous reports that the addition of the electron donor decreased the *cis*-selectivity of the system owing to the monomeric nature of the active species. More significantly, they established the correlation between the properties and the microstructure of polybutadiene [72]. The linear high *cis*-1,4-regulated and narrow molecular weight-distribution polybutadiene showed excellent tensile and dynamic properties such as low heat build-up and high abrasion resistance but poor processability in view of high compound viscosity and hardness. Whilst the slightly branched, low *cis*-1,4-regulated polybutadiene with broad molecular weight distribution generated with increase in Nd concentration, exhibited improved processability for better mixing and milling with filler and other polymers in terms of low compound viscosity, and good tensile and dynamic properties such as hardness because of increased miscibility with carbon black [73–76]. The polybutadiene prepared by Ni-based catalyst showed a very low cold flow because of a broad MWD, indicating the good processability, however, low tensile and dynamic properties, especially high heat build-up (34.3°C) and abrasion (17.0 mg) owing to branching [75, 77].

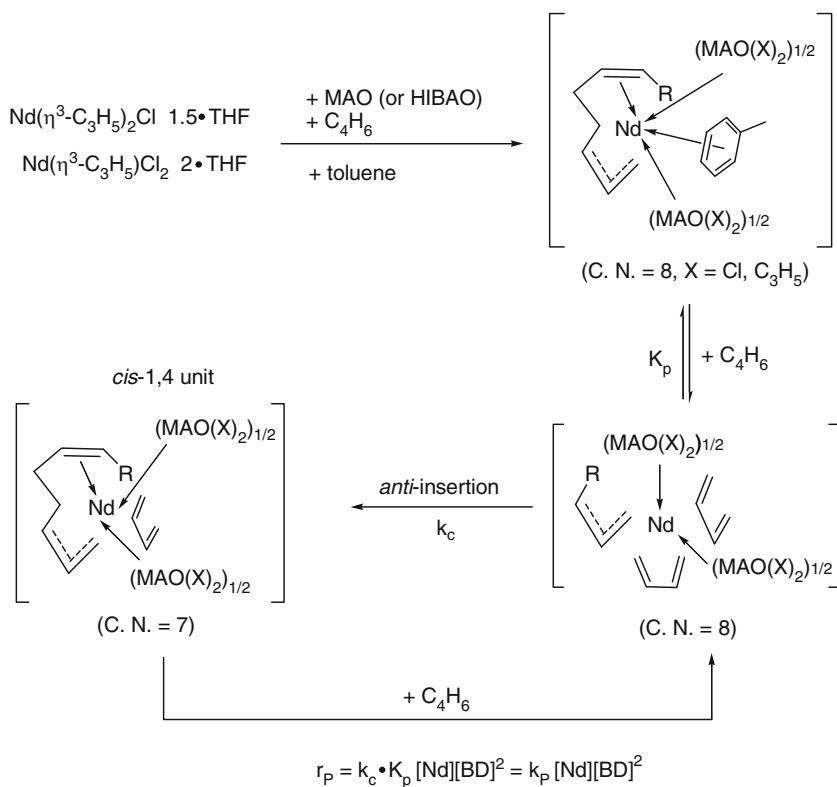
An important kind of Ziegler–Natta catalyst precursors reported by Taube were the allyl neodymium chloride complexes such as $\text{Nd}(\text{C}_3\text{H}_5)_2\text{Cl}\cdot 1.5\text{THF}$ and $\text{Nd}(\text{C}_3\text{H}_5)_2\text{Cl}\cdot 2\text{THF}$, which could be activated by adding MAO or HIBAO to produce *cis*-1,4-polybutadiene. At the ratio of $\text{Al}/\text{Nd} = 30$, a turnover frequency (TOF) of about $1.08 \times 10^6 \text{ g}/(\text{mol}_{\text{Nd}} \text{ h})$ and *cis*-selectivity of 95–97% in moderate yields were achieved under standard conditions (Table 6). Molecular weight determinations indicated a low polydispersity ($M_w/M_n = 1\text{--}1.5$), the formation of only one polymer chain per neodymium and the linear increase of the polymerization degree with the conversion, as observed for living polymerization. From the proven dependence of the polymerization rate (first order in neodymium, second order in butadiene concentration), it followed that two butadiene molecules might take part in the insertion reaction in the transition state of the allyl neodymium complex; the formation of an $\eta^3\text{-butenyl-bis}(\eta^4\text{-butadiene})\text{neodymium(III)}$ complex of the composition $[\text{Nd}(\eta^3\text{-RC}_3\text{H}_4)(\eta^4\text{-C}_4\text{H}_6)_2(\text{X} - \{\text{AlOR}\}_n)_2]$ ($\text{X}^- = \text{Cl}^-$ or C_3H_5^-) was assumed to be the true active species for the chain propagation (Scheme 6) [78]. When 2 equiv. AlMe_2Cl (DMAC) were used to replace MAO, the resultant combination was highly active for the polymerization of butadiene with an activity doubled compared with MAO, $1.9 \times 10^6 \text{ g}/(\text{mol}_{\text{Nd}} \cdot \text{h})$ and narrower than 1.3 polydispersity albeit low *cis*-1,4-selectivity (of 90%). A chloro complex at the Nd(III) center as a consequence of allyl anion transfer to Al(III) (Scheme 7) was proposed to be the active species, in which the coordination of two butadiene monomers was requisite by the coordination number of 8 of Nd(III) [79]. However, employing AlR_3 to activate the solvated $\text{Nd}(\text{C}_3\text{H}_5)_2\text{Cl}\cdot 1,4\text{-dioxane}$ and $\text{Nd}(\text{C}_3\text{H}_5)_2\text{Cl}_2\cdot 2(\text{THF})$ or solvent-free $\text{Nd}(\text{C}_3\text{H}_4\text{R})_3$ ($\text{R} = (\text{C}_4\text{H}_6)_n\text{C}_3\text{H}_5$), respectively, low activity and *cis*-1,4-selectivity were obtained, which might be attributed to the formation of probable chloride-bridged dimeric structure of the mono- or dichloride allyl precursors or the formation of the chloride cluster of resultant active species for the triallyl precursors.

Table 6 Polymerization of butadiene by employing Nd(C₃H₅)₂Cl·1.5THF/HIBAO^a [78]

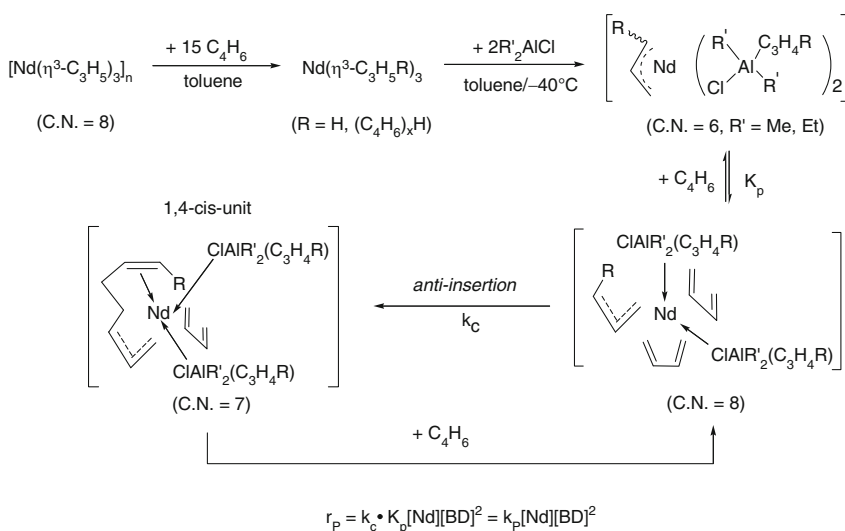
Run	<i>m</i> _K (mg)	[Nd] (mol L ⁻¹)	[BD] ₀ /[Nd]	Time (min)	Yield (%)	TOF	<i>cis/trans</i> /1,2 (%)	<i>M</i> _n × 10 ⁻⁴ (LS)	<i>M</i> _n (V)	<i>M</i> _w × 10 ⁻⁴ (LS)	PDI	<i>M</i> _n (LS)/ <i>M</i> _n (V)
1	27.3	1 × 10 ⁻³	2,000	4	64	19,400	95/4/1	11.1	6.8	12.5	1.13	1.02
2	28.4	1 × 10 ⁻³	2,000	4	60	17,800	95/4/1	10.4	6.5	11.6	1.12	0.99
3	22.4	8 × 10 ⁻⁴	2,500	4	57	21,300	95/4/1	12.4	7.7	14.0	1.13	1.00
4	20.3	8 × 10 ⁻⁴	2,500	4.5	58	19,700	95/4/1	12.7	8.4	14.2	1.12	0.94
5	18.5	6 × 10 ⁻⁴	3,350	6	58	19,100	96/3/1	14.2	9.4	17.8	1.25	1.10
6	18.2	6 × 10 ⁻⁴	3,350	6	60	19,900	95/4/1	15.8	9.2	18.9	1.19	1.17
7	14.2	4 × 10 ⁻⁴	5,000	10	52	15,900	95/4/1	21.9	13.6	27.9	1.27	1.04
8	11.5	4 × 10 ⁻⁴	5,000	7	52	22,200	96/3/1	23.6	14.0	28.9	1.22	1.00
9	8.9	2 × 10 ⁻⁴	10,000	10	41	24,600	97/2/1	42.7	21.3	57.2	1.34	1.04
10	6.8	1.5 × 10 ⁻⁴	13,300	12	29	19,300	98/1/1	57.2	21.5	83.7	1.46	0.97

*m*_K: amount of the neodymium complex; [BD]₀: initial butadiene concentration; TOF: turnover frequency, mol BD/(mol Nd h); *M*_n: determined by light scattering (LS) or viscosimetrically (V)

^aPerformed in toluene, 35°C [BD]₀ = 2.0 mol L⁻¹, [Al]/[Nd] = 30



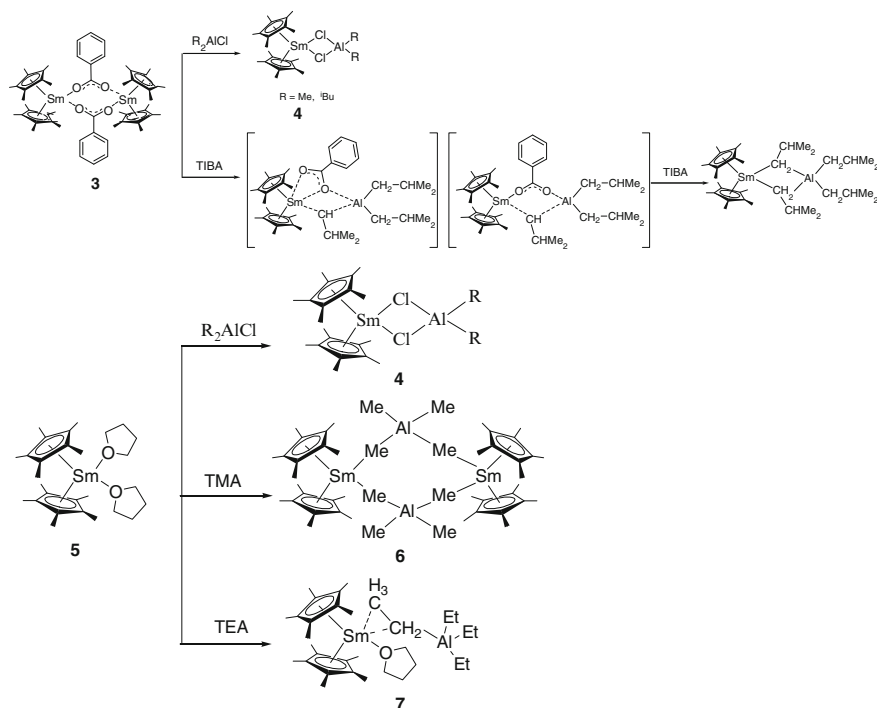
Scheme 6 Formation of catalytically active species and pathway of butadiene insertion (CN coordination number)



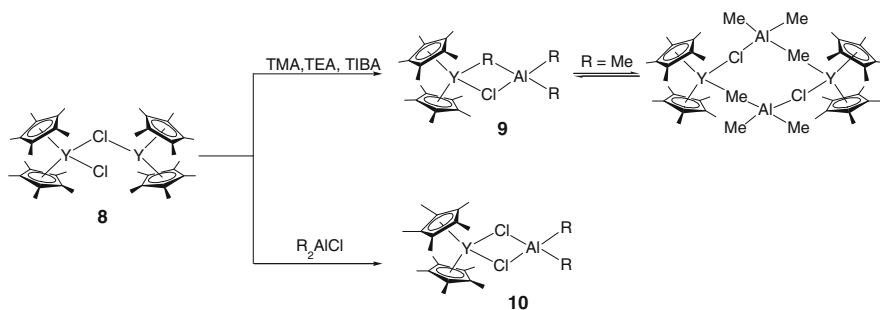
Scheme 7 Formation of allyl neodymium/aluminum complex

2.1.2 Modified Ziegler–Natta Rare-Earth Metal Precursors

The conventional Ziegler–Natta catalyst recipe contains both binary and ternary systems comprising 10–30-fold excess of aluminum trialkyl reagents except the single-component divalent lanthanide iodides [80], even though stoichiometric TIBA is sufficient with the fully defined carboxylate precursors [81]. And in all cases, chloride is included, which is generally believed to be crucial to the success of the polymerization [81–91]. Therefore, although heterobimetallic complexes with alkylated rare-earth metal centers have been proposed to promote 1,3-diene polymerization via an allyl insertion mechanism, details of the polymerization mechanism and the structure of the catalytically active center(s) are still elusive [92]; hence, improvement and optimization of the catalytic system have been achieved only empirically [93–95]. The interaction of the “cationizing” chloride-donating reagent with alkylated rare-earth metal centers is not well understood [96–98]. To mimic these conventional Ziegler–Natta catalytic precursors, the research works have been directed to the tailor-made and well-defined rare-earth metal carboxylates as models for diene polymerization catalysts. Evans designed the neodymium and lanthanum carboxylates $\{\text{Nd}[\text{O}_2\text{CC}(\text{CH}_3)_2\text{CH}_2\text{CH}_3]_3\}_n$ (**1**) and $\{\text{La}[\text{O}_2\text{CC}(\text{CH}_3)_2\text{CH}_2\text{CH}_3]_3\}_n$ (**2**) combined with DEAC and DIBAH to initiate the high *cis*-1,4-isoprene polymerization with high activity. Although the attempt to isolate the active intermediate of the process by crystallization of the reaction product of **1** with DEAC was unsuccessful by giving base-adduct LnCl_3 , the probable active species were recognized to contain minimally the lanthanide and aluminum as well as halide and ethyl ligands in a formula $\text{Ln}_2\text{AlCl}_5(\text{Et}_2(\text{O}_2\text{CR}))$ [81–91]. When the cyclopentadienyl ligand was introduced into the carboxyl complexes, some reaction intermediates had been successfully isolated. For instance, by treatment of $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{O}_2\text{CC}_6\text{H}_5)]_2$ (**3**) with R_2AlCl ($\text{R} = \text{Me}, \text{Et}, {}^i\text{Bu}$) a dichloro complex $(\text{C}_5\text{Me}_5)_2\text{Sm}(\mu\text{-Cl})_2\text{AlR}_2$ (**4**) was successfully obtained where carboxylate ligands were replaced indeed by chloride in the reaction (Scheme 8). A divalent precursor $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2$ (**5**) reacted with DEAC, TMA, and TEA, respectively, afforded **4**, and the corresponding aluminates $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{AlMe}_4)]_2$ (**6**) and $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})-(\mu\text{-}\eta^2\text{-Et})\text{AlEt}_3$ (**7**). The mixed chloride/alkyl-bridged complexes $(\text{C}_5\text{Me}_5)_2\text{Ln}(\mu\text{-Cl})(\mu\text{-R})\text{AlR}_2$ (**9**), the mimic intermediates, could be prepared by treatment of $(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-Cl})\text{YCl}(\text{C}_5\text{Me}_5)_2$ (**8**) with aluminum compounds [96]. Complexes **9** were usually monomeric but adopted dimeric structure when TMA was used (Scheme 9). These studies proved at least that the well-defined coordination environment provided by two Cp ligands; R_2AlCl reagents reacted with a lanthanide carboxylate ligand to deliver chloride indeed. The product was not a simple chloride carboxylate exchange product, however, a mixed metal complex containing aluminum bridged by two chloride ligands, $[(\text{C}_5\text{Me}_5)_2\text{-Ln}(\mu\text{-Cl})_2\text{AlR}_2]$ (**10**). The isolation and identification of the mimic intermediates and the probable active species in the polymerization of dienes by Ziegler–Natta catalysts systems were realized by Anwender, who utilized the substituted homoleptic rare-earth metal carboxylate complexes $\{\text{Ln}(\text{O}_2\text{CC}_6\text{H}_2\text{R}_3\text{-2,4,6})_3\}_n$ (**11**) ($\text{R} = \text{Me}, {}^i\text{Pr}, {}^t\text{Bu}, \text{Ln} = \text{Y}$,

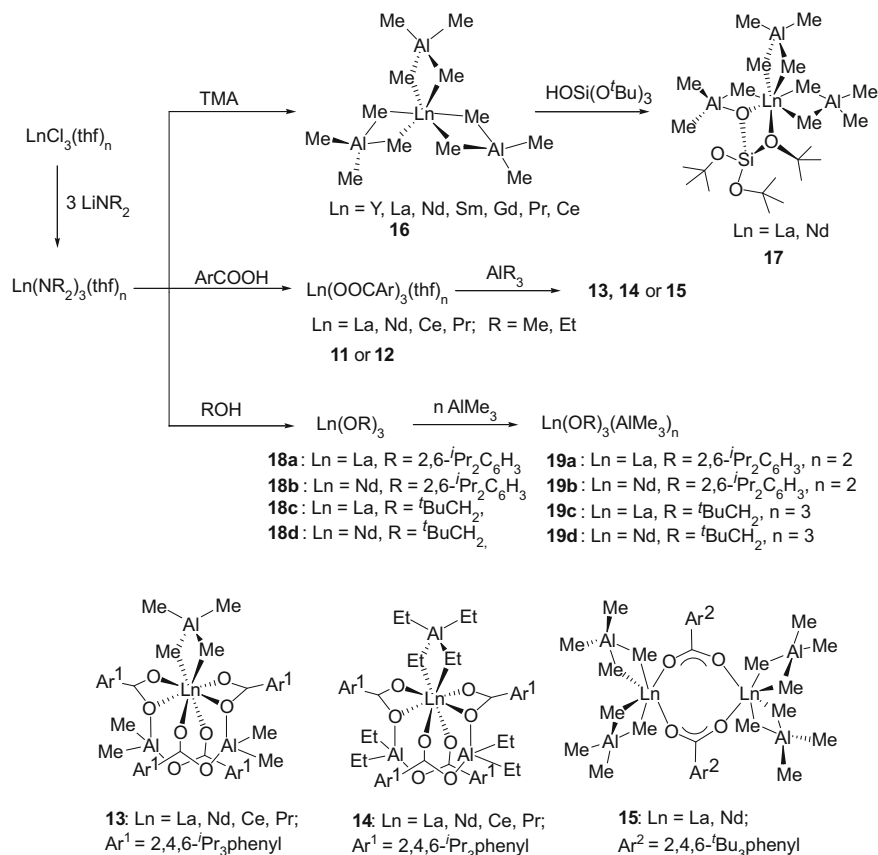


Scheme 8 Synthesis of chloride- and alkyl-bridged Sm–Al bimetallic complexes



Scheme 9 Activation of **8** with different aluminum compounds

La, Nd, Gd, Lu) and $\{Ln(O_2CC_6H_3R_{2-2,6})_3(THF)\}_n$ (**12**) ($R = Ph, Mes, Ln = Y, La$) without a Cp ligand to react with stoichiometric amount of AlR_3 ($R = Me, Et$). The resultant hexane-soluble complexes **13–15** featuring a η^2 -coordinating tetraalkylaluminate ligand and a novel ancillary $AlMe_2$ -bridged bis(carboxylate) ligand, were coordinated by mono- or di-tetraalkylaluminate ligands depending on the steric demand of the benzoate moieties and aluminum alkyls (Scheme 10). Upon activation with 1–2 equiv. DEAC, the resultant Ziegler–Natta catalyst



Scheme 10 Syntheses of heterobimetallic complexes

systems efficiently polymerized isoprene (*cis*-1,4 > 99%, Table 7), the performance of which depended significantly on the metal center ($\text{Nd} > \text{Gd} > \text{La}$) and the degree of alkylation (" $\text{Ln}(\text{AlMe}_4)_2$ " > " $\text{Ln}(\text{AlMe}_4)$ "). Equimolar reaction of $[\text{Me}_2\text{Al}(\text{O}_2\text{CC}_6\text{H}_2^i\text{Pr}_{3-2,4,6})_2]_2\text{Ln}[(\mu\text{-Me})_2\text{AlMe}_2]$ (**14**) with R_2AlCl ($\text{R} = \text{Me, Et}$) quantitatively produced $[\text{Me}_2\text{Al}(\text{O}_2\text{CC}_6\text{H}_2^i\text{Pr}_{3-2,4,6})_2]$ and the proposing initiating species " Me_2LnCl ." When the lanthanide aryloxide complexes $\text{Ln}(\text{OR})_3$ were employed, the degree of preactivation by TMA influenced the initiating capability distinctly. The heterobimetallic bis-TMA adducts $\text{Ln}(\text{OAr}^i\text{Pr})_3(\text{TMA})_2$ and *tris*-TMA adducts $\text{Ln}(\text{OCH}_2^i\text{Bu})_3(\text{TMA})_3$ ($\text{Ln} = \text{La, Nd}$) under the activation of DEAC (Cl-to-Ln ratio of 2) produced the same highly reactive and stereoselective (*cis*-1,4 > 99%) initiators $[\text{Me}_2\text{LnCl}]$, whereas the mono-TMA adducts $\text{Ln}(\text{OAr}^i\text{Bu})_3(\text{TMA})$ were catalytically inert. The alkoxide-based *tris*-TMA adducts gave narrower molecular weight distributions than the aryloxide-based bis-TMA adduct complexes ($M_w/M_n = 1.74\text{--}2.37$ vs. $2.03\text{--}4.26$) [102]. Homoleptic $\text{Ln}(\text{AlMe}_4)_3$ (**16**) was spotted as a crucial reaction intermediate

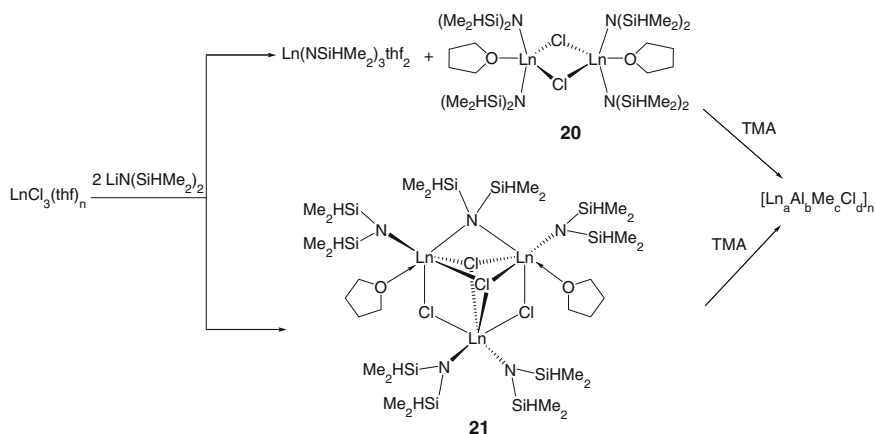
Table 7 Polymerization of isoprene with different lanthanide precatalyst^a

Run	Precatalyst	Yield (%)	<i>cis</i> -1,4 (%)	M_n ($\times 10^3$)	M_w ($\times 10^3$)	PDI	References
1	LaCl ₃ (thf) _n /3LiNR ₂ /3Ar ¹ COOH/6TMA	70	98.1	180	816	4.52	[99]
2	NdCl ₃ (thf) _n /3LiNR ₂ /3Ar ¹ COOH/6TMA	>99	98.6	271	621	2.29	[99]
3	CeCl ₃ (thf) _n /3LiNR ₂ /3Ar ¹ COOH/6TMA	>99	>98	149	532	3.59	[99]
4	PrCl ₃ (thf) _n /3LiNR ₂ /3Ar ¹ COOH/6TMA	>99	>98	158	650	4.11	[99]
5	LaCl ₃ (thf) _n /3LiNR ₂ /3Ar ¹ COOH/6TEA	>99	96.6	91	454	4.98	[99]
6	NdCl ₃ (thf) _n /3LiNR ₂ /3Ar ¹ COOH/6TEA	>99	95.6	92	266	2.88	[99]
7	LaCl ₃ (thf) _n /3LiNR ₂ /3Ar ² COOH/6TMA	>99	>99	175	564	3.23	[99]
8	NdCl ₃ (thf) _n /3LiNR ₂ /3Ar ² COOH/6TMA	>99	>99	250	705	2.82	[99]
9	YCl ₃ (thf) _n /3LiNR ₂ /8TMA	97	75.9	101	400	3.95	[100]
10	LaCl ₃ (thf) _n /3LiNR ₂ /8TMA	99	>99	184	600	3.26	[100]
11	NdCl ₃ (thf) _n /3LiNR ₂ /8TMA	>99	>99	117	326	2.78	[100]
12	SmCl ₃ (thf) _n /3LiNR ₂ /8TMA	7	>99	ND	ND	ND	[100]
13	GdCl ₃ (thf) _n /3LiNR ₂ /8TMA	>99	>99	146	377	2.58	[100]
14	CeCl ₃ (thf) _n /3LiNR ₂ /8TMA	>99	>98	152	469	3.08	[100]
15	PrCl ₃ (thf) _n /3LiNR ₂ /8TMA	>99	>98	320	735	2.30	[100]
17	NdCl ₃ (thf) _n /3LiNR ₂ /8TMA/ ^f Bu ₃ OSiOH	>99	>99	116	233	2.00	[101]
18	CeCl ₃ (thf) _n /3LiNR ₂ /8TMA/ ^f Bu ₃ OSiOH	>99	>98	535	807	1.51	[80]
19	PrCl ₃ (thf) _n /3LiNR ₂ /8TMA/ ^f Bu ₃ OSiOH	>99	>98	446	762	1.71	[101]
21	LaCl ₃ (thf) _n /3LiNR ₂ /3Ar ³ OH/2TMA	54	>99	390	870	2.23	[102]
22	NdCl ₃ (thf) _n /3LiNR ₂ /3Ar ³ OH/2TMA	>99	>99	223	453	2.03	[102]
23	LaCl ₃ (thf) _n /3LiNR ₂ /3NpOH/3TMA	>99	>99	517	954	1.85	[102]
24	NdCl ₃ (thf) _n /3LiNR ₂ /3NpOH/3TMA	>99	>99	384	670	1.74	[102]

ND not determined, Ar¹=2,4,6-*i*-Pr₃(C₆H₂), Ar²=2,4,6-*t*-Bu₃(C₆H₂), Ar³=2,6-*i*-Pr₂(C₆H₃), Np neopentyl

^aPolymerization procedure: 0.02 μmol precatalyst, 8 mL hexane, 0.04 μmol DEAC (2 equiv.), 20 mmol isoprene; 24 h, 40 °C

and was used for the high-yield synthesis of the various alkylated carboxylate complexes according to a novel “tetraalkylaluminate” route. Upon activation with 1–3 equiv. of DEAC, complexes **16** initiated the polymerization of isoprene in quite an efficient manner to yield highly stereospecific *cis*-1,4 > 99% polymers within 24 h [99–101]. The aforementioned Ln/Al heterobimetallic complexes such as [LnAl₃Me₈(O₂CC₆H₂^{*i*}Pr₃-2,4,6)₄], [Ln(OR)₃(AlMe₃)_n] (R = neopentyl, 2,6-*t*-Bu₂C₆H₃, 2,6-*i*-Pr₂C₆H₃), and [Ln(AlMe₄)₃] can be considered as the alkylated intermediates which, upon further activation with DEAC (or immobilized with MCM-48 [103]), gave similar highly efficient initiators for isoprene polymerization. The actual initiating active species were proposed to be [Me₂LnCl]_n and [MeLnCl₂]_n, which were generated by sequential alkylation–chlorination scenario. This was confirmed by their recent result utilizing lanthanide trichlorides as the starting reagent, which were treated with LiN(SiHMe₂)₂ to yield a mixture of homoleptic Ln{N(SiHMe₂)₂}₃(thf)_n and a monoamido derivatives



Scheme 11 Formation of chloro-bridged lanthanide amide complexes

$[\text{Ln}\{\text{N}(\text{SiHMe}_2)_2\}_2\text{Cl}_2(\text{thf})_n]$ (**20**) and a dimeric species $[\{\text{Ln}\{\text{N}(\text{SiHMe}_2)_2\}_2(\mu\text{-Cl})(\text{thf})\}_2]$ (**21**) (Scheme 11). Further addition of excess TMA to the above mixture gave $[\text{Ln}_a\text{Al}_b\text{Me}_c\text{Cl}_d]_n$ ($a + b = 1, a > b; c + d = 3, c > d$; determined by elemental analysis and magic-angle-spinning NMR technique) of single component catalyst ($\text{Ln} = \text{Nd}$) that provided an over 99% *cis*-1,4-selectivity with moderate to high activity (24 h, 40°C, >99% yield) [103]. The intrinsic Nd effect was observed in all these systems.

2.2 The Cationic Catalytic System

As the homogeneous catalyst system can provide more controlled polymerization especially the molecular weight of the resulting polydiene products, and the precursor of these systems are usually well defined that facilitate the investigation of the polymerization intermediate as well as the mechanism, thus the single-site homogeneous catalysts have attracted increasing attention. In these systems the organoborates are usually used to activate the precursors to give the cationic active species.

2.2.1 Lanthanocene Precursors

For the (modified) Ziegler–Natta systems although the structures of the precatalysts are still elusive, it is commonly accepted that the active center involves the formation of the Ln –alkyl or Ln –H species and cationization via Al-to-Ln chloride transfer. Therefore, well-defined Ln –C bond-containing complexes have attracted an increasing attention, among which the lanthanocene derivatives occupy notable positions. Coming to the first are samarocene divalent or trivalent complexes such as $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2$ (**5**) or $(\text{C}_5\text{Me}_5)_2\text{LnR}$ ($\text{R} = \text{H}$ or alkyl) which

are known to be efficient catalysts or precatalysts for polymerization of ethylene and methyl methacrylate in a living way to give monodispersed high molecular weight polymers in good yields [104–109]. However, they are almost inert for polymerization of dienes due to easy formation of stable η^3 -allyl intermediates that seem to be somewhat of a thermodynamic sink [105]. Strikingly, Kaita discovered that in combination with a cocatalyst such as MMAO, these complexes could efficiently initiate the polymerization of butadiene with an over 98% *cis*-1,4-regularity and high molecular weight and narrow molecular weight distribution ($PDI = 1.69$). TIBA/[Ph₃C][B(C₆F₅)₄] can also be used as cocatalysts in stead of MMAO. The resultant three-component catalyst system could initiate smooth polymerization of butadiene in a “living” mode to a large extent to provide polybutadiene with high *cis*-1,4-content (94.2–95.0%) and narrow molecular weight distribution ($PDI = 1.31$ – 1.39). When the polymerization was carried out at low temperature (-20°C), a dramatic increase in the *cis*-1,4-content of polybutadiene had been obtained ($>99.5\%$) [105–109]. The pronounced enhancements both in activity and in *cis*-1,4-selectivity were brought in by introducing bulky substituents on the Cp ligand or reducing the ionic radius of the central metal ions. For instance, complexes (C₅Me₄R)₂Sm(THF)_x (**22–26**, Fig. 2) under the activation with MMAO showed catalytic activity for the polymerization of butadiene depending on the R group; when it was ^{*i*}Pr, the highest activity was obtained [110]. (C₅Me₅)₂Ln[(μ-Me)AlMe₂(μ-Me)]₂Ln(C₅Me₅)₂ (**27**, Scheme 12), in situ generated from the reaction of (C₅Me₅)₂LnTHF_x with 8 equiv. TMA, when treated with [Ph₃C][B(C₆F₅)₄]/TIBA, showed catalytic activity in a trend of Gd \gg Nd \gg Pr and

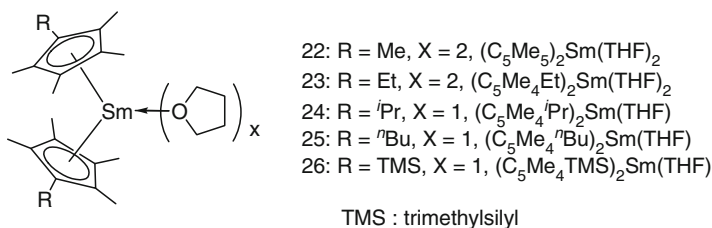
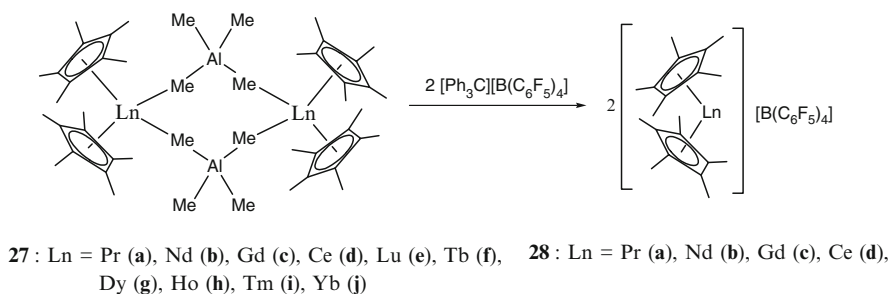


Fig. 2 Divalent samarocene complexes



Scheme 12 Activation of complex **27** with organoborate

the regularity of the resulting polymer following the similar trend Gd(97.5%) > Nd (91.3%) > Pr (90.2%) (*cis*-1,4-selectivity at 50°C), which were inverse of the size of metal ion. The activity of the Gd complex/TIBA system was so high that the polymerization could be performed fluently at low temperature -78°C to give perfect *cis*-1,4-stereospecific (>99.9%) polybutadiene with sharp molecular weight distribution ($M_w/M_n = 1.45$) under reasonable yields [111].

In contrast, the system based on Ce precursor **27d** with almost similar cocatalysts, TIBA/[Ph₃C][B(C₆F₅)₄], yielded polybutadiene with a low *cis*-1,4-content (38.8%, Table 8). Switching to TMA/[Ph₃C][B(C₆F₅)₄], surprisingly, highly *trans*-1,4-polybutadiene was obtained (93.8%, Table 9), suggesting that the type of the cocatalysts have also dramatic influence on the catalytic performances. Moreover,

Table 8 Polymerization of 1,3-butadiene with **27** and **6** in the presence of TIBA and [Ph₃C][B(C₆F₅)₄]^a [112]

Run	Cat.	Yield (%)	Microstructure (%)			$M_n (\times 10^3)$	M_w/M_n
			1,4- <i>cis</i>	1,4- <i>trans</i>	1,2-		
1	27a	28	55.3	43.9	0.8	22.8	1.27
2	27b	63	65.9	32.5	1.6	40.1	1.24
3	27c	~100	97.3	2.0	0.7	82.5	1.32
4	27d	15	38.8	59.8	1.4	12.8	1.24
5	27e	54	87.7	2.5	9.8	95.8	1.66
6	27f	~100	96.2	3.0	0.8	96.4	1.39
7	27g	~100	95.3	2.9	1.8	94.6	1.53
8	27h	~100	96.6	1.6	1.8	108.9	1.32
9	27i	~100	87.5	4.7	7.8	98.7	1.58
10	27j	0					
11	27c	~100	>99.9			113.7	1.70
12 ^b	6	~100	86.0	13.2	0.8	59.8	1.36

^aConditions: toluene: 20 mL, 25°C; 15 min; butadiene = 1×10^{-2} mol; Ln = 5×10^{-5} mol; [TIBA]₀/[Ln]₀ = 5; [Ph₃C][B(C₆F₅)₄]₀/[Ln]₀ = 1

^b−40°C, 5 h

Table 9 Polymerization 1,3-butadiene with **27** and **6** in the presence of AlMe₃ and [Ph₃C][B(C₆F₅)₄]^a

Run	Cat.	Yield (%)	Microstructure (%)			$M_n (\times 10^3)$	M_w/M_n
			1,4- <i>cis</i>	1,4- <i>trans</i>	1,2-		
1	27a	72	9.6	89.6	0.8	56.0	1.25
2	27b	87	13.8	85.2	1.0	65.0	1.25
3	27c	76	59.7	38.8	1.5	111.5	1.59
4	27d	35	4.9	93.8	1.3	38.0	1.41
5	27e	24	40.9	50.0	9.1	43.4	1.82
6	27f	43	72.4	26.6	1.4	91.2	1.84
7	27g	69	56.0	41.1	2.9	144.2	1.88
8	27h	48	64.8	32.5	2.7	72.0	1.60
9	27i	4	47.8	46.8	5.4	29.5	1.60
10	27j	0					
11 ^b	6	80	33.2	65.2	1.6	71.6	1.46

^aConditions: toluene: 20 mL, 25°C, 30 min; butadiene = 1×10^{-2} mol; Ln = 5×10^{-5} mol; [TMA]₀/[Ln]₀ = 3; { [Ph₃C][B(C₆F₅)₄]₀/[Ln]₀ = 1

^b24 h

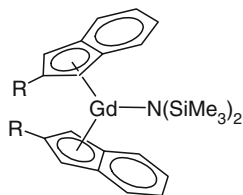
when the Al/Ln ratio was 3–5, the alkylaluminum worked as an activator; the polymerization systems showed somewhat living-like nature to afford polybutadiene with the M_n proportional to monomer consumption whilst the molecular weight distribution stayed constant. In the presence of excess amount of alkylaluminum, it worked as a chain transfer agent to adjust the molecular weight of polybutadiene conveniently [112, 113]. These lanthanocene catalyst systems showed lower activity for isoprene polymerization as compared with butadiene (Table 10). The monomer reactivity ratios by applying the Fineman–Ross method, $r_{\text{butadiene}} = 4.7$ and $r_{\text{isoprene}} = 0.02$, indicated that isoprene is two orders of magnitude less reactive than butadiene and also low specific regularity (*cis*-1,4-content of butadiene unit 98.4–96.9%, 1,4-content of isoprene unit 54.2–51.5%) [114]. As shown above in striking contrast to the intrinsic “Nd effect” of the conventional Ziegler–Natta catalysts, the catalytic performances of these cationic lanthanocene-based systems were governed significantly by the concerted effects of the specific environment around the reaction centers, the types of lanthanide ions and cocatalysts.

Tardif reported recently that the cationic half-sandwich lanthanide amido complexes $[(\text{Ind})\text{Ln}\{\text{N}(\text{SiMe}_3)_2\}][\text{B}(\text{C}_6\text{F}_5)_4]$ (**29**, Fig. 3) were also highly efficient and *cis*-1,4-selective for butadiene polymerization [115]. Meanwhile, Visseaux demonstrated that the half-sandwich scandium borohydride complex $\text{Cp}^*\text{Sc}(\text{BH}_4)_2(\text{THF})$ (**30**, Fig. 3) combined with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ and TIBA led to the very active and highly stereoselective isoprene polymerization (>90% *cis*-1,4, Table 11) as well as styrene (>99.9% syndio, Table 12). Improvement of the control of the polymerization was performed at lower temperature at -10°C that the *cis*-1,4-ratio increased up to 97.2% followed by the decrease of PDI down to 1.7 [116]. This

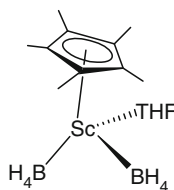
Table 10 Polymerization isoprene with **27c**/[Ph₃C][B(C₆F₅)₄]/TIBA^a [114]

Run	Temp (°C)	[TIBA] ₀ / [Gd] ₀	Yield (%)	Microstructure (%)			<i>M</i> _w (×10 ³)	<i>M</i> _n (×10 ³)	<i>M</i> _w / <i>M</i> _n	<i>T</i> _g (°C)	
				1,4- <i>cis</i>	1,4- <i>trans</i>	3,4-					
1	RT		2 h	97	32.6	18.8	48.6	370.9	179.1	2.07	−31.7
2	−20		6 days	22	44.9	3.0	52.2	114.6	114.6	10.01	−25.9
3	RT	10	1 h	~10	50.8	12.7	36.5	112.7	65.3	1.73	−51.2
4	0	20	5 h	93	98.7	0.0	1.3	902.0	461.5	1.95	−67.5
5	−20	50	10 h	88	>99.99			1,494.5	675.0	2.21	−68.4

^aConditions: in toluene; isoprene: 0.03 mol; **27c**: 2×10^{-5} mol



29: R = H (**a**), Me (**b**), Ph (**c**)



30

Fig. 3 Structures of lanthanide complexes **29** and **30**

Table 11 *cis*-1,4-Polymerization of isoprene (IP) using **30**/[Ph₃C][B(C₆F₅)₄]/TIBA [116]

Run	[IP]/[Sc]	[B]/[Sc]	TIBA	Temp (°C)	Time (min)	Yield (%)	Activity (kg (mol h) ^{−1})	<i>M</i> _n (×10 ³)	PDI	<i>cis</i> -1,4 (%)
1	1,000	1	10	20	9	39	177	36.7	4.1	90.7
2	1,000	2	10	20	7	76	443	92.6	2.7	94.2
3	1,000	2	20	0	25	55	90	96.4	2.4	97.0
4	1,000	2	20	−10	35	41	48	39.9	1.7	97.2
5	3,000	2	10	20	1	38	4,651	166.7	2.2	96.3
6	3,000	2	20	20	15	41	334	115.3	2.6	96.4
7	1,000	1	10	20	10	44	179	36.4	3.9	90.2
8	410	1	10	20	1,440	92	1.1	–	–	94.6

Table 12 Syndiospecific polymerization of styrene (ST) using **30**/[Ph₃C][B(C₆F₅)₄]/TIBA^a [116]

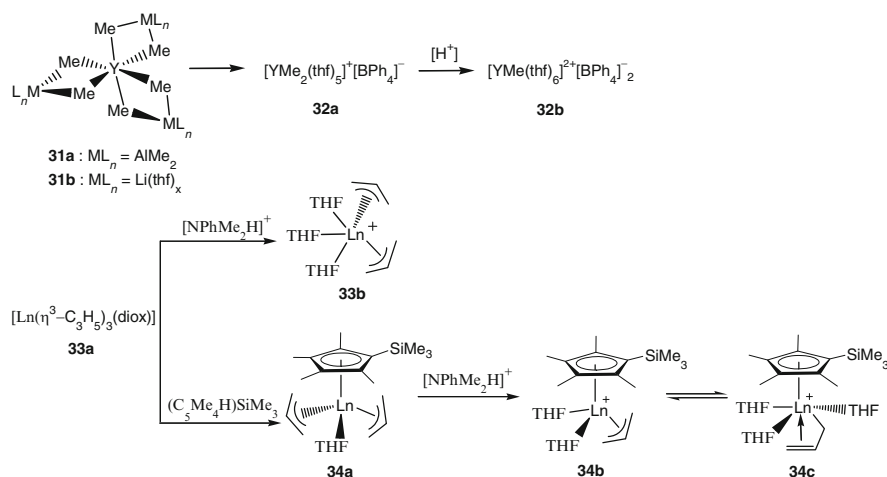
Run	[ST]/[Sc]	Time	Yield (%)	Activity (kg (mol h) ^{−1})	<i>M</i> _n (×10 ³)	PDI	sPS (%)	<i>T</i> _f (°C)
1	100	1 min	32	200	24.3	3.68	>99.9	269
2 ^b	200	17 h	80	1.0	6.0	3.64	>99.9	265
3	500	3 h 30 min	21	3.1	8.5	2.68	>99.9	270
4 ^c	500	18 h	25	0.7	–	–	>99.9	268
5 ^d	200	2 h 30 min	62	5.1	86.6	3.83	95 ^f	267
6 ^e	400	1 h 30 min	88	24.4	3.0	3.29	Atactic	–

^aConditions: T = 50°C, [TIBA]/[Sc]/[Ph₃C][B(C₆F₅)₄] = 10/1/1, toluene/monomer = 1^bT = 20°C^cToluene/monomer = 5^dSynthesized in situ^eIn the absence of TIBA^fCorresponds to 95% pure sPS along with an atactic fraction as evidenced by the high melting point

distinguished performances might be attributed to the introduction of the bulky Cp* ligand, because the analogous Sc(BH₄)₃(THF)_{1.5}/[Ph₃C][B(C₆F₅)₄]/(10TIBA) in toluene afforded polyisoprene quantitatively in 10 min at 20°C albeit with less controlled microstructure (mixture of *cis*-1,4-, *trans*-1,4-, and 3,4-units), whereas its neodymium analogue, the in situ-generated ternary catalytic system Nd(BH₄)₃(THF)₃/[HNMe₂Ph][B(C₆F₅)₄]/TIBA, exhibited better performances with a 92% *cis*-1,4-selectivity together with good control of *M*_n and PDI [117,118].

2.2.2 Noncyclopentadienyl Lanthanide Precursors

Non-Cp ligands [119–127] those containing heteroatom compounds have been extensively explored as spectator ligands by virtue of their strong metal–heteroatom bonds and exceptional and tunable steric and electronic features required for compensating coordinative unsaturation of metal centers and for catalytic activity toward polymerization. The elegant non-Cp-ligated cationic yttrium aluminate species applied in the polymerization of 1,3-dienes was reported by Okuda. Both the yttrium aluminates (**31a**) and their lithium ate complexes (**31b**) upon activation



Scheme 13 Synthesis of the mono- and dicationic yttrium methyl complexes **33** and **34** from yttrium aluminate **31** or hexamethyl yttrium **32**

with $[PhNHMe_2][B(C_6F_5)_4]$ catalyzed the polymerization of 1,3-dienes albeit at low activity and gave crosslinked product. The in situ-generated monocation $[YMe_2(solv)_x]^+$ (**32a**) produced polybutadiene in only 90% *cis*-1,4-tacticity and had a significantly lower polymerization activity (no polybutadiene was obtained after 30 min) than the dications (18–26% conversion). Under the presence of TIBA, the activity increased and *cis*-1,4-enriched polybutadienes were produced. Remarkably, the in situ-generated dication $[YMe(thf)_x]^{2+}$ (**32b**) gave *cis*-1,4-polybutadiene in up to 97% tacticity at 100% conversion after 14 h. In addition the molecular weight of the resultant polybutadiene by dicationic species was as high as that obtained with the monocation, indicating either a dication with one growing chain or a monocation with two growing chains (Scheme 13, Table 13) [128]. Very recently, the same group successfully isolated the yttrium bisallyl monocationic and yttrium monoallyl dicationic complexes (**33b**, **34**), which could initiate polymerization of butadiene with about 90% *cis*-1,4-selectivity [129].

Cui successfully isolated the non-Cp pyrrolyl aldiminate-ligated rare-earth metal bis(alkyl)s (**35**, Fig. 4), which combined with aluminum *tris*(alkyl)s and borate, initiated the polymerization of isoprene with *cis*-1,4-enriched regularity [130]. Increasing the ligand steric bulkiness, the indolyl-stabilized counterpart (**36**, Fig. 4) provided higher *cis*-1,4-selectivity and polyisoprene with more controllable molecular weight and narrow molecular weight distribution. The concerted influence of the environmental hindrance around central metals arising from the bulky substituents (*i*Pr vs. Me) of the ligands as well as the sterically demanding aluminum *tris*(alkyl)s, and the Lewis-acidic rare-earth metal ion, endowed the scandium combination **36d**/[Ph₃C][B(C₆F₅)₄]/TIBA the highest activity and the regioselectivity ($M_n = 2.65 \times 10^5$, $M_w/M_n = 1.07$, *cis*-1,4 = 98.2%, -60°C) [131].

Table 13 1,3-Diene polymerization by **31** activated by $[\text{PhNHMe}_2][\text{B}(\text{C}_6\text{F}_5)_4]^{\text{a}}$ [128]

Run	B:Y		Time (min)	Conversion (%)	Selectivity ^b	$M_n^c (\times 10^3)$	M_w/M_n
<i>1,3-Butadiene polymerization</i>							
1 ^d	1		30	<5			
2 ^e	1		240	73		186	4.4
3	1	TIBA	840	100	90:8:2	50	2.6
4	2		30	26	95:3:2	140	2.0
5 ^e	2		240	93		312	2.6
6	2	TIBA	30	18	95:3:2	61	1.7
7	2	TIBA	840	100	97:2:1	100	2.1
<i>Isoprene polymerization</i>							
8	1		10	56	60:26:14	117	1.6
9	1	TIBA	10	86	89:0:11	315	2.1
10	2		10	65	67:13:20	260	1.5
11	2	TIBA	10	78	90:0:10	133	2.9

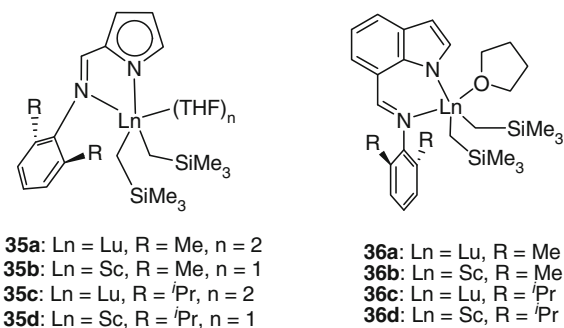
^aConditions: **31**: 5 μmol , 25°C. 1,3-Butadiene polymerization: $V_{\text{butadiene}} = 7.5 \text{ mL}$ (14 wt% in toluene); $V_{\text{total}} = 30 \text{ mL}$. Isoprene polymerization: $V_{\text{isoprene}} = 1 \text{ mL}$; $V_{\text{total}} = 30 \text{ mL}$.

^bRatio *cis:trans*: 1,2 for 1,3-butadiene; ratio *cis:trans*: 3,4 for isoprene

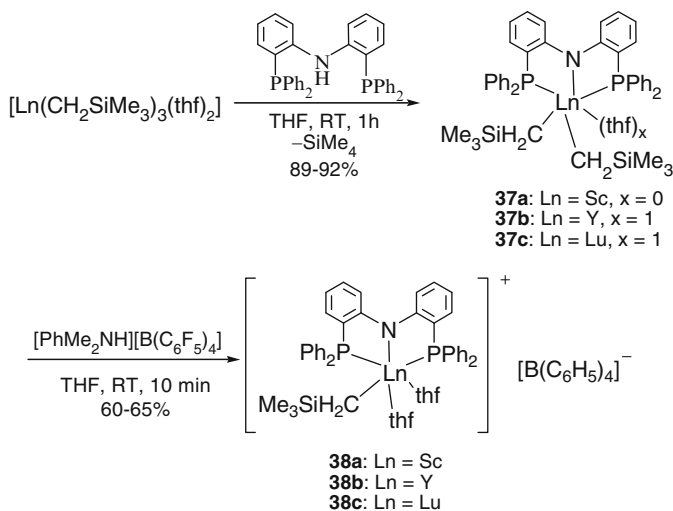
^cDetermined by GPC

^dNot determined

^eMicrostructure not determined because of crosslinking; molecular weight determined for the soluble fraction

Fig. 4 Pyrrolyl- and indenyl-stabilized dialkyl lanthanide complexes

The fascinating homogeneous catalysts based on rare-earth metal bis(alkyl) complexes (**37**) bearing bis(phosphinophenyl)amido (PNP) ancillary ligand were reported by Hou. The cationic alkyl species were generated in situ by treatment of **37** with equimolar $[\text{PhMe}_2\text{NH}][\text{B}(\text{C}_6\text{F}_5)_4]$ in $\text{C}_6\text{D}_5\text{Cl}$ (Scheme 14), among which the yttrium complex **37b** showed extremely high *cis*-1,4-selectivity (99%) and excellent livingness ($M_w/M_n = 1.05\text{--}1.13$) for the polymerization of isoprene and butadiene without addition of an aluminum additive (Table 14). The similar catalytic activity was observed for the Sc and Lu analogues, albeit with slightly lower *cis*-1,4-selectivity (96.5–97.1%). The excellent *cis*-selectivity was slightly influenced by increasing polymerization temperature up to 80°C, indicating that the active species were thermal stable. In addition a cationic alkyl lutetium complex



Scheme 14 Synthesis of neutral and cationic rare-earth metal alkyl complexes bearing a bis(2-diphenylphosphinophenyl)amido (PNP^{Ph})ligand

Table 14 Living *cis*-1,4-polymerization of isoprene (IP) initiated by **37** and borate (or borane)^a [132]

Run	Cat.	Temp (°C)	Time (min)	Yield (%)	M_n^b ($\times 10^5$)	M_w/M_n^b	Microstructure ^c		T_g^d (°C)	Eff. ^e (%)
							<i>cis</i> -1,4-	3,4-		
1	37	RT	60	0						
2	37a/A ^f	RT	60	100	1.6	1.10	96.5	3.5	−66	26
3	37b/A ^f	RT	60	100	2.3	1.10	99.3	0.7	−69	18
4	37c/A ^f	RT	60	100	1.9	1.09	97.1	2.9	−67	22
5	37b/B ^f	RT	60	79	3.2	1.11	99.3	0.7	−69	10
6	37b/C ^f	RT	60	0						
7	37b/A ^g	RT	10	40	0.5	1.05	99.3	0.7	−69	33
8	37b/A ^g	RT	15	90	1.0	1.05	99.3	0.7	−69	37
9	37b/A ^g	RT	20	100	1.2	1.07	99.3	0.7	−69	34
10	37b/A ^{g,h}	RT	40	150	1.8	1.08	99.3	0.7	−69	34
11	37b/A ^{g,h}	RT	60	200	2.3	1.08	99.3	0.7	−69	36
12	37b/A ^g	0	180	100	1.3	1.06	99.6	0.4	−69	31
13	37b/A ⁱ	50	10	90	0.7	1.05	98.7	1.3	−68	53
14	37b/A ^{i,j}	50	20	188	1.4	1.05	98.7	1.3	−68	55
15	37b/A ⁱ	80	2	66	0.6	1.05	98.5	1.5	−68	45
16	37b/A ⁱ	80	5	100	0.8	1.05	98.5	1.5	−68	51

^aConditions: C₆H₅Cl (10 mL); Ln (25 μmol); [IP]₀/[Ln]₀ = 600; [Ln]₀/[activator]₀ = 1:1 (activator = [PhMe₂NH][B(C₆F₅)₄] (**A**), [Ph₃C][B(C₆F₅)₄] (**B**), B(C₆F₅)₃ (**C**))

^bDetermined by GPC

^cDetermined by ¹H and ¹³C NMR spectroscopy

^dMeasured by DSC

^eCatalyst efficiency

^fIn runs 2–6, IP was added to **37b**/activator

^gIn runs 7–12, **A** was added to complex/IP

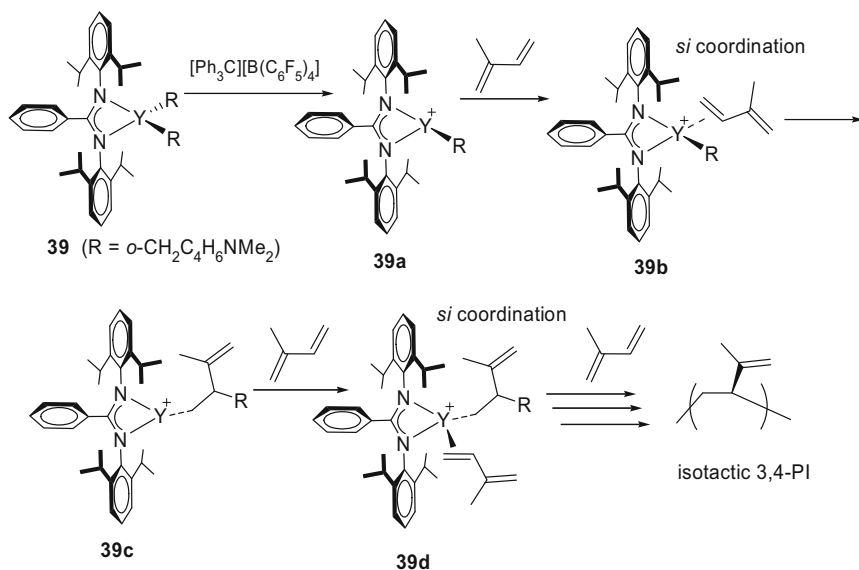
^hAnother equivalent of IP was added

ⁱIn runs 13–16, **37b** and IP in C₆H₅Cl (3 mL) was added to **A**

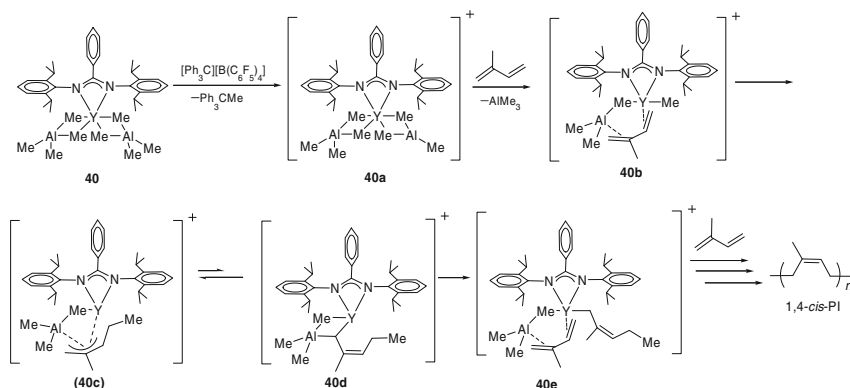
^j[IP]₀/[**37b**]₀ = 1,200

38c was successfully isolated and characterized, which represented in some degree a structural model for the true active species and for the mechanistic understanding of the polymerization process [132]. When PNP ligand was replaced by *N,N'*-bis(2,6-diisopropylphenyl)benzamidine (NCN^{dipp}H), the corresponding mono(amidinate) bis(aminobenzyl) complex **39** behaved quite differently. In the presence of 1 equiv. $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, it converted isoprene quantitatively into polyisoprene with high 3,4-regioselectivity (91%) and some degree of isotacticity (*mm* = 50%). When the polymerization was carried out at low temperature (-10°C), an even higher regio- and stereoselectivity was achieved and almost perfect isotactic 3,4-polyisoprene was obtained (3,4-selectivity up to 99.5%, *mmmm* up to 99%). The addition of TIBA or TEA had little effect on the polymerization; however, addition of 3 equiv. TMA, the resultant system changed the regio- and stereoselectivity of the polymerization dramatically from 3,4-isospecific to *cis*-1,4-selective that increased to as high as 98% at 5 equiv. TMA at -10°C or below. They explained that the steric hindrance and C_2 symmetry of the (NCN^{dipp})Y unit made isoprene coordinate to the Y center preferably in a 3,4- η^2 fashion, leading to the formation of isotactic 3,4-polyisoprene (Scheme 15); when 5 equiv. TMA was added, the resultant heterotrinnuclear Y/Al complex **40** preferred the coordination of isoprene in a μ -*cis*-1,4- η^4 fashion by replacement of an TMA unit. The 1,4-addition of a methyl group to the coordinated isoprene gave a μ - π -*anti*-allyl species and its equilibrium isomer μ - σ -allyl species, leading to *cis*-1,4-polyisoprene eventually (Scheme 16) [133].

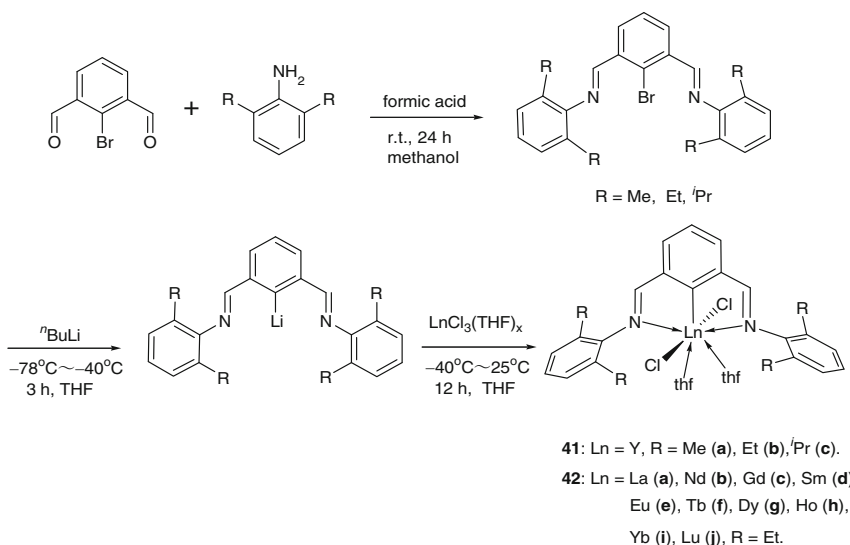
To date, the characteristic of the mentioned systems are based on lanthanide alkyl complexes, and showed intrinsic Nd or Sm or Gd or Y effects. The Ti, Co, Ni, and Nd metal chlorides, on the other hand, the first innovated to initiate the



Scheme 15 Possible mechanism for 1,4-selective polymerization of isoprene with **39**



Scheme 16 Possible mechanism for the *cis*-1,4-polymerization with **40**



Scheme 17 Synthesis of pincer-type lanthanide dichloride

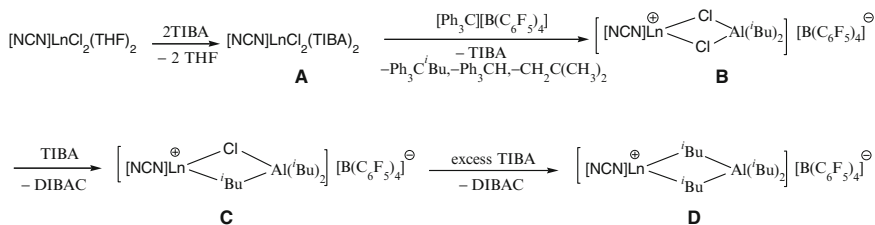
polymerization of butadiene in the early 1960s, are highly active to give polymers with 98% *cis*-1,4-selectivity but heterogeneous, leading to gel formation [134,135]. The addition of an electron donor to lanthanide trichlorides improves the catalytic activity and selectivity slightly, whereas the system is still heterogeneous [37]. Modifying the lanthanide chloride species with Cp or *ansa*-Cp and Flu moieties generated an inert system for the polymerization of butadiene, although which was active for copolymerization with ethylene, affording *trans*-1,4-butenyl units [136]. Cui's group successfully introduced the aryldiimino NCN-pincer ligand into rare-earth metal chloride compounds via covalent bond to afford complexes **41** and **42** (Scheme 17) [137]. These complexes in combination with aluminum alkyls

Table 15 Polymerization of butadiene induced by (NCN)LnCl₂THF₂/TIBA/[Ph₃C][B(C₆F₅)₄]^a [137]

Run	Complex	[BD]/ [Ln]	Temp (°C)	Time (min)	Yield (%)	M_n^b ($\times 10^4$)	M_w/M_n^b	Microstructure (%) ^c		
								<i>cis</i> -1,4-	<i>trans</i> -1,4-	1,2-
1	41a	500	25	60	80	3.96	1.47	98.5	1.3	0.2
2	41b	500	25	60	100	8.60	2.23	99.7	0.3	–
3	41c	500	25	60	68	2.63	1.31	95.3	4.2	0.5
4	42a	500	25	60	87	7.01	1.59	99.3	0.5	0.2
5	42b	500	25	15	100	18.00	2.08	99.5	0.4	0.1
6	42c	500	25	10	100	32.21	2.18	99.7	0.3	–
7	42d	500	25	120	0					
8	42e	500	25	120	0					
9	42f	500	25	10	100	21.00	2.43	99.7	0.3	–
10	42g	500	25	10	100	26.00	2.24	99.4	0.6	–
11	42h	500	25	15	100	14.22	2.44	99.4	0.6	–
12	42i	500	25	120	0					
13	42j	500	25	60	90	9.75	2.48	99.3	0.6	0.1
14	41b	1,000	25	60	100	18.63	2.31	99.3	0.7	
15 ^d	41b	2,000	25	60	93	39.50	2.40	99.4	0.6	–
16 ^e	41b	4,000	25	180	90	79.20	2.13	99.7	0.3	–
17 ^f	41b	5,000	25	180	85	133.00	1.79	99.9	0.1	–
18 ^g	41b	500	25	60	43	31.88	2.11	66.5	31.7	1.8
19 ^h	41b	500	25	60	65	17.40	1.68	51.5	47.5	1.0
20	42c	500	0	30	85	33.10	1.89	100		
21	42c	500	40	5	100	21.35	2.03	99.3	0.7	–
22	42c	500	60	5	100	11.70	1.87	97.6	2.1	0.3
23	42c	500	80	5	80	10.23	1.95	96.9	3.0	0.5

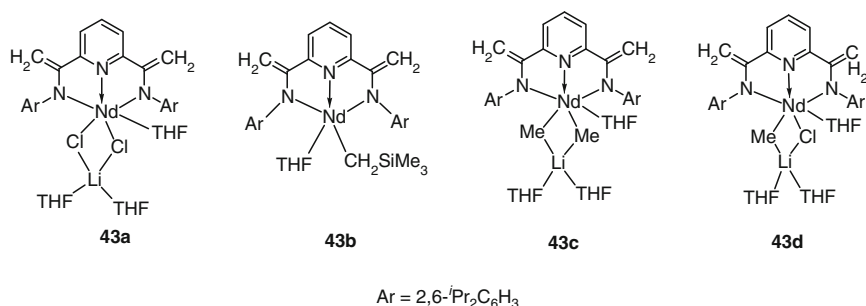
^aC₆H₅Cl (5 mL), complex (20 μmol), [Ln]₀/[TIBA]₀/[B]₀ = 1:20:1 (B = [Ph₃C][B(C₆F₅)₄])^bDetermined by GPC^cDetermined by ¹³C NMR spectrum^dC₆H₅Cl (15 mL)^eC₆H₅Cl (20 mL)^fC₆H₅Cl (30 mL)^g[Y]₀/[TMA]₀/[B]₀ = 1:20:1^h[Y]₀/[TEA]₀/[B]₀ = 1:20:1

and organoborate generated a new type of homogeneous Ziegler–Natta catalyst systems that displayed high activities and distinguished *cis*-1,4-selectivities for the polymerizations of butadiene and isoprene (Table 15). These excellent catalytic performances did not show obvious metal-type dependence except the inert Yb, Sm, and Eu counterparts but were influenced significantly by the spatial sterics of the auxiliary ligand and the sterically demanding alkylaluminum. The *cis*-selectivity of this system was found to be influenced by the *ortho*-substituents of the *N*-aryl ring of the ligands, reaching as high as 99.7% for **41b** bearing *o*-ethyl, which dropped slightly for **41a** bearing *o*-methyl (98.5%) and even more in the case of **41c** with the bulky *o*-isopropyl (95.3%). This might be ascribed to the different steric environment of the center metal that was pinched by the two *ortho*-substituted *N*-aryl rings. The dihedral angle formed by the aryl rings was 118.56(13)° in **41a**, 109.9° in **41b**, and 133.28(15)° in **41c**, respectively. The smaller the dihedral angle is, the

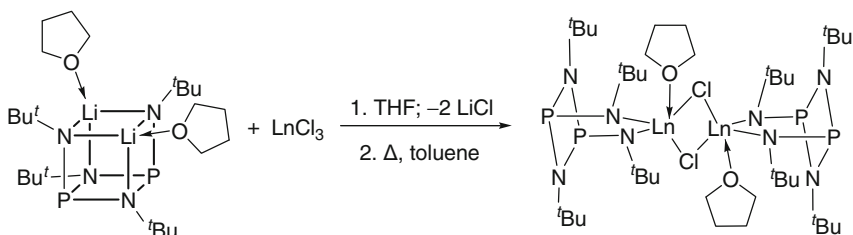


Scheme 18 Probable mechanism for diene polymerization

bulkier the metal center is, the higher *cis*-1,4-selectivity is. Remarkably, the high *cis*-1,4-selectivity remained at elevated polymerization temperatures up to 80°C. These results were in striking contrast to the conventional Ziegler–Natta systems in the specific selective polymerization of dienes. The identification of the active species was depicted in Scheme 18. The pincer yttrium dichloride (**41b**) was first treated with TIBA in C₆D₅Cl. The alkylation did not take place at room temperature within 12 h, suggesting that the Ln–Cl bond in **41b** was strengthened by the chelating NCN-pincer donor as compared to LnCl₃. Instead, an intermediate **A** [NCN]LnCl₂(TIBA)₂, the TIBA adduct of **41b**, was generated. It was reasonable that **A** could not induce the polymerization of butadiene at room temperature. When activated with [Ph₃C][B(C₆F₅)₄], **A** was swiftly transformed into the ion pair **B**. **B** was still inert to the polymerization. When adding one more equivalent of TIBA to **B**, a heteroleptic alkyl/chloride-bridged bimetallic intermediate **C**, [NCN]Ln[(μ-Cl)(μ-ⁱBu)(Al(ⁱBu)₂)] [B(C₆F₅)₄], was given. Under the presence of excess TIBA, **C** initiated the polymerization of butadiene (isoprene) immediately [137]. This result strongly suggested that the intermediate or active species generated by different catalyst systems might be different even though they showed the same high *cis*-1,4-selectivity toward the diene polymerizations. Onward Gambarotta [138] reported the 2,6-diiminopyridine ligand-stabilized rare-earth metal dichloride lithium ate complexes 2,6-[2,6-(ⁱPr)₂C₆H₃N=C(CH₃)₂(C₅H₃N)Nd(THF)(μ-Cl)₂][Li(THF)₂].0.5(hexane) (**43a**), and its analogues **43b–d** (Fig. 5). Addition of a solution of **43a** in cyclohexane to a cyclohexane solution of butadiene containing excess MMAO at 50°C started a polymerization affording polybutadiene with 95–97% *cis*-1,4-configuration in good yield (about 70%). Such high stereoselectivity in addition to the high catalyst activity, the high molecular weight, the relatively narrow polydispersity, and other desirable rheological properties placed this catalyst above other transition metal-based catalysts [139–142] and NdCl₃(THF)₂ [5], but below the remarkably performing Cp*₂Sm(THF)₂ [105] and the aryldiimino NCN-pincer-ligated rare-earth metal dichlorides (2,6-(2,6-C₆H₃R₂N=CH)₂–C₆H₃)LnCl₂(THF)₂ [137]. The mixed alkyl/chloride complex **43d** showed similar catalytic performances to **43a**, suggesting that partial alkylation occurred during the treatment of **43a** with MMAO. Meanwhile, the complex **43c** was also a potent polymerization catalyst when activated by alkylaluminum derivatives. Although the activity was somewhat lower than **43a**, the molecular weight of the polymer produced by **43c** was higher (Table 16).

**Fig. 5** Structures of complexes **43****Table 16** Polymerization of butadiene catalyzed by **43** and MMAO [138]

Run	Complex	Time (min)	Activity (kg (mmol h) ⁻¹)	Yield (%)	<i>cis</i> -1,4 (%)	<i>trans</i> -1,4 (%)	<i>trans</i> -1,4 1,2-(%)	<i>M_w</i> (×10 ⁴)	<i>M_n</i> (×10 ⁴)	<i>M_z</i> (×10 ⁴)	<i>M_w</i> / <i>M_n</i>
1	43d	15	0.74	77.3	97.0	2.5	0.5	65.9	26.3	122.0	2.5
2	43d	15	0.12(5)	67.5	95.0	4.5	0.5	38.0	16.4	71.5	2.31
3	43d	15	0.034(5)	84.8	96.1	4.5	3.4	38.5	16.4	72.7	2.34
4	43a	10	0.71	78.6	97.0	2.3	0.7	72.5	26.2	144.0	2.8
5	43c	15	0.40	17.2	95.9	3.3	0.8	91.0	15.5	220.0	4.9
6	43b	30	0.048	75.0	61.8	36.4	1.8	9.6	4.4	23.5	2.18

**44:** Ln = Y (a), La (b), Nd (c), Sm (d)**Scheme 19** Synthesis of complexes **44**

Recently Roesky et al. [143] demonstrated the synthesis of dimeric lanthanide chloro complexes featuring bis(amido)cyclodiphosph(III)azane (**44**) through salt metathesis methodology (Scheme 19). In the presence of MMAO, the neodymium complex **44c** displayed considerably high activity ($\text{TOF} \approx 17,000 \text{ h}^{-1}$) for polymerization of butadiene with 94% *cis*-1,4-selectivity. The number-average molecular weight of the afforded polybutadiene reached to $287,000 \text{ g mol}^{-1}$ and the molecular weight distribution was narrow ($\text{PDI} = 2.1$). When the cocatalyst MMAO was replaced by organoborate $[\text{R}_2(\text{Ph})\text{NH}][\text{B}(\text{C}_6\text{F}_5)_4]$ ($\text{R} = \text{octadecyl}$) and AlMe_3 , the resultant ternary catalyst system exhibited nearly six times higher activity whilst the molecular weight and molecular weight distribution remained almost unchanged.

3 *trans*-1,4-Polymerization of 1,3-Conjugated Dienes

trans-1,4-Polydienes [144, 145], and particularly *trans*-1,4-polyisoprene produced naturally as gutta-percha rubber, appear well suited for the elaboration of high-performance tires [146], and have found application in the fabrication of golf ball and insulating materials. Moreover, *trans*-polymerization may also allow incorporation of α -olefin into a polydiene chain, affording high-value-added copolymers [147–149]. Therefore, *trans*-1,4-selective polymerization of dienes has attracted an increasing attention. In the investigation of active centers (ACs) with NdCl_3 based catalyst system for butadiene polymerization by Monakov, six kinds of ACs were proposed to relate the microstructures of polybutadiene (Fig. 6). The first five involved a π -allyl binding of the terminal unit of the growing polymer chain, which was deemed to be responsible for the *cis*-regulated polybutadiene, whilst only the last one characterized as a σ -alkyl structure led to *trans*-regulated polybutadiene [150]. Thus, the reports on the production of *trans*-1,4-polymers by rare-earth metal complexes remain less owing to few suitable active centers compared with the *cis*-1,4-polymerization.

Visseaux reported that neodymium borohydrido complexes were very efficient catalysts toward isoprene polymerization. Upon activation with alkylaluminum or MAO, these borohydrido complexes yielded polydienes rich in *cis*-1,4-units, whereas *trans*-1,4-polydienes with very high stereoregularity were produced in the presence of dialkyl magnesium activator [150–156]. Although the mechanism was still unclear and no obvious regularity could be drawn, the selectivity was dependent on the metal center [154]. For instance, $\text{Nd}(\text{BH}_4)_3\text{THF}_3$ (**45a**) displayed high activity and selectivity while Sm and Y congeners (**45b**, **45c**) were totally inactive (Table 17). Unlike trialkylaluminum additives which can remarkably change the regioselectivity, varying dialkyl magnesium exhibited no evident effect on the *trans*-1,4-selectivity. Higher activity was realized at elevated temperature albeit sacrificing the selectivity and molecular weight distribution. The used solvent also affected the activity and selectivity. Noncoordinating solvents such as toluene or aliphatic hydrocarbon had no influence on the selectivity, but low activity was observed in

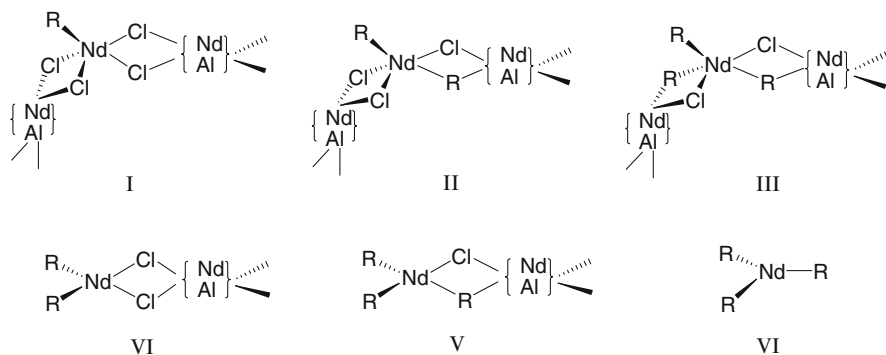


Fig. 6 The probable six kinds of active centers

Table 17 Polymerization of isoprene with borohydride complexes and magnesium activator

Run	Precatalyst ^a	[IP]/ [Ln]	Solvent	Temp (°C)	Time (h)	Yield (%)	<i>trans</i> - 1,4 ^b (%)	<i>M_n</i> ^c (×10 ³)	PDI ^c	References
1	45a /1 MgBuEt	1,000	Toluene	50	3	92	96.4	43.2	1.37	[154]
2	45a /1 Mg(Hex) ₂	1,000	Toluene	50	3	80	96.2	42.2	1.75	[154]
3	45a /1 MgBu ₂	1,000	Toluene	50	3	85	94.5	46.5	1.59	[154]
4	45a /1 Mg(CH ₂ TMS) ₂	1,000	Toluene	50	1	50	86.1	82.7	1.61	[154]
5	45a /1 Mg(C ₃ H ₅) ₂	1,000	Toluene	50	1	80	96.3	35.1	1.34	[154]
6	45b /1 MgBuEt	1,000	Toluene	50	24	0				[154]
7	45c /1 MgBuEt	1,000	Toluene	50	24	0				[154]
8	45a /0.5 MgBuEt	1,000	Toluene	50	2	67	93.0	61.5	1.40	[154]
9	45a /1 MgBuEt	1,000	Toluene	50	2	87	95.5	52.1	1.35	[154]
10	45a /2 MgBuEt	1,000	Toluene	50	2	66	93.9	27.8	1.55	[154]
11	45a /3 MgBuEt	1,000	Toluene	50	24	0				[154]
12	45a /3 MgBuEt	1,000	Toluene	50	48	30	60.7	15.0	2.05	[154]
13	45a /3 MgBuEt	1,000	Toluene	90	24	58	64.8	8.6	3.20	[154]
14	45a /5 MgBuEt	1,000	Toluene	50	24	0				[154]
15	45a /1 MgBuEt	1,000	Toluene	50	2	87	95.5	NG	1.35	[154]
16	45a /1 MgBuEt	1,000	Cyclohexene	50	2	52	95.2	NG	1.48	[154]
17	45a /1 MgBuEt	1,000	Pentane	50	2	54	95.8	NG	1.52	[154]
18	45a /1 MgBuEt	1,000	Toluene/ THF	50	2	33	96.5	NG	1.60	[154]
19 ^d	45a /1 MgBuEt	1,000	THF	50	24	0				[154]
20	45a /1 MgBuEt	1,000	CH ₂ Cl ₂	50	6	18	87.8	NG	2.18	[154]
21	45a /1 MgBuEt	1,000	Toluene	50	3	66	96.4	NG	1.82	[154]
22 ^c	45a /1 MgBuEt	1,000	Toluene	50	24	94	94.2	NG	1.82	[154]
23 ^c	45a /1 MgBuEt	1,000	Toluene	20	3	31	97.7	21.5	1.35	[154]
24	45a /1 MgBuEt	1,000	Toluene	50	3	92	95.5	63.6	1.37	[154]
25	45a /1 MgBuEt	1,000	Toluene	70	3	92	93.7	63.3	1.82	[154]
26	45a /1 MgBuEt	1,000	Toluene	80	3	93	93.2	59.0	2.22	[154]
27	46 /1 MgBu ₂	600	Toluene	50	22	60	98.4	15.4	2.01	[153]
28 ^d	47 /0.9 MgBu ₂	120	Toluene	50	2.75	>99	98.5	9.5	1.15	[153]
29	47 /52 MgBu ₂	120	Toluene	50	20	60	57.7	ND	ND	[153]
30	48 /1.2 MgBu ₂	160	Toluene	50	NG	NG	98.2	9.7	1.22	[153]
31	48 /1 MgBuEt	1,000	Toluene	50	2	80	97.4	52.3	1.18	[153]
32	49 /1 MgBuEt	1,000	Toluene	50	2	84	98.2	58.2	1.16	[155]
33	50 /1 MgBuEt	1,000	Toluene	50	2	41	95.2	31.6	1.57	[155]
34	51 /1 MgBuEt	1,000	Toluene	50	2	59	96.2	35.5	1.32	[155]

NG not given, ND not determined

^aPrecatalyst: 10 μmol solvent: 1 mL^bDetermined by ¹H NMR^cDetermined by GPC^d[thf]/[Ln] = 3^eToluene: 3 mL

the latter, probably due to the poor solubility of the thus formed polymer. In contrast, the coordinating THF or CH₂Cl₂ were deleterious, owing to their competitive coordination to active sites with dienes. The *trans*-selectivity could be improved by means of enhancing the steric hindrance at the metal center. Thus, the bulky half-metallocene derivatives **46–51** provided more than 98% *trans*-1,4-polyisoprene [152, 153] (Fig. 7, Table 17) as compared with the combination of the homoleptic Nd(BH₄)₃(THF)₃ and MgBu₂ (96%) [156]. Obviously, *trans*-stereospecific character of these catalysts was tentatively attributed to the concerted effects arising from both Nd and Mg ions, evidenced by the formation of Nd(μ-BH₄)Mg bridging

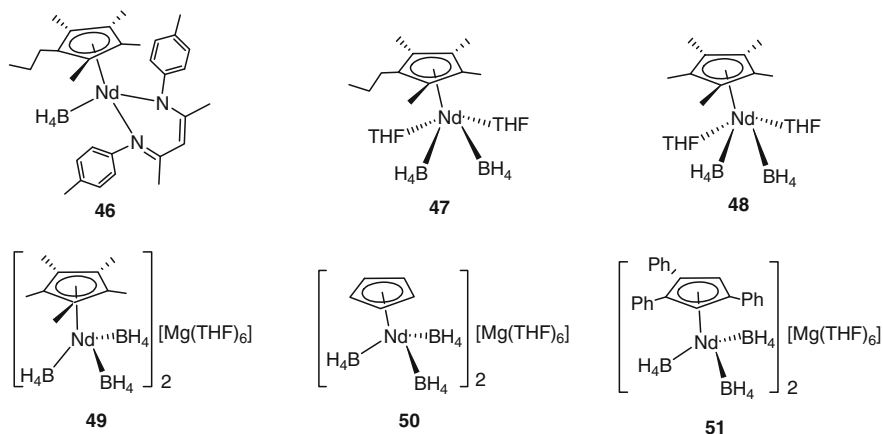
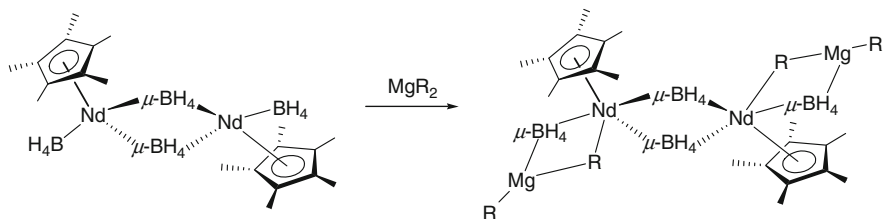


Fig. 7 Structures of half-sandwich neodymium borohydrido complexes **46–51**



Scheme 20 Probable heterobimetallic active species

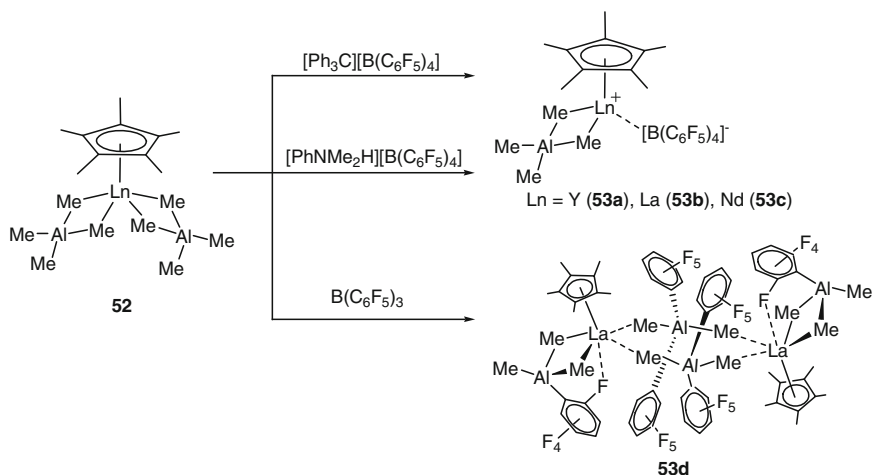
active species according to ^1H NMR analysis (Scheme 20) [154, 155]. Therefore, introducing a long-chain *n*-butyl ethyl magnesium, a living *trans*-1,4-polymerization of isoprene could be achieved [156, 157]. The surplus amount of dialkyl magnesium, however, resulted in a lowered *trans*-selectivity with the increase of 3,4-units in the afforded polymer. Surprisingly, when BuLi was used instead of MgR_2 , the combination with $(\text{C}_5\text{H}^i\text{Pr}_4)\text{Ln}(\text{BH}_4)_2(\text{THF})$ ($\text{Ln} = \text{Sm}, \text{Nd}$), or $(\text{C}_5\text{H}^i\text{Pr}_4)\text{U}(\text{BH}_4)_3$ enabled not only the *trans*-1,4 (95%) polymerization of isoprene to give high molecular weight product ($M_n = 590,000$, $\text{IP} = 1.5$, 5 h, 50°C) but also syndioselective (75%) polymerization of styrene (16 h, 50°C , yield 90%, $M_n = 530,000$, $\text{IP} = 1.6$) [158].

Half-sandwich lanthanide aluminate (**52**) with the activation of organoborate or borane displaying good to excellent activities for the *trans*-1,4-polymerization of isoprene was reported by Anwander [159]. They found that neutral borane $\text{B}(\text{C}_6\text{F}_5)_3$ exhibited superior performance as compared with organoborate, and the larger the rare-earth metal was, the higher the selectivity was. Thus, polyisoprene with very high *trans*-1,4-content (99.5%) and very narrow molecular weight distributions ($M_w/M_n = 1.18$) could be obtained from a combination of $\text{Cp}^*\text{La}(\text{AlMe}_4)_2$ and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_3]$ (**53b**), suggesting a living catalyst system (Table 18). Remarkably, a cationic and well-characterized complex **53d** isolated from the reaction between $\text{Cp}^*\text{La}(\text{AlMe}_4)_2$ and $\text{B}(\text{C}_6\text{F}_5)_3$ (Scheme 21) could serve as a single-component catalyst to produce the *trans*-polymer with almost the same properties, which also provided the structure model of the true active center in this

Table 18 Polymerization of isoprene catalyzed by heterobimetallic complexes and borate (or borane)

Run	Precat.	Cocat.	$M_n (\times 10^4)$	M_w/M_n	<i>trans</i> -1,4/ <i>cis</i> -1,4	References
1	52a	A	2	8.95	20.6/60.5	[159]
2	52a	B	6	1.59	28.7/43.5	[159]
3	52a	C	9	1.78	93.6/1.9	[159]
4	52c	A	3	2.87	69.7/14.0	[159]
5	52c	B	4	1.16	79.9/6.9	[159]
6	52c	C	13	1.35	92.4/3.8	[159]
7	52b	A	7	1.28	87.0/3.5	[159]
8	52b	B	6	1.22	79.5/3.4	[159]
9	52b	C	24	1.18	99.5/–	[159]
10	53d	–	23	1.19	99.0/0.2	[159]
11	54a	A	19	2.18	9.0/60.0	[160]
12	54a	B	12	1.77	4.0/63.0	[160]
13	54a	C	27	1.74	40.0/52.0	[160]
14	54b	A	6	1.28	80.3/14.5	[160]
15	54b	B	6	1.22	79.4/15.3	[160]
16	54b	C	33	1.52	89.3/–	[160]
17	55a	A	1	24.41	26.4/38.1	[160]
18	55a	B	3	1.74	34.6/38.3	[160]
19	55a	C	5	1.73	80.8/3.4	[160]
20	55b	A	9	1.45	81.4/3.4	[160]
21	55b	B	6	1.20	87.7/10.5	[160]
22	55b	C	20	1.26	95.6/2.2	[160]
23	56a	A	8	1.67	21.2/45.5	[160]
24	56a	B	9	1.25	19.0/53.0	[160]
25	56a	C	5	1.50	56.0/31.0	[160]
26	56b	A	8	1.41	60.0/20.0	[160]
27	56b	B	8	1.22	50.0/30.0	[160]
28	56b	C	11	1.41	90.0/6.0	[160]

A: $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, B: $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$, C: $\text{B}(\text{C}_6\text{F}_5)_3$

**Scheme 21** Activation of Ln/Al complex with different organoborate or borane

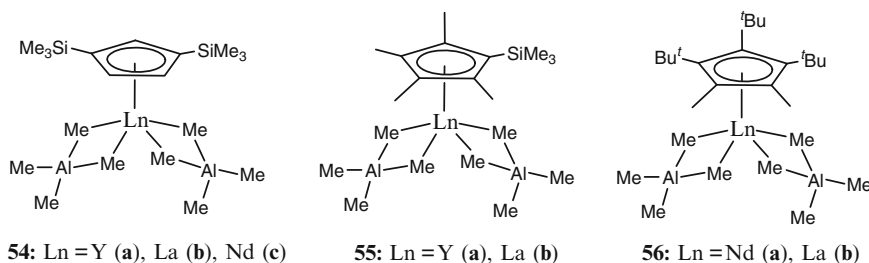
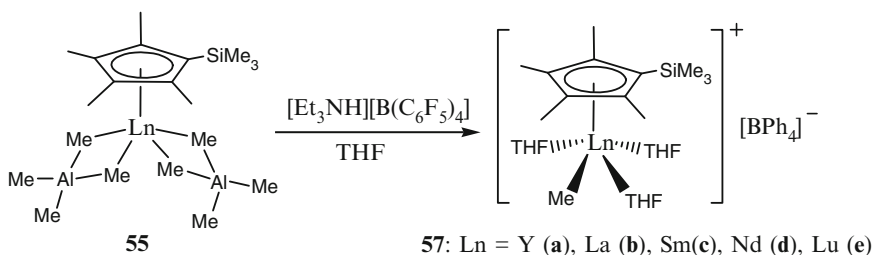


Fig. 8 Structures of half-sandwich heterobimetallic lanthanide/aluminum complexes **54–56**

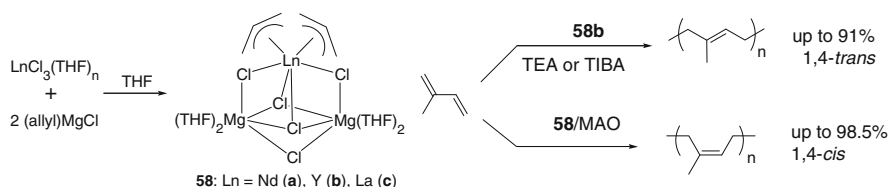


Scheme 22 Isolation of ion pair complex from **55** and organoborate

polymerization process. The regioselectivity could be improved with the complexes (**54–56**, Fig. 8) bearing the ancillary ligands that stabilized the cationic species generated in situ from reaction of catalyst precursor and borane as was disclosed by online NMR technique, although there seemed no correlation between the degree of steric shielding of the ancillary ligand with the catalytic activity and the selectivity [160].

Meanwhile, Okuda investigated the catalytic behavior for the polymerization of butadiene with the same half-sandwich rare-earth metal tetramethylaluminate complexes [Ln(η⁵-C₅Me₄SiMe₃){(μ-Me)₂(AlMe₂)₂}₂] (**55**, Ln = Y, La, Nd, Sm, Gd, Lu) [161]. Upon activation with [NEt₃H]⁺[B(C₆F₅)₄][−], the resultant cationic species enabled the polymerization of butadiene in the presence of TIBA to give *trans*-1,4-polybutadiene with narrow polydispersities (*M_w*/*M_n* = 1.05–1.09). Different from Anwander's result where heterobimetallic species was isolated, mononuclear ion pair was obtained from the reaction with borate (Scheme 22). Unfortunately, no catalytic data of **57** were given by the authors.

Nd(η³-C₃H₅)₃ and its derivatives were also evaluated as catalysts toward the polymerization of butadiene by Taube [162, 163]. Polymers with *trans*-1,4-unit around 85% were formed by using Nd(η³-C₃H₅)₃ in toluene at 50°C. Detailed study revealed that the *M_n* of the polymer increased linearly with the conversion and the polydispersity remained narrow. For the solvated precursor Nd(η³-C₃H₅)₃(C₄H₈O₂), higher *trans*-1,4-selectivity of 94% was achieved. Interestingly, the *trans*-1,4-selectivity can be switched to *cis*-1,4 by addition of trialkylaluminum or MAO. Introducing a Cp ligand, the resultant half-

**Scheme 23** Polymerization of isoprene initiated by **58** with alkylaluminum activator**Table 19** Polymerization of conjugated dienes by lanthanide precatalyst and different activator

Run	Catalyst	Monomer	Temp (°C)	$M_n (\times 10^3)$	M_w/M_n	1,4- <i>cis</i> / 1,4- <i>trans</i> (%)	References
1	58a /MAO	Isoprene	20	78	1.38	96.0/2.3	[164]
2	58b /MAO	Isoprene	20	33	6.5	75.2/22.8	[164]
3	58b /TEA	Isoprene	20	12	8.6	8.3/90.7	[164]
4	58b /TIBA	Isoprene	20	12	6.7	8.8/90.0	[164]
5	59a /MAO	Butadiene	25	NG	NG	0/>99	[165]
6	59a /Mg(Bu) ₂ /B(C ₆ F ₅) ₃	Butadiene	25	NG	NG	20/80	[165]
7	59b /MAO	Butadiene	25	NG	NG	76/17	[165]
8	59a /Mg(Bu) ₂ /B(C ₆ F ₅) ₃	Butadiene	25	NG	NG	30/70	[165]
9	59c /MAO	Butadiene	25	NG	NG	65/35	[165]
10	59c /Mg(Bu) ₂ /B(C ₆ F ₅) ₃	Butadiene	25	NG	NG	0/>99	[165]

NG not given

sandwich allyl complex $\text{Cp}^*\text{Nd}(\eta^3\text{-C}_3\text{H}_5)_2(0.7\text{C}_4\text{H}_8\text{O}_2)$, unfortunately, was inactive for the polymerization of butadiene, which in conjunction with MAO became extremely active albeit without selectivity. It was interesting to find that the central metal ion played a significant role in determining the selectivity of the system. Carpentier reported that the bimetallic neodymium–magnesium $\text{Nd}(\text{allyl})_2\text{Cl}(\text{MgCl}_2)_2(\text{THF})_4$ (**58a**, Scheme 23) combined with TEA or TIBA was highly active and *cis*-1,4-selective for the polymerization of isoprene (average TOFs up to ca. $5 \times 10^4 \text{ mol}(\text{mol h})^{-1}$ at 20°C). Whereas the yttrium analogue **58b**/MAO displaying lower activity enabled the formation of either *cis*-1,4-enriched (75%) or *trans*-1,4-enriched (91%) polyisoprenes, simply replacing the MAO activator by TEA or TIBA, respectively (Table 19) [164].

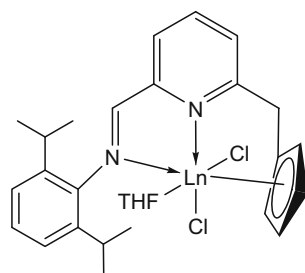
The strong dependence of the catalytic performances on the lanthanide metal ions and the trialkylaluminum compounds were also found in the systems based on lanthanocenes reported by Kaita et al. Lanthanocene complexes **27** in the presence of trialkylaluminum and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ could initiate the living polymerization of butadiene [112]. The most active gadolinium system gave perfectly *cis*-1,4-regulated polybutadiene at -40°C , whilst the analogous cerium complex and TMA and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ displayed high *trans*-1,4-selectivity (93.8%) toward the polymerization of butadiene in a quasiliving mode (Table 9).

The linked half-sandwich ligand brought about obvious improvement in *trans*-1,4-selectivity for the attached active metal center as reported by Napoli [165]. The yttrium complex **59a** (Fig. 9) in conjunction with MAO produced polybutadiene

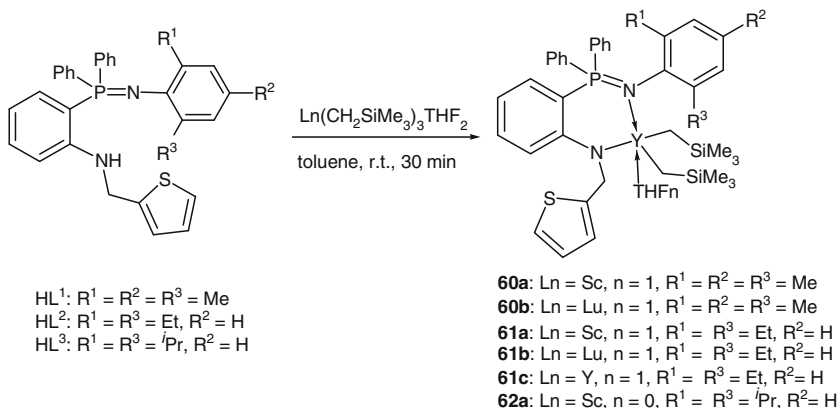
with >99% *cis*-1,4-regularity, whereas the samarium (**59b**) and neodymium (**59c**) analogues were *cis*-1,4-selective enriched. Replacing MAO by MgBu_2 and $\text{B}(\text{C}_6\text{F}_5)_3$, in contrast, **59c** exhibited an as high as *trans*-1,4 > 99% selectivity, whereas *trans*-1,4-selectivity of **59a** system reduced to 80% (Table 19). This proved further that the active species in the *trans*-polymerization of dienes were probably bimetallic.

Up to date, all these complexes showing high *trans*-1,4-selectivity for the polymerization of dienes are rare-earth metal complexes bearing a Cp ligand by virtue of their steric hindrance. Cui's group recently reported the first rare-earth metal bis(alkyl) complexes featuring a non-Cp *N,N'*-bidentate auxiliary ligand (L^{1-3}) $\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_n$ (**60–62**, Scheme 24), which, in combination with AlR_3 and borate, showed medium activity and good *trans*-1,4-selectivity for the polymerization of butadiene. The resultant polymer had moderate molecular weight ($M_n = 10,000\text{--}18,000$) with narrow molecular weight distribution ($M_w/M_n < 1.6$) and *trans*-1,4-regularity varying from 49.2% up to 91.3%. The catalyst performances were strongly dependent on the *ortho*-substituent of the *N*-aryl ring, the type of aluminum alkyls and the lanthanide metal used. Higher

Fig. 9 Linked half-metalocene complexes of lanthanide



59 : Ln = Y (**a**), Sm (**b**), Nd (**c**)



Scheme 24 Synthesis of dialkyl lanthanide complexes bearing anilido-phosphoimino ligand

trans-1,4-selectivity could be reached with bulky substituents or by employing smaller metal. Furthermore, the introduction of a pendant moiety capable of coordinating to the metal center benefited the *trans*-1,4-regularity [166, 167].

4 3,4-Polymerization of Isoprene

As compared with the explosive number of reports on 1,4-polymerization of dienes, 3,4-selective polymerization of isoprene has remained less explored, although 3,4-regulated polyisoprene is an important component of high-performance rubbers such as those with wet-skid resistance or low-rolling resistance tread [168, 169]. Early researches revealed that diene monomers insert into active lanthanide center to generate $\text{Ln-}\eta^3\text{-allyl}$ transition state (Scheme 2). As a consequence of the strong lanthanide allyl bond and higher ionic charge on the lanthanide, the negative charges shifted to C1 atom from C3 atom. Thus, the nucleophilicity of the C3 atom was lessened, suppressing the formation of 3,4-unit by the nucleophilic attack of the diene via C3 atom. Therefore the 3,4-polymerization of isoprene is more impossible. The first efficient 3,4-selective systems were the patented organolithium and ferric acetylacetonate [170–172] and the transition metal complexes such as $\text{AlEt}_3\text{-Ti(OR)}_4$ [22], $(\text{dmpe})_2\text{CrCl}_2\text{-MAO}$ [23], and ferric complexes chelated by nitrogen ligands [22–25]. Medium to high 3,4-regularity or strain-crystalline polyisoprene could be obtained by lowering the polymerization temperature. The catalyst systems based on rare-earth metals were achieved only recently by Hou's group using a dimeric yttrium monoalkyl complex **63a** (Fig. 10) bearing bulky linked half-sandwich ligand and a cocatalyst $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$. The polymerization of isoprene proceeded rapidly to yield 3,4-polyisoprene (99%) with isotactic-rich stereotacticity ($mm = 80\%$, $mmmm = 30\%$) and a relatively narrow molecular weight distribution ($M_w/M_n = 1.8$, Table 20). When polymerization was carried out at -20°C , a polyisoprene with almost perfect isotactic 3,4-microstructure (3,4-selectivity 100%, $mmmm > 99\%$) was obtained. The active species were unstable, easily decomposed, or changed to other species; thus, bimodal molecular weight

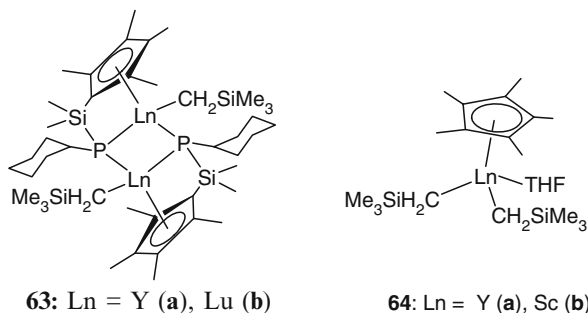


Fig. 10 Structures of half-metalloccenes of lanthanide alkyl complexes

Table 20 Polymerization of isoprene under various conditions lanthanide alkyl complexes^a [173]

Run	Cat.	Temp (°C)	Time (h)	Yield (%)	M_n^b ($\times 10^5$)	PDI ^b	Microstructure (%)			T_g/T_m^d
							3,4-	<i>mm</i>	<i>mmmm</i>	
1	63a	25	2	0						
2	A	25	2	80	0.3	7.9	<5 ^c			ND
3	B	25	2	0						
4	C	25	2	0						
5	63a + A	25	2	92	1.0	1.8	99	80	30	42/–
6	63a + A	–10	16	41	4.3; 0.3	1.6; 1.4	100	96	80	28/148
7	63a + A	–20	48	50	3.2; 0.3	1.7; 1.4	100	100	>99	30/154
8	63a + A	25	2	100	1.2	1.3	99	80	30	41/–
9	63a + A	–10	16	60	3.7	1.6	100	96	80	31/138
10	63a + A	–20	48	87	5.0	1.6	100	100	>99	33/162
11 ^f	63a + A	25	2	65	0.8	1.6	99	25		38/–
12	63a + B	25	2	85	1.4	1.3	99	40		ND
13	63a + C	25	2	63	1.1	1.4	99	38		ND
14	63a + A	25	2	17	1.3	1.6	89			ND
15	64a + A	25	2	100	0.9	1.06	66 ^g			ND

ND not determined

^aConditions: C₆H₅Cl, 10 mL; neutral complex, 2.5×10^{-5} mol; [isoprene]₀/[complex]₀ = 600, [complex]₀/[activator]₀ = 1:1, **A** = [Ph₃C][B(C₆F₅)₄], **B** = [PhMe₂NH][B(C₆F₅)₄], **C** = B(C₆F₅)₃. In runs 5–7, isoprene was added to **63a** and **A**. In runs 8–15, an activator was added to neutral complex and isoprene

^bDetermined by GPC against polystyrene standard

^cDetermined by ¹H and ¹³C NMR

^dDetermined by DSC

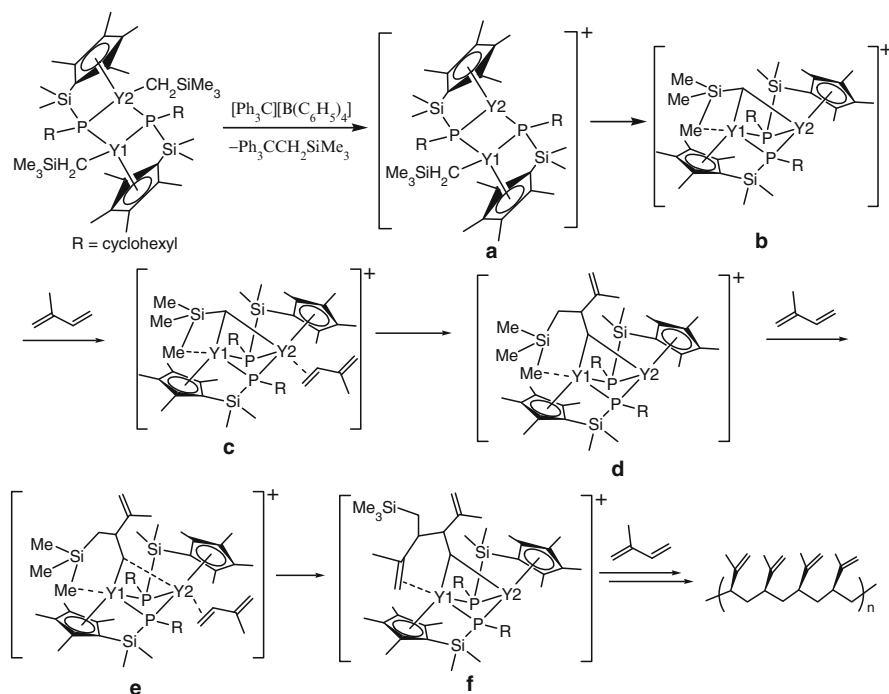
^eThe *trans*-1,4-unit is a major component

^fIn toluene

^g1,4-unit: 34%

distribution was observed. To avoid this isoprene should be added to the reaction mixture prior to the activator to stabilize the formed active species. By means of DFT calculation, the mechanism was supposed as shown in Scheme 25. It seemed that the steric environment enforced isoprene to adopt η^2 -coordination to the active metal center; meanwhile, the agostic interaction of the silylmethyl or vinyl chain-end groups with metal ion contributed to the isotacticity. For comparison, the unlinked half-sandwich yttrium dialkyl complex **64a** was employed for the isoprene polymerization to give 66% 3,4-selectivity. This confirmed further that a more steric environment around the metal center benefited 3,4-selectivity [173].

Cui's group successfully synthesized indenyl- and fluorenyl-modified *N*-heterocyclic carbene, a new kind of linked half-sandwich ligand, attached rare-earth metal bis(alkyl) complexes (**65**, **66**) (Fig. 11). In the presence of TIBA and [Ph₃C][B(C₆F₅)₄], complexes **65b–65d** exhibited high activity, medium syndio but remarkably high 3,4-regioselectivity. More strikingly, this system realized for the first time the livingness mode for the 3,4-polymerization of isoprene. Moreover, such distinguished catalytic performances could be maintained under various monomer-to-initiator ratios (500–5,000) and broad range of polymerization temperatures (25–80°C) (Table 21). The resultant polymers are crystalline, having syndiotactic enriched (racemic enchainment triad *rr* = 50%, pentad *rrrr* = 30%)



Scheme 25 Possible polymerization mechanism

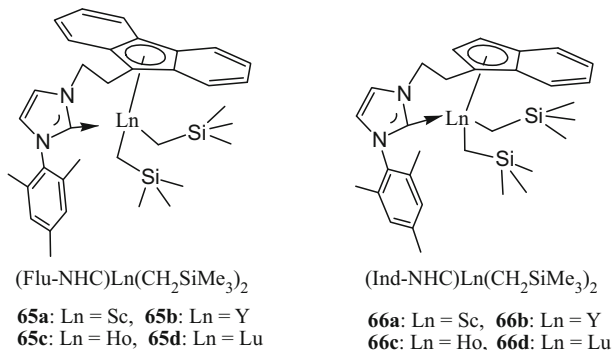


Fig. 11 Fluorenyl- and indenyl-functionalized carbene lanthanide dialkyl complexes

3,4-regulated (99%) microstructure and high glass transition temperatures (40–49°C). In contrast, complex **65a** was almost inert, probably resulting from the overcrowded environment induced by a smaller radius of scandium. For the less sterically hindered carbene–indenyl complexes **66a–66d**, low activity or selectivity was observed. This is in agreement with the assumption that tuning the spatial hindrance at the metal centers effectively changes the regioselectivity [174, 175].

Sequentially, the same group developed a variety of rare-earth metal bis(alkyl) complexes featuring NPN ligands (Scheme 26). Under the assistance of borate

Table 21 Polymerization of isoprene by using rare-earth metal precursors **65a–d** and **66a–d** and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ and TIBA^a [174]

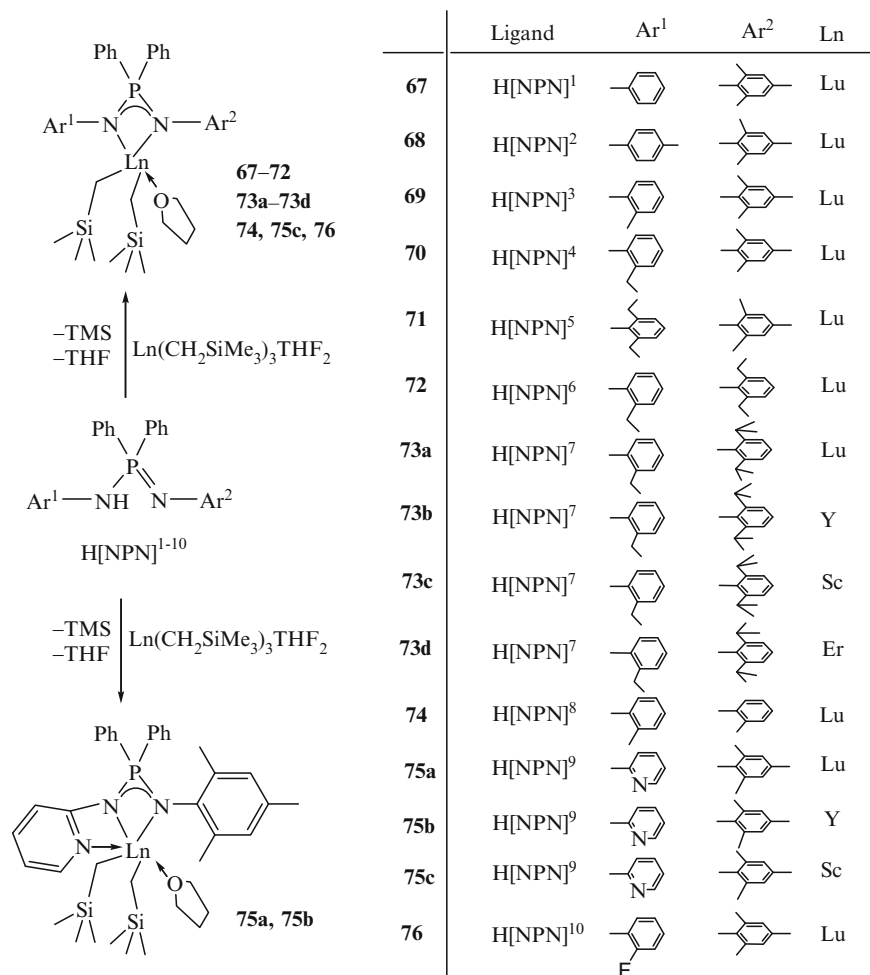
Run	Cat.	[IP]/[Ln]	Temp (°C)	Time (h)	Yield (%)	3,4- (%)	$M_n (\times 10^4)$	M_w/M_n	T_g (°C)	Eff. (%)
1	65a	500	25	6	Trace	ND	ND	ND	ND	ND
2	65b	500	25	4	100	98.2	4.72	1.06	41	72.2
3	65c	500	25	3	100	98.3	3.94	1.07	43	86.4
4	65d	500	25	6	100	99.0	4.08	1.05	45	83.5
5	65d	1,000	25	12	100	98.6	8.61	1.11	45	79.1
6	65d	2,000	25	24	100	96.6	16.7	1.12	48	81.6
7	65d	3,000	25	36	100	96.7	25.1	1.22	48	81.4
8	65d	4,000	25	48	100	96.5	32.9	1.27	48	82.8
9	65d	5,000	25	72	93	95.2	39.4	1.29	47	80.4
10	65d	500	40	5	100	97.4	3.90	1.22	49	87.3
11	65d	500	50	4	100	97.3	3.73	1.27	48	91.3
12	65d	500	60	3	100	95.4	3.85	1.19	47	88.5
13	65d	500	70	3	100	95.4	4.02	1.19	46	84.7
14	65d	500	80	2	100	94.5	3.91	1.22	46	87.1
15	65d^b	500	25	12	100	98.1	3.86	1.38	40	88.2
16	65d^c	500	25	2	100	98.2	4.26	1.10	45	80.0
17	66a	500	25	6	Trace	ND	ND	ND	ND	ND
18	66b	500	25	6	50	89.4	2.03	1.36	23	83.9
19	66c	500	25	6	93	76.1	3.81	1.40	3	83.1
20	66d	500	25	6	15	91.0	ND	ND	ND	ND

ND not determined

^aConditions: toluene (3.0 mL); Ln (10 μmol); $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (10 μmol); TIBA (100 μmol)^bHexane as solvent^cChlorobenzene as solvent

and trialkylaluminum, these complexes displayed extremely high activity and 3,4-selectivity for the polymerization of isoprene [176, 177] which represented the first non-Cp-ligated rare-earth metal-based catalyst system possessing such distinguished performances. Systematic study revealed that the complexes bearing alkyl substituents in the aryl rings of the ligands exhibited higher activity than those bearing electron-withdrawing substituents, irrespective of the central metal type (Table 22). Meanwhile, the sterics and electronics of the ligands played significant roles in governing the 3,4-selectivity of the complexes. With the increase of bulkiness of the *ortho*-substituents of the aryl rings of the ligands as well as reducing the size of the metal ion, the resultant complexes provided an increasing 3,4-selectivity, as the steric shielding around metal center led to isoprene η^2 -coordination. The complexes bearing electron-donating ligands showed higher 3,4-selectivity, as the space-filled and electronegative metal center facilitated isoprene η^2 -coordination. In contrast, an electrophilic metal center attached by ligands with electron-withdrawing groups favored isoprene η^4 -coordination, resulting in moderate 3,4-regulated or even *cis*-1,4-enriched polyisoprene. These results elucidated for the first time the correlation of molecular structures of complexes and catalytic behaviors in 3,4-selective isoprene polymerization.

Similarly, yttrium dialkyl complexes **39**, **39a**, and **40** bearing amidinate ligand, a geometry analogue of NPN-imidophosphine amido ligand, in combination with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, established cationic species for the polymerization of isoprene,

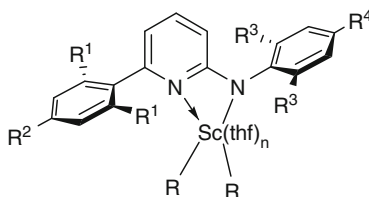
**Scheme 26** Synthesis of NPN-ligated lanthanide dialkyl complexes

giving isotactic 3,4-polyisoprene (Scheme 15) [133]. Meanwhile, Kempe reported 2-amidopyridine-ligated scandium dialkyl complexes **77a–d** (Fig. 12) where the ligand could be formally viewed as a variation of amidinate and coordinated to scandium in a N, N' - η^2 -mode. These complexes were activated with organoborate or borane to show more than 95% 3,4-selectivity at room temperature. Further investigation of the monomer-to-initiator ratio with **77a**/[C₆H₅NH(CH₃)₂][B(C₆F₅)₄] disclosed that the number of polymer chain was proportional to that of the metal pre-catalyst, suggesting a controlled polymerization. In contrast to the previous reports the addition of aluminum alkyl additives was detrimental to the polymerization, resulting in a decreased 3,4-selectivity or broadening of the molecular weight distribution. Although organoscandium cations could be isolated by treatment of **77a–77c**

Table 22 Polymerization of isoprene catalyzed by NPN-ligated lanthanide dialkyl complexes^a [177]

Run	Cat.	Temp (°C)	Time (min)	Yield (%)	Microstructures (%)			$M_n (\times 10^4)$	M_w/M_n	Eff. (%)
					3,4-	<i>cis</i> -1,4	<i>trans</i> -1,4			
1	67	20	15	100	81.6	17.5	0.9	5.44	1.8	1.25
2	68	20	15	100	82.0	17.3	0.7	6.92	1.7	0.98
3	69	20	15	100	95.1	4.2	0.7	7.53	1.7	0.90
4	70	20	15	100	96.6	3.0	0.4	6.50	1.8	1.05
5	71	20	15	100	95.1	4.3	0.6	6.57	2.0	1.04
6	72	20	15	100	96.8	3.0	0.2	6.07	1.9	1.12
7	73a	20	15	100	97.8	2.0	0.2	7.43	1.9	0.92
8	73b	20	15	100	92.3	6.9	0.8	8.74	1.2	0.78
9	73c	20	15	100	98.1	1.8	0.1	6.48	1.2	1.05
10	73d	20	15	100	93.8	5.9	0.3	10.97	1.3	0.62
11	73c	40	10	100	91.6	8.2	0.2	5.03	1.4	1.35
12	73c	0	30	89	98.5	1.4	0.1	11.49	1.4	0.59
13	73c	−20	360	81	99.4	0.6	0	14.90	1.5	0.46
14	74	20	15	100	84.4	15.1	0.5	6.45	1.9	1.05
15	75a	20	60	100	85.0	14.6	0.4	4.28	1.8	1.59
16	75b	20	15	100	85.5	14.0	0.5	14.60	1.8	0.47
17	75c	20	360	80	33.3	65.9	0.8	15.90	1.9	0.43
18	76	20	15	100	77.5	21.6	0.9	3.94	1.6	1.73

^aConditions: toluene 5 mL, complex 10 μ mol, $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ 10 μ mol, TIBA 100 μ mol, $[\text{IP}]_0:[\text{Ln}]_0 = 1,000$



77a: $\text{R}^1 = \text{R}^2 = \text{R}^3 = i\text{Pr}$, $\text{R}^4 = \text{H}$, $\text{R} = \text{CH}_2\text{SiMe}_3$, $n = 1$

77b: $\text{R}^1 = \text{R}^2 = i\text{Pr}$, $\text{R}^3 = \text{R}^4 = \text{Me}$, $\text{R} = \text{CH}_2\text{SiMe}_3$, $n = 1$

77c: $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{H}$, $\text{R}^3 = i\text{Pr}$, $\text{R}^4 = \text{H}$, $\text{R} = \text{CH}_2\text{SiMe}_3$, $n = 1$

77d: $\text{R}^1 = \text{R}^2 = \text{R}^3 = i\text{Pr}$, $\text{R}^4 = \text{H}$, $\text{R} = \text{CH}_2\text{Ph}$, $n = 1$

77e: $\text{R}^1 = \text{R}^2 = \text{R}^3 = i\text{Pr}$, $\text{R}^4 = \text{H}$, $\text{R} = \text{N}(\text{SiHMe}_2)_2$, $n = 0$

Fig. 12 Amidopyridine scandium dialkyl and diamide complexes

with borate, their inability to initiate polymerization of isoprene suggested a different pathway from that proposed by Hou [178]. Interestingly, the scandium diamide analogue **77e** produced *cis*-1,4-polyisoprenes (selectivity = 96%) in the presence of borate and trialkylaluminum, which might be attributed to the ligand transfer from scandium to aluminum [179].

5 Copolymerization of Conjugated Dienes with Alkenes

The copolymerization of dienes with alkenes provides a methodology to prepare high-performance rubbers, however, it usually encounters problems of low activity owing to different mechanisms. Recently, some breakthroughs have been achieved by virtue of the fast development of organolanthanide chemistry. Boisson et al. reported the copolymerization of ethylene with butadiene using a series of neodymocene catalysts (Fig. 13), the performances of which were significantly influenced by the ligand framework, the anionic counterion as well as the activator. The lanthanocene chloride complexes **78–80** initiated the copolymerization of ethylene with butadiene in the presence of BuLi/DIBAH to afford random copolymer containing a small ratio of butadiene [178]. The silylene-bridged bis-Flu neodymium chloride and borohydride complexes **81–89** were able to catalyze the copolymerization of ethylene with butadiene but behaved quite differently (Table 23) [149, 180–182], among which **81** could produce a copolymer with high incorporation of butadiene units up to 62 mol% with the increase of butadiene feed ratio. However, in contrast, the yttrium and samarium counterparts **82** and **83** displayed an inferior activity by giving a copolymer with lower butadiene content (13.6%) [149]. An interesting catalytic performance was found for the *ansa*-Flu neodymium complex **84** (or **87**) in the presence of alkylating reagents to afford polymer with *trans*-1,2-cyclohexane rings in the backbone of macromolecular chains. This system could randomly

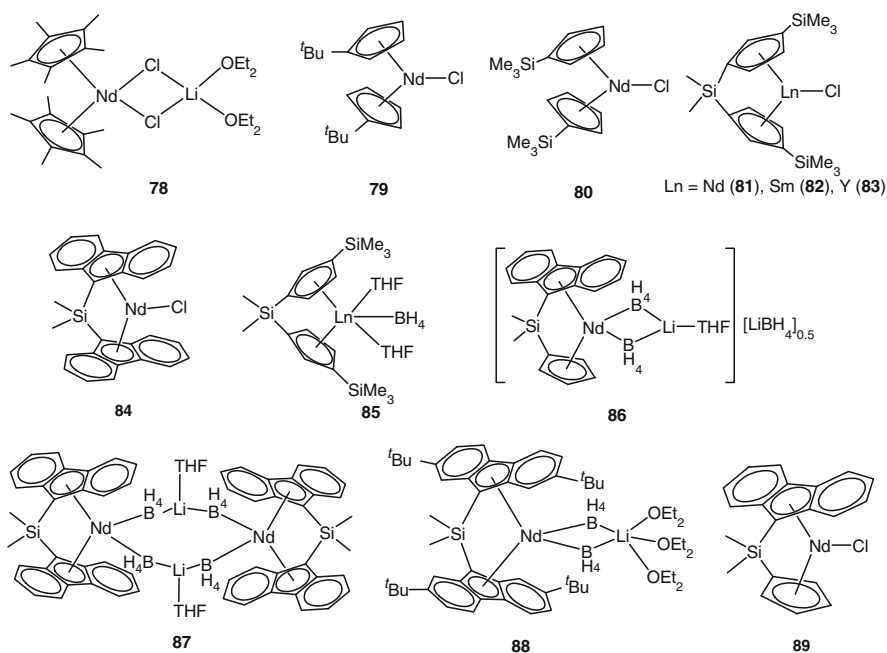


Fig. 13 Structures of lanthanide metallocene catalysts **78–89**

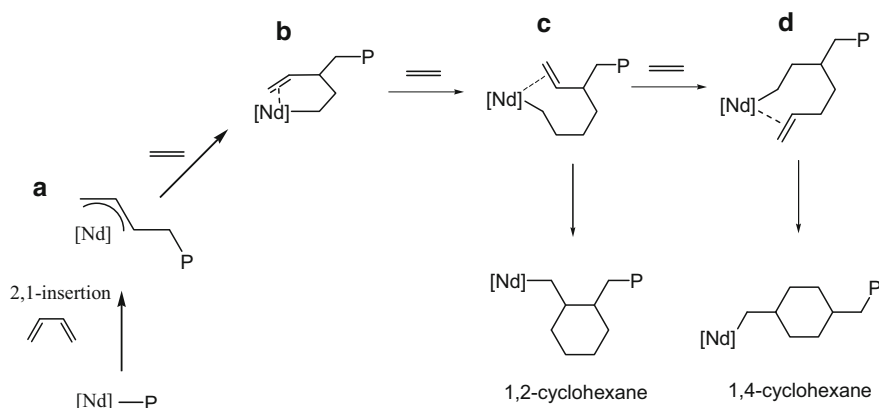
Table 23 Copolymerization of ethylene with butadiene with **84**, **87**, and **88** in the presence of BuMg(Oct)

Run	Catalyst	BD% in polymer	<i>trans</i> -1,4	Vinyl	<i>trans</i> -1,2-cyclohexane	<i>cis</i> -1,2-cyclohexane	<i>trans</i> -1,4-cyclohexane	<i>T_g</i> (°C)	References
1	84 + 2 equiv. Mg	13.3	27.1	20.1	52.8			-31	[180]
2	84 + 2 equiv. Mg	15.0	25.8	22.9	51.3			-34	[180]
3	84 + 2 equiv. Mg	19.3	27.6	28.4	44.0			-37	[180]
4	87 + 5 equiv. Mg	26.7	31.8	35.2	33.0			-36.0	[181]
5	87 + 2 equiv. Mg	25.3	31.9	31.9	36.1			-33.0	[181]
6	87 + 2 equiv. Mg	19.3	27.6	28.4	44.0			-37.0	[181]
7	87 + 10 equiv. Mg	28	32.3	38.9	28.8			-35.3	[181]
8	87 + 2 equiv. Mg	12.9	25.3	39.6	35.1			-36.0	[181]
9	87 + 2 equiv. Mg	30.8	29.6	50.3	20.2			-45.6	[181]
10	88 + 5 equiv. Mg	12.8	17.5	20.2	41.9	5.5	14.7	-33.6	[181]
11	88 + 5 equiv. Mg	21.6	19.2	32.8	34.3	4.2	9.6	-35.7	[181]
12	88 + 5 equiv. Mg	32.1	21.5	57.5	19.0	2.0	ND	-28.3	[181]
13	88 + 5 equiv. Mg	10.2	25.4	7.6	45.9	5.2	15.9	ND	[181]

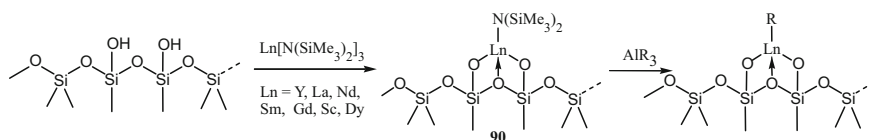
incorporate 30 mol% of α -olefin into two *trans*-1,4-butadiene units [180, 181, 183]. When an ate complex **88** bearing the steric t Bu substituents was employed, both *cis*-1,2-cyclohexane and *trans*-1,4-cyclohexane rings were formed along the macromolecular chains in addition to *trans*-1,2-cyclohexane units [181]. Remarkably, alternating copolymerization of ethylene with butadiene was realized by **89** combined with butyloctylmagnesium in a higher activity than that of homopolymerization of each monomer [137]. A possible mechanism of 2,1-insertion was proposed as Scheme 27.

Bochmann [184] developed a heterogeneous catalyst system of silica-supported neodymium amides (Scheme 28) that in conjunction of TIBA displayed activity for the copolymerization of ethylene and butadiene to give copolymer with relatively broad molecular weight distribution and *trans*-1,4-regulated butadiene sequences.

Barbier-Baudry [147, 148, 185–188] studied in detail the *ansa*-samarocene allyl and chloride complexes **91–93** (Fig. 14) as the single-component catalysts for the copolymerization of a series of α -olefins with conjugated dienes. The resultant copolymers contained about 6% linear α -olefins. Each olefin unit randomly inserted between two *trans*-1,4-isoprenes. It was worth noting that the afforded copolymers with different precatalysts were characterized with almost the same properties, denoting the same catalytic active species formed during polymerization [147, 186]. In addition, these catalysts were able to copolymerize isoprene with ϵ -caprolactone to form diblock copolymers [186, 187] and triblock copolymer poly[isoprene-*co*-



Scheme 27 Possible mechanism for the formation of 1,2- or 1,4-cyclohexane unit



Scheme 28 Silica-supported lanthanide compound

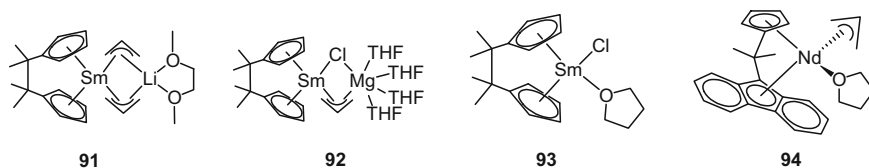


Fig. 14 Structures of *ansa*-metallocenes of samarium and neodymium

Table 24 Isoprene/ α , ω -diene co-(ter-) polymerization catalyzed by **92**/Li(allyl)(1,4-dioxane) [148]

Run ^a	Monomers	Toluene (mL)	Sm (μ mol)	[M] ₀ /[Sm] ^b	Time (h)	Yield (%)	Comonomer content (%) ^c	M_n^d ($\times 10^3$)	PDI ^d	T_g^e ($^{\circ}$ C)
1	1/1/0		6.9	720	20	73	8.2	50	1.3	−60
2	1/0.5/0		7.4	900	20	98	4.5	f	f	f
3	0.5/1/0		6.9	480	40	99	5.4	38	1.6	−58
4	1/1/0	4	1.4	720	27	80	4	f	f	f
5	0.5/0.5/0.5		6.5	520	17	28	4.6 ^g , 6.3 ^h	39.5	1.5	−62
6	1/1/0		6.9	720	19	93 ⁱ	i	f	f	−45
7	0.9/0.9/0	1.8	3.8	650	20	97 ⁱ	i	f	f	f
8	0.5/0.5/0	1	5.5	450	63	64	6.5	50	1.8	−69
9	0.5/0.5/0	2	4.6	360	17	79	4.3	f	f	f
10	0.5/1/0	2	4.7	300	21	24	10	f	f	f
11	0.25/0.5/0.25		11.1	450	16	58 ⁱ	i	f	f	f
12	0.5/0.4/0.1		11.1	450	5	87 ⁱ	i	f	f	f
13	0.5/0.1/0.4		11.1	450	17	82	4 ^j , 4.8 ^h	41.4	2.0	−66

^aIsoprene/hexa-1,5-diene (runs 1–5), isoprene/octa-1,7-diene/hex-1-ene (runs 6–13), volumes in mL

^bInitial concentration of isoprene

^cOn the basis of ¹H NMR integration

^dDetermined by SEC

^eDetermined by DSC

^fNot given

^gHexa-1,5-diene

^hHex-1-ene

ⁱCrosslinked: does not take octa-1,7-diene into account

^jOcta-1,7-diene

(hexene)]-*b*-poly(ϵ -caprolactone) with narrow molecular weight distribution [187]. Moreover, the copolymerization of isoprene with α , ω -dienes was achieved albeit with low incorporation of nonconjugated dienes (ca. 4–10%) (Table 24) [148, 187]. For instance the copolymerization of isoprene with 1,5-hexadiene resulted in the formation of five-membered ring in the polymer backbone, whilst with 1,7-octadiene afforded vinyl pendent copolymers, indicating that only one double bond was involved in the reaction with isoprene (Fig. 15).

Copolymerization of styrene and conjugated dienes is another attractive subject which provides the most commonly used styrene–butadiene rubbers (SBRs). Boisson reported that by using neodymium amide Nd{N(SiMe₃)₂}₃ and TIBA and DEAC, SBRs with 10–15 mol% of styrene were produced [189], although drops in both activity and molecular weight were observed as compared with those of

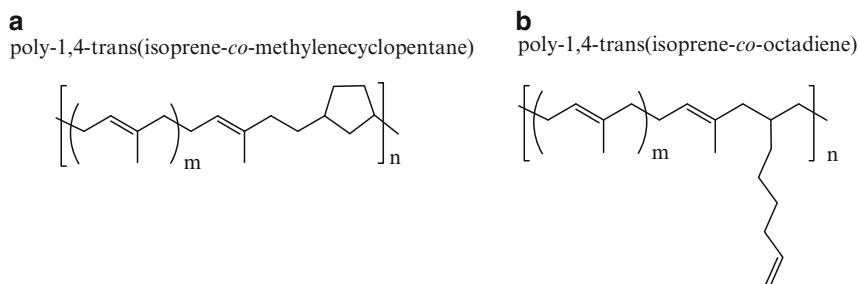


Fig. 15 Structures of copolymers of isoprene/hexa-1,5-diene (**a**) and isoprene/octa-1,7-diene (**b**)

homopolymerizations. ^{13}C NMR analysis disclosed that the microstructure of the butadiene units adopted *cis*-1,4-configuration domain, whereas 95% butadiene units inserted after the styrene unit was *trans*-1,4-regulated. The addition of organoborate to the system showed similar results. By employing conventional Ziegler–Natta catalyst system $\text{Nd}(\text{naph})_3/\text{TIBA}/\text{DIBAC}$ Shen et al. successfully synthesized SBRs with varying content of styrene, in which the inserted butadiene was highly *cis*-1,4-tactic (93%); however, this stereoregularity dropped with the increase of the styrene content [190–192]. By using the same catalyst, Wu et al. conducted the polymerization of styrene in CHCl_3 at 70°C followed by adding butadiene at low temperature to obtain diblock SBRs with high molecular weight albeit with wide molecular weight distribution, in which the butadiene block was highly *cis*-1,4-regulated ($\sim 97\%$), almost independent of the content of styrene units [193].

It is noteworthy that when magnesium alkyls were used as activators, the resultant systems provided SBRs possessing usually *trans*-1,4-butadiene units. Mortreux and Carpentier reported catalyst system $\text{Nd}(\text{O}-2, 6\text{-}^t\text{Bu}_2\text{-4-Me-C}_6\text{H}_2)_3(\text{THF})/\text{Mg}(n\text{-Hex})_2$ that gave SBRs containing 8–13 mol% styrene. Each styrene unit was inserted into *trans*-1,4-polybutadiene blocks [194]. Visseaux et al. [195] investigated the combination of $\text{Nd}(\text{BH}_4)_3\text{THF}_3/\text{BuMgEt}$ that could effectively incorporate styrene into polyisoprene. Introducing Cp^* ligand to neodymium borohydride led to a higher uptake of styrene (30%) and a narrower molecular weight distribution. The polyisoprene backbone was highly *trans*-1,4-regulated up to 98% and the styrene units randomly inserted into two *trans*-1,4-isoprene blocks (Table 25).

Carpentier et al. used a marvelous single-component catalyst the *ansa*-neodymocene allyl complex $(\text{CpCMe}_2\text{Flu})\text{Nd}(\text{C}_3\text{H}_5)(\text{THF})$ (**94**) to achieve the copolymerization of isoprene and styrene [196]. The resultant copolymers had high molecular weight and narrow molecular weight distributions in which the polystyrene units were syndiotactic separated by discrete isoprene unit (Table 26). Strikingly, this system enabled the copolymerization of styrene/ethylene/isoprene to afford terpolymers with different T_m and T_g values varying with the initial monomer feed ratios (Table 27).

Hou and Wakatsuki [197] reported a cationic ternary system composed of samarocene aluminate $\text{Cp}^*_2\text{Sm}(\mu\text{-Me})_2\text{AlMe}_2$ (**95**) and TIBA and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, showing living mode for the copolymerization of butadiene and styrene

Table 25 Copolymerization of styrene and isoprene by borohydrido lanthanide complex and MgBuEt^a [195]

Run	Catalyst	St in feed	St in poly-mer	<i>trans</i> -1,4-PI	<i>cis</i> -1,4-PI	3,4-PI	M_n ($\times 10^3$)	PDI	T_g ($^{\circ}\text{C}$)
1	Nd(BH ₄) ₃ THF ₃	0	—	96	2	2	72	2.0	−66
2	Nd(BH ₄) ₃ THF ₃	20	5	98	<0.5	2	65	1.6	−61
3	Nd(BH ₄) ₃ THF ₃	50	15	97	1	2	43	1.8	−54
4	La(BH ₄) ₃ THF ₃	50	11	94	4	2	15	1.5	−63
5	Nd(BH ₄) ₃ THF ₃	80	27	98	2	<0.5	23	1.8	−40
6	Nd(BH ₄) ₃ THF ₃	100	—	—	—	—	10	1.6	ND
7	Cp [*] Nd(BH ₄) ₂ THF ₂	0	—	98	0	2	67	1.8	−66
8	Cp [*] Nd(BH ₄) ₂ THF ₂	20	5	97	0	3	66	1.6	−66
9	Cp [*] Nd(BH ₄) ₂ THF ₂	50	16	98	0	2	47	1.4	−51
10	Cp [*] Nd(BH ₄) ₂ THF ₂	80	32	96	<0.5	4	27	1.4	−30
11	Cp [*] Nd(BH ₄) ₂ THF ₂	100	—	—	—	—	8	1.5	ND

^a 2 h reaction at 50 $^{\circ}\text{C}$ in 0.5 mL of toluene; molar ratio monomer/Nd/Mg: 2,000/1/1**Table 26** Copolymerization of styrene–isoprene complex **94**^a [196]

Entry	[St]/[Nd]	[St]	[IP]	Temp ($^{\circ}\text{C}$)	Time (min)	Yield (%)	Activity (kg (mol h) ^{−1})	St content	M_n ($\times 10^3$)	PDI	T_m ($^{\circ}\text{C}$)	T_g^b ($^{\circ}\text{C}$)	T_g^c ($^{\circ}\text{C}$)
1	600	8.7	—	60	5	2.3	1,710	100	54	1.73	264	—	ND
2	600	0	10	60	35	2.0	122	0	27	1.09	49	—	ND
3	600	4.7	4.0	60	6	2.4	550	70	55	1.54	—	—	63
4	600	6.0	3.0	60	15	3.8	165	85	91	1.25	—	62	67
5	600	7.9	0.9	60	10	9.6	380	94	63	1.62	218	77	ND
6	600	8.3	0.5	60	4	9.2	957	97 \pm 2	12	3.25	228	77	84
7	600	8.3	0.5	80	3.5	8.8	1,025	97 \pm 2	20	2.95	227	83	91
8	1,700	8.3	0.5	60	7	1.8	309	97 \pm 2	73	1.33	245	—	112

^aGeneral conditions: 0.05–0.15 mmol Ln; total volume 10 mL; reactions were conducted in neat monomers^bMelting and glass transition temperatures determined by DSC^cGlass transition determined by DMA

(Fig. 16). Thus, block copolymers were produced with highly *cis*-1,4-regulated butadiene fragments (99%) and up to 33.2% styrene content. Meanwhile, the random copolymers with various styrene contents (4.6–33.2 mol%), highly *cis*-1,4-selective polybutadiene sequences (95.1–80.3%), and high molecular weights ($M_n = 1.01 \times 10^5$ – 2.34×10^4 , PDI = 1.42) were obtained when the polymerization was performed at 50 $^{\circ}\text{C}$. Noteworthy was that the molecular weight distribution became wider and the *cis*-1,4-regularity declined with the increase of styrene content (Table 28). These results were in consistent with Boisson's results that a butadiene inserted after a styrene unit adopted *trans*-1,4-configuration.

The cationic system based on half-sandwich scandium borohydrides Cp^{*}Sc(BH₄)₂THF/[Ph₃C][B(C₆F₅)₄]/TIBA was found by Visseaux et al. to be active toward the copolymerization of isoprene and styrene, although low styrene incorporation and drop of *cis*-1,4-microstructure of isoprene units were observed as compared with the homopolyisoprene obtained using the same system (94% vs. 97%) [116]. The cationic system based on the half-sandwich scandium alkyl complex (C₅Me₄SiMe₃)Sc(CH₂SiMe₃)₂(THF) (**96**, Fig. 16) and [Ph₃C][B(C₆F₅)₄]

Table 27 Styrene–ethylene–isoprene terpolymerization catalyzed by complex **94**^a [196]

Entry	[Nd]	[St]	[IP]	P (bar)	Temp (°C)	Time (min)	Yield (%)	Activity (kg (mol h) ^{−1})	St (mol%)	IP (mol%)	Et (mol%)	M _n (×10 ³)	PDI	T _m (°C)	T _g ^b (°C)	T _g ^c (°C)
1	1,800	–	10	4	60	15	11.4	138	–	76	24	112	1.61	–	–	ND
2	600	2.2	2.2	5	60	60	7.2	33	41	34	25	73	2.41	–	–	35
3	600	7.9	0.9	1	60	15	8.9	244	96 ± 2	3	<1	41	2.84	204	76	ND
4	600	4.1	0.5	4	60	15	25.6	235	71	6	23	83	1.18	219	56	55
5	600	4.1	0.5	4	80	15	40.5	375	71	6	23	ND	ND	ND	ND	ND
6	600	4.1	0.5	1	60	30	18.7	86	81	3	16	ND	ND	–	60	84

^aGeneral conditions: 0.02–0.35 mmol Ln; total volume 1–60 mL^bMelting and glass transition temperatures determined by DSC^cGlass transition determined by DMA

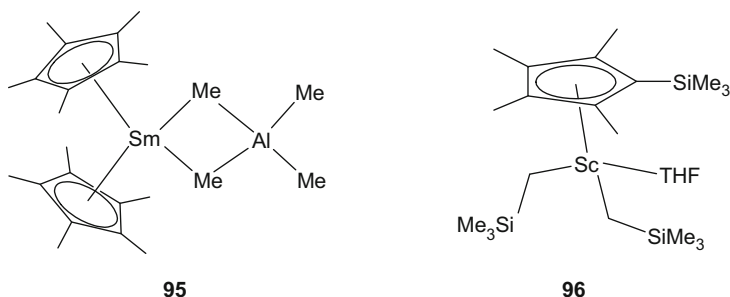


Fig. 16 Structures of half-sandwich lanthanide aluminate and bis(alkyl) complexes **95** and **96**

Table 28 Random copolymerization of butadiene and styrene initiated by **95**/TIBA/[Ph₃C][B(C₆F₅)₄]^a [197]

Run	Styrene in feed (mol%)	Time (h)	Yield (%)	Microstructure (%)			Styrene content (mol%)	M_n ($\times 10^3$)	PDI
				<i>cis</i> -1,4	<i>trans</i> -1,4	1,2-			
1	40	0.5	21	94.6	4.4	1.0	4.6	101	1.41
2	50	1	22	95.1	3.9	1.0	7.2	78.6	1.59
3	60	6	20	91.7	7.2	1.1	11.4	73.9	1.69
4	70	12	23	87.4	11.7	0.9	19.1	38.7	1.75
5	80	50	21	80.3	18.7	1.0	33.2	23.4	2.23

^aPolymerization conditions: in toluene; $T_g = 50^\circ\text{C}$; [butadiene]₀ + [styrene]₀ = 6.0 M (3.0×10^{-2} mol); [**95**]₀ = 0.006 M (3.0×10^{-5} mol); [TIBA]₀/[cat]₀ = 3; {[Ph₃C][B(C₆F₅)₄]}₀/[**95**]₀ = 1

reported by Hou et al. has demonstrated distinguished catalytic activity and selectivity for the copolymerization of isoprene and styrene [198]. The system behaved in a living fashion to give diblock and triblock copolymers of AB and ABA, respectively, in which the styrene fragments were perfectly syndiotactic whilst the isoprene blocks were random. Moreover, the random copolymerization could also be realized without detectable formation of homopolyisoprene or atactic polystyrene in the process; meanwhile, the amount of inserted styrene can be adjusted by varying the initial feed ratio. More recently, Hou et al. investigated in detail the catalytic performances of the cationic system based on the half-sandwich scandium alkyl complexes **97**–**102** analogous to **96** but bearing different substituents (Fig. 17) [199]. By varying the substituents on the Cp ring, the catalytic activity for the polymerization of styrene and isoprene could be adjusted; the highest active system belonged to complex **100**. These variations of the ligands also influenced the selectivity; therefore, copolymers with polyisoprene sequences containing *cis*-1,4-contents varying from 85 to 92% were obtained. More remarkably, almost perfect alternating copolymerization of ethylene with isoprene was achieved.

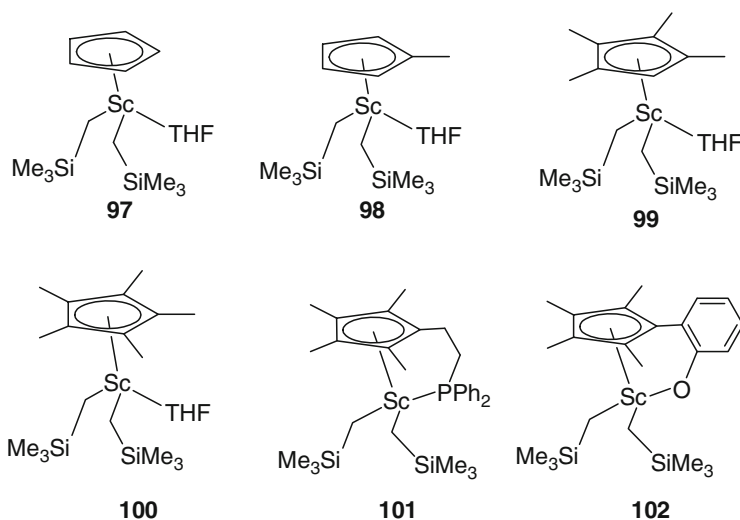


Fig. 17 Structures of half-sandwich scandium alkyl complexes **97** to **102**

6 Conclusions and Perspective

There is no doubt that the rapid development of rare-earth metal coordination catalysts has significantly advanced the syntheses of polydienes and the copolymers with precisely controlled microstructures that in turn determine their unique properties and versatile applications. The homogeneous single-site catalyst systems based on well-defined rare-earth metal complexes offer a decisive enhancement on catalytic activity and *cis*-1,4-, *trans*-1,4-, and 3,4-regioselectivity, and 3,4-stereoselectivity, which can be achieved by tuning the sterics and electronics of the ancillary ligands and the geometry of the ligand frameworks, as well as the types of cocatalysts such as aluminum or magnesium *etc* metal compounds or addition of organoborate cationization agents. In addition, successful isolation of some probable reaction intermediates facilitates further investigation of mechanism and guides the design of new catalysts. Meanwhile, modifying the conventional Ziegler–Natta catalyst systems focusing on increase of their catalytic activity, efficiency, and specific selectivity, control of the molecular weight and molecular weight distribution and identification of the active species, has gained obvious improvements by optimizing the catalyst recipe and polymerization conditions, and by employing the mimic tailor-made Ziegler–Natta catalyst systems.

Despite these encouraging progresses in this area, there still have many problems to be solved. The single-site lanthanide catalysts containing metal carbon bond are generally complicated in preparation, high cost, extremely sensitive to moisture and oxygen, and therefore less thermally stable, which hinder large-scale production. The cationic systems are usually heterogeneous in the industry-used aliphatic alkane medium owing to the addition of borates. The selectivity is not satisfactory

at room temperature or higher for most of present systems. The catalyst systems of highly active and selective for *trans*-1,4- and 3,4-polymerization of dienes still remain scarce, and those initiate copolymerization of dienes with alkene still need further investigation. Moreover, the successful copolymerization of dienes and alkenes goes along with an increase of 1,2- and *trans*-1,4-configuration. Sometimes, even 1,2-cyclohexane units are formed. For various applications, copolymers with a high *cis*-content are of high interest. It is not clear neither from experimental nor from theoretical point of view whether copolymers with a *cis*-1,4-content are feasible and how the respective catalysts have to be modified in order to meet this requirement. More importantly, the mechanism of polymerization is not clear at present and the correlation between structure of catalyst and stereoregularity as well as activity has not been established yet, which impede the search of potent catalysts for diene polymerization and their copolymerization with olefins or polar monomers.

Acknowledgements This work was partly supported by The National Natural Science Foundation of China for project No. 20934006. The Ministry of Science and Technology of China for projects Nos. 2005CB623802; 2009AA03Z501.

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Molecular Catalysis of Rare-Earth Elements

Roesky, P.W. (Ed.)

2010, XIII, 250 p. 48 illus., Hardcover

ISBN: 978-3-642-12810-3