Polymer Chemistry

Neodymium Catalysts for Polymerization of Dienes, Vinyl Monomers, and ε-Caprolactone

Journal:	*Polymer Chemistry*
Manuscript ID	PY-REV-09-2021-001270.R1
Article Type:	Review Article
Date Submitted by the Author:	06-Nov-2021
Complete List of Authors:	Stefan, Mihaela; The University of Texas at Dallas, Chemistry and Biochemistry Calubaquib, Erika; University of Texas at Dallas, Chemistry and Biochemistry Wang, Hanghang; The University of Texas at Dallas, Chemistry and Biochemistry Cue, John Michael; University of Texas at Richardson, Chemistry and Biochemistry Miller, Justin; The University of Texas at Dallas, Chemistry and Biochemistry Taslimy, Somayeh; The University of Texas at Dallas, Chemistry and Biochemistry Kularatne, Ruvanthi; The University of Texas at Dallas, Chemistry and Biochemistry

REVIEW

Neodymium Catalysts for Polymerization of Dienes, Vinyl Monomers, and ε-Caprolactone

Hanghang Wang,‡ John Michael O. Cue,‡ Erika L. Calubaquib,‡ Ruvanthi N. Kularatne,‡ Somayeh Taslimy,‡ Justin T. Miller,‡ Mihaela C. Stefan‡*

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Among the rare-earth catalysts, neodymium-based catalysts are systematically investigated due to their efficiency and versatility. Still, the correlation between the complex structure and the catalytic coordination polymerization is not yet fully established. The discovery of new neodymium catalytic systems that are homogeneous, well-defined, thermally stable, and producing polymers in high yield and stereospecificity is an important research direction. Ziegler-Natta catalysts were developed to polymerize olefins and dienes and showed good activity. Later, lanthanide-based Ziegler-Natta type catalysts were reported for improved stereospecificity and activity for the polymerization of dienes. Out of the lanthanide catalysts reported, neodymium-based catalysts exhibit better catalytic performance for the polymerization of dienes and are also valuable for making vinyl polymers and polycaprolactones. This review discusses various neodymium catalysts for stereospecific polymerization of dienes, vinyl monomers, and ε-caprolactone.

1. Introduction

The lanthanide metals differ in their reactivities as a catalyst due to their varying ionic radius and number of 4f electrons. Among the lanthanide series, neodymium (Nd)-based catalysts are the most studied due to their availability, efficiency, and versatility for polymerizing dienes, vinyl monomers, and cyclic esters.

Nd-based catalysts can come in the form of Ziegler-Natta (ZN) type catalytic systems, binary catalytic systems containing an alcohol initiator, and single-component systems. One of the essential applications of Nd-based catalysts, particularly ZN-type catalytic systems, is the synthesis of elastomeric polybutadiene, which has similar properties to natural rubber and polyisoprene. The mechanical and rheological properties of polydienes are strongly affected by their molecular weight, molecular weight distribution, and microstructures (Figure 1). The synthesis of polybutadiene rubber allows different chemo- and stereoselectivities such as 1,4-*cis*, 1,4-*trans*, or 1,2-(or 3,4- for polyisoprene) additions. A slight increase in 1,4-*cis* stereoregularity affects the strain-induced crystallization of raw rubbers and vulcanizates, ultimately affecting mechanical properties. The conventional ZN catalysts were initially utilized for the polymerization of ethylene and propylene. Still, the development of the catalysts soon expanded to the polymerization of styrene and 1,3-conjugated dienes.[1, 2] These catalysts are readily prepared from metal carboxylates, and Lewis acid co-catalysts are used commercially. However, they produce polydienes with relatively low *cis* content and poor molecular weight control due to varying initiation sites.[3] Lanthanide-based ZN catalysts were discovered in the 1960s and soon became the primary focus of research on diene polymerization. Studies on lanthanide-based ZN catalysts showed higher reactivity and selectivity than the conventional titanium- and cobalt-based catalysts for the polymerization of dienes.[4]

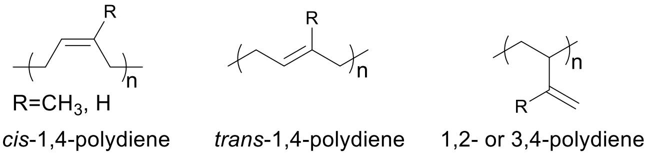


Figure 1. Microstructures of polydienes.

Previous overviews on ZN diene polymerization focused on different lanthanide metal centers and carboxylate ligand system.[5-7] A review on the polymerization of dienes by lanthanide catalytic systems was compiled by Marina and co-workers in 1991.[8] This review focused on the influence of different lanthanide catalytic systems and polymerization conditions in the polybutadiene rubber *cis*-content. In 1993, Porri and co-workers presented a review on diene polymerization using ZN-type catalysts.[9] In 2006, Friebe and co-workers gave a comprehensive review of Nd-based Ziegler catalysts for the polymerization of dienes, a mechanistic understanding of the organoaluminum-promoted activation complexes containing various ligands, and their industrial applications. The organoaluminum-promoted activation of Nd complexes with different ligand environments and their proposed mechanistic models were presented.[6] Zhang and co-

† The Department of Chemistry and Biochemistry, The University of Texas at Dallas, 800 W. Campbell Road, Richardson, Texas, 75080, USA
* Corresponding author. Email: mihaela@utdallas.edu
* Email: mihaela@utdallas.edu
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

workers compiled another review in 2010, wherein they discussed the rare-earth catalyzed synthesis of homopolymers and copolymers of dienes, particularly isoprene.[4]

Nd-based complexes have also been utilized to synthesize aliphatic polyesters, which are particularly important in biomedical applications, through ring-opening polymerization (ROP), mainly as a single-component catalyst. Among the aliphatic polyesters, polycaprolactone (PCL) is the most prominent due to its useful structural, thermal, and rheological properties.[6, 10, 11] Several reviews have discussed the different alkali, alkaline, and transition metal catalysts to polymerize ε-CL. However, few reviews are available for lanthanide complexes, particularly Nd-based complexes. In 2000, Greiner reviewed the organolanthanide complexes for the homopolymerization of lactones and block- and graft copolymerization with polylactones, polylactides, and polyolefins.[12] Edelmann's review mainly focused on lanthanide amidinate and guanadinate complexes for the polymerization of various monomers.[13] More recently, Trifonov et al. published a review on the polymerization of lactides and lactones using different rare-earth metal complexes.[14] The comprehensive review of lanthanide borohydrides by Visseaux and Bonnet includes using these complexes to polymerize cyclic esters.[15]

This review discusses various Nd catalysts for stereospecific polymerization of dienes, vinyl monomers, and ε-caprolactone (ε-CL). The first part focuses on the Nd-based ZN-type catalysts and the effects of different co-catalysts and polymerization conditions for the polymerization of dienes. This part also covers the polymerization of styrene, methyl methacrylate, and methyl acrylate vinyl monomers. In the second part, we give an up-to-date report of the different Nd-based catalysts used as single component initiators for the polymerization of ε-CL.

2. Neodymium-based catalysts for the polymerization of dienes and vinyl monomers

One of the most used catalytic systems developed for the industrial production of 1,4-*cis*-polydiene, neodymium versatate, is based on the rare earth metal neodymium. The effectiveness of the catalyst for the regio- and stereoselective polymerization depends on the metal center, ligands, and activators. These catalysts are primarily reported as neodymium (III) precursors based on: carboxylates, alcoholates, phosphates, phosphonates, allyl compounds, cyclopentadienyl derivatives, amides, boranes and acetylacetonates. The specific catalytic systems with their activators are discussed in the next sections.

2.1. Neodymium-based complexes for polymerization

Neodymium carboxylates and alcoholates

As early as the 1960s, neodymium carboxylates were studied as catalysts due to their solubility, catalytic activity, stereospecificity, and molar mass control. Versatate, octanoate, isooctanoate, and naphthenate are the most common ligands for neodymium (III) carboxylates (Figure 2 (A), complexes **1**-**4**). These catalysts are employed with alkylaluminum co-catalysts to generate the active species for polymerization. Some significant factors influence the performance of Nd carboxylates, such as chemical structure, length of aliphatic chains, and electron-withdrawing properties. Wilson et al. showed that isocarboxylates $Nd(OCOCH_2R)_3$ have a lower activity than neocarboxylates ($Nd(OCOCR_3)_3$). Moreover, isocarboxylates with longer hydrocarbon chains showed higher polymerization activities than the ligands with shorter alkyl chains.[16]

In addition to conventional carboxylates, neodymium-based metal-organic frameworks (MOFs) combined with methylaluminoxane (MAO) or modified MAO (MMAO), which is a mixture including some isobutylaluminoxane, provide polydienes with high selectivity. M. J. Vitorino et al. showed that the activity and selectivity of polymerization of isoprene could be changed based on the microstructure of Nd polycarboxylate-based MOFs. Materials with high porosity have higher activity and produce mainly cis-selective polyisoprenes at low temperatures, shifting to trans-selectivity at higher temperatures. A possible explanation is the well-known syn-trans equilibrium or the arrangement of monomers within the MOF micro-cavities and the activation of Nd centers near the pores by the Al co-catalyst.[17] I. Rodriques et al. group showed that the use of sterically demanding carboxylates and non-aqueous solvents could yield water-free MOFs such as Nd(2,6-naphthalenedicarboxylate)(formate) and $Nd(formate)_3$. In the presence of aluminoxanes, these precatalysts polymerize isoprene highly cis-selectively and efficiently.[18] S. Russell et al. exploited the often undesired remnants of the catalytic MOF in the synthesized polymer to produce a luminescent and durable cis-1,4 polyisoprene/MOF composite through the use of an Eu- or Tb-doped Nd-carboxylate MOF catalyst.[19]

Nd alcoholates are called pseudo-organometallics because the neodymium and oxygen (Nd-O) bond readily undergoes hydrolysis, unlike the Nd-Cl or Nd-O (carboxylate) coordination bonds. This well-known class of rare earth metal compounds includes highly soluble discrete complexes of a well-defined number of coordinated ligands depending on the bulkiness of the alkyl group. The Nd-alcoholates that are frequently mentioned in the literature include $Nd(butanolate)_3$, $Nd(isopropoxide)_3$, $Nd(methanolate)_3(AlMe_3)_4$, and Nd aryl oxides (Figure 2(A), complex **5**).[7, 20]

Neodymium phosphate and phosphonates

Reports on applying neodymium phosphate-based catalysts (Figure 2(B), complexes **6**-**9**) for the polymerization of isoprene date back to 1978.[21] Nd bis(2-ethylhexyl)phosphate (NdP) is a predominant Nd phosphate in the context of diene polymerization. NdP-based catalysts are also used for the polymerization of non-diene monomers in both binary and ternary systems. NdP/triethylaluminum (TEA) and NdP/triisobutylaluminum as the binary catalytic systems have been applied to polymerize acetylene and for the copolymerization of carbon dioxide and epichlorohydrin, respectively. The ternary system NdP/TEA/water polymerizes lactide, and NdP/dibutylmagnesium/

tetraethylmethylenediamine was used for homopolymerization of methyl methacrylate.[7]

One of the most studied phosphate catalysts is the $NdCl_3 \cdot n$TBP (TBP=tributylphosphate) binary catalytic system, which was demonstrated to produce high 1,4-*cis*-polyisoprene content.[4, 6, 22, 23] Disadvantages of this system include its multi-site nature, which causes difficulty in controlling the molecular weight,[4, 6] and poor solubility in organic solvents which frustrates industrial applications.

Neodymium allyl complexes

The synthesis of polydienes by ZN catalysts was performed in the 1960s by introducing allyl ligands in the Nd active species for polymerization.[6] Neodymium-allyl-group (Figure 2(C), complexes **10**-**12**) is a critical element in the insertion of dienes into the neodymium-carbon bond. It is assumed that the π-bonding conditions in the neodymium-allyl bond push the diene insertion to undergo the σ-allyl mechanism, which will be discussed in detail in the mechanism section. Taube et al. improved stereospecific dienes polymerization by

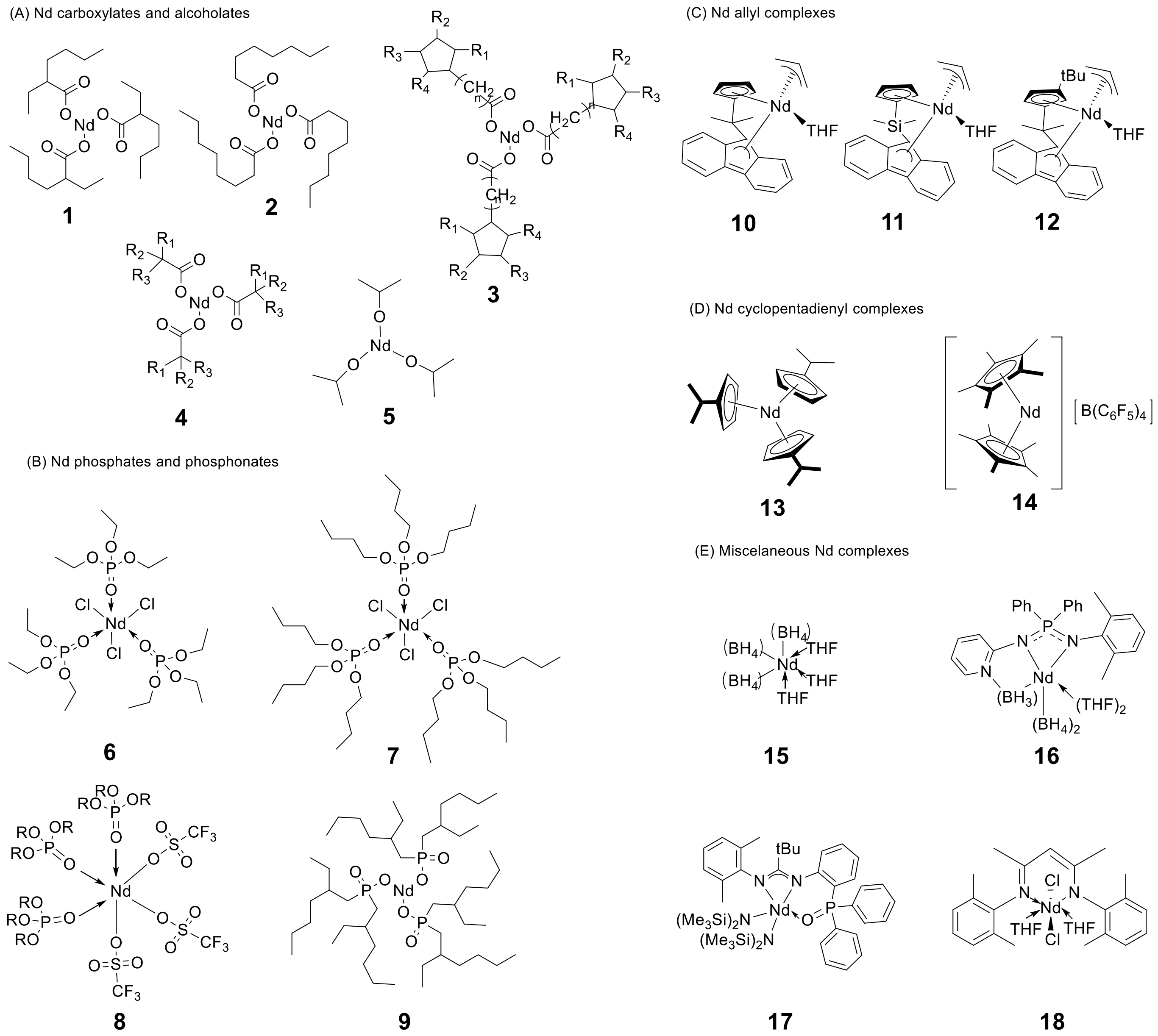


Figure 2. Selected examples of neodymium-based catalysts for the polymerization of dienes: (A) Neodymium catalysts **1**-**5** with carboxylate and alcoholate ligands, (B) Neodymium catalysts **6**-**9** with phosphate and phosphonate ligands, (C) Neodymium catalysts **10**-**12** with allyl complexes, (D) Neodymium catalysts **13**-**14** with cyclopentadienyl ligands, and (E) Neodymium complexes **15**-**18** with miscellaneous ligands

synthesizing Nd-allyl complexes with high activity and stereospecificity. They synthesized tri(allyl) neodymium, $Nd(\eta^3\text{–}C_3H_5)_3\cdot$dioxane, by using tetra(allyl) neodymium complexes and tetra(ethyl) boron (Scheme 1), which led to polydienes with high 1,4-*trans*-content (94%).[6] The addition of Lewis acids such as diethylaluminum chloride (DEAC) and methylaluminoxane (MAO) to the Nd allyl precursor led to higher catalytic activity and higher *cis* content.[24] This is due to the formation of cationic allyl neodymium complexes by the co-catalyst.

$Nd(\eta^3\text{–}C_3H_5)_2Cl \cdot THF/MAO$ catalytic system had higher activity than tris-allyl Nd-complexes because the abstraction of one chlorine atom from the central neodymium is more accessible than the abstraction of an allyl group, which facilitated the formation of a vacant coordination site on neodymium (Scheme 1).[6]

Visseaux's group reported several allyl lanthanide complexes for styrene polymerization without requiring aluminum cocatalysts, obtaining syndiotactic-rich and isotactic-rich polystyrene with different systems.[25]

$$(C_3H_5)_3Nd \cdot L_n + MAO \longrightarrow [(C_3H_5)Nd^{2+} \cdot 2(C_3H_5)^- \cdot MAO \cdot L_n]$$

$$(C_3H_5)NdCl_2 \cdot L_n + MAO \longrightarrow [(C_3H_5)Nd^{2+} \cdot 2Cl^- \cdot MAO \cdot L_n]$$

Scheme 1. Activation of Nd-allyl and Nd-allyl chloride complexes by MAO (L = dioxane or THF).[6]

Neodymium cyclopentadienyl complexes

Neodymium cyclopentadienyl (Cp) complexes, like dicyclopentadienyl lanthanide alkyl or halide complexes and monocyclopentadienyl lanthanide dialkyl or dihalide complexes, share electronic and structural similarities and thus often catalyze similar polymerization reactions.[6] Various types of Nd-based cyclopentadienyl (Cp) derivatives have been studied so far, with the majority showing only limited solubility in non-polar solvents. CpNd complexes (Figure 2(D), complexes **13**-**14**) have shown an excellent ability to polymerize various alkenes such as α-olefins, styrene, α,ω-dienes, and polar acrylates.[26, 27] Most of the studies using CpNd complexes focused on butadiene polymerization because mono cyclopentadienyl lanthanide dichlorides with trialkyl aluminum compounds as co-catalysts resulted in polybutadiene with 98% *cis*-1,4-content.[6] A significant class of exceptions to this is Cp-borohydro-Nd complexes, which are a recent and growing class of catalysts for the *trans*-1,4-selective polymerization of isoprene and the polymerization of styrene. A wide variety of lanthanidocene and half-lanthanidocene borohydride complexes have been developed for use as polymerization catalysts. However, it is worth noting that other lanthanides see more use than neodymium in these applications.[15]

Miscellaneous Neodymium complexes

The use of Nd-borohydride complexes as polymerization catalysts is a relatively recent development. In 2004, the polymerization of isoprene by $Nd(BH_4)_3(THF)_3$ (Figure 2(E), complex **15**) was reported by Barbier-Baudry.[28] Cui used this complex as a precursor to the organoborate complex $[N(C_6H_3\text{-}2,6\text{-}Me_2)PPh_22\text{-}pyrN(BH_3)]Nd(BH_4)_2(thf)_2$ (Figure 2(E), complex **16**), which was also used for *trans*-1,4-specific isoprene polymerization.[29] $[Nd(BH_4)_2(thf)_5][B(C_6F_5)_4]$ has been used by Visseaux for the cationic, *cis*-selective polymerization of isoprene.[30]

Aryldiimine complexes of several metals, including Nd, were used for stereospecific diene polymerization by Cui in 2008, achieving good activity and excellent *cis*-1,4 selectivity.[31] These "NCN-pincer" complexes were soon followed by "CCC-pincer" complexes exhibiting even greater *cis*-1,4 selectivity, with the Nd examples possessing the greatest activity of the metals tested.[32] Cui also investigated β-diketiminate complexes for isoprene polymerization, including $[(2,6\text{-}C_6H_3Me_2)NH{=}C(Me)CH{=}C(Me)N(2,6\text{-}C_6H_3Me_2)]NdCl_2(THF)_2$ (Figure 2(E), complex **18**), again finding good *cis*-1,4 selectivity.[33,34]

2.2. 1,4-*Cis* selective polymerization of dienes

The polymerization of dienes using neodymium catalysts requires specific activators to achieve high activity and high *cis*-content of the polydiene. The effect of the activators will be summarized in the following subsections showing various binary, and ternary catalytic systems reported.

2.2.1. Binary catalytic systems. Neodymium-based binary catalytic systems are composed of a neodymium-containing precursor, such as $NdCl_3$, and an alkyl aluminum co-catalyst. These binary systems are very active in diene polymerization, but they result in high dispersity (Đ) of the polymers due to the insoluble catalytically active species formed. The addition of electron-donating ligands, such as alcohols, tetrahydrofuran, pyridine, dimethyl sulfoxide, phosphates, and amines, to the Nd–Al bimetallic species significantly improves their solubility in hydrocarbon solvents as well as increases the catalyst activity while maintaining stereospecificity.[4, 6, 35, 36] These catalytic systems can polymerize butadiene and isoprene with high (>98%) *cis*-1,4 stereoselectivity.[6, 8] Some of the reported binary neodymium catalytic systems are shown in Table 1. More studies are needed for the improvement of the binary neodymium catalytic systems to achieve *livingness* of polymerization producing polydienes with high *cis* content and well-defined molecular weights.[4, 6, 37-41] Moreover, the modification of the ligand structure and the Nd catalyst could also result in better solubility of binary catalytic systems.[4, 6] The addition of organoaluminum with neodymium-based precursors forming binary catalytic systems showed higher activity for diene polymerizations than typical ternary systems.[4, 6] The effects of different polymerization conditions (varying co-catalyst, solvents, and temperature) will be discussed in detail.

2.2.1.1. Effect of the co-catalyst. The co-catalyst is combined with the neodymium complex to form a bimetallic, catalytically active species. The added co-catalyst additionally helps to control the molecular weight of the synthesized polymers. The co-catalysts commonly used for binary systems are composed of aluminum, magnesium, or boron-based Lewis acids. Generally, organoaluminum Lewis acids favor the formation of *cis*-polydienes. In contrast, organomagnesium Lewis acids favor the generation of *trans*-polydienes.[42, 43] One exception to this is the neodymium acetylacetonate and dibutylmagnesium system used by Zhang and coworkers to synthesize 94.8% 1,4-cis-polyisoprene.[44] Commonly used aluminum co-catalysts include trimethylaluminum (TMA), triethylaluminum (TEA), triisobutylaluminum (TIBA), diisobutylaluminum hydride (DIBAH), methylaluminoxane (MAO), and modified methylaluminoxane (MMAO). The type and amount of aluminum co-catalyst can influence the 1,4-*cis* content and the molecular weight, regardless of the type of catalytic system. TIBA is generally utilized for both ternary and binary systems to generate high activity and high 1,4-*cis* content. TMA, on the other hand, tends to yield the lowest activities and lower 1,4-*cis* content. The aluminum co-catalysts are typically added in excess to facilitate the alkylation of the Nd complex. Moreover, using an excess of organoaluminum co-catalyst can aid in scavenging water and oxygen impurities. The amount of co-catalyst added should be optimized since it may act as a chain transfer agent when added in excess. Zhang and co-workers conducted the polymerization of isoprene using $NdCl_3{\cdot}3TBP$/TIBA and $NdCl_3{\cdot}3TBP$/DIBAH and observed that the increased [Al]/[Nd] ratio for the polymerization led to a decrease in molecular weights while the *cis*-1,4 content remained at 96%.[45]

Iovu and co-workers reported an increase in the content of *cis*-1,4-polyisoprene from 92% to 96% as the amount of aluminum co-catalyst increased for the $NdCl_3{\cdot}3TBP$/TIBA catalytic system.[46] Hsieh et al. studied the effect of different aluminum co-catalysts on 1,4-*cis*-specificity in polybutadiene polymerization. TIBA achieved the highest 1,4-*cis* content, with the others decreasing in the order of TIBA > DIBAH > DEAH > TEA.[47]Lopez et al. examined the TEA, TIBA, DIBAH, and MAO co-catalysts in terms of the catalytic activity and 1,4-*cis* content for $NdCl_3{\cdot}(C_5H_{11}O)_3$ binary system for the polymerization of butadiene. They determined that the catalytic activity followed the order TEA > TIBA > DIBAH > MAO. The 1,4-*cis* content decreased as following TIBA > DIBAH > TEA > MAO.

Liu et al. reported the polymerization of butadiene using Nd triflate coordinated with phosphate ligands and TIBA co-catalyst. The Nd triflate coordinated with tris(2-ethylhexyl)phosphate gave polybutadiene with ~98% 1,4-*cis,* and narrow Đ of 1.32.[48] Stefan et al. investigated a halide-free coordination polymer with Nd coordinated with bridging bidentate diethyl phosphate ligands. TIBA's use resulted in the polymerization of myrcene with 96% 1,4-*cis* content, and Đ of 1.8.[49] Meermann et al. performed the isolation and characterization of the active species of Nd-based Ziegler catalysts. In the case of the chlorination-alkylation sequence, the pre-formed heterogeneous catalyst $[Nd_aAl_bMe_cCl_d]_n$ prepared from Nd complex with $[N(SiHMe_2)]^-$ ligands and excess trimethylaluminum gave 99% 1,4-*cis* content and Đ close to two. However, the alkylation-chlorination sequence with $[Nd(AlMe_4)_3]/Et_2AlCl$ afforded 99% 1,4-*cis* content and Đ close to three with high efficiency. The *cis* stereoregularity was decreased to 64% when the $[B(C_6F_5)_4]^-$ was used instead of the chloride source. Controlling the molecular weight and Đ proved difficult using this catalytic system, which is a common problem in Ziegler mixed catalysts.[50]

2.2.1.2. Effect of the solvent. The choice of solvent for polymerization of dienes plays a role in the catalytic activity, molecular weight, and 1,4-*cis* content. Alkane and cycloalkane solvents are most often used for polymerization. Optimization of the amount of the added solvent is necessary due to the solvent cage effect when the solvent is used in excess.

Table 1. Polymerization of dienes with different binary Nd ligand complexes

Nd compound	**Ligand**	**Co-catalyst**	**Monomer**	***cis*-1,4 (%)**
$NdCl_3{\cdot}2.5EHOH$[52]	2-ethylhexanol (EHOH)	TEA	Butadiene	>99
$NdCl_3$[53]	C_6H_5Me	MCl_x–masked silica [MCl_x = BCl_3, $AlCl_3$, $TiCl_4$]	Butadiene	99
$NdCl_3{\cdot}(C_5H_{11}OH)_3$[35]	Pentanol	TEA	Butadiene	>99
$NdCl_3{\cdot}3EHOH$[37]	EHOH	TEA	Isoprene	96
$NdCl_3{\cdot}3{}^iPrOH$[37]	Isopropanol (^{i}PrOH)	TEA	Isoprene	96
$NdCl_3{\cdot}3TBP$[46]	TBP	TIBA	Butadiene Isoprene	97 96
$NdCl_3{\cdot}3TBP$[45]	TBP	MAO	Isoprene	96
$NdCl_3{\cdot}(C_5H_{11}O)_3$[54]	Pentanolate	TIBA	Butadiene	96
Nanosized $NdCl_3{\cdot}1.5THF$[39]	THF	TIBA and DIBAH	Butadiene	96
$NdCl_3{\cdot}(C_5H_{11}O)_3$[55]	Pentanolate	TIBA	Butadiene	98
$NdCl_3{\cdot}$(2-methyl-8-hydroxyquinolate)$_3$[56]	2-methyl-8-hydroxyquinolate	TIBA	Isoprene	97
$NdCl_3{\cdot}3{}^iPrOH$[57]	^{i}PrOH	MMAO	Isoprene	97
$NdCl_3{\cdot}2THF$[58]	THF	TIBA	Isoprene	99
$NdCl_3{\cdot}3TEP$[59]	TEP	TIBA	Myrcene	96

Some aromatic solvents can also give rise to competitive coordination with the diene, reducing the catalyst activity.[4, 51] Homogeneous systems are preferred over partially soluble or heterogeneous systems for the industrial production of rubber due to gel formation.

Neodymium complexes can achieve the required solubility with appropriate ligands, enhancing the solubility in different solvents such as toluene, n-hexane, and cyclohexane. Common neodymium salts with good solubility in hydrocarbon solvents include carboxylates, alcoholates, and phosphates. These are based on branched or cyclic aliphatic groups, preferably containing eight or more carbon atoms.

Hseih et al. studied the effect of a variety of solvents on the activity of binary catalytic systems towards the polymerization of dienes, and they noticed that the activities decreased in the following order: cyclohexane ~ n-hexane > n-heptane > chlorinated aromatic hydrocarbons > toluene > 1-hexene > tetrachloroethylene ≥ styrene.[47] The effect of the solvents on the *cis*-1,4 content was minimal, while toluene caused a decrease in the molecular weight. Dong and co-workers determined the effect of a range of solvents, including heptane, cyclohexane, toluene, and dichloromethane, on the yield of polymerization, molecular weight, and 1,4-*cis* content for $Nd(O\textit{i}Pr)_3$/MMAO and $Nd(O\textit{i}Pr)_3$/MAO (O*i*Pr = isopropoxide) catalyzed polymerizations of isoprene. Cyclohexane and heptane gave higher polymer yield and molecular weight than toluene for both catalytic systems. The lowest polymer yield was measured in dichloromethane when an insoluble polymer was formed. The highest 1,4-*cis* content (~ 93%) was obtained using toluene, and the lowest 1,4-*cis* content (~ 91%) using heptane.[60, 61]

***2.2.1.3. Effect of temperature*.** The temperature affects the rate of polymerization, molecular weight, 1,4-*cis* content, and dispersity. Iovu et al. studied the effect of varying temperatures for the $NdCl_3{\cdot}3TBP$/TIBA binary catalytic system at 20, 30, 40, 60, and 80 °C. The molecular weight decreased from ~400 kDa to ~150 kDa, and the 1,4-*cis* content decreased from 97% to 91% with the increase in temperature. The highest molecular weight and 1,4-*cis* content were achieved at 20 °C with ~400 kDa and 97%, respectively. The dispersity of the synthesized polyisoprene increased from 3.7 to 7.6 upon increasing temperature from 20 to 60 °C. At higher temperatures, lower molecular weight and 1,4-*cis* content, and higher dispersity were attributed to the chain transfer reactions that occurred with TIBA.[46]

Zhang et al. studied the effect of temperature (0, 25, and 50°C) on $NdCl_3{\cdot}3TBP$/MAO binary catalytic system for the polymerization of isoprene in which a lower molecular weight and 1,4-*cis* content were observed. Iovu et al. also noticed the same trend; however, there was a slight increase for the Đ as the temperature was increased (1.35 at 0 °C increased to 1.56 at 50°C).[45] Rao et al. observed similar results wherein the 1,4-*cis* content for the $NdCl_3{\cdot}2.5EHOH$/TEA binary system dropped from 99.2% at 25 °C to 95.6% at 75 °C.[52] The polymerization of butadiene using $NdCl_3{\cdot}(C_5H_{11}O)_3$/TIBA exhibited similar results upon increasing the temperature from 40°C to 60°C with the yield increasing from 66% to 100% and the Đ from 3.7 to 6.7. The molecular weight decreased from 63 kDa to 22 kDa and the 1,4-*cis* content from 96.2% to 95.8%.[54]

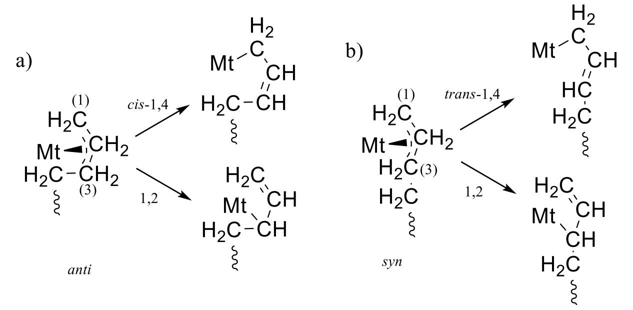
***2.2.1.4. Binary catalyst polymerization mechanism*.** Coordination polymerization was initially developed for the polymerization of ethylene and was later extended to other monomers, such as propylene, dienes, and styrene. In 1953, Karl Ziegler discovered that the combination of $TiCl_3(s)$ and $AlEt_3$ produced an active heterogeneous catalyst for the polymerization of ethylene. Later, Giulio Natta extended the method to other olefins like propylene and developed variations of the Ziegler catalyst based on his findings on the mechanism of the polymerization reaction. The Ziegler-Natta catalyst family includes halides of titanium, chromium, vanadium, and zirconium, typically activated by alkyl aluminum compounds. Ziegler and Natta received the Nobel Prize in Chemistry for their work in 1963.[62, 63]

Conventional Ziegler-Natta catalysts are relatively easy to synthesize, so they were used in industry to polymerize dienes. These catalysts produce polydienes with relatively low *cis*-1,4-content and poor molecular weight control due to multiple initiation sites. Catalysts based on lanthanides (Nd, Pr, Gd, and La) with suitable activators have been proposed and applied to make stereoregular polymers of isoprene, butadiene, and 1,3-pentadiene. Neodymium produced the most effective catalysts due to its greater ionic size and coordination modes to produce at least 98% 1,4-*cis*-polybutadiene. Rubbers produced from these catalysts have excellent properties such as excellent abrasion and fatigue performance, making them superior to those made from Ti, Co, and Ni analogues.[64]

The neodymium-catalyzed diene polymerization mechanism is not yet fully understood, and different proposed mechanisms were presented in various studies. Several proposed reaction mechanisms have contradictory results. The polymerization mechanism could be well understood if the structure of the active site were known. However, most of the proposed mechanisms are derived only from speculations on the structure of the active site. The mechanism of diene polymerization involves different coordination modes and propagating chain-end structure, which makes it challenging to design a general catalyst to give polydienes with predictable microstructures.[65]

In 1984, Marina and co-workers reviewed the development of lanthanide catalysts from early binary systems up to the common ternary systems. Different factors impacting activity and microstructure were discussed, including the effect of solvent, neodymium complex type, varying the molar ratio of catalyst components, type of alkylaluminum, and temperature.[66] Marina and Monakov reported that $NdCl_3{\cdot}3TBP$ (tributylphosphate) with the co-catalyst TIBA forms the same species regardless of the amount of the co-catalyst used. Elemental analysis showed that the active species do not contain any phosphorous.[67] When TIBA was added, TBP preferentially coordinated with TIBA, forming a TIBA-TBP bimetallic complex. This complex was found to be heterogenous, containing species with both one and two moles of TIBA per Nd center. Due to this heterogeneity, the researchers were unable to provide any single structure of the complex.[67]

Later, Porri proposed a 1,3-diene polymerization mechanism (Scheme 2) where the allylic unit can exist as *anti* and *syn* forms with reactive positions at C1 and C3. A new monomer reacting at the C1 position, produces a 1,4-unit which can either be in the *cis* form when the allylic unit is in the *anti* form or *trans* when the allylic unit is in the *syn* form. A 1,2 unit is produced when the entering monomer reacts at the C3 position.[68-70]



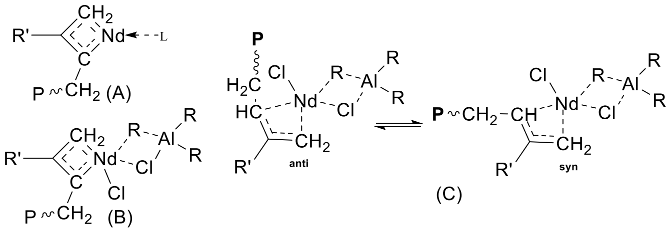
Scheme 2. Formation of 1,4- and 1,2-polydiene microstructure from (a) anti and (b) syn Mt-η3-butenyl group.[64]

Porri had a strong influence on the design of new 1,3-diene polymerization catalysts based on transition metals and lanthanide complexes with ligands such as phosphines, imines, iminopyridines, and ketoimines. The catalytic systems have been proven to be particularly active and selective, having control over the polymer microstructure, molecular weight, and dispersity to synthesize novel stereoregular polydienes from different petroleum-based and natural monomers. His studies initiated the correlations among catalyst structure, monomer structure, and polymer microstructure to conceptualize the polymerization mechanism of dienes.[63]

Porri's proposed mechanism was supported by Iovu and co-workers where they studied the $NdCl_3 \cdot 3TBP/TIBA$ catalyzed polymerization of isoprene and butadiene and proposed two possible models for the active sites.[46] One model showed the coordination of the TBP ligands with Nd (Scheme 3, (A)), and the other model showed Nd and TIBA bridged complex formed due to the excess TIBA (Scheme 3, (B)) entirely replacing the ligands. The active center B was speculated to be more stable to enable the "anti" to "syn" conversion. The "syn" species were proposed to form the 1,4-*trans* product, and the "anti" species were speculated to give 1,4-*cis* product. This results in a decrease of 1,4-*cis* unit content when excess co-catalyst is used (Scheme 3, (C)), causing an increase in the rate of isomerization from "anti" to "syn".[46] The observations of Marina and Monakov, along with the work of Iovu and co-workers, make a case for the bridged complex formed by the complete replacement of the phosphate ligands as the real active site of the $NdCl_3 \cdot 3TBP/TIBA$ catalytic system.[46, 67]

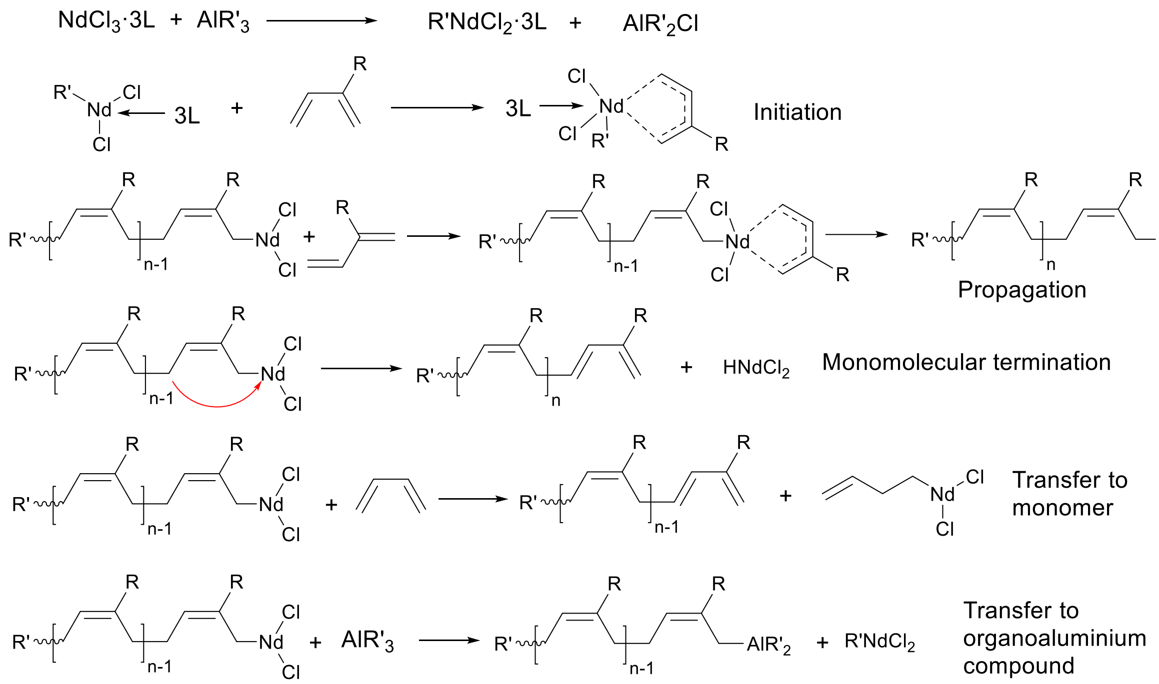
Iovu and co-workers fitted the experimental results for the polymerization of butadiene and isoprene using $NdCl_3 \cdot 3TBP/TIBA$ system to a pair of proposed mathematical models.[71] One of the models included a possible monomolecular termination, while the second model considered the absence of termination reactions. The experimental data fit supported the mechanism without termination reactions.[72, 73] The mechanism proposed by Iovu and co-workers is shown in Scheme 4, in which the organoaluminum co-catalyst alkylates the neodymium halide to yield the catalytically active species. In this mechanism, the active species contains all the ligands, contradicting earlier reports.[46] Monomolecular termination and chain transfer to monomer reactions have been proposed for some reported neodymium catalytic systems, and the organoaluminum cocatalyst may participate in these side reactions (Scheme 4).[71] The researchers also reported bimodal molecular weight distributions, which suggests the involvement of multiple active species and/or termination reactions.[71]

Taube explored mono- to tetra-substituted allyl rare earth complexes during the 1980s and 1990s. Studied complexes included $Nd(allyl)_3$, $Nd(allyl)_2Cl$, and $Nd(allyl)Cl_2$ and were observed to be quite active in the polymerization of butadiene and isoprene in combination with alkylaluminum.[74] The polymerization mechanism of allyl neodymium complexes is shown in Scheme 5. Compared to transition-metal catalyzed polymerization of diene, the neodymium ions do not have d-orbitals for π-back bonding. Thus, the neodymium metal center can interact covalently with the allyl anion and incoming butadiene monomer. The allyl lanthanide bond should resemble the allyl alkali metal bond due to their ionic contribution. This is supported by ab initio quantum mechanical calculations. For the allyl lanthanide complexes, butadiene insertion occurs via σ-allyl insertion mechanism. The *cis*-η4 coordinated butadiene can react only in a supine arrangement, as observed by Porri. Furthermore, The η2 coordinated butadiene reacts via *syn* insertion in its stable single *trans* configuration. The *trans* or *cis* polydiene structure can arise if the butadiene monomer is η2 or *cis*-η4 coordinated.[24]

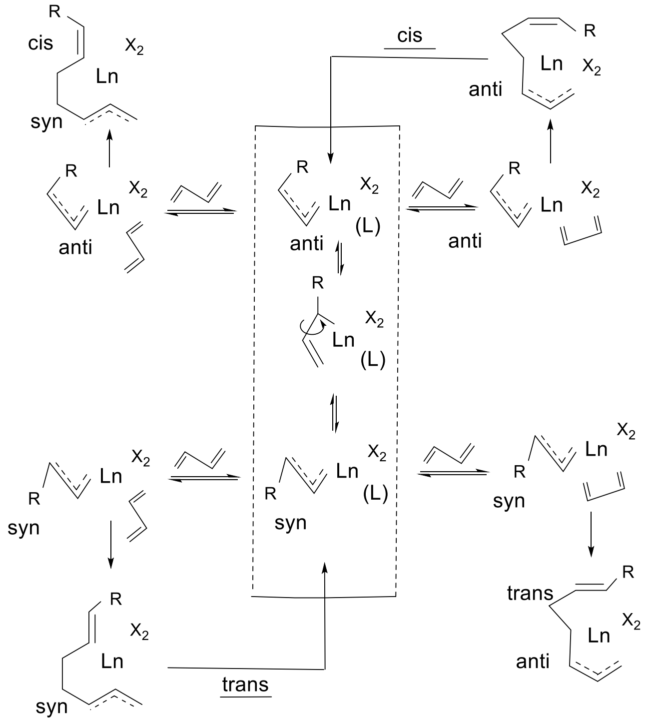


Scheme 3. Structures of the two types of active centers (A) and (B) for the polymerization $NdCl_3 \cdot 3TBP/TIBA$ catalytic system, and the "anti" and "syn" structures (C) of the chain ends of polydiene with $NdCl_3 \cdot 3TBP/TIBA$ catalytic system.[46]

Monakov et al. proposed an active site structure for the $NdCl_3 \cdot 3TBP/DIBAH$ system based on quantum chemical calculations. In the proposed structure, the DIBAH molecules compete with the monomer to coordinate to the active center, lowering the effective reactivity of the catalyst. The proposed structure is given in Figure 3 for the "syn" active site for $C_4H_7NdCl_2 \cdot Al(CH_3)_3$ and an active center for $(CH_3)_3AlH$.[75]



Scheme 4. The proposed mechanism for polymerization of dienes with the catalytic system $NdCl_3 \cdot 3TBP$/TIBA.[71]



Scheme 5. General reaction scheme for the allyl lanthanide complex catalyzed cis and trans 1,4-polymerization of butadiene.[24]

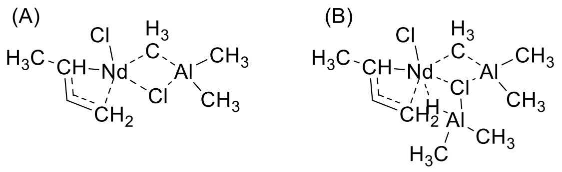


Figure 3. Proposed active site structures for (A) $C_4H_7NdCl_2 \cdot Al(CH_3)_3$ and (B) $(CH_3)_3AlH$.[75]

2.2.2. Ternary catalytic systems. Ternary systems are composed of a co-catalyst (Figure 4(A)), a halide donor (Figure 4(B)), and a halide-free neodymium precursor (such as Nd-carboxylates from versatates, octanoates, and naphthenates). They have the general formula of $NdL_3/AlR_3/R_2AlH$ or R_2AlX, where L= phosphates, carboxylates, alkyl/aryl oxides; R= alkyl groups; and X= halogen. The neodymium precursors usually contain long aliphatic chains to increase the solubility in hydrocarbon solvents.[6] The halide donor in the system significantly increases the 1,4-*cis*-content and the catalytic activity over halide-free systems (Figure 4). The halogenation of the Nd metal happens through exchange reactions. Some examples of ternary systems are shown in Table 2. Other ternary systems replace the required halide donor with the use of boron-based compounds. The most common are perfluorinated organoborates and boranes that act as a pseudohalogen activating the neodymium complex for the polymerization of dienes. The addition of the boron-based activators aids in the generation of cationic heterometallic species that are active for polymerization.[76]

In the early 1980s, Bayer started developing ternary catalytic systems of neodymium carboxylates. Some common carboxylate catalytic systems are neodymium versatate, neodymium 2-ethylhexanoate, neodymium octanoate, and neodymium naphthenate. For synthesizing 1,4-*cis* polybutadiene, ternary systems are favored in industrial settings for their solubility advantages over binary systems. Herein, we will discuss the effects of different co-catalysts and donor ligands, temperature, and solvents upon the polymerization of dienes by ternary catalytic systems.

Table 2. Ternary neodymium catalytic systems used for polymerization of dienes

Nd complex	**Co-catalyst**	**Halide donor**	**Monomer**	***cis*-1,4 (%)**
$Nd(vers)_3$[77] (vers= versatate)	TEA	Diisobutylaluminum chloride (DIBAC)	Isoprene	98
$Nd(vers)_3$[78]	TIBA	DEAC	Butadiene	97
$Nd(vers)_3$[79]	TIBA	DIBAC	Pentadiene	70
$Nd[N(SiMe_3)_2]_3$[80]	TIBA	DEAC	Butadiene	98
$Nd(vers)_3$[81]	DIBAH	Ethylaluminum sesquichloride*	Butadiene	97
$Nd(vers)_3$[38]	DIBAH	$SiCl_4$	Butadiene	97
Neodymium isopropoxide[60]	MMAO	DEAC/ *t*-BuCl	Isoprene	95
Neodymium carboxylates $\{Nd[O_2CC(CH_3)_2CH_2CH_3]_3\}_x$ [82]	TIBA	DEAC	Butadiene/Isoprene	98
$Nd(C_7H_{15}COO)_3$[83]	TIBA	DEAC	Butadiene/Isoprene	95
$Nd(vers)_3$[84]	TIBA	DEAC	Myrcene	98
$Nd(vers)_3$[85]	DIBAH	*t*-BuCl	Butadiene	98
$[Nd_2(Ph_2CHCOO)_6(THF)_x]_x$[86]	TIBA	Ethylaluminum sesquichloride	Butadiene	99
$[Nd_2(Ph_2CHCOO)_6(THF)_x]_x$[86]	TIBA	Ethylaluminum sesquichloride	Isoprene	94
$[Ln(\kappa_2\text{-}Ph_3CCOO)_3(THF)_3]$[86]	TIBA	Ethylaluminum sesquichloride	Butadiene	98
$[Ln(\kappa_2\text{-}Ph_3CCOO)_3(THF)_3]$[86]	TEA	Ethylaluminum sesquichloride	Isoprene	95
$2\text{-}[Ph_2P(O)]C_6H_4NC(tBu)N(2,6\text{-}Me_2C_6H_3)\}Nd(N(SiMe_3)_2)_2$[87]	TIBA, DIBAH	$[PhNHMe_2][B(C_6F_5)_4]$, $[Ph_3C][B(C_6F_5)_4]$	Isoprene	89
$Nd(C_5H_4t\text{-}Bu)_3$[26]	TIBA	Trityl borate $[CPh_3][B(C_6F_5)_4]$	Isoprene	96

*Ethylaluminum sesquichloride is the product of equilibrium mixtures of ethylaluminum dichloride and diethylaluminum chloride

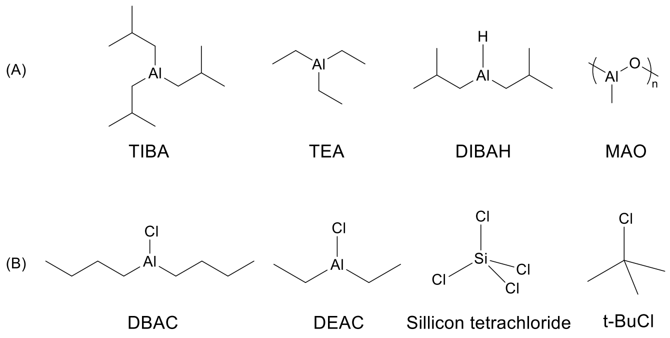


Figure 4. (A) Structures of the co-catalysts in ternary catalytic systems: triisobutylaluminum (TIBA), triethylaluminum (TEA), diisobutylaluminum hydride (DIBAH), and methaylaluminoxane (MAO). (B) Structures of the halide donors in ternary catalytic systems: dibutylaluminum chloride (DBAC), diethylaluminum chloride (DEAC), silicon tetrachloride, and *tert*-butyl chloride (*t*-BuCl).

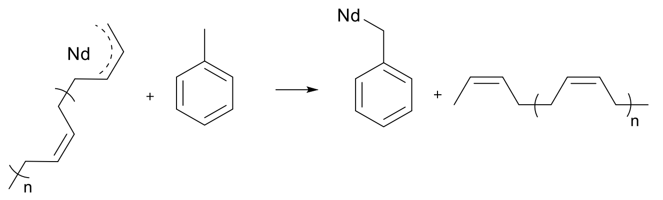
2.2.2.1. Effect of the co-catalyst. For the ternary systems, an organoaluminum, organoboron, or organomagnesium can be used as a co-catalyst. Uribe and co-workers observed a decrease in molecular weights for the ternary catalytic system $Nd(vers)_3$/TIBA/DEAC when the [Al]/[Nd] ratio was increased from 10 to 30 (the DEAC concentration was kept constant) during the polymerization of myrcene.[84] Wilson et al. studied the effect of different alkyl substituents of the aluminum co-catalyst in the $Nd(vers)_3/AlR_3$/*t*-BuCl catalytic system on the *cis*-stereoregularity of polybutadiene. The 1,4-*cis* content shows the following decreasing order of the aluminum co-catalyst: TIBA > TMA > DIBAH > $Al(n\text{-}Dodec)_3$ > $Al(n\text{-}Pro)_3$ > $Al(n\text{-}Hex)_3$ > $Al(n\text{-}Bu)_3$ = $Al(n\text{-}Oct)_3$ > TEA (Dodec = dodecyl, Pr = propyl, Hex = hexyl, Bu= butyl, Oct = octyl).[88] According to their study, no evident trend was observed for the varying alkyl chains of the co-catalyst. The activity of some aluminum co-catalysts for the ternary system Nd octanoate/DEAC/AlR_3, shows the following decreasing trend of TIBA ≈ DIBAH > TEA > TMA.[89]

Among the aluminum derivatives, TMA demonstrated the lowest activity in both binary and ternary diene polymerization catalytic systems. Wilson and co-workers investigated the effect of varying aluminum co-catalyst on the polymerization of butadiene using the ternary system $Nd(vers)_3/AlR_3$/*tert*-butylchloride, and the catalytic activity was decreasing in the following order: $Al(n\text{-}Pr)_3$ > $Al(n\text{-}Dodec)_3$ = $Al(n\text{-}Oct)_3$ = $Al(n\text{-}Hex)_3$ > DIBAH = TIBA > TEA > TMA. The catalytic systems containing methyl substituents in the aluminum co-catalyst showed low or no yield. Ethyl substituents resulted in a higher yield than the methyl ones, while the propyl substituent gave the highest yield. No significant increase was observed in the yield for longer alkyl chain length from 4 to 10.[88] Roitershtein et al. synthesized ternary catalysts consisting of Nd di- and triphenylacetates, ethylaluminum sesquichloride, and co-catalysts: TIBA, DIBAH, and TEA. Among the three co-catalysts studied, TIBA gave a high *cis* content up to 98.9%, high molecular weight, and low dispersity. DIBAH resulted in the highest *cis*-content, up to 99.2%; however, the yield was low, but the dispersity was high (Scheme 6).[86]

Tolpygin et al. synthesized a bis(amido) Nd complex coordinated by tridentate amidinate with a pendant Lewis base $Ph_2P{=}O$ group in NCN ligand ({2-[$Ph_2P(O)$]$C_6H_4NC(tBu)$ $N(2,6\text{-}Me_2C_6H_3)$}Ln[$N(SiMe_3)_2$]$_2$) (Figure 2(E), complex **17**). The synthesis of polyisoprene using this catalyst with borate and TIBA was characterized by high Đ (2.25–9.46), while using DIBAH produced a low Đ range of 1.21 to 1.58. This was due to DIBAH being a more efficient chain transfer agent than TIBA.[87]

***2.2.2.2. Effect of the solvent*.** Wilson et al. studied Nd(vers)$_3$/MAO/*t*-BuCl for the polymerization of butadiene in which the following trend was observed for the catalytic activity: cyclopentane = cyclohexane = methylcyclohexane = hexane = 1,2-dichlorobenzene >> toluene > xylene. Insoluble polymers were observed when chloroform and dichloromethane solvents were used. Using aromatic solvents in the polymerization caused a dramatic reduction in the catalytic activity, with the polymer yield decreasing from 100% to < 20%, but this was not observed for 1,2-dichlorobenzene. The presence of deactivating chlorine groups on the aromatic ring of 1,2-dichlorobenzene decreased solvent competition with the monomer for coordinating to the catalyst.[90] Leon et al. reported the synthesis of polybutadiene using the ternary catalytic system, Nd(vers)$_3$/DIBAH/EASC, and styrene as a solvent, which resulted in the incorporation of 6.3- 15.4% of styrene into the polymer.[91]

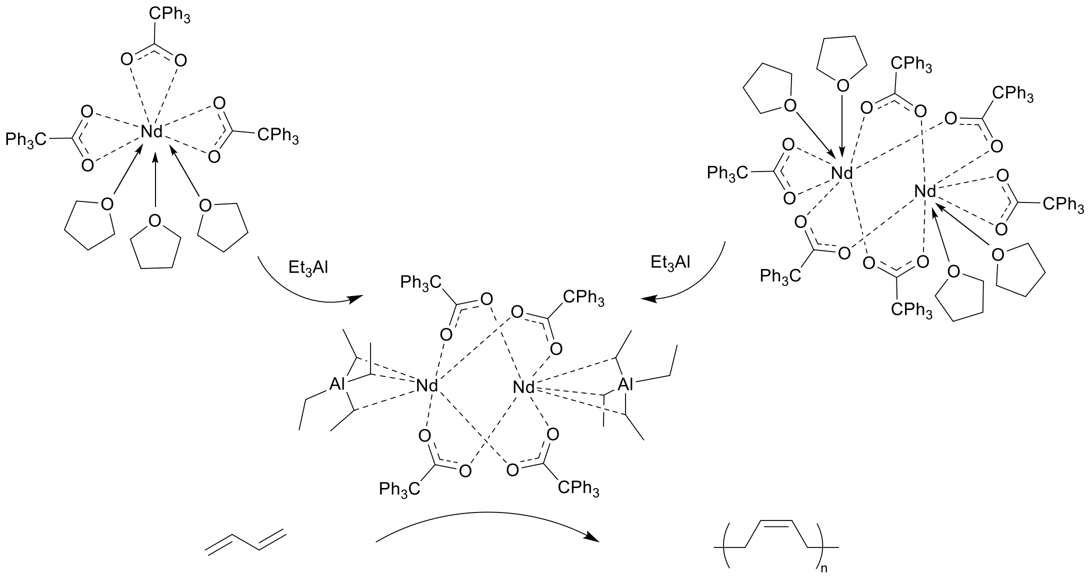
The use of aromatic solvents in the system causes competition with the monomer to coordinate to the catalyst, thereby reducing the effective catalytic activity. Additionally, Friebe et al. reported that a chain transfer reaction occurs when toluene is used, where a proton from toluene is abstracted by the allyl at the end of the growing polydiene chain (Scheme 7).[6, 51]



Scheme 7. Chain transfer to solvent between the allyl end of a growing polybutadiene chain and toluene. (Ligands and co-catalysts are not shown for simplification).[6, 51]

Schmidt et al. observed that toluene tends to coordinate with the neodymium metal center, affecting the polymerization activity. They suggested a catalytic system with Nd{$C(SiHMe_2)_3$}$_3$, two equivalents of a strong Lewis acid $B(C_6F_5)_3$, and TIBA in heptane to produce polybutadiene with 91% 1,4-*cis* content and Đ of 1.48. They identified the 'best' catalyst by characterizing the pre-catalysts, active formation of cationic or zwitterionic species from catalyst initiation, diene insertion for chain propagation, and chain-transfer steps.[25] Tanaka et al. synthesized chloride-bridged bimetallic Nd borohydride complexes, which can be used as catalysts for the polymerization of isoprene activated by tri(*n*-octyl)aluminum. They showed that methylcyclohexane significantly increased the polymerization activity compared to the system with toluene and toluene coordinates to the cationic Nd metal center preventing the insertion of the monomer.[92]

Overall, aliphatic solvents increase the catalyst's activity and the polymer yields compared to aromatic ones. However, polymerization in aliphatic hydrocarbon solvents will cause catalyst deactivation at temperatures >50 °C.[8] In addition, aromatic solvents can affect polydienes' stereospecificity, decreasing cis-1,4 content and increasing trans-1,4 content. C. Boisson et al. reported this behavior with heptane and toluene used



Scheme 6. The general reaction of Nd triphenylacetates with triethylaluminum to produce the catalysts for the stereospecific polymerization of dienes.[86]

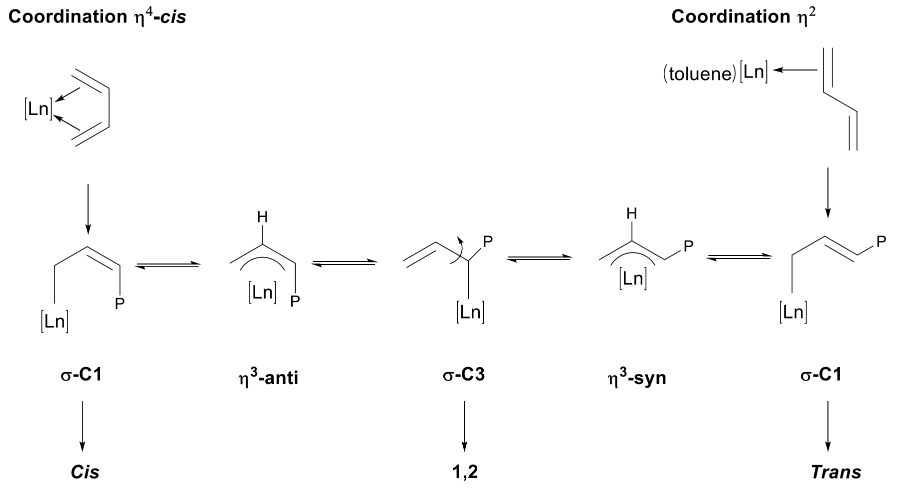
as solvents during polymerization of butadiene in the presence of $Nd\{N(SiMe_3)_2\}_3$ /Al(iBu)$_3$ /AlEt$_2$Cl catalytic system. As a result of switching from heptane to toluene, cis-1,4 content decreased from 97.6% to 93.1%, whereas trans-1,4 content increased from 1.6% to 6.0%. Boisson suggests two possible causes for this observation. First, coordination of toluene as a new ligand to the active center changes the coordination state of butadiene from η^4 to η^2. Second, a decrease in the propagation rate facilitates *anti-syn* isomerization of the last inserted unit (Scheme 8).[80]

***2.2.2.3. Effect of temperature*.** Ternary systems such as Nd(vers)$_3$/MAO/*t*-BuCl,[90] Nd(vers)$_3$/DIBAH/EASC,[93] and Nd(vers)$_3$/DIBAH/*t*-BuCl[94] also exhibit a decrease in molecular weight when the temperature is increased. However, the dispersity for Nd(vers)$_3$/DIBAH/EASC system increases upon increasing the temperature. As a general rule, regardless of the type of catalytic system, a temperature increase will reduce the molecular weight and 1,4-*cis* content while increasing the catalytic activity and Đ.

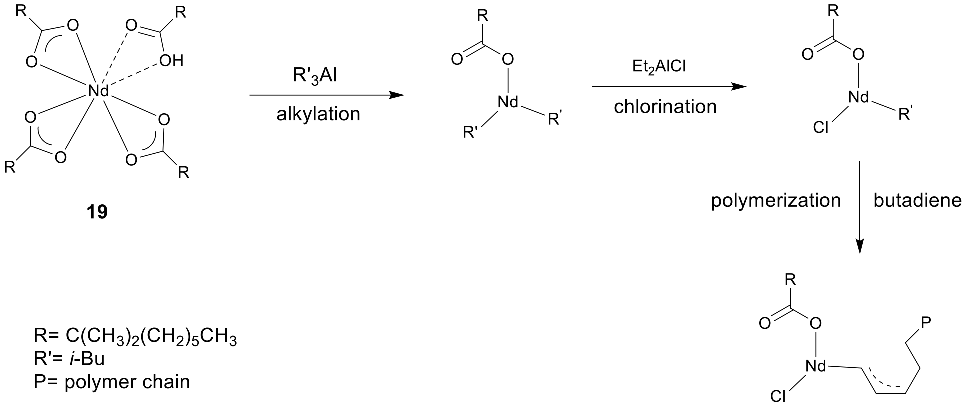
The most significant effect of temperature is on the rate of polymerization. Several studies have reported the activation energies for the polymerization of different dienes. In general, the lower the activation energy (E_a), the higher the polymerization rate. Because the lower the energy of an intermediate, the faster the transition from reactants to products will be at a given temperature. Hsieh et al. reported the activation energies of $NdCl_3{\cdot}nROH/AlR_3$ system for isoprene and butadiene; E_a (isoprene) = 34.3 kJ mol^{-1}, and E_a (butadiene) = 34.1 kJ mol^{-1}.[47] The activation energy for the ternary system Nd(vers)$_3$/DIBAH/EASC was determined to be 53.0 kJ mol^{-1}, which is higher than what is observed for the binary catalytic systems.[95] The binary catalytic systems show lower E_a when compared to the conventional ZN catalysts where E_a = 40-60 kJ mol^{-1}.[96]All parameters mentioned above could affect the following properties significantly, including the catalytic activity, microstructure, molecular weight, and dispersity of the polymer; however, these effects could be positive or negative as described. Nonetheless, to achieve polydienes with desired properties, optimization of those parameters seems necessary.

***2.2.2.4. Ternary catalyst polymerization mechanism*.** A proposed mechanism was reported by Kwag and co-workers for butadiene polymerization using Nd(vers)$_3$ (Scheme 9, complex **19**)/TIBA/DEAC, where the Nd precursor is alkylated with the aluminum compound and subsequent chloride transfer from the chlorinated aluminum compound. The insertion of butadiene forms the Nd-C bond during the alkylating step (Scheme 9). The mechanism was developed from the synchrotron X-ray absorption and UV-Vis spectroscopic data. According to Kwag and co-workers, the presence of one excess versatic acid (VA) molecule in Nd(vers)$_3$ (Nd(vers)$_3$·VA) will break the Nd(vers)$_3$ cluster into discrete monomer species to make all the Nd centers more accessible for alkylation.[97]

Recently, Guo and co-workers proposed a mechanism for Nd(vers)$_3$/TIBA/DIBAC ternary catalytic system from the X-ray absorption fine structure (XAFS) analysis.[98] It was found that Nd(vers)$_3$ formed an oligomer with two Nd-O subshells around neodymium. These aggregates were disturbed when TIBA was added due to alkylation, where the alkyl chains in TIBA are attached to Nd by Nd-C bonds. When the Al/Nd ratio was increased from 2.5/1 to 10/1, the oxygen atoms in the shells around the Nd center reduced from four to two. The DIBAC chlorination prevented the formation of Nd(vers)$_3$ aggregates, where the DIBAC coordinates to the Nd center through Nd-Cl bonds. After alkylation and chlorination, there were no oxygen atoms around the Nd center.[99] Upon adding isoprene to the alkylated, chlorinated Nd catalyst, an exchange reaction takes place between the alkyl groups and isoprene. However, the chlorine atoms are attached.[98]



Scheme 8. Stereospecificity of lanthanide catalysts in butadiene polymerization in the presence of aromatic solvent. R: Polymer chain.[80]



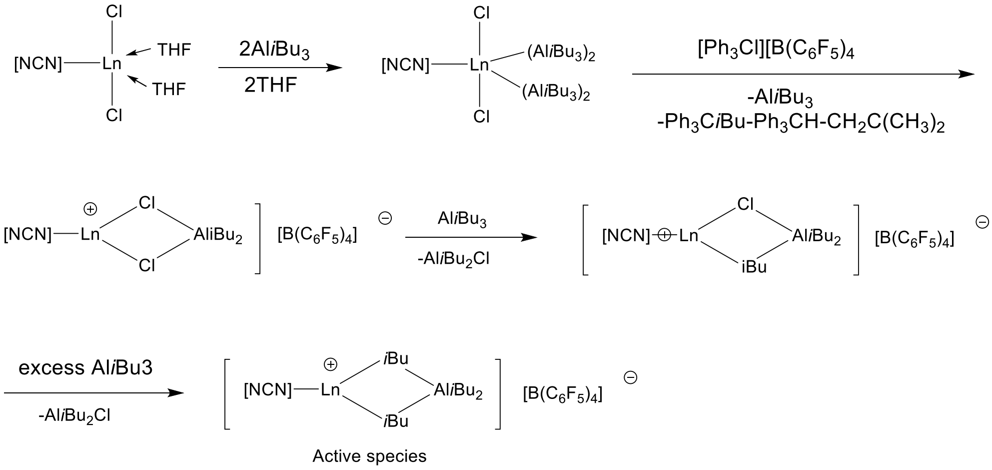
Scheme 9. Proposed activation and propagation mechanism for Nd(vers)$_3$ (complex **19**).[97]

Roitershtein and co-workers reported neodymium diphenylacetate and triphenylacetate derivatives which are active for the polymerization of isoprene and butadiene using ethylaluminum sesquichloride and diisobutylaluminum hydride co-catalysts. They have successfully isolated a Nd-Al adduct, which shows that the ethyl group from the triethylaluminum is bonded to the Nd metal center. Nd triphenylacetates were reacted with excess triethylaluminum in a 1:5 ratio forming pale blue crystals $[Nd_2(Ph_3CCOO)_4(AlEt_4)_2]$ in hexanes. The structure of the complex was resolved by X-ray diffraction. It formed a dimer with two Nd atoms bridging carboxylate ligands bearing two $[AlEt_4]^-$ moieties (Scheme 6). The stable dineodymium complex can be a prototype formed from the activation of Nd carboxylates with trialkylaluminum. This adduct is the catalytically active species commonly observed in diene polymerization.[86]

In addition to ternary systems with halide activators, boron-based activators are also proposed to initiate the polymerization of dienes. Cui and co-workers reported *livingness* in isoprene polymerization using a constrain-geometry-conformation aminophenyl functionalized lanthanide bis(allyl) precursors.[100] The Nd/Al*i*Bu$_3$/$[PhMe_2NH][B(C_6F_5)_4]$ system showed the highest polymerization activity. In some cases, the triisobutylaluminum can act as a chain transfer agent to adjust the molecular weight. The polydispersities are sometimes broad due to active site deactivation and excess aluminum co-catalyst. In 2008, Cui and Gao successfully synthesized aryldiimine NCN-pincer neodymium dichloride complex. The complex forms a ternary catalytic system with organoaluminum and organoborates to synthesize polybutadiene with high *cis* content up to 99.9%. They have deduced the actual active species different from early models of ZN catalysis using NMR spectroscopy and polymerization data. They observed that active species containing an alkyl bridged Ln-Al bimetallic cation (Scheme 10). This observation contrasts with the ZN catalysts with a two-step activation forming the reactive Ln-alkyl or Ln-hydride and aluminum to Ln chlorine transfer.[31]

2.3. 1,4-*Trans* selective polymerization of dienes

The 1,4-*trans*-polydiene has been less explored since the reported work of Natta.[101] These polymers are usually synthesized using catalysts based on metals of group IV, V, chromium, iron, cobalt, and rhodium. The material has attracted commercial application due to its low rolling resistance, hardness, abrasion resistance, etc. The incorporation of 1,4-*trans*-polydiene to polyolefins helps in the reinforcement of important commercial materials.[34]



Scheme 10. Formation of the active species for the aryldiimine NCN-pincer Nd catalyst.[31]

The *trans*-1,4 content can be influenced by the solvent. As mentioned earlier, aromatic solvents promote *trans* stereospecificity by coordinating to the metal and changing the coordination state of butadiene from η^4 to η^2, as well as facilitating *anti-syn* isomerization by decreasing the propagation rate. Toluene is the most used solvent for high-*trans* polymerization. Moreover, a neodymium-based pre-catalyst and a magnesium-based co-catalyst generally afford 1,4-*trans*-polydiene. Monakov and co-workers obtained 91.7% 1,4-*trans*-polyisoprene using the $NdCl_3$(tributylphosphate)$_3$/MgR_2 catalytic system, finding higher *trans* content using toluene as a solvent compared to using heptane.[102] A simple catalytic system was reported by Zheng and co-workers introduced the Nd(Oi-Pr)$_3$/dibutylmagnesium catalytic system for the 1,4-*trans*-specific polymerization of 1,3-butadiene up to 96% (Mn=1.0-2.3 x 104, Đ~1.7). The polymerization occurs via coordination chain transfer polymerization with dibutylmagnesium acting both as a co-catalyst and a chain transfer agent. The catalytic system was also used to prepare block copolymers consisting of 1,4-*trans*-polybutadiene and poly(cyclic ester).[103] Barbier-Baudry and co-workers reported the stereospecific synthesis of 1,4-*trans*-polyisoprene with 96% incorporation using Nd trisborohydride complex (Figure 5, complex **20**) and dibutylmagnesium (compared to a triethylaluminum co-catalyst).[28] This is in agreement with results obtained by Visseaux and co-workers, where they synthesized half sandwich Nd-based complexes (Figure 5, complexes **21**-**23**) using "borohydride/alkylroute" method. The catalytic systems exhibited a high 1,4-*trans*-stereospecificity of 91.4-98.2% and Đ of 1.16-1.90.[104] Cui and co-workers reported a Nd borohydride complex for the synthesis of 1,4-*trans*-polyisoprene (97%) with organoborates and Mg^nBu_2 in a *living* type polymerization. A similar system was reported by Ventura and co-workers where the catalytic system based on neodymium borohydrido complexes, $Nd(BH_4)_3(THF)_3$ or $Cp^*Nd(BH_4)_2(THF)x$ ($Cp^*=C_5(CH_3)_5$), with butylethylmagnesium co-catalyst, affords up to 96.7% 1,4-trans-polybutadiene (Mn=47, 000, Đ=1.38). An excess amount of the co-catalyst in the polymerization, lead to chain transfer reactions between the neodymium and magnesium with an increase in the 1,2 regio-defects.[101]

Anwander and coworkers proposed a mono(cyclopentadienyl) neodymium complex, $(Cp^*)Nd(AlMe_4)_2$. The X-ray structure of the neodymium complex shows a distinctive tetramethylaluminum coordination (one η^2 and one bent η^2). The neodymium complex added with perfluorinated organoborates, $[Ph_3C][B(C_6F_5)_4]$ and $[PhNMe_2H][B(C_6F_5)_4]$, generates cationic species that are active for the polymerization of isoprene. This forms up to 79.2% 1,4-trans-polyisoprene with 1,4-cis and 3,4-regio defects.[105] Higher 1,4-*trans* content was obtained by Napoli and co-workers when they utilized an ansa-mono cyclopentadienyl-imino-pyridine dichloride Nd complex. Using the complex and a co-catalyst, Mg*n*Bu_2/$B(C_6F_5)_3$, high 1,4-*trans*-polybutadiene (99%) was obtained, but the activities and 1,4-*trans* content were lower than the catalyst/methylaluminoxane co-catalyst system.[106] A bis-arylated phosphazene (NPNPN-type) Nd complex/ Mg*n*Bu_2 catalytic system yielded high 1,4-*trans*-polyisoprene (97%) and 1,4-*trans*-polybutadiene (94%).[107]

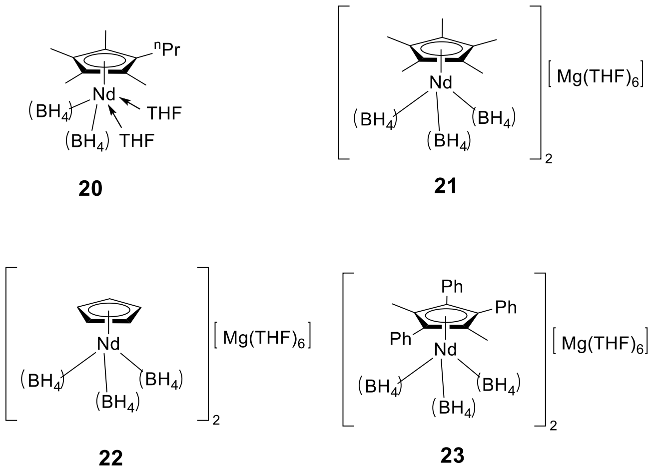
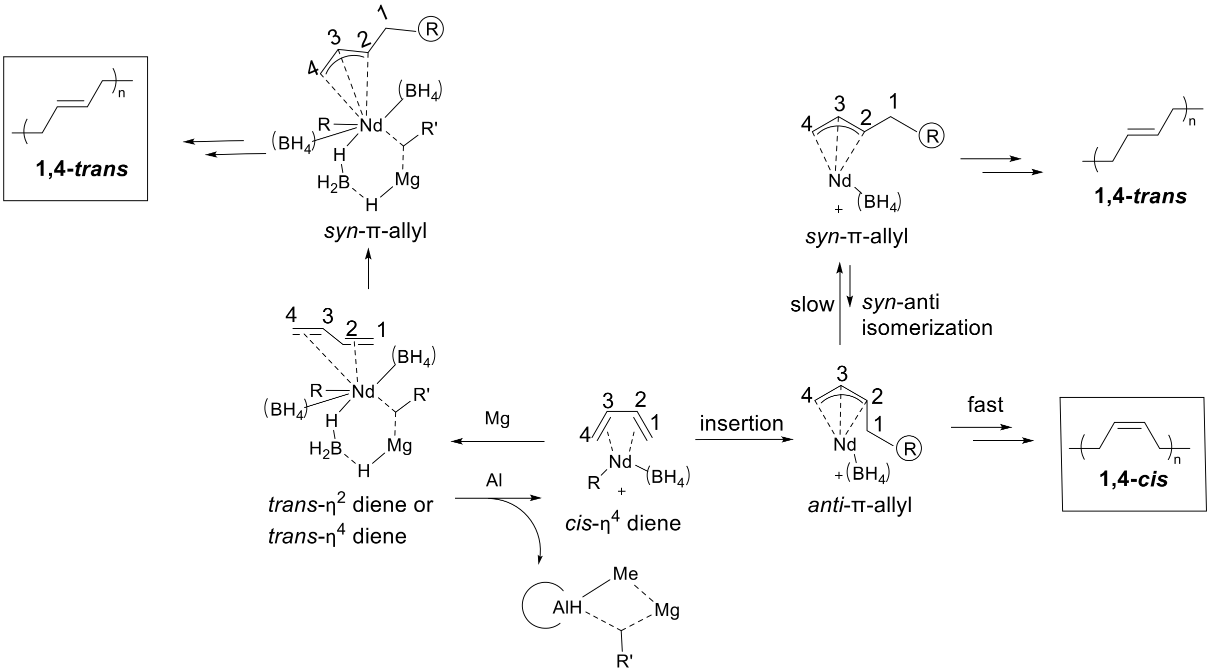


Figure 5. Nd borohydride complexes **20**-**23** for the synthesis of 1,4-*trans*-polydiene.

The majority of the catalysts mentioned contain a cyclopentadienyl ligand to get high 1,4-*trans*-selectivity due to their steric hindrance. Bulky substituents with pendant groups can also be used to facilitate the synthesis of higher 1,4-*trans*-polydiene. Alkylmagnesium was shown to be an alkylating agent from NMR analysis showing a Nd-Mg bimetallic species.[108, 109] Taube and co-workers reported the 1,4-*trans*-polybutadiene initiated by a single-component Nd(η^3-C_3H_5)$_3$, and the stereoselectivity comes from the steric hindrance of the propagating chain forming the *trans*-η^4 diene or *trans*-η^2 diene.[110] Tanaka and co-workers reported the same mechanism for the 1,4-*trans*-stereoselectivity utilizing $Nd(BH_4)_3(THF)_3$-dibutylmagnesium catalytic system (Scheme 11). The 1,4-*trans*-polydiene comes from the syn-π-allyl intermediate formed from the *trans*-η^4 diene or *trans*-η^2 diene intermediate due to the steric hindrance of alkylmagnesium.[111] Moreover, a cationic neodymium intermediate from $Nd(BH_4)_3(THF)_3$ or neutral dialkyl neodymium $(C_3H_5)_2NdCl$ promotes 1,4-*cis*-polydiene. The magnesium in the previous bimetallic complex forms a dimer with alkylaluminum forcing the coordination of a diene to the Nd precursor in a *cis*-η^4 manner. [30, 99, 112, 113]

2.4. Polymerization of vinyl monomers

Polar and non-polar vinyl monomers are usually polymerized by anionic, cationic, and radical polymerizations. The Ziegler-Natta catalysts based on Ti, Co, and Ni get deactivated with the addition of polar vinyl monomers due to the monomer's irreversible coordination to the active catalytic site. Thus, Ti, Co, and Ni catalysts are only utilized to polymerize non-polar dienes and olefins. Nd-based cyclopentadienyl catalysts are applicable for the polymerization of olefins, dienes, styrene, and polar vinyl monomers. Unfortunately, the catalytic systems mentioned show poor solubility in non-polar solvents, and their alkyl derivatives are unstable in solution, making them prone to



Scheme 11. Active species and mechanism of stereoselectivities in the polymerization of conjugated dienes using Nd-Mg/Al.[111]

decomposition. The development of neodymium-based single-site and Ziegler-Natta catalysts for these monomers is scarce. The majority of these reports are focused on styrene polymerization and a few methacrylate and acrylate polymerization; none for vinyl acetate polymerization. Studies for the homopolymerization of styrene are primarily concerned with the ability of the catalytic system to make copolymers with dienes and to make polystyrene with different tacticities.

Polystyrene can be prepared using single-component catalytic systems, often with cyclopentadienyl ligands. Carpentier and co-workers reported the syndiospecific polymerization of styrene using neutral allyl ansa-neodymocene (Figure 2(C), complexes **10**-**12**).[114] The catalytic system gave remarkably high activity with a high number average molecular weight of $1.35x10^5$ g/mol and unimodal narrow dispersity (Đ=1.2-2.1), which indicates single-site catalysis. A structurally similar dimethylsilylene ansa-neodymocene complex gave lower activity due to a hindered coordination sphere than the previous neutral allyl ansa-neodymocene. Lower activities were observed for the cyclopentadienyl ligand with the substituted *tert*-butyl group, which indicates that steric and electronic effects might affect the polymerization activity.[34, 114, 115] D. Baudry-Barbier and coworkers used anionic bisally-ansa-neodymocene, $[Me_4C_2Cp_2Nd(C_3H_5)_2]Li$(dioxane), for the synthesis of isotactic polystyrene without the use of a co-catalyst. Having a bridge between the two cyclopentadienyl rings prevented the redistribution of ligands and the formation of tris(cyclopentadienyl) complexes. Also, it contributed to improved activity by relieving steric hindrance around the metal center.[25]

D. Baudry-Barbier et al. reported other allyl-neodymium complexes that did not require a cocatalyst in order to polymerize dienes with specific stereoselectivity. It was found that tetra-allyl-neodymium anionic, $[Nd(C_3H_5)_4]Li(dioxane)_{1.5}$, (1) and tris-allyl-neodymium, $Nd(C_3H_5)_3(dioxane)_{1.5}$, (2) lead to syndiotactic and isotactic polyisoprene, respectively. In the presence of solvents or monomers, the catalyst is in the equilibrium $[(allyl)_4Ln]Li \leftrightarrow (allyl)_3Ln + (allyl)Li$. Stereoselectivity is the result of simultaneous catalytic processes independent of allyl-lithium and tris-allyl-neodymium. The neutral tris-allyl-neodymium acts as a polymerization initiator, but the allyl-lithium protects the neodymium active species. The allylneodymium complex can easily coordinate styrene and provide isotactic polymers in high yield.[25]

A single-component neutral allyl ansa-neodymocene with bridged bis(indenyl) ligand was reported to produce nearly pure isotactic heptad >99%. The catalyst can stand high temperatures up to 120°C. The complexes with no tetrahydrofuran showed higher catalytic activities than the complexes with bulky initiators.[116]

Borohydride-based binary catalytic systems have been reported by P. Zinck and co-workers. They investigated the polymerization of styrene using $Nd(BH_4)_3(THF)_3$(**1**), $La(BH_4)_3(THF)_3$(**2**), and $Sm(BH_4)_3(THF)_3$(**3**)/n-butylethylmagnesium catalytic systems, and found that the stereoselectivity was independent of the metal identity while activity was strongly affected. The activity increased in the following order: La>Nd>Sm; The lower the initiation efficiency and the hypothetical transfer efficiency, the lower the activity. The stereoselectivity of all synthesized polyisoprenes was atactic.[117] Also, in 2007, this group used

$Cp^*Nd(BH_4)_2(THF)_2$ and the same cocatalyst to prepare the first polystyrene catalyzed chain growth (CCG) with 100% transfer efficiency for reversible transmetallation (Scheme 12). The catalytic system leads to syndioselective oligomerization of styrene with a narrow dispersity (Đ=1.2 or 1.3) and well-controlled molecular weights. Furthermore, this pseudo-living system affords the synthesis of new polystyrene-block-(1,4-trans polyisoprene) copolymers.[118]

Oehme and co-workers reported the polymerization of styrene using $Nd(Oct)_3/CCl_4$/TIBA catalytic system. The tacticity of the polystyrene was not determined, but they obtained a M_n of 3.6 kDa with a Đ of 1.5.[119] A similar catalytic system was reported by Yang and co-workers using $Nd(naph)_3/CCl_4$/TIBA to obtain syndiotactic polystyrene. The addition of CCl_4 or $CHCl_3$ to the polymerization increases the conversion up to >95 %, while increasing the co-catalyst Al/Nd ratio from 4/1 to 12/1, immensely increases the conversion from 7.5 to 98.1%. Upon increasing the CCl_4/Al ratio to 2/1, complete conversion was obtained. Furthermore, the effect of utilizing different ligands for the Nd complex and the catalytic activity decreased in the following manner: $Nd(P_{507})_3$ ~ $Nd(P_{204})_3$ > $Nd(naph)_3$ > $Nd(acac)_3 \cdot H_2O$ (where, acac= acetylacetonate, naph= naphthenate, Figure 6).[120] Gong and co-workers reported the synthesis of isotactic polystyrene using the $Nd(P_{507})_3/H_2O$/TIBA system. The addition of water increased the yield of isotactic polystyrene from 15% to 48%. Moreover, three solvent systems were used to study the effect of solvent polarity; hexane (ε = 1.89, ε= effective dielectric constant), hexane/toluene 40:1 (v/v) (ε = 1.92) and hexane/o-dichlorobenzene 40:1 (v/v) (ε = 2.30). When the polarity of the solvent system was increased, the conversion increased from 62 to 74%, and the isotactic yield decreased from 48 to 24%.[121] $Nd(carboxylate)_3$/trichloroethane/TIBA system was used by Wang et al.. The polystyrene obtained was mainly atactic. The carboxylate ligand used was not specified in this article.[122]

A series of $Nd(OCOR)_3$/DEAC/TIBA ternary systems, where R can be CF_3, CCl_3, $CHCl_2$, CH_2Cl, and CH_3, was reported by Kobayashi and co-workers for the homopolymerization of styrene. The polymerization was carried out at 50 °C in hexane for 6 h for all different catalytic systems with varying alkyl groups. The highest activity was obtained for the catalytic system with R= CCl_3.[123] Zhang and co-workers obtained polystyrene using $Nd(acac)_3/CHCl_3/Bu_2Mg$ catalytic system with ~28% yield at 60 °C in toluene for 4 h.[44] The use of $Nd(naph)_3$/DIBAC/TIBA system for the polymerization of styrene gave only a 2% yield upon performing the polymerization reaction at 50 °C in toluene for 18 h.[124] Nd(O-2,6-t-Bu_2-4-Me-Ph)$_3$(THF)/Mg(n-Hex)$_2$ (O-2,6-t-Bu_2-4-Me-Ph = 2,6-di-*tert*-butyl-4-methylphenol, Figure 6) for the polymerization of styrene was used by Gromada et al., where a 30% yield and a M_n of 2.4 kDa was obtained.[125]

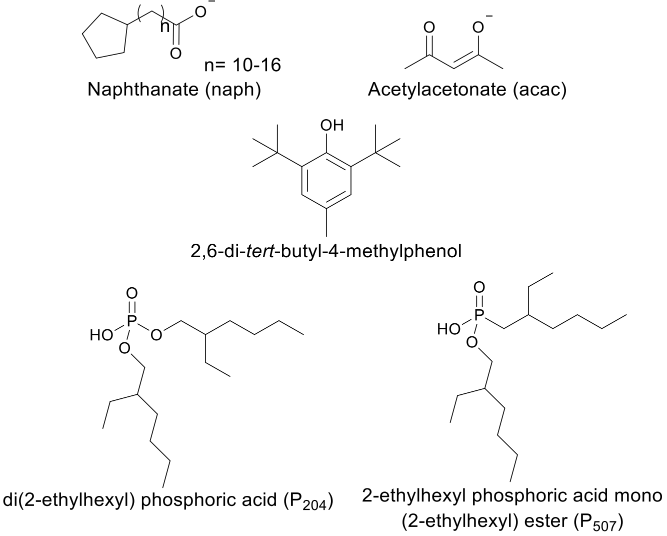
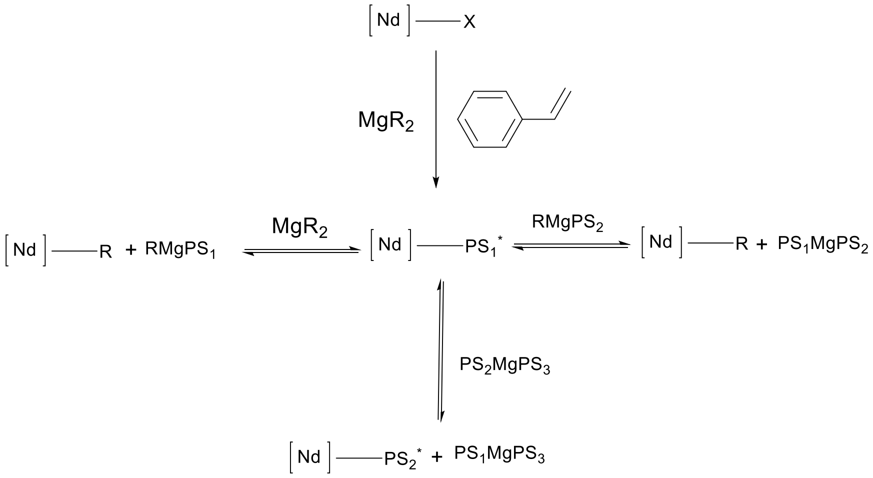


Figure 6. Structures of naphthenate, acetylacetonate, 2,6-di-tert-butyl-4-methylphenol, P_{204}, and P_{507}.



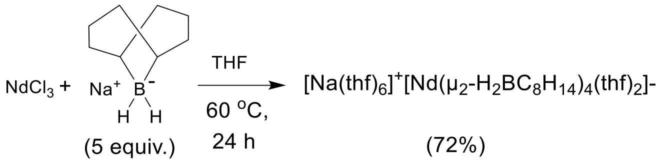
Scheme 12. Mechanism of the transfer polymerisation of styrene in the presence of half-lanthanidocene/dialkylmagnesium systems. X represents a BH_4 group, R is *n*-butylethyl, and PSi* is a growing polystyrene chain.[118]

Like polystyrene, poly(methyl methacrylate) (PMMA) can be synthesized in a variety of tacticities by neodymium catalysts. Barbier-Baudry et al. investigated a number of cyclopentadienyl- and diketiminate- borohydrido neodymium complexes for this purpose and found that the co-catalyst and solvent used substantially impacted the stereospecificity of the polymerization. Syndiotactic polymer was obtained in a polar solvent (THF), isotactic polymer was obtained with BuLi in a nonpolar solvent (toluene), and the atactic polymer was obtained with Mg^nBu_2 in a nonpolar solvent.[126] N. Barros et al. investigated for the first time the role of the borohydride ligand in the polymerization of acrylate, methyl methacrylate (MMA), by combining experimental/synthetic in the presence $[Nd(BH_4)_3(THF)_3]$ complex and density functional theory (DFT)-based theoretical/mechanistic study using the model complexes $[Eu(BH_4)_3]$, $[Eu(BH_4)(Cp)_2]$, and $[Eu(Cp)_2(H)]$ (Cp=η5C$_5$H$_5$). It has been demonstrated that the energy barrier to the formation of the active species, a borate, from the reaction between $[Eu(BH_4)_3]$ and $[Eu(BH_4)(Cp)_2]$ with the first MMA molecule is responsible for the observed uncontrolled polymerization. In addition, comparing $[Eu(BH_4)_3]$ with $[Eu(BH_4)(Cp)_2]$ revealed that the latter gives products with lower stability because the Cp ligands raise the energy value. As the formation of an enolate is more energetically favored, MMA polymerization based on hydride precursors followed a well-controlled method as already reported experimentally by Yasuda for [Sm-(Cp*)$_2$(H)$_2$].[127]

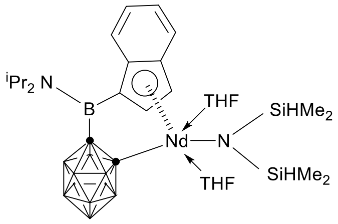
Gromada published several articles describing the homo- and copolymerization of ethylene and methyl methacrylate (MMA) using the Nd_3(O-t-Bu)$_9$(THF)$_2$ catalytic system.[128, 129] Homopolymerization of MMA gave predominantly syndiotactic PMMA (76-79% *rr*; Đ of 1.06-1.12). This provides a new alternative to lanthanocenes for the syndiotactic polymerization of MMA.[130] Nd(O*i*Pr)/TIBA system was used to produce syndiotactic PMMA by Sun et al., and the activation energy was determined to be 43.5 kJ mol^{-1}.[131, 132] Liu et al. reported the homopolymerization of MMA at low temperature (-22 °C) with Nd(naph)$_3$/BuLi, where BuLi was used as the co-catalyst.[133] Tanaka et al. reported the synthesis of poly-MMA by $[Na(thf)_6]^+[Nd(\mu_2\text{-}H_2BC_8H_{14})_4(THF)_2]^-$ (Scheme 13) in the absence of a co-catalyst and with isotactic stereoregularity. This stereochemistry is mainly obtained by alkali metal compounds such as BuLi and lithium enolate as the initiator in non-polar solvents. The high activity of this catalyst is attributed to the stronger attack of hydride to β-carbon of MMA (its anionic nature) rather than those on neutral complexes. Use of excess amount of Bu_2Mg resulted in atactic PMMA with Đ=18.8, and syndiotactic PMMA was obtained by addition of MMAO. The reason for this change is due to the formation of mononuclear aluminum enolate and participation of Bu_2Mg as a catalyst.[65]

Stefan et al. reported $NdCl_3$.3TEP/TIBA (TEP=triethylphosphate) for polymerization of MMA, MA, and VA. The synthesized PMMA, which is obtained by a binary catalytic system, was comprised of 62% syndiotactic triad (rr), 35% heterotactic triad (mr), and 3% isotactic triad (mm). Nonetheless, all previous studies have reported only isotactic PMMA using the neodymium catalysts.[53] Skvortsov et al. reported the polymerization of MMA using a Nd complex (Scheme 14, complex **24**). The conversion degree of the polymerization by using Nd catalyst increased to 77% within 3h with M_w= 199900, M_n=20100, and a high dispersity (Đ=9.95) at room temperature.[134]

Based on the work of Zi, the environment around the Nd metal center in catalytic systems plays a significant role in the reactivity of polymerization. The [η5:σ-*i*Pr$_2$NB(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)]NdN(SiHMe$_2$)$_2$(THF)$_2$ (Figure 7, complex **25**) with the sterically encumbered environment around Nd led to syn-rich PMMA with the low conversion of MMA.[135]

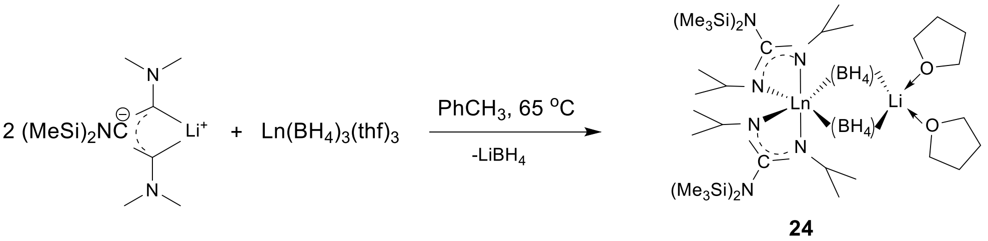


Scheme 13. Synthesis of Nd alkylborohydride complex.[65]



25

Figure 7. Structure of [η5:σ-*i*Pr$_2$NB(C$_9$H$_6$)(C$_2$B$_{10}$H$_{10}$)]NdN(SiHMe$_2$)$_2$(THF)$_2$.[135]



24

Ln = Nd, Sm

Scheme 14. Synthesis of Nd complexes **24**.[134]

3. Neodymium-based complexes for the ring-opening polymerization of ε-caprolactone

3.1. Polymerization of ε-caprolactone

Aliphatic polyesters are indispensable in the biomedical field due to their biocompatibility and biodegradability and their useful structural, thermal, and rheological properties.[10, 11] Among the aliphatic polyesters, PCL is the most exploited material, and it is used in a range of applications from sutures to drug delivery systems.[136-139] PCL can be synthesized by the ROP of ε-CL through different routes, including anionic, cationic, enzymatic, and coordination-insertion.[10, 11, 14] Anionic polymerization yields polymers with well-defined molecular weights; however, the nucleophiles are highly reactive, resulting in chain transfer reactions. Cationic polymerization is poorly controlled, and high molecular weight polymers are rarely produced. Enzymatic polymerization is unfavorable because of the low polymer yields and molecular weights, even though it is a greener method. Coordination-insertion polymerization is a more controlled method, yields high molecular weight, and often follows quasi-*living* kinetics.

Catalysts comprised of Sn[140, 141], Zn[142, 143], or Al[144, 145] metal centers are extensively utilized for coordination-insertion ROP, with tin(II) 2-ethylhexanoate (Sn(Oct)$_2$) as the most exploited in the biomedical field for the polymerization of non-functionalized and functionalized ε-CL.[11, 136, 137, 146-149] Although Sn(Oct)$_2$ gives good catalytic activity, the difficulty of removing it from the polymer can be a disadvantage. This is often not a problem – the Food and Drug Administration approved the utilization of Sn(Oct)$_2$ as a drug additive.[150] However, concerns were raised as it was found that Sn(Oct)$_2$ is a cell growth inhibitor.[151] A promising alternative is rare earth metal catalysts taking their high activity for the ROP of ε-CL into account.[152] These catalysts include ZN type catalytic systems, single-component systems, and binary catalytic systems with an alcohol initiator. Organocatalysis for ROP is growing fast and is another alternative to metal catalysis.[153] Commonly used organocatalysts include 1,4,7-triazabicyclodecen[154-156], 1,8-diazabicycloundec7-ene[154], phosphazene bases[157, 158] ect. In this review, we will focus on Nd-based metal catalysts for coordination-insertion ROP of ε-CL.

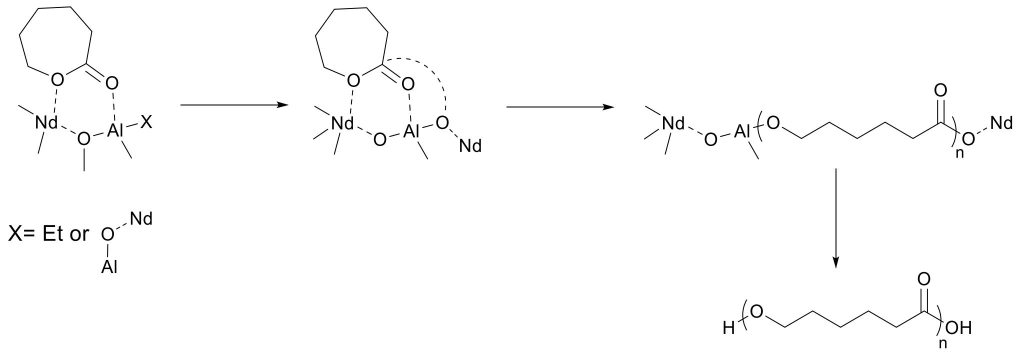
3.2. Polymerization mechanism

Most of our knowledge of the mechanism is derived from the end group analysis of resulting polymers. Several reaction models have been proposed based on hypothesized structures of the active site. In this section, the polymerization mechanisms for the ZN type catalytic systems, binary catalytic systems using an alcohol initiator, and single-component systems for the ROP of ε-CL will be discussed.

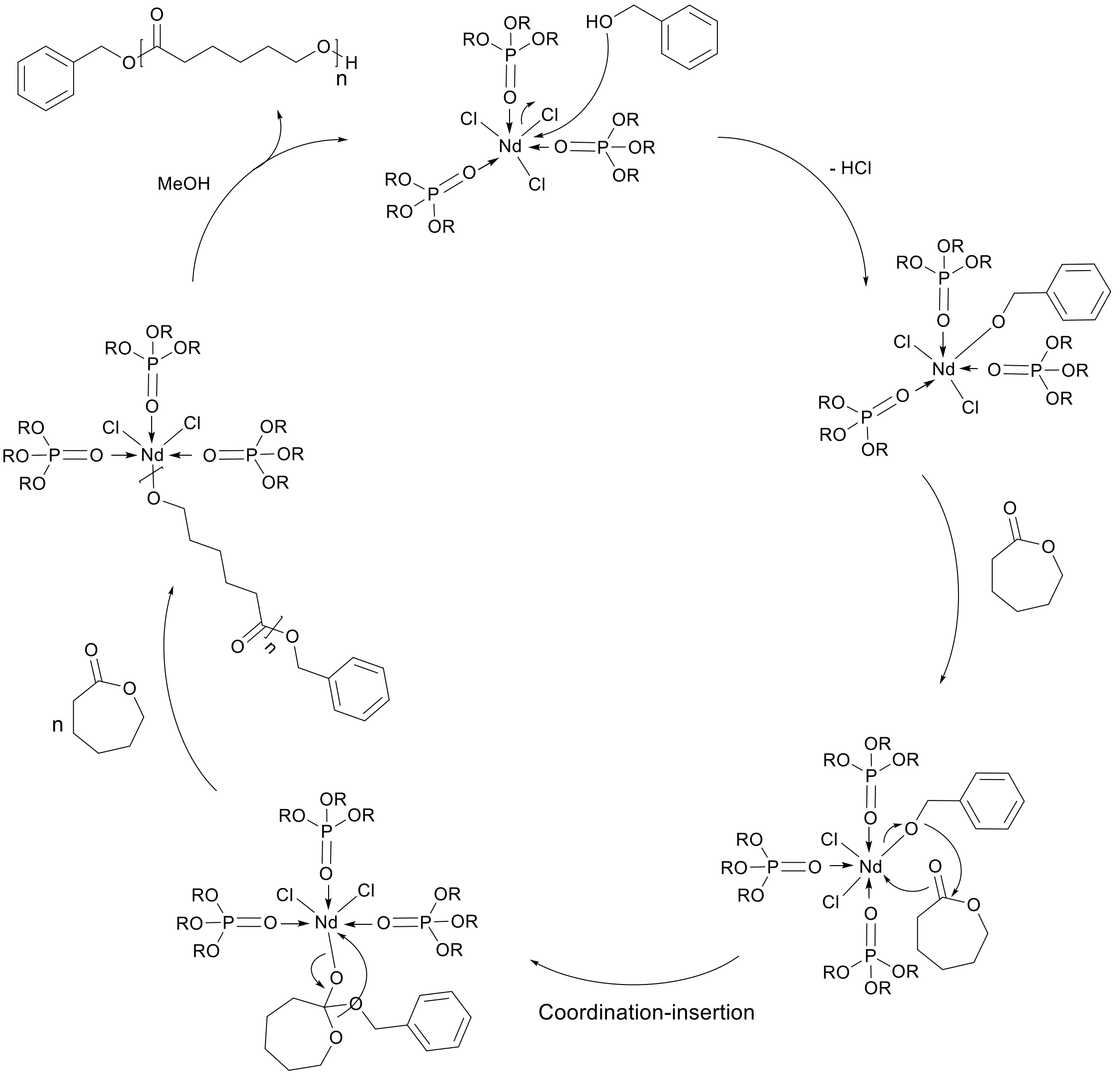
In the early 1990s, Z. Shen's group proposed the polymerization mechanism using ZN type catalytic systems Nd(acac)$_3$·3H$_2$O/TEA for ε-CL polymerization (Scheme 15).[159] The mechanism was determined by IR, NMR, and end-group analysis, demonstrating the exocyclic oxygen's coordination to aluminum and the endocyclic oxygen to Nd.

Nd-based complexes with alcohol as initiators are also used for the ROP of ε-CL. In 2018, Stefan's group reported Nd-phosphate catalysts NdCl$_3$·3L (L = triethyl phosphate or tris(2-ethylhexyl) phosphate) for ε-CL polymerization using benzyl alcohol as an initiator.[160] A detailed coordination-insertion mechanism is given in Scheme 16. The benzyl alcohol coordinates with Nd to form an active alkoxide complex to initiate the polymerization.

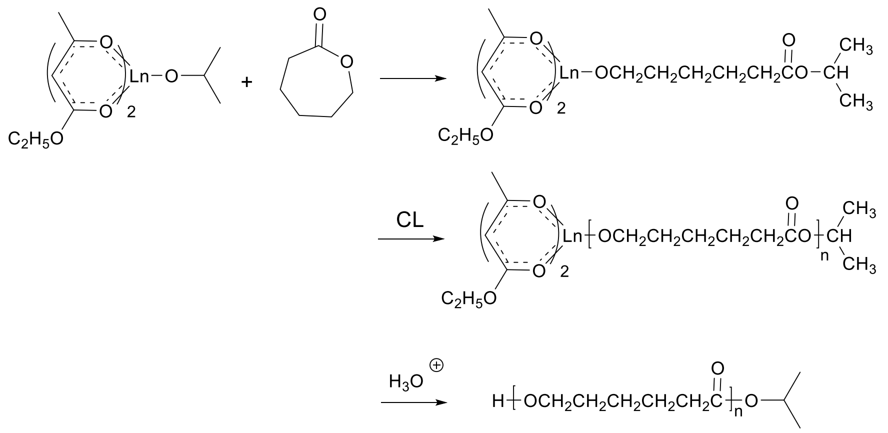
In alkoxide-based catalysts, the ligands can act as the initiator for single component neodymium-based complexes. In 1996, Z. Shen's group reported the *living* polymerization of ε-CL initiated by the single component neodymium alkoxide (diethyl acetoacetate)$_2$NdO*i*Pr.[161] The NMR analysis of the polymer end groups revealed that the polymerization was only initiated by the O*i*Pr group, with one polymer chain initiated by each (EA)$_2$NdO*i*Pr molecule (Scheme 17). Transesterification reactions were found to be suppressed by the bulky ligands.[161]



Scheme 15**.** The mechanism for the ROP of ε-CL using ZN type catalytic system Nd(acac)$_3$·3H$_2$O/TEA.[159]



Scheme 16. Proposed mechanism for the benzyl alcohol-initiated coordination-insertion ROP of CL by $NdCl_3 \cdot 3L$ phosphate complexes.[160]



Scheme 17. Proposed mechanism for the ROP of ε-CL initiated by the single component Nd-based alkoxide (diethyl acetoacetate)$_2$NdOiPr.[161]

In addition to neodymium-based alkoxides being used as single component initiators for the ROP of ε-CL, neodymium-based complexes with nitrogen-based ligands and borohydride-based ligands were also used to initiate the polymerization. In 2003, Q. Shen's group reported a single-component neodymium-based complex with guanidinate ligand for the coordination-insertion ROP of ε-CL.[162] Oligomer analysis confirmed that a terminal diisopropylamido group is present. The lactone carbonyl carbon is attacked by the amido-nitrogen, followed by cleavage of acyl-oxygen bond and formation of a lanthanide alkoxide complex (Scheme 18).[162] Guillaume's and Sun's groups used a single component $Nd(BH_4)_3(THF)_3$ to polymerize ε-CL.[163, 164 165] The complex serves as a precursor in the initiation process, which results in the formation of the actual initiator, a trisalkoxide compound. The proposed pseudo-anionic coordination-insertion mechanism shows that three polymer chains grow in every neodymium center, and two hydroxyl groups terminate the polymers.[163]

In the 21st century, single component neodymium-based complexes have been extensively explored as initiators for the ROP polymerization of ε-CL and showed good activity.[14] Ligand selection was significant to the design and performance of these catalysts. A wide variety of ligands have been investigated. In the following sections, the polymerization performance of single component Nd-based complexes with phenolate-based ligands, nitrogen-based ligands, borohydride-based ligands, and other types of ligands will be discussed.

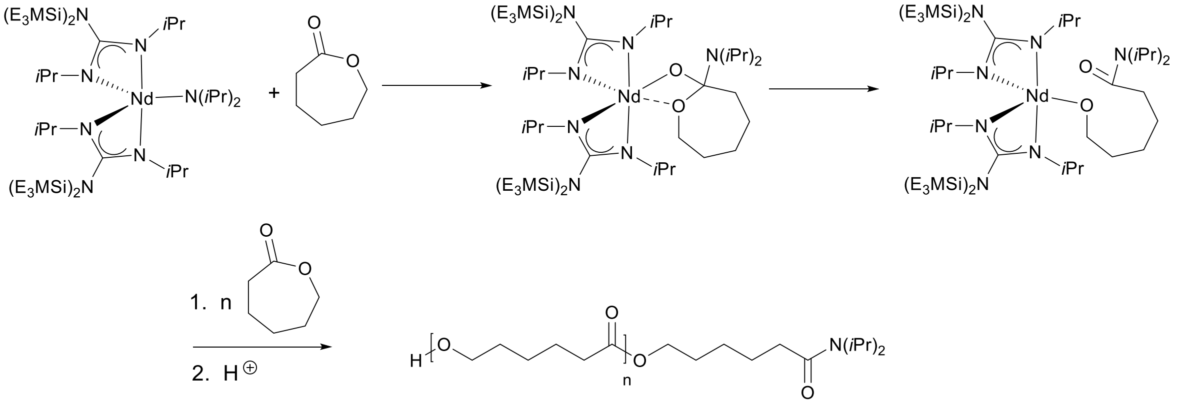
3.3. Neodymium-based complexes with phenolate-based ligands

3.3.1. Mono phenolate ligands. In 2003, Z. Shen's group reported a novel Nd-tris(4-*tert*-butylphenolate) ($Nd(OTBP)_3$) single component initiator for ε-CL polymerization.[166] The initiator can efficiently polymerize ε-CL under mild conditions (e.g., 60 °C) in toluene with a molar ratio of [ε-CL]/[Nd] = 500, to produce PCL with M_n of 3.11×10^4 g/mol over 80% conversion within 2 hours. Single component and Nd-tris(2,4,6-tri-*tert*-butylphenolate) ($Nd(OTTBP)_3$) initiators were reported by the same group and Zhang's group, respectively.[167] $Nd(OTTBP)_3$ can polymerize ε-CL at 20 °C in toluene with a ratio of [ε-CL]/[Nd] = 800 yielding PCL with M_n = 2.69×10^4 g/mol and11.4% conversion.[167] Meanwhile, researchers became interested in bulkier bridged bis(phenolate) ligands. A summary of the polymerization performance is shown in Table 3.

3.3.2. Bridged bis(phenolate) ligands. In 2005, Yao and Q. Shen et al. reported Nd alkoxides with a carbon-bridged bis(phenolate) ligand, i.e. 2,2'-methylenebis(6-*tert*-butyl-4-methylphenoxo), ($[(MBMP)Nd(\mu\text{-}OR)(THF)_2]_2$, R = Pr^i (**26**), Me (**27**), CH_2Ph (**28**)) (Figure 8) in a joint work.[168] These alkoxides showed improved activity over mono(phenoate) ligated complexes for controlled ε-CL polymerization. At 50 °C in toluene with a molar ratio of [ε-CL]/[Nd] = 200 or 300, ε-CL was consumed entirely in one hour, producing PCL with high M_n (3.65×10^4 - 6.94×10^4 g/mol) and narrow Đ (1.17 – 1.29).

In 2006, Yao's group reported controlled ROP of ε-CL in toluene by a new Nd isopropoxide with a carbon-bridged bis(phenolate) ligand 2,2'-ethylene-bis(4,6-di-*tert*-butylphenoxo) ($[(EDBP)Nd(\mu\text{-}OPr^i)(THF)_2]_2$, **29**) (Figure 8).[169] The polymerization was completed in 4 min at 50 °C at [ε-CL]/[Nd] = 200, and 96% conversion was obtained in 12 min increasing [ε-CL]/[Nd] to 300. Even at a lower temperature of 22 °C, 77.5% conversion was achieved. The higher catalytic activity of complex **29** than complexes **27**-**28** is probably due to the larger steric hindrance of the EDBP ligand.

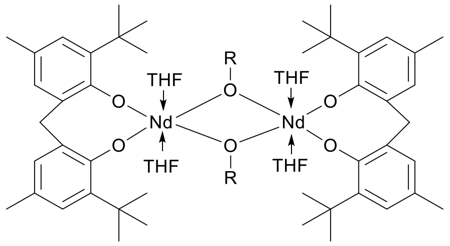
In another joint work of Yao and Q. Shen et al., a neutral Nd amide and an anionic Nd amide with the carbon-bridged 2,2'-methylenebis(6-tert-butyl-4-methylphenoxo) ligand ($(MBMP)Nd[N(TMS)_2](THF)_2$, **30**; $[Li(THF)_4][(MBMP)Nd\{N(TMS)_2\}_2]$, **31**) (Figure 9) were reported.[170] A study of the effect of the bis(phenolate) ligand on the catalytic activities of Nd amides for ε-CL polymerization was carried out. The results revealed that the neutral Nd amide showed lower activity than the anionic Nd amide even though both amides were efficient catalysts for ε-CL polymerization and produced PCL with high molecular weights and narrow Đ.



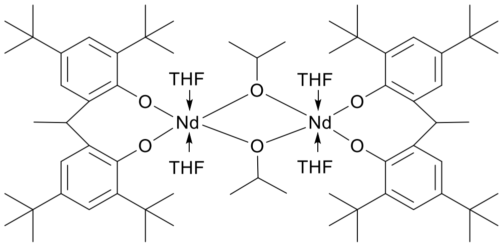
Scheme 18. Proposed initiation mechanism for the ROP of ε-CL by the single component Nd-based complex with nitrogen-based ligand $[(SiMe_3)_2NC(NiPr)_2]_2NdN(iPr)_2$.[162]

Table 3. Summary of the polymerization of ε-CL using Nd-based complexes with phenolate ligands

Nd complexes (Initiator)	**[ε-CL]/[I] (molar ratio)**	**Temp. (ºC)**	**Time (h)**	**Conv. (%)**	**Mn^{SEC} (× 10^4) g/mol**	**Mn/Mw (Đ)**
Nd(OTBP)$_3$[166]	500	60	2	82.8	-	-
Nd(OTTBP)$_3$[167]	800	20	0.33	11.4	2.69	-
26[168]	600	50	1	100	5.23	1.14
27[168]	600	50	1	100	6.94	1.29
28[168]	600	50	1	100	6.40	1.25
29[169]	600	50	0.2	96.0	6.63	1.28
30[170]	500	50	0.25	88	13.07	1.19
31[170]	500	25	0.25	88	10.13	1.24

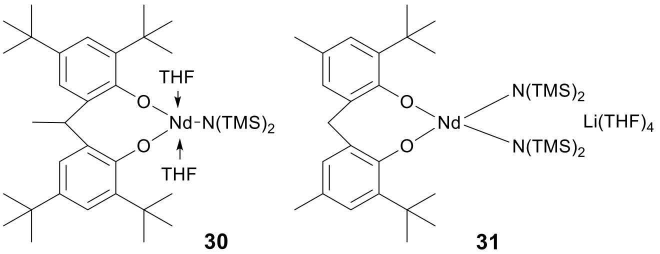


R = Pr^i, **26**; R = Me, **27**; R = CH$_2$Ph, **28**



29

Figure 8. The structures of Nd alkoxides **26**-**28** with carbon-bridged bis(phenolate) ligand MBMP and Nd isopropoxide **29** with carbon-bridged bis(phenolate) ligand EDBP



30 **31**

Figure 9. The structures of Nd amides **30** (neutral) and **31** (anionic) with a carbon-bridged bis(phenolate) ligand MBMP

3.4. Neodymium-based complexes with nitrogen-based ligands

Nitrogen-based ligands also received significant attention due to their ability to stabilize highly electrophilic organolanthanide complexes.[171] In this section, Nd complexes bearing amidinate, β-diketiminate, guanidinate, pyrrole, and amido-based ligands will be discussed, as well as less common ligands such as ketoiminate and scorpionate. These ligands are attractive because of their polydenticity and the tunability of their electronic and steric properties through functional modification of the nitrogen and carbon atoms and by the introduction of pendant Lewis base groups that can coordinate to the metal ion.[172]

3.4.1. Amidinate-based ligands. Amidinate ligands [RC(NR')$_2$]$^-$ are pseudo-allyl ligands that are electronically flexible and are compatible with transition metals in a range of oxidation states.[173] They commonly act as bidentate or bridging monodentate four-electron donors through metal-nitrogen σ-bonds, and π-bonded compounds.[174] Figure 10 shows the structures of the different complexes, and Table 4 gives a summary of the catalytic activity of the amidinate-based complexes. In 2002, Weng and co-workers synthesized homoleptic amidinate Nd complexes: [CyNC(Me)NCy]$_3$Nd (complex **32**) and [CyNC(Ph)NCy]$_3$Nd·2THF (complex **33**) (where Cy = cyclohexyl, Me = methyl, Ph = phenyl), which exhibited high catalytic activity for the ROP of ε-CL.[175] For complex **7**, a 100% yield was obtained in 15 min for a [ε-CL]/[Nd] = 500 at 25 °C and 40 °C. With an increase in the ε-CL ratio (1000:1), a high yield could still be achieved, while lowering the temperature to -5 °C, resulted in a 64% yield. Complex **8** gave lower activity with yields of 89-94% at 25 °C under the same polymerization conditions, which could be due to its less open coordination environment around the metal. Polymers obtained from the reaction of complex **7** showed lower M$_n$ (3.34 – 4.67 x 10^4 g/mol) and Đ (1.71 – 1.81) compared to those obtained from complex **8** (M$_n$: 20.48 – 21.74 x 10^4 g/mol and Đ: 1.90 – 2.18). Due to the versatility of the amidinate ligands to carry different functionalities, heteroleptic complexes were also explored. For instance, Wang et al. studied the use of Nd complex with an ansa-bis(amidinate) ligand and a rigid *o*-phenylene linker (complex **34**).[176] The polymerization only resulted in 74% conversion with M$_n$ of 5.48 x 10^4 g/mol and Đ of 2.03. Even when the polymerization time was extended, the conversion did not change. In 2019, a Nd amido complex supported by tetradentate amidinate ligands (complex **35**) was reported by Trifonov and co-workers, which high catalytic activity for the polymerization of ε-CL at different [ε-CL]/[Nd] ratios in the absence or presence of isopropyl alcohol.[172] Polymerization was completed in less than 1 minute. In the absence of alcohol, the PCL obtained had M$_n$ of 7.83 – 27.15 x 10^4 g/mol with broad Đ (1.6-2.6). These molecular weight values were much higher than what would be expected from the [ε-CL]/[Nd] ratio, which is often observed in ROP initiated by rare earth amide complexes. This can be due to the low initiation rate caused by the lower nucleophilicity of the amido group compared to the alkoxide propagating chain. With the use of an alcohol initiator, polymers with lower M$_n$ (3.41 – 5.49 x 10^4 g/mol) and lower Đ (1.3 – 1.7) were obtained. In 2020, the same group reported the synthesis of a Nd bis(amidinate) monoallyl complex

Table 4. Summary of the polymerization of ε-CL using Nd-based complexes with amidinate-based ligands

Nd complexes (Initiator)	[ε-CL]/[I] (molar ratio)	Temp. (ºC)	Time (h)	Conv. (%)	Mn^{SEC} ($\times 10^4$) g/mol	M_n/M_w (Đ)
32[175]	1000	25	0.25	96.1	4.67	1.71
33[175]	1000	25	0.25	89.3	20.48	2.18
34[176]	500	20	0.5	73.5	5.48	2.03
35[172]	500	25	0.017	100	27.15	1.6
36[177]	500	20	0.033	100	11.43	1.87

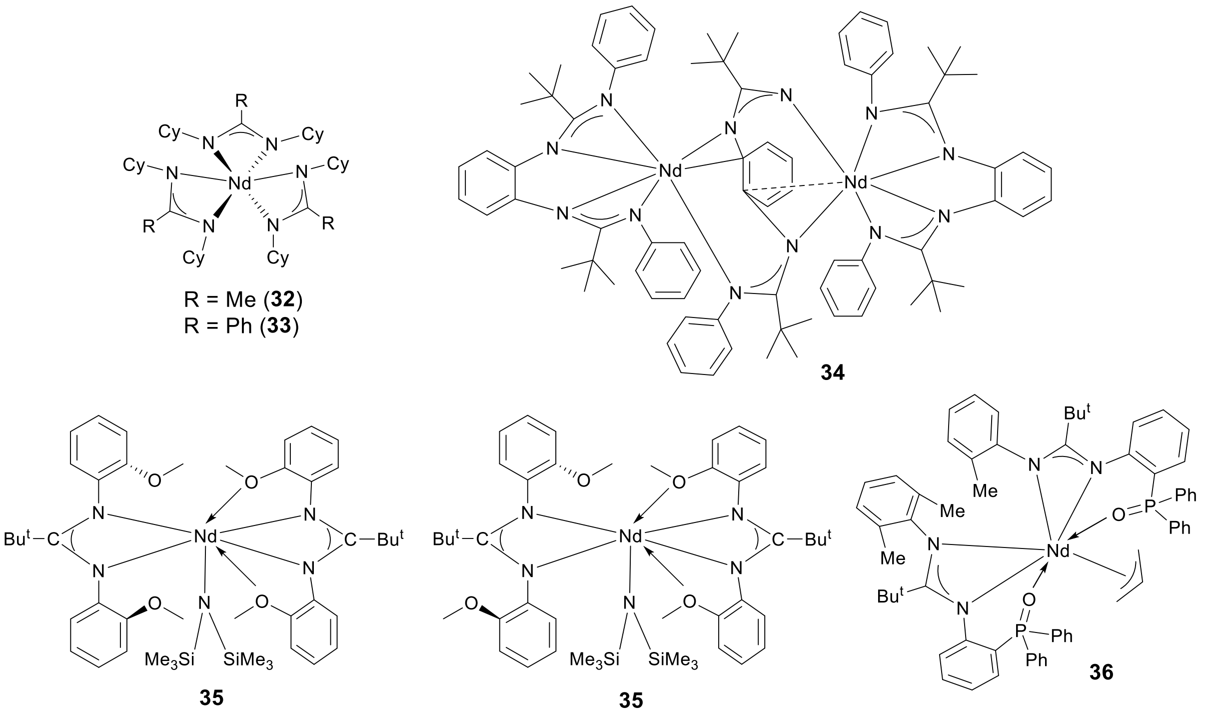


Figure 10. The structures of Nd-based complexes **32**–**36** with amidinate-based ligands

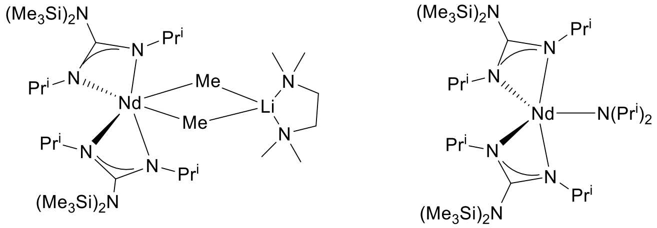
(complex **36**) and its utilization on the polymerization of ε-CL.[177] The PCL had high M_n ranging from 11.43 - 23.75 x 10^4g/mol and broad Đ in the range of 1.87-2.40 within 0.5 to 2 min. Nd complex development is also now moving into the combination of amidinate ancillary ligands with borohydrides to obtain a more efficient polymerization, which will be discussed in the borohydrides section.[172, 176, 178]

3.4.2. Guanidinate-based ligands. Guanidinate anions $[(RN)_2C{=}NR]^-$ are another type of ligand that are structurally similar to amidinates. In comparison to amidinates, guanidinates have a more flexible π-donor ability and are more compatible with electron deficient metals.[173] Figure 11 shows the structures of the different complexes, and Table 5 summarizes the catalytic activity of the guanidinate-based complexes. In 2003, Weng et al. showed that the guanidinate methyl lanthanide complex $[(SiMe_3)_2NC(N\textit{i}Pr)_2]Nd(\mu\text{-}Me)_2Li(TMEDA)$ (complex **37**) had a moderate activity for the ROP of ε-CL at 20 °C, giving M_n of 6.35 – 11.03 x 10^4 g/mol within 15 min to 1 h but with a broad Đ ranging from 1.92 – 2.54.[179] When they modified the complex to a bis(guanidinate) Nd diisopropylamido, $[(SiMe_3)_2NC(N\textit{i}Pr)_2]_2NdN(\textit{i}Pr)_2$ (complex **38**), ε-CL polymerization gave 80-100 % yield within 5 min at 15 °C, with M_n ranging from 11.06 – 32.29 x 10^4 g/mol but still with a broad Đ (1.87-2.26).[162] In this complex, an increase in steric bulk was observed due to the orientation of $N(SiMe_3)_2$ groups relative to the N-C-N-Nd plane. Also, the hard Lewis base of the guanidinate ligand makes the Nd center more electronic-deficient. Although not published, they mentioned that under the same polymerization conditions, $[(SiMe_3)_2NC(N\textit{i}Pr)_2]_3Ln$ are unable to initiate the ROP of ε-CL, which demonstrates the importance of having the Ln-N(*i*Pr)$_2$ σ-bond. A terminal diisopropylamido group was confirmed when the oligomer was analyzed, showing that the polymerization initiation follows the mechanism shown in Scheme 14.[162]

3.4.3. β-Diketiminate-based ligands. The β-diketiminate anion, an isoelectronic alternative to cyclopentadienyl ligand, has also been utilized in organolanthanide complexes. β-diketiminates can coordinate to the metal center in a series of bonding modes from purely σ to π donation.[180] Figure 12 shows the structures of the different complexes, and Table 6 gives a summary of the catalytic activity of the β-diketiminate-based complexes. In 2005, Zhang et al. synthesized a salt-free

Table 5. Summary of the polymerization of ε-CL using Nd-based complexes with guanidinate-based ligands

Nd complexes (Initiator)	[ε-CL]/[I] (molar ratio)	Temp. (°C)	Time (h)	Conv. (%)	Mn^{SEC} (× 10^4) g/mol	M_n/M_w (Đ)
37[179]	500	20	0.25	100	9.18	1.99
38[162]	2000	15	0.083	98	32.29	1.87

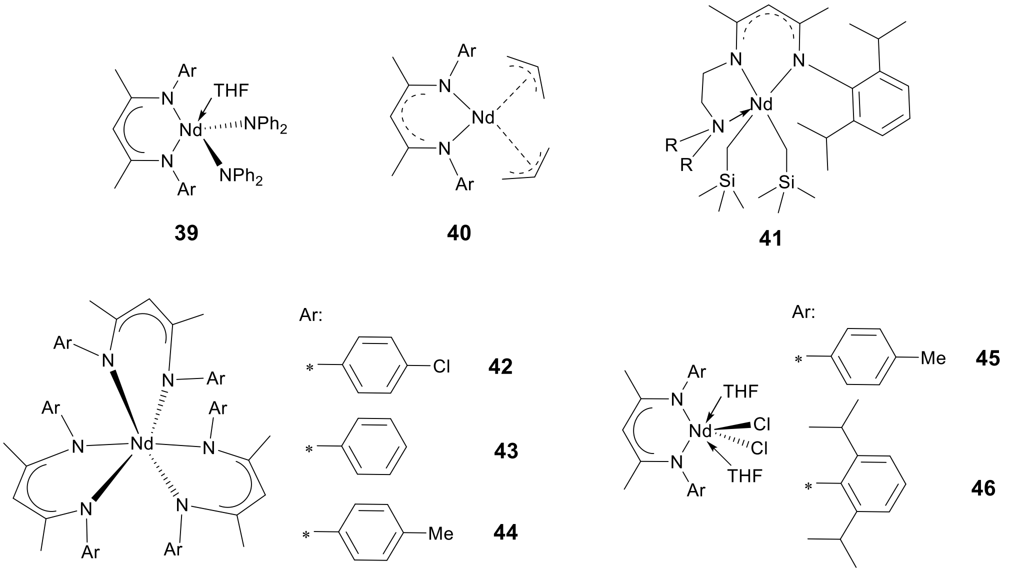


37 **38**

Figure 11. The structures of Nd-based complexes **37** and **38** with guanidinate-based ligands

Table 6. Summary of the polymerization of ε-CL using Nd-based complexes with β-diketiminate-based ligands

Nd complexes (Initiator)	[ε-CL]/[I] (molar ratio)	Temp. (°C)	Time (h)	Conv. (%)	Mn^{SEC} (× 10^4) g/mol	Mn/Mw (Đ)
39[181]	1000	0	0.25	100	15.97	1.50
40[180]	200	0	0.017	99	2.95	1.8
41[171]	2000	26	0.33	89	2.94	1.35
42[182]	2000	0	0.5	100	27.5	1.81
43[182]	2000	25	0.5	100	19.7	1.89
44[182]	1000	25	0.25	97	11.6	1.69
45[182]	100	25	3	0	-	-
46[182]	100	25	3	0	-	-



39 **40** **41**

Figure 12. The structures of Nd-based complexes **39**-**46** with β-diketiminate-based ligands

diamido complex bearing β-diketiminate ligand, (N,N'-bis(2,6-dimethylphenyl)-2,4-entanediiminate))Nd(NPh$_2$)$_2$(THF) (complex **39**).[181] The complex showed high activity for the ROP of ε-CL at 0 °C and 25 °C with quantitative yield and M_n of 9.86 – 15.97 x 10^4 g/mol within 3 – 15 min. The polymerization afforded a Đ ranging from 1.50 – 1.90, where the lowest Đ was obtained at low temperatures. In 2005, Bochmann et al.[180] explored the use of mixed ligands: bis(allyl)diketiminato and tris(allyl) Nd complex, Nd(η^3-C_3H_5)$_2${κ^2-HC(MeCN(2,6-C_6H_3*i*Pr_2))$_2$} (complex **40**). The complex was highly active for ε-CL polymerization, where a 99% conversion was achieved within 1 min at 0 °C with M_n of 2.95 x 10^4 g/mol and Đ of 1.8. The catalyst's high efficiency is attributed to the presence of allyl ligands, which are adequately nucleophilic for the attack on the lactone without the need for an activator or scavenger. From end group analysis, they were able to confirm the presence of an allyl terminus, proving that a nucleophilic route of polymerization takes place. The transfer of an allyl ligand to the monomer initiates the polymerization with metal alkoxide as the propagating species. Another way to mitigate the tendency of the ligand to undergo redistribution, dimerization, and elimination reactions is through the introduction of neutral pendant arms that will allow the stabilization of the complex. This was exemplified in the work of Sun et al.[171] in 2008 where they utilized a Nd dialkyl complexes containing tridentate monoanionic ligand with nitrogen donors (complex **41**) to polymerize ε-CL. 89 % yield was obtained within 20 min at room temperature, with a molecular weight of 2.94×10^4 g/mol and Đ of 1.35. In 2009, Q. Shen et al. synthesized a series of Nd complexes having a tris-β-diketiminate ligand to obtain a more sterically crowded complex.[182] $Nd[(4\text{-}ClPhNC(Me)_2CH^-]_3$ (complex **42**, with Cl at the para position), $Nd[(PhNC(Me)_2CH^-]_3$ (complex **43**), no substituent), and $Nd[(4\text{-}MePhNC(Me)_2CH]^-]_3$ (complex **44**), with Me group at para-position) were synthesized to compare the effect of electron density. More acute bite angles were observed for these complexes compared to the mono-β-diketiminate complexes.

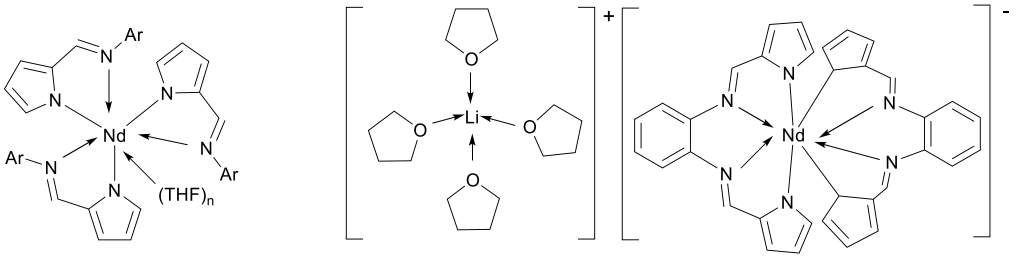
These complexes were highly active initiators for the ROP of ε-CL, yielding polymers with high M_n ($7.78 - 27.50 \times 10^4$ g/mol) and moderate distributions ranging from 1.38 – 1.89. Complex **44** exhibited the lowest activity, which can be attributed to the increase in the electron density of the ligand around the Nd center resulting in less favored coordination of ε-CL to Nd. β-diketiminate Nd dichlorides complexes were also synthesized for comparison - $[(4\text{-}MePhNC(Me)_2CH^-]NdCl_2(thf)_2$ (complex **45**), with Me group at the para position) and $[(2,6\text{-}iPr_2Ph)NC(Me)_2CH^-]NdCl_2(thf)_2$ (complex **46**), with isopropyl group at the ortho positions). No polymerizations were observed, which means that the steric environment around the metal is a crucial factor to be considered when designing complexes.

3.4.4. Pyrrolyl-based ligands. Pyrrolyl-based ligands have also been considered in organolanthanide chemistry because it is a six π-electron system similar to cyclopentadienyl. Also, tunable steric and electronic properties can be achieved due to the ability of the nitrogen in the ring to form σ-bonds.[183] [184] Figure 13 shows the structures of the different complexes, and Table 7 gives a summary of the catalytic activity of the pyrrolyl-based complexes. In 2011, Wang et al. synthesized rare-earth metal complexes with iminopyrrolyl ligand, $[2\text{-}(2,6\text{-}Et_2C_6H_3NCH)C_4H_3N]_3Nd(THF)$ (complex **47**), which showed high catalytic activity where >99% conversion was achieved at 60 °C within 30 s in both toluene and THF solvents.[183] High M_n in the ~5.0×10^4 g/mol range was obtained with moderately good Đ (1.52 and 1.63). Li et al. reported Nd complex supported by a pyrrolide Schiff base ligand H_2bppda (H2bppda = N,N'-bis(2-pyrrylmethylidene)-1,2-phenylenediamine).[184] The complex, $[Li(THF)_4][Nd(bppda)_2]\cdot THF$ (complex **48**), has a discrete ion-pair structure consisting of an anion $[Nd(bppda)_2]^-$, a cation $[Li(THF)_4]^+$, and a solvate THF molecule. The complex can initiate the polymerization of ε-CL, and all the obtained polymers have high M_n ($2.84 - 10.20 \times 10^4$ g/mol) and relatively narrow Đ (1.09 – 1.39). The influences of temperature and solvents were also studied. In dimethoxyethane (DME) solvent, a higher temperature is needed for the polymerization to give high conversions. Toluene gave complete conversion in a relatively short time while etherate solvents were slower, which can be attributed to the competitive binding to Nd by the solvent.

3.4.5. Amido-based ligands. Amides such as the $N(SiMe_3)_2$ group and (phosphanyl)amides are another type of bulky ligand that has been shown to coordinate with lanthanides for use as catalysts for the ROP of ε-CL. Figure 14 shows the structures of the different complexes, and Table 8 gives a summary of the catalytic activity of the amido-based complexes. In 2004, Q. Shen et al. used bulky bis(trimethylsilyl) amido ligands to synthesize two Nd complexes with different coordination numbers - complex **49**

Table 7. Summary of the polymerization of ε-CL using Nd-based complexes with pyrrolyl-based ligands

Nd complexes (Initiator)	[ε-CL]/[I] (molar ratio)	Temp. (°C)	Time (h)	Solvent	Conv. (%)	Mn^{SEC} (× 10^4) g/mol	Mn/Mw (Đ)
47[183]	500	60	0.0083	Toluene	> 99	5.16	1.52
	500	60	0.0083	THF	> 99	4.57	1.63
48[184]	200	40	48	DME	50	2.84	1.26
	200	40	33	THF	93	4.64	1.39
	200	40	10	Toluene	97	9.57	1.12

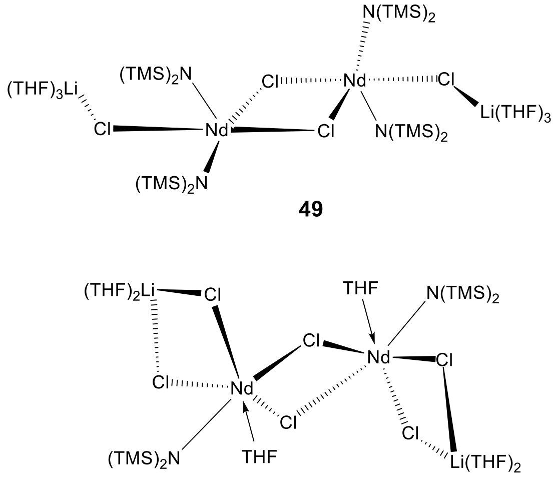


47 **48**

Figure 13. The structures of Nd-based complexes **47** and **48** with pyrrolyl-based ligands

Table 8. Summary of the polymerization of ε-CL using Nd-based complexes with amido-based ligands

Nd complexes (Initiator)	[ε-CL]/[I] (molar ratio)	Temp. (°C)	Time (h)	Conv. (%)	Mn^{SEC} (× 10^4) g/mol	Mn/Mw (Đ)
49[185]	800	25	2	99	5.11	1.91
50[185]	800	25	2	61	5.23	1.87
51[186]	150	r.t.	0.017	95	1.72	1.12



49

50

51

Figure 14. The structures of Nd-based complexes **49**-**51** with amido-based ligands

with a coordination number of 5 and complex **50** with a coordination number of 6.[185] The monosubstituted silylamido complex **50** showed poorer catalytic activity than the corresponding disubstituted complex **49** under the same conditions due to the more strictly restricted environmentaround the Nd metal of the former. Complex **49** gave 99% conversion at room temp within 2 h, giving an M_n of 5.11 x 10^4 g/mol and Đ of 1.91. Complex **25** only gave 61% yield, but the M_n obtained was higher (5.23 x 10^4 g/mol), and Đ was slightly narrower (1.87). Greiner et al. synthesized a Nd complex of chelating bis(phosphanyl)amide (complex **41**).[186] Bis(phosphanyl)amide, $(Ph_2P)_2N^-$ was used as a possible precursor to synthesize stable Ln complexes because of its more sterically hindered structure compared to mono(phosphanyl)amide. Phosphorus can be easily replaced by a hard donor atom such as oxygen because phosphorus only forms weak Lewis acid-base adducts with the Nd. Using this complex, quantitative polymerization of ε-CL was observed with M_n of 1.72 x 10^4 g/mol and Đ of 1.12 within 1 min. Compared to amido group, alkoxide group -OR (R is the growing polymer chain) exhibits a higher initiation rate resulting from the ring-opening of ε-CL and the insertion of the resulting fragment into the $M\text{-}N(SiMe_3)_2$ bond.[172]

3.4.6. Other types of nitrogen-based ligands. Other types of nitrogen-based Nd complexes that have been reported are β-ketoiminate and heteroscorpionate ligands (Figure 15). Table 9 gives a summary of the catalytic activity of these types of Nd complexes. In 2011, Q. Shen et al. explored using a ferrocene-containing N-aryloxo-β-ketoiminate Nd complex (complex **52**) for the polymerization of ε-CL.[187] In their previous studies, they showed that lanthanide aryloxo and amido complexes based on N-aryloxo functionalized ketoiminate ligand are active initiators for the ROP of ε-CL. However, stable dimeric structures can be formed, resulting in lower catalytic activity than another organolanthanide catalyst. Hence, they decided to use a bulky ligand to form complex **52,** which was able to initiate ε-CL polymerization with moderate activity. All the polymers obtained have high molecular weights and relatively broad Đ (1.33 – 2.02). Complex **52** quantitatively polymerized the ε-CL within two h in toluene at 50 °C with M_n of 16.77 x 10^4 g/mol. Higher activity was observed in toluene than in THF and CH_2Cl_2, which can be attributed to solvent coordination resulting in catalyst deactivation.

Scorpionate ligands are also extensively used in various applications. Rodriguez et al. were interested in extending the scope to synthesize heteroscopionate complexes of rare earth metals.[188] They reported new chiral and achiral rare earth metal silylamide complexes supported by heteroscorpionate ligands (complexes **53**–**57**). Complex **53** was isolated as an enantiopure compound, complex **54** was isolated as a racemic mixture of two diastereomers, and complexes **55** and **56** did not have any chirality element. The ligand can coordinate with the metal centers in different ways due to the versatility of the acetamide heteroscorpionate and its ability to form different tautomers. This led to the synthesis of a bis(amido)dimeric complex (complex **57**) where the heteroscorpionate ligands are coordinated bridging to the Nd centers. Nd complexes **53**-**56** acted as efficient single-site initiators for the controlled

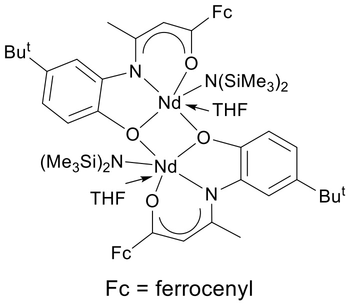
ROP of ε-CL, while no polymerization was observed for complex **57**. For complex **53**, the reaction was rapid, wherein 77% conversion was observed in 30 s at 25 °C. A decrease in temperature to 0 °C and -40 °C resulted in lowering conversion and lower Đ. At the same time, an increase in the [ε-CL]/[Nd] ratio gave polymers with higher M_n with the Đ almost unchanged. A linear correlation between M_n and the percentage conversion was observed. Under the same conditions, complex **54** gave 100% conversion but with broader Đ, while decreased reactivity was observed for complex **55** and even lower for complex **56**. The Đ values were broader than those obtained for complex **53**. A nucleophilic route is proposed due to the presence of $N(SiHMe_2)_2$ termini. They reported the first example of the activation of a C-H bridge methine group with subsequent coordination of the carbon atom in this class of heteroscorpionate.

3.5. Neodymium-based complexes containing borohydride-based ligands

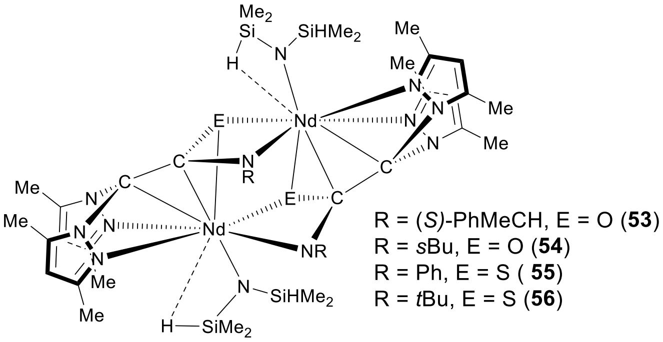
Borohydrides are another class of ligands that exhibit highly versatile catalytic ability towards the polymerization of various monomers. In this section, simple catalysts bearing borohydride groups are discussed. Moreover, the current trend is towards tailoring new complexes with the incorporation of different functional groups. Most of the recent works which employ borohydrides combined with various ligands such as allyl, phenoxy, and amidinates, will also be presented (Figure 16). A summary of the catalytic activity of these complexes is presented in Tables 10 and 11.

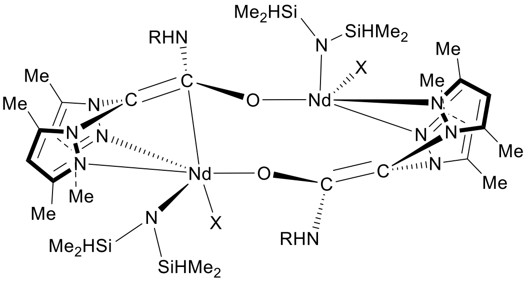
Table 9. Summary of the polymerization of ε-CL using Nd-based complexes with other types of nitrogen-based ligands

Nd complexes (Initiator)	[ε-CL]/[I] (molar ratio)	Temp. (ºC)	Time (h)	Solvent	Conv. (%)	Mn^{SEC} (× 10^4) g/mol	Mn/Mw (Đ)
52[187]	400	50	2	Toluene	90	16.77	1.69
	400	50	2	THF	53	8.62	1.33
	400	50	2	CH_2Cl_2	25	1.86	1.45
53[188]	500	25	0.028	Toluene	100	5.21	1.29
54[188]	500	25	0.033	Toluene	100	5.45	1.48
55[188]	500	25	0.042	Toluene	80	4.90	1.33
56[188]	500	25	0.028	Toluene	42	2.171	1.39
57[188]	500	25	1	Toluene	traces	-	-



52





R = *s*Bu, X = $N(SiHMe_2)_2$ **57**

Figure 15. The structures of Nd-based complexes **52**-**57** with other types of nitrogen-based ligands

Table 10. Summary of the polymerization of ε-CL using Nd-based complexes with simple borohydride-based ligands

Nd complexes (Initiator)	[ε-CL]/[I] (molar ratio)	Temp. (ºC)	Time (h)	Solvent	Conv. (%)	Mn^{SEC} (× 10⁴) g/mol	Mn/Mw (Đ)
58[163]	348	21	0.083	THF	100	1.03	1.2
	117	21	0.083	CH_2Cl_2	100	0.48	1.5
58[164]	663	21	0.25	Toluene/THF	100	1.70	1.4
58[165]	470	60	0.23	Acetone/THF	90	0.959	1.39
59[189]	500	19	0.0083	THF	100	1.48	1.25

Table 11. Summary of the polymerization of ε-CL using Nd-based complexes with borohydride combined with other groups of ligands

Nd complexes (Initiator)	[ε-CL]/[I] (molar ratio)	Temp. (ºC)	Time (h)	Solvent	Conv. (%)	Mn^{SEC} (×10⁴) g/mol	Mn/Mw (Đ)
60[190]	550	25	0.0083	Toluene + a few drops of THF	89	2.4	1.57
61[191]	10,000	25	0.013	THF	95	12.0	1.53
62[192]	1000	25	0.5	Toluene	100	4.85	1.8
63[178]	1000	20	0.033	Toluene	> 99	12.1	1.34
	1000	20	0.033	THF	77	7.7	1.41
64[172]	500	25	0.011	Toluene	100	5.33	1.6

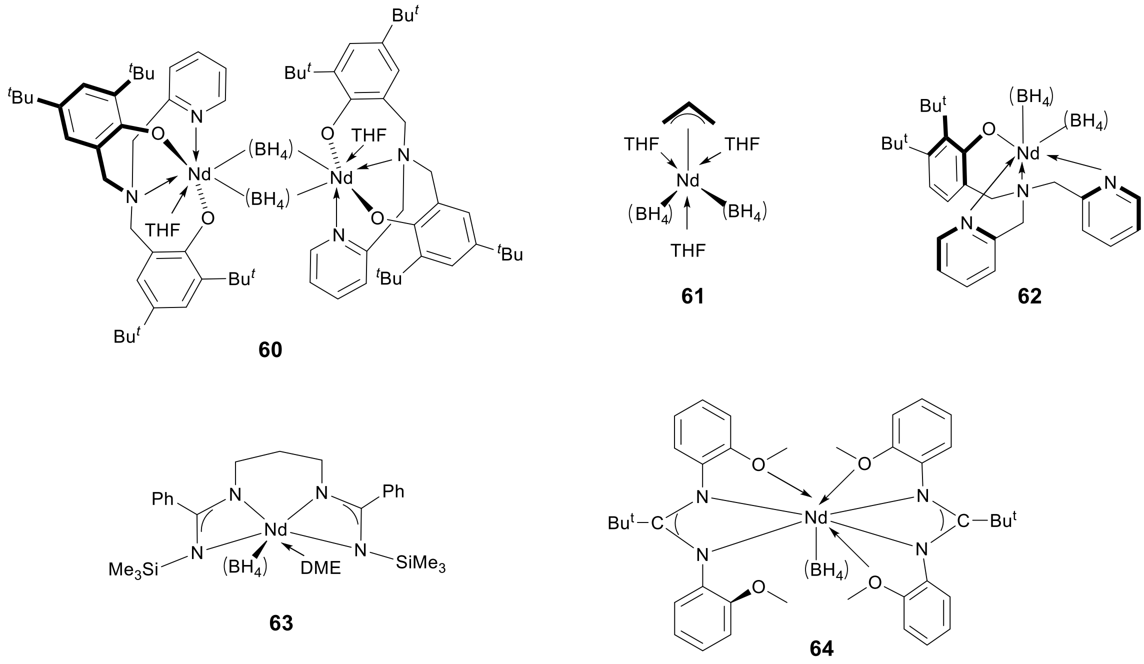


Figure 16. The structures of Nd-based complexes **60**-**64** with borohydride combined with other group of ligands

3.5.1. Simple borohydride-based ligands. The group of Soum, Guillaume,[163, 164] and Z. Shen,[165] reported a single component $Nd(BH_4)_3(THF)_3$ (complex **58**) for the ROP of ε-CL. In the work of Soum and Guillaume in 2003 and 2005, within 5 to 15 min into the polymerization, quantitative yield is obtained with M_n ranging from 0.30 – 1.70 x 10^4 g/mol and Đ in the range of 1.2 - 1.5. Z. Shen et al. utilized the same complex for one-pot synthesis of carbonyl end-capped PCL by an in situ reduction-initiation strategies.[165] Various carbonyl compounds were treated with the complex followed by feeding of ε-CL. Among the carbonyls, the use of benzaldehyde as an end-capping agent was the fastest, which took 14 min to obtain 90% yield of PCL, with the end-capping degree of 0.84, M_n of 0.96 x 10^4 g/mol, and Đ of 1.39. In 2008, a monocationic bis(borohydride) complex, $[Nd(BH_4)_2(THF)_5]^+[BPh_4]^-$ (complex **59**), was also reported to catalyze the polymerization of ε-CL affording a polymer with M_n of 1.48 x 10^4 g/mol and Đ of 1.25.[189]

3.5.2. Borohydride combined with other groups of ligands. A more complex Nd borohydride complex supported by diaminobis(phenoxide) ligands (complex **60**) was reported by Mountford and his group.[190] This complex was able to polymerize ε-CL within 30 s in 89% yield with M_n of 2.40 x 10^4 g/mol and Đ of 1.57. Attempts to make a block copolymer of ε-CL and ʟ-LA or *rac*-LA were successful when ε-CL was added first. When ʟ-LA is added first, and when random copolymerization was attempted, only homopolymers of ʟ-LA were obtained. A Nd complex bearing both the borohydride and the allyl complex (complex **61**) was first reported in 2016 by Visseaux's group.[191] PCL with M_n ranging from 0.54 – 12.00 x 10^4 g/mol were obtained as the ratio [ε-CL]/[Nd] increases from 100 to 10000 along with relatively narrow Đ (1.17 – 1.59), which was achieved in less than a minute. Polymer analysis showed the presence of hydroxyl group in both ends of the polymer. Hence it can be proposed that the polymerization was initiated through the Nd-borohydride bond instead of the insertion into the allyl group, which was also supported by DFT calculations.[193]

The catalytic activity of this allyl-borohydride complexes is higher than the Nd bis(amidinate) monoallyl complex.[177] This complex was then used for the statistical copolymerization of ε-CL and ʟ-LA.[194] The [LA]/[ε-CL] feed monomer ratio was set to 100:100 and 100:200, and the reactions were carried out in toluene at 70 °C, either in the absence or presence of benzyl alcohol, which is a chain transfer agent. In all cases, the conversion of ʟ-LA was almost complete, whereas the conversion of ε-CL was limited. The presence of benzyl alcohol slowed down the polymerization and resulted in more incorporation of ε-CL of up to 40%, but high molecular weights were not obtained. In 2019, a Nd-borohydride complex coordinated by tetradentate phenoxide ligand (complex **62**) was reported.[192] The M_n of the obtained PCL range from 0.76 – 4.85 x 10^4 g/mol as the ratio [ε-CL]/[Nd] increases from 100 to 1000 along with Đ in the range of 1.7 – 2.3, which was achieved in 5 – 30 mins with 100% conversion. In 2012, Q. Shen et al. reported a more efficient Nd complex containing borohydrides with a bridged bis(amidinate) ligand, $(Me_3SiNC(C_6H_5)N)_2(CH_2)_3Nd(BH_4)(DME)$ (where DME = dimethoxyethane) (complex **63**).[178] Quantitative yields were obtained within 1 minute for a [ε-CL]:[Nd] ratios of 200:1 to 1000:1 with moderately good Đ in the range of 1.34-1.52. In 2019, Trifonov and co-workers reported a Nd borohydrido complex having tetradentate amidinate ligands (complex **64**), which they compared to a Nd amino complex having the same amidinate ancillary ligand.[172] Polymerizations were conducted with various [ε-CL]/[Nd] ratios and were completed in less than 1 min. The Nd borohydrido complex provided a better matching between the calculated and experimental M_n of the obtained PCLs (1.07 – 5.33 x 10^4 g/mol), however moderate Đ values (1.5 – 1.8) were obtained.

3.6. Neodymium-based complexes with other types of ligands

In addition to the classes of complexes described above, few various Nd complexes have proved to be efficient single component initiators for ε-CL polymerization. These include phenyl[195] and allyl[196, 197] complexes, metallocenes,[198] thiolates[199], and metal alkoxide clusters (Figure 17). [200-202] A summary of their catalytic activity is presented in Table 12.

The triphenyl Nd complex $(C_6H_5)_3Nd$ (complex **65**) initiated bulk polymerization of ε-CL by a coordination-deprotonation-insertion (Scheme 19) process with a [ε-CL]/[Nd] ratio of 500 at 25°C, 60 °C, and 80°C.[195] With the

Table 12. Summary of the polymerization of ε-CL using Nd-based complexes with other types of ligands

Nd complexes	[ε-CL]/[I] (molar ratio)	Temp. (°C)	Time (h)	Solvent	Conv. (%)	Mn^{SEC} (×10^4) g/mol	Mn/Mw (Đ)
65[195]	500	60	0.5	THF	92	13.4	-
66[196, 197]	500	50	0.017	-	85.8	12.7	1.3
67[198]	1000	25	6	Toluene	86	14.5	1.65
68[199]	600	25	0.25	THF/ toluene	99	2.87	1.40
Cluster $[Nd_2Na_8(OCH_2CH_2NMe_2)_{12}(OH)_2]$[200]	15000	20	0.017	Toluene	100	9.0	1.58
Cluster $NdNa_8[OC(CH_3)_3]_{10}(OH)$[201]	8000	25	0.017	Toluene	98	11.1	2.04
Cluster $Nd_4(OCH_2CH_2NMe_2)_{26}(OH)_6K_{20}$[202]	20000	25	0.017	Toluene	100	5.89	1.75

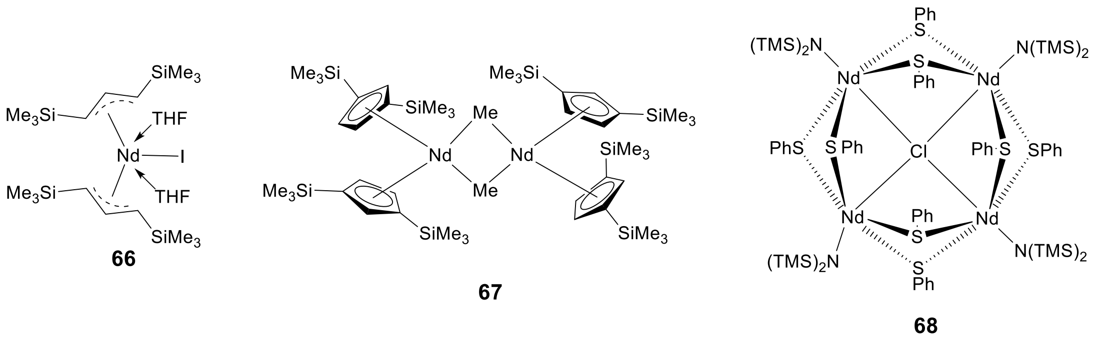
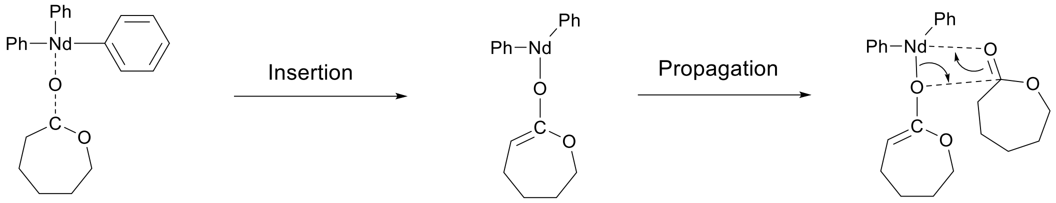


Figure 17. The structure of Nd-based complexes **66**-**68** with other types of ligands



Scheme 19. The structure of Nd-based complex **65** and coordination-deprotonation-insertion mechanism.[195]

increase of temperature, enhanced yield (from 80% to 96%) and molecular weight (from 7.90 × 10^4 to 14.60 × 10^4) was obtained. However, decreased yield and molecular weight were observed after 30 min at 60 °C, which might be caused by the decomposition of the polymer. Woodman et al. and Bochmann et al. reported a highly effective bulky allyl Nd complex $[1,3\text{-}C_3H_3(SiME_3)_2]_2NdI(THF)_2$ (complex **66**) for ε-CL polymerization at 50 °C, which achieved 86% conversion within 1 min with M_n of 12.70 × 10^4 and low Đ 1.3.[196, 197]

The tetra(trimethylsilyl) substituted metallocene methyl complex (complex **67**) was investigated for polymerization of ε-CL in an effort to produce a very inexpensive catalyst.[198] In toluene at 25 °C, a conversion of 86%, Mn 14.5 × 10^4, and Đ of 1.65 was achieved in 6 h – much slower than many of the other catalysts. The Nd thiolate complex $[(TMS)_2N]_3Nd(\mu\text{-}Cl)Li(THF)_3$ ($(TMS)_2N$ = bis(trimethylsilyl)amide) (complex **68**) polymerized ε-CL at 25 °C achieving a conversion of 99% in 8 min with a [ε-CL]/[Nd] ratio of 100, and in 15 min with a [ε-CL]/[Nd] ratio of 150 in THF/toluene with fairly narrow Đ of 1.34 – 1.40.[199]

Mixed-metal alkoxide clusters of Nd and alkali metals were also explored for ε-CL polymerization as single component initiators. Examples include $[Nd_2Na_8(OCH_2CH_2NMe_2)_{12}(OH)_2]$,[200] $NdNa_8[OC(CH_3)_3]_{10}(OH)$,[201] and $Nd_4(OCH_2CH_2NMe_2)_{26}(OH)_6K_{20}$.[202] These clusters have high catalytic activity, achieving complete polymerization with a [ε-CL]/[Nd] ratio ranging from 5,000 – 8,000 within 1 min at room temperature in toluene. These catalysts were proposed to follow a coordination-insertion mechanism. As of the moment, these are some of the most active catalytic systems in the literature. The resulting material had accordingly high molecular weights and had Đ slightly higher than other catalysts we have discussed (1.58 to 2.04).

Although PCL is a valuable polymer in the biomedical field, its utilization has been limited by its hydrophobic nature and poor wettability. To enhance its suitability for biomedical applications, various functional groups can be attached to the polymer to tune its physicochemical properties. Functionalization also provides a strategy to graft small molecules or drugs to the polymer backbone. The $Sn(Oct)_2$ system most commonly used to polymerize ε-CL struggles with functionalized monomers, yielding much slower polymerizations and often transesterification side products, which sometimes become the major product.

Nd-based complexes have been shown to be an efficient single-component catalyst for the polymerization of non-functionalized ε-CL but have not been extensively investigated for functionalized ε-CL. Stefan and co-workers demonstrated that an ester functionalized ε-CL, γ-4-phenylbutyrate ε-CL, was polymerized using a binary catalytic system composed of $NdCl_3 \bullet 3TEP/TIBA$ (TEP=triethylphosphate) in a 1:10 ratio, with a conversion of 73%.[203] However, with this system, block copolymers cannot be attained. Moreover, alkyl aluminum complexes can polymerize ε-CL, thus the incorporation of TIBA as co-catalyst might influence the polymerization. Hence, it would be beneficial to the field to develop a complex that can polymerize functionalized ε-CL in a *living* manner to allow the synthesis of block copolymers without the use of co-catalysts.

4. Summary and outlook

Nd-based ZN systems exhibit improved stereospecificity and activity compared to conventional Ziegler-Natta catalysts and other lanthanide-based ZN systems for the polymerization of dienes. The catalytic systems also have the capability to polymerize polar vinyl monomers. The polymerization reactions can be easily tuned with the variation of ligands, co-catalysts, temperature, solvent, and [co-catalyst]/[catalyst] ratios. Polydienes and some vinyl polymers are precisely produced from coordination-insertion polymerizations. Copolymers which incorporate polar functionality into non-polar polymers are important to generate new materials that are useful for adhesives, dyeing agents, material moisture absorption, surface modification, compatibilizers, and elastomers.[204] As we have seen, neodymium-based catalytic systems are able to polymerize both dienes and lactones, and copolymers of ε-caprolactone and butadiene can be produced with a single catalyst. Such copolymers have been produced with both *cis*- and *trans*-stereospecificity.[205, 206]

For polar vinyl monomers, polymerization through coordination-insertion is difficult due to the poisoning of the catalytically active species from heteroatoms in the monomer, side reactions, and mismatch between the orbital energies of the monomer and catalyst. The ability to form copolymers between polar and non-polar monomers is one of the best features of the Nd-based Ziegler-Natta systems. Unfortunately, these systems are not true *living* systems. Therefore, further development of neodymium-based catalysts that offer control over the polymerization (*living* character and stereoselectivity) and tolerance for chemical functionality (polar and non-polar monomers), optimization of reaction conditions, and the proper understanding of the polymerization mechanism are crucial.

A great deal of effort has also been put into developing Nd-based catalysts for ε-CL polymerization, and ligands of different natures are combined to generate well-defined complexes for controlled polymerization. However, research on the polymerization of functionalized ε-CL remains scarce. It would be beneficial to develop new Nd-based catalysts that can polymerize functionalized ε-CLs in a *living* manner to facilitate the synthesis of block copolymers and functionalized PCLs with adjustable physiochemical properties.

Upon addressing all the issues, these systems have the potential to replace many catalytic systems that are used in industry, providing more opportunities to make polydienes, vinyl polymers, copolymers consisting of non-polar and polar monomers, bio-based polymers like poly(myrcene), and substituted polyesters with adjustable physiochemical properties for various applications.

Author Contributions

The manuscript was written through the contributions of all authors.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We gratefully acknowledge the financial support from the National Science Foundation (CHE-1609880) and Welch Foundation (AT-1740). Mihaela Stefan acknowledges the generous financial support from the Eugene McDermott Foundation.

References

1. K. Ziegler, E. Holzkamp, H. Breil and H. Martin, *Angew. Chem.*, 1955, **67**, 426.
2. G. Natta, P. Pino, P. Corradini, F. Danusso, E. Mantica, G. Mazzanti and G. Moraglio, *Journal of the American Chemical Society*, 2002, **77**, 1708-1710.
3. L. Wang, D. Cui, Z. Hou, W. Li and Y. Li, *Organometallics*, 2011, **30**, 760-767.
4. Z. Zhang, D. Cui, B. Wang, B. Liu and Y. Yang, in *Molecular Catalysis of Rare-Earth Elements*, Springer Berlin Heidelberg, 2010, vol. 137, ch. Chapter 16, pp. 49-108.
5. S. Zhiquan, *Inorganica Chimica Acta*, 1987, **140**, 7-14.
6. L. Friebe, O. Nuyken and W. Obrecht, in *Neodymium Based Ziegler Catalysts – Fundamental Chemistry*, Springer Berlin Heidelberg, 2006, vol. 204, ch. Chapter 94, pp. 1-154.
7. A. Fischbach and R. Anwander, in *Neodymium Based Ziegler Catalysts – Fundamental Chemistry*, Springer Berlin Heidelberg, 2006, vol. 204, ch. Chapter 93, pp. 155-281.
8. N. G. Marina, Y. B. Monakov, Z. M. Sabirov and G. A. Tolstikov, *Polymer Science U.S.S.R.*, 1991, **33**, 387-417.
9. L. Porri, A. Giarrusso and G. Ricci, *Makromol Chem-M Symp*, 1993, **66**, 231-243.
10. K. E. Washington, R. N. Kularatne, V. Karmegam, M. C. Biewer and M. C. Stefan, *Wiley Interdiscip Rev Nanomed Nanobiotechnol*, 2017, **9**, e1446-n/a.
11. A. C. Albertsson and I. K. Varma, *Biomacromolecules*, 2003, **4**, 1466-1486.
12. S. Agarwal, C. Mast, K. Dehnicke and A. Greiner, *Macromol Rapid Comm*, 2000, **21**, 195-212.
13. F. T. Edelmann, *Chem Soc Rev*, 2012, **41**, 7657-7672.
14. D. M. Lyubov, A. O. Tolpygin and A. A. Trifonov, *Coordin Chem Rev*, 2019, **392**, 83-145.
15. M. Visseaux and F. Bonnet, *Coordin Chem Rev*, 2011, **255**, 374-420.
16. D. J. Wilson, *Polymer*, 1993, **34**, 3504-3508.
17. M. J. Vitorino, T. Devic, M. Tromp, G. Ferey and M. Visseaux, *Macromol Chem Phys*, 2009, **210**, 1923-1932.
18. I. Rodrigues, I. Mihalcea, C. Volkringer, T. Loiseau and M. Visseaux, *Inorg Chem*, 2012, **51**, 483-490.
19. S. Russell, T. Loiseau, C. Volkringer and M. Visseaux, *Inorganics*, 2015, **3**, 467-481.
20. *U.S. Pat.,* EP0638598, 1996.
21. A. A. Berg, Y. B. Monakov, V. P. Budtov and S. R. Rafikov, *VYSOKOMOLEKULYARNYE SOEDINENIYA SERIYA B*, 1978, **20**, 295-299.
22. J. H. Yang, M. Tsutsui, Z. Chen and D. E. Bergbreiter, *Macromolecules*, 1982, **15**, 230-233.
23. Z. Hou, S. Kaita and Y. Wakatsuki, *Pure and Applied Chemistry*, 2001, **73**, 291-294.
24. R. Taube, H. Windisch and S. Maiwald, *Macromolecular Symposia*, **89**, 393-409.
25. D. Baudry‐Barbier, E. Camus, A. Dormond and M. Visseaux, *Applied organometallic chemistry*, 1999, **13**, 813-817.
26. I. Rodrigues, T. Y. Xue, P. Roussel and M. Visseaux, *Journal of Organometallic Chemistry*, 2013, **743**, 139-146.
27. K. Osakada and D. Takeuchi, *Polymer Synthesis*, 2004, 137-194.
28. F. Bonnet, M. Visseaux, A. Pereira, F. Bouver and D. Barbier-Baudry, *Macromol Rapid Comm*, 2004, **25**, 873-877.
29. Y. Yang, K. Lv, L. Wang, Y. Wang and D. Cui, *Chem Commun (Camb)*, 2010, **46**, 6150-6152.
30. M. Visseaux, M. Mainil, M. Terrier, A. Mortreux, P. Roussel, T. Mathivet and M. Destarac, *Dalton T*, 2008, DOI: 10.1039/b806669h, 4558-4561.
31. W. Gao and D. Cui, *J Am Chem Soc*, 2008, **130**, 4984-4991.
32. K. Lv and D. M. Cui, *Organometallics*, 2010, **29**, 2987-2993.
33. D. Li, S. Li, D. Cui and X. Zhang, *Organometallics*, 2010, **29**, 2186-2193.
34. J. M. Huang, Z. H. Liu, D. M. Cui and X. L. Liu, *Chemcatchem*, 2018, **10**, 42-61.

35. G. S. Srinivasa Rao, V. K. Upadhyay and R. C. Jain, *Journal of Applied Polymer Science*, 1999, **71**, 595-602.
36. M. C. Gallazzi, F. Bianchi, L. Depero and M. Zocchi, *Polymer*, 1988, **29**, 1516-1521.
37. C. Y. Ren, G. L. Li, W. M. Dong, L. S. Jiang, X. Q. Zhang and F. S. Wang, *Polymer*, 2007, **48**, 2470-2474.
38. R. P. Quirk and A. M. Kells, *Polym Int*, 2000, **49**, 751-756.
39. G. Kwag, D. Kim, S. Lee and C. Bae, *Journal of Applied Polymer Science*, 2005, **97**, 1279-1283.
40. A. Oehme, U. Gebauer, K. Gehrke and M. D. Lechner, *Angew Makromol Chem*, 1996, **235**, 121-130.
41. D. E. Bergbreiter, L. B. Chen and R. Chandran, *Macromolecules*, 1985, **18**, 1055-1057.
42. Y. B. Monakov, N. V. Duvakina and I. A. Ionova, *Polym Sci Ser B+*, 2008, **50**, 134-138.
43. N. V. Duvakina and Y. B. Monakov, *Dokl Chem*, 2002, **384**, 129-131.
44. Q. S. Zhang, X. F. Ni, Y. F. Zhang and Z. Q. Shen, *Macromol Rapid Comm*, 2001, **22**, 1493-1496.
45. Y. M. Hu, C. Q. Zhang, X. G. Liu, K. K. Gao, Y. M. Cao, C. Y. Zhang and X. Q. Zhang, *Journal of Applied Polymer Science*, 2014, **131**, n/a-n/a.
46. H. Iovu, G. Hubca, E. Simionescu, E. G. Badea and M. Dimonie, *Angew Makromol Chem*, 1997, **249**, 59-77.
47. H. L. Hsieh and H. C. Yeh, *Rubber Chem Technol*, 1985, **58**, 117-145.
48. J. Liu, X. D. Fan, X. Min, X. Z. Zhu, N. Zhao and Z. C. Wang, *Rsc Adv*, 2018, **8**, 21926-21932.
49. Y. X. Ren, J. T. Miller, S. T. Polderman, T. D. Vo, A. C. M. Wallace, J. M. O. Cue, S. T. Tran, M. C. Biewer and M. C. Stefan, *Rsc Adv*, 2019, **9**, 3345-3350.
50. C. Meermann, K. W. Tornroos, W. Nerdal and R. Anwander, *Angew Chem Int Ed Engl*, 2007, **46**, 6508-6513.
51. L. Friebe, J. M. Müller, O. Nuyken and W. Obrecht, *Journal of Macromolecular Science, Part A*, 2006, **43**, 841-854.
52. C. S. S. Rao, V. K. Upadhyay and R. C. Jain, *Angew Makromol Chem*, 1997, **251**, 193-205.
53. F. Barbotin, R. Spitz and C. Boisson, *Macromol Rapid Comm*, 2001, **22**, 1411-1414.
54. J. Enríquez-Medrano Francisco, V. López Luis Alexandro, A. de Santiago-Rodríguez Yair, S. Corral Florentino, S. Caballero Hened, L. L. Quintanilla María and D. de León-Gómez Ramón, *polyeng*, 2015, **35**, 105-111.
55. L. A. Valencia López, F. J. Enríquez-Medrano, H. Maldonado Textle, F. Soriano Corral, H. R. López González, C. St Thomas, F. Hernández Gámez, J. L. Olivares Romero and R. E. Díaz de León Gómez, *Journal of the Mexican Chemical Society*, 2016, **60**, 141-147.
56. Z. H. Wang, Y. Q. Qian, W. J. Zhang, J. Y. Wang, L. X. He, Q. J. Lin and W. H. Sun, *Polym Int*, 2015, **64**, 1030-1036.
57. G. L. Li, C. Y. Ren, W. M. Dong, L. S. Jiang, X. Q. Zhang and F. S. Wang, *Chinese J Polym Sci*, 2010, **28**, 157-164.
58. Y. Phuphuak, F. Bonnet, G. Stoclet, M. Bria and P. Zinck, *Chem Commun (Camb)*, 2017, **53**, 5330-5333.
59. R. N. Kularatne, A. Yang, H. Q. Nguyen, G. T. McCandless and M. C. Stefan, *Macromol Rapid Commun*, 2017, **38**, 1700427.
60. W. M. Dong and T. Masuda, *J Polym Sci Pol Chem*, 2002, **40**, 1838-1844.
61. W. M. Dong and T. Masuda, *Polymer*, 2003, **44**, 1561-1567.
62. J. B. Nickaf, R. P. Burford and R. P. Chaplin, *J Polym Sci Pol Chem*, 1995, **33**, 1125-1132.
63. G. Ricci, G. Pampaloni, A. Sommazzi and F. Masi, *Macromolecules*, 2021, **54**, 5879-5914.
64. G. Ricci and G. Leone, 2014.
65. R. Tanaka, Y. Shinto, R. Matsuzaki, Y. Nakayama and T. Shiono, *Dalton T*, 2019, **48**, 7267-7273.
66. N. Marina, Y. B. Monakov, S. Rafikov and K. K. Gadeleva, *Polymer Science USSR*, 1984, **26**, 1251-1268.
67. Z. G. Shamaeva, N. G. Marina, Y. B. Monakov and S. R. Rafikov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1982, **31**, 743-746.
68. L. Porri, A. Giarrusso and G. Ricci, *Macromolecular Symposia*, 2002, **178**, 55-68.
69. L. Porri, A. Giarrusso and G. Ricci, *Polymer science*, 1994, **36**, 1421-1432.
70. L. Porri, A. Giarrusso and G. Ricci, *Prog Polym Sci*, 1991, **16**, 405-441.
71. H. Iovu, G. Hubca, D. Racoti and J. S. Hurst, *Eur Polym J*, 1999, **35**, 335-344.
72. H. Iovu, G. Hubea and S. J. Hurst, *Acta Polym*, 1996, **47**, 450-454.
73. H. Iovu, G. Hubca, E. Simionescu, E. Badea and J. S. Hurst, *Eur Polym J*, 1997, **33**, 811-814.
74. J. Jothieswaran, S. Fadlallah, F. Bonnet and M. Visseaux, *Catalysts*, 2017, **7**, 378.
75. Z. M. Sabirov, N. K. Minchenkova, V. N. Urazbaev and Y. B. Monakov, *Journal of Polymer Science Part A: Polymer Chemistry*, 1993, **31**, 2419-2421.
76. Y. Taniguchi, W. Dong, T. Katsumata, M. Shiotsuki and T. Masuda, *Polymer Bulletin*, 2005, **54**, 173-178.
77. H. L. Guo, J. F. Bi, J. Y. Wang, X. Q. Zhang, S. C. Jiang and Z. H. Wu, *Polymer*, 2017, **119**, 176-184.
78. M. L. Méndez-Hernández, J. L. Rivera-Armenta, U. Páramo-García, S. Corona Galvan, R. García-Alamilla and B. A. Salazar-Cruz, *International Journal of Polymer Science*, 2016, **2016**.
79. X. Y. Jia, Y. M. Hu, Q. Q. Dai, J. F. Bi, C. X. Bai and X. Q. Zhang, *Polymer*, 2013, **54**, 2973-2978.
80. C. Boisson, F. Barbotin and R. Spitz, *Macromol Chem Phys*, 1999, **200**, 1163-1166.
81. L. Friebe, O. Nuyken, H. Windisch and W. Obrecht, *Macromol Chem Phys*, 2002, **203**, 1055-1064.
82. W. J. Evans, D. G. Giarikos and J. W. Ziller, *Organometallics*, 2001, **20**, 5751-5758.
83. A. Oehme, U. Gebauer, K. Gehrke, P. Beyer, B. Hartmann and M. D. Lechner, *Macromol Chem Phys*, 1994, **195**, 3773-3781.
84. R. E. Díaz de León Gómez, F. J. Enríquez-Medrano, H. Maldonado Textle, R. Mendoza Carrizales, K. Reyes Acosta, H. R. López González, J. L. Olivares Romero and L. E. Lugo Uribe, *The Canadian Journal of Chemical Engineering*, 2016, **94**, 823-832.

85. I. L. Mello and F. M. B. Coutinho, *Journal of Applied Polymer Science*, 2009, **112**, 1496-1502.
86. D. M. Roitershtein, A. A. Vinogradov, A. A. Vinogradov, K. A. Lyssenko, Y. V. Nelyubina, I. V. Anan'ev, I. E. Nifant'ev, V. A. Yakovlev and N. N. Kostitsyna, *Organometallics*, 2013, **32**, 1272-1286.
87. A. O. Tolpygin, O. A. Linnikova, T. A. Glukhova, A. V. Cherkasov, G. K. Fukin and A. A. Trifonov, *Rsc Adv*, 2016, **6**, 17913-17920.
88. D. J. Wilson, *J Polym Sci Pol Chem*, 1995, **33**, 2505-2513.
89. G. Ricci, S. Italia, F. Cabassi and L. Porri, *Polym Commun*, 1987, **28**, 223-226.
90. D. J. Wilson, *Polym Int*, 1996, **39**, 235-242.
91. R. Díaz de León, F. Soriano Corral, F. J. Enríquez-Medrano, G. Bosques Ibarra, P. de León Martínez, F. Hernández Gámez, H. R. López-González and L. F. Ramos de Valle, *International Journal of Polymer Science*, 2016, **2016**.
92. R. Tanaka, Y. Nakayama and T. Shiono, *Organometallics*, 2020, **39**, 1855-1860.
93. G. Sylvester and W. Wieder, in *Elastomers and Rubber Elasticity*, AMERICAN CHEMICAL SOCIETY, 1982, vol. 193, ch. 3, pp. 57-72.
94. N. M. T. Pires, F. M. B. Coutinho and M. A. S. Costa, *Eur Polym J*, 2004, **40**, 2599-2603.
95. L. Friebe, *Butadienpolymerisation mit Neodym-Ziegler-Katalysatoren*, Verlag Dr. Hut, 2004.
96. C. C. Loo and C. C. Hsu, *The Canadian Journal of Chemical Engineering*, 1974, **52**, 381-386.
97. G. Kwag, *Macromolecules*, 2002, **35**, 4875-4879.
98. H. L. Guo, J. F. Bi, Q. Y. Wu, J. Y. Wang, W. Q. Shi, X. Q. Zhang, S. C. Jiang and Z. H. Wu, *Rsc Adv*, 2017, **7**, 14413-14421.
99. H. Guo, J. Bi, J. Wang, X. Zhang, S. Jiang and Z. Wu, *Dalton Trans*, 2015, **44**, 9130-9139.
100. Z. Jian, D. Cui, Z. Hou and X. Li, *Chem Commun (Camb)*, 2010, **46**, 3022-3024.
101. A. Ventura, T. Chenal, M. Bria, F. Bonnet, P. Zinck, Y. Ngono-Ravache, E. Balanzat and M. Visseaux, *Eur Polym J*, 2013, **49**, 4130-4140.
102. Y. B. Monakov, Z. M. Sabirov, V. N. Urazbaev and V. P. Efimov, *Kinet Catal+*, 2001, **42**, 310-316.
103. W. J. Zheng, N. Yan, Y. T. Zhu, W. P. Zhao, C. Y. Zhang, H. X. Zhang, C. X. Bai, Y. M. Hu and X. Q. Zhang, *Polym Chem-Uk*, 2015, **6**, 6088-6095.
104. M. Visseaux, M. Terrier, A. Mortreux and P. Roussel, *Cr Chim*, 2007, **10**, 1195-1199.
105. M. Zimmermann, J. Volbeda, K. W. Tornroos and R. Anwander, *Cr Chim*, 2010, **13**, 651-660.
106. G. Paolucci, A. Zanella, M. Bortoluzzi, S. Sostero, P. Longo and M. Napoli, *J Mol Catal a-Chem*, 2007, **272**, 258-264.
107. W. F. Rong, D. T. Liu, H. P. Zuo, Y. P. Pan, Z. B. Jian, S. H. Li and D. M. Cui, *Organometallics*, 2013, **32**, 1166-1175.
108. F. Bonnet, M. Visseaux, A. Pereira and D. Barbier-Baudry, *Macromolecules*, 2005, **38**, 3162-3169.
109. F. Bonnet, H. E. Dyer, Y. El Kinani, C. Dietz, P. Roussel, M. Bria, M. Visseaux, P. Zinck and P. Mountford, *Dalton Trans*, 2015, **44**, 12312-12325.
110. S. Maiwald, H. Weißenborn, C. Sommer, G. Müller and R. Taube, *Journal of Organometallic Chemistry*, 2001, **640**, 1-9.
111. R. Tanaka, K. Yuuya, H. Sato, P. Eberhardt, Y. Nakayama and T. Shiono, *Polym Chem-Uk*, 2016, **7**, 1239-1243.
112. S. Maiwald, C. Sommer, G. Muller and R. Taube, *Macromol Chem Phys*, 2002, **203**, 1029-1039.
113. G. Kwag, H. Lee and S. Kim, *Macromolecules*, 2001, **34**, 5367-5369.
114. E. Kirillov, C. W. Lehmann, A. Razavi and J. F. Carpentier, *J Am Chem Soc*, 2004, **126**, 12240-12241.
115. A. S. Rodrigues, E. Kirillov, C. W. Lehmann, T. Roisnel, B. Vuillemin, A. Razavi and J. F. Carpentier, *Chem. Eur. J.*, 2007, **13**, 5548-5565.
116. A. S. Rodrigues, E. Kirillov, T. Roisnel, A. Razavi, B. Vuillemin and J. F. Carpentier, *Angew Chem Int Ed Engl*, 2007, **46**, 7240-7243.
117. P. Zinck, M. Visseaux and A. Mortreux, *Z Anorg Allg Chem*, 2006, **632**, 1943-1944.
118. P. Zinck, A. Valente, A. Mortreux and M. Visseaux, *Polymer*, 2007, **48**, 4609-4614.
119. A. Oehme, U. Gebauer, K. Gehrke and M. D. Lechner, *Macromol Rapid Comm*, 1995, **16**, 563-569.
120. M. Yang, C. Cha and Z. Shen, *Polymer Journal*, 1990, **22**, 919-923.
121. L. Liu, Z. Gong, Y. L. Zheng and X. B. Jing, *Macromol Rapid Comm*, 1997, **18**, 859-864.
122. J. Wang, Y. X. Wu, X. Xu, H. Zhu and G. Y. Wu, *Polym Int*, 2005, **54**, 1320-1325.
123. E. Kobayashi, N. Hayashi, S. Aoshima and J. Furukawa, *J Polym Sci Pol Chem*, 1998, **36**, 1707-1716.
124. Q. S. Zhang, W. S. Li and Z. Q. Shen, *Eur Polym J*, 2002, **38**, 869-873.
125. M. Gromada, L. le Pichon, A. Mortreux, F. Leising and J. F. Carpentier, *Journal of Organometallic Chemistry*, 2003, **683**, 44-55.
126. D. Barbier-Baudry, F. Bouyer, A. S. M. Bruno and M. Visseaux, *Applied Organometallic Chemistry*, 2006, **20**, 24-31.
127. N. Barros, M. Schappacher, P. Dessuge, L. Maron and S. M. Gullaume, *Chem-Eur J*, 2008, **14**, 1881-1890.
128. J. Gromada, A. Mortreux, T. Chenal, J. W. Ziller, F. Leising and J. F. Carpentier, *Chem-Eur J*, 2002, **8**, 3773-3788.
129. J. Gromada, T. Chenal, A. Mortreux, F. Leising and J. F. Carpentier, *J Mol Catal a-Chem*, 2002, **182**, 525-531.
130. J. Gromada, C. Fouga, T. Chenal, A. Mortreux and J. F. Carpentier, *Macromol Chem Phys*, 2002, **203**, 550-555.
131. J. Q. Sun, *Acta Polym Sin*, 1998, 96-100.
132. J. Q. Sun, *Chem Res Chinese U*, 1997, **13**, 344-349.
133. J. F. Liu, Z. Q. Shen and J. Q. Sun, *Eur Polym J*, 1996, **32**, 883-886.
134. G. G. Skvortsov, M. V. Yakovenko, G. K. Fukin, E. V. Baranov, Y. A. Kurskii and A. A. Trifonov, *Russian Chemical Bulletin*, 2007, **56**, 456-460.
135. G. Zi, H.-W. Li and Z. Xie, *Organometallics*, 2002, **21**, 1136-1145.
136. E. A. Rainbolt, K. E. Washington, M. C. Biewer and M. C. Stefan, *Polym Chem-Uk*, 2015, **6**, 2369-2381.

137. J. Hao, E. A. Rainbolt, K. Washington, M. C. Biewer and M. C. Stefan, *Curr Org Chem*, 2013, **17**, 930-942.
138. Y. Xiao, M. Yuan, J. Zhang, J. Yan and M. Lang, *Curr Top Med Chem*, 2014, **14**, 781-818.
139. V. Guarino, G. Gentile, L. Sorrentino and L. Ambrosio, *Encyclopedia of polymer science and technology*, 2002, 1-36.
140. R. F. Storey and J. W. Sherman, *Macromolecules*, 2002, **35**, 1504-1512.
141. A. Kowalski, J. Libiszowski, T. Biela, M. Cypryk, A. Duda and S. Penczek, *Macromolecules*, 2005, **38**, 8170-8176.
142. J. Hao, P. C. Granowski and M. C. Stefan, *Macromol Rapid Commun*, 2012, **33**, 1294-1299.
143. M. Honrado, A. Otero, J. Fernandez-Baeza, L. F. Sanchez-Barba, A. Garces, A. Lara-Sanchez and A. M. Rodriguez, *Organometallics*, 2016, **35**, 189-197.
144. P. Hao, Z. Yang, W. Li, X. Ma, H. W. Roesky, Y. Yang and J. Li, *Organometallics*, 2014, **34**, 105-108.
145. Y. Wei, S. Wang and S. Zhou, *Dalton Trans*, 2016, **45**, 4471-4485.
146. Y. Cheng, J. Hao, L. A. Lee, M. C. Biewer, Q. Wang and M. C. Stefan, *Biomacromolecules*, 2012, **13**, 2163-2173.
147. S. Zhou, X. Deng and H. Yang, *Biomaterials*, 2003, **24**, 3563-3570.
148. E. A. Rainbolt, J. B. Miller, K. E. Washington, S. A. Senevirathne, M. C. Biewer, D. J. Siegwart and M. C. Stefan, *J Mater Chem B*, 2015, **3**, 1779-1787.
149. K. E. Washington, R. N. Kularatne, J. Du, Y. X. Ren, M. J. Gillings, C. X. Geng, M. C. Biewer and M. C. Stefan, *Journal of Materials Chemistry B*, 2017, **5**, 5632-5640.
150. C. Jerome and P. Lecomte, *Adv Drug Deliv Rev*, 2008, **60**, 1056-1076.
151. M. C. Tanzi, P. Verderio, M. G. Lampugnani, M. Resnati, E. Dejana and E. Sturani, *J Mater Sci-Mater M*, 1994, **5**, 393-396.
152. A. Arbaoui and C. Redshaw, *Polym Chem-Uk*, 2010, **1**, 801-826.
153. N. E. Kamber, W. Jeong, R. M. Waymouth, R. C. Pratt, B. G. Lohmeijer and J. L. Hedrick, *Chem Rev*, 2007, **107**, 5813-5840.
154. B. G. G. Lohmeijer, R. C. Pratt, F. Leibfarth, J. W. Logan, D. A. Long, A. P. Dove, F. Nederberg, J. Choi, C. Wade, R. M. Waymouth and J. L. Hedrick, *Macromolecules*, 2006, **39**, 8574-8583.
155. L. Simon and J. M. Goodman, *J Org Chem*, 2007, **72**, 9656-9662.
156. R. C. Pratt, B. G. Lohmeijer, D. A. Long, R. M. Waymouth and J. L. Hedrick, *J Am Chem Soc*, 2006, **128**, 4556-4557.
157. S. F. Liu, C. L. Ren, N. Zhao, Y. Shen and Z. Li, *Macromol Rapid Comm*, 2018, **39**, 1800485.
158. L. Zhang, F. Nederberg, R. C. Pratt, R. M. Waymouth, J. L. Hedrick and C. G. Wade, *Macromolecules*, 2007, **40**, 4154-4158.
159. Z. Shen, X. Chen, Y. Shen and Y. Zhang, *Journal of Polymer Science Part A: Polymer Chemistry*, 1994, **32**, 597-603.
160. Y. Ren, R. N. Kularatne, J. T. Miller, S. T. Polderman, T. D. Vo, M. C. Biewer and M. C. Stefan, *Journal of Polymer Science Part A: Polymer Chemistry*, 2018, **56**, 1289-1296.
161. Y. Shen, Z. Shen, Y. Zhang and K. Yao, *Macromolecules*, 1996, **29**, 8289-8295.
162. Y. Yao, Y. Luo, J. Chen, Z. Zhang, Y. Zhang and Q. Shen, *Journal of organometallic chemistry*, 2003, **679**, 229-237.
163. S. M. Guillaume, M. Schappacher and A. Soum, *Macromolecules*, 2003, **36**, 54-60.
164. I. Palard, A. Soum and S. M. Guillaume, *Macromolecules*, 2005, **38**, 6888-6894.
165. G. Wu, W. Sun and Z. Shen, *Reactive and Functional Polymers*, 2008, **68**, 822-830.
166. C. Yu, L. Zhang and Z. Shen, *Eur Polym J*, 2003, **39**, 2035-2039.
167. L. Zhang, Y. Niu, Y. Wang, P. Wang and L. Shen, *Journal of Molecular Catalysis A: Chemical*, 2008, **287**, 1-4.
168. Y. Yao, X. Xu, B. Liu, Y. Zhang, Q. Shen and W.-T. Wong, *Inorg Chem*, 2005, **44**, 5133-5140.
169. X. Xu, Y. Yao, M. Hu, Y. Zhang and Q. Shen, *Journal of Polymer Science Part A: Polymer Chemistry*, 2006, **44**, 4409-4419.
170. X. Xu, Z. Zhang, Y. Yao, Y. Zhang and Q. Shen, *Inorg Chem*, 2007, **46**, 9379-9388.
171. X. Xu, X. Xu, Y. F. Chen and H. Sun, *Organometallics*, 2008, **27**, 758-763.
172. G. G. Skvortsov, A. S. Shavyrin, T. A. Kovylina, A. V. Cherkasov and A. A. Trifonov, *Eur J Inorg Chem*, 2019, **2019**, 5008-5017.
173. P. J. Bailey and S. Pace, *Coordin Chem Rev*, 2001, **214**, 91-141.
174. A. B. Xia, H. M. El-Kaderi, M. J. Heeg and C. H. Winter, *Journal of Organometallic Chemistry*, 2003, **682**, 224-232.
175. Y. Luo, Y. Yao, Q. Shen, J. Sun and L. Weng, *Journal of organometallic chemistry*, 2002, **662**, 144-149.
176. F. Wang, X. Zhao, X. Meng and S. Wang, *Dalton Trans*, 2019, **48**, 12193-12198.
177. A. Tolpygin, O. Linnikova, T. Kovylina, A. Cherkasov, G. Fukin and A. Trifonov, *Russian Chemical Bulletin*, 2020, **69**, 1114-1121.
178. W. Li, M. Xue, J. Tu, Y. Zhang and Q. Shen, *Dalton Trans*, 2012, **41**, 7258-7265.
179. Y. Luo, Y. Yao, Q. Shen, K. Yu and L. Weng, *Eur J Inorg Chem*, 2003, **2003**, 318-323.
180. L. F. Sánchez-Barba, D. L. Hughes, S. M. Humphrey and M. Bochmann, *Organometallics*, 2005, **24**, 3792-3799.
181. M. Xue, Y. Yao, Q. Shen and Y. Zhang, *Journal of organometallic chemistry*, 2005, **690**, 4685-4691.
182. M. Xue, R. Jiao, Y. Zhang, Y. Yao and Q. Shen, *Eur J Inorg Chem*, 2009, **2009**, 4110-4118.
183. S. L. Zhou, C. W. Yin, H. Wang, X. C. Zhu, G. S. Yang and S. W. Wang, *Inorg Chem Commun*, 2011, **14**, 1196-1200.
184. X.-Q. Zhang, M.-S. Lin, B. Hu, W.-Q. Chen, L.-N. Zheng, J. Wu, Y.-M. Chen, F.-Y. Zhou, Y.-H. Li and W. Li, *Polyhedron*, 2012, **33**, 273-279.
185. H.-X. Li, Q.-F. Xu, J.-X. Chen, M.-L. Cheng, Y. Zhang, W.-H. Zhang, J.-P. Lang and Q. Shen, *Journal of organometallic chemistry*, 2004, **689**, 3438-3448.
186. P. W. Roesky, M. T. Gamer, M. Puchner and A. Greiner, *Chem. Eur. J.*, 2002, **8**, 5265-5271.

187. L. L. Huang, X. Z. Han, Y. M. Yao, Y. Zhang and Q. Shen, *Applied Organometallic Chemistry*, 2011, **25**, 464-469.
188. A. Otero, A. Lara-Sanchez, J. Fernandez-Baeza, C. Alonso-Moreno, I. Marquez-Segovia, L. F. Sanchez-Barba, J. A. Castro-Osma and A. M. Rodriguez, *Dalton Trans*, 2011, **40**, 4687-4696.
189. D. Robert, M. Kondracka and J. Okuda, *Dalton Trans*, 2008, 2667-2669.
190. F. Bonnet, A. R. Cowley and P. Mountford, *Inorg Chem*, 2005, **44**, 9046-9055.
191. S. Fadlallah, M. Terrier, C. Jones, P. Roussel, F. Bonnet and M. Visseaux, *Organometallics*, 2016, **35**, 456-461.
192. N. Rad'kova, V. Rad'kov, A. Cherkasov, T. Kovylina and A. Trifonov, *Inorganica Chimica Acta*, 2019, **489**, 132-139.
193. S. Fadlallah, J. Jothieswaran, I. Del Rosal, L. Maron, F. Bonnet and M. Visseaux, *Catalysts*, 2020, **10**, 820.
194. S. Fadlallah, J. Jothieswaran, F. Capet, F. Bonnet and M. Visseaux, *Chem. Eur. J.*, 2017, **23**, 15644-15654.
195. X. Deng, M. Yuan, C. Xiong and X. Li, *Journal of applied polymer science*, 1999, **73**, 1401-1408.
196. T. J. Woodman, M. Schormann, D. L. Hughes and M. Bochmann, *Organometallics*, 2003, **22**, 3028-3030.
197. T. J. Woodman, M. Schormann, D. L. Hughes and M. Bochmann, *Organometallics*, 2004, **23**, 2972-2979.
198. Y. Satoh, N. Ikitake, Y. Nakayama, S. Okuno and H. Yasuda, *Journal of organometallic chemistry*, 2003, **667**, 42-52.
199. H. X. Li, Z. G. Ren, Y. Zhang, W. H. Zhang, J. P. Lang and Q. Shen, *J Am Chem Soc*, 2005, **127**, 1122-1123.
200. H. Sheng, F. Xu, Y. Yao, Y. Zhang and Q. Shen, *Inorg Chem*, 2007, **46**, 7722-7724.
201. H. Sheng, J. Li, Y. Z. Y. Yao and Q. Shen, *Journal of Applied Polymer Science*, 2009, **112**, 454-460.
202. H. Sheng, Y. Feng, Y. Zhang and Q. Shen, *Eur J Inorg Chem*, 2010, **2010**, 5579-5586.
203. R. N. Kularatne, K. E. Washington, C. Bulumulla, E. L. Calubaquib, M. C. Biewer, D. Oupicky and M. C. Stefan, *Biomacromolecules*, 2018, **19**, 1082-1089.
204. W. Li, X. Jiang, Y.-M. So, G. He and Y. Pan, *New Journal of Chemistry*, 2020, **44**, 121-128.
205. F. Wang, C.-y. Zhang, Y.-m. Hu, X.-y. Jia, C.-x. Bai and X.-q. Zhang, *Polymer*, 2012, **53**, 6027-6032.
206. F. Wang, H. Liu, Y. M. Hu and X. Q. Zhang, *Sci China Technol Sc*, 2018, **61**, 1286-1294.