

**BUTADIENE RUBBER: SYNTHESIS, MICROSTRUCTURE, AND ROLE OF CATALYSTS**

AMIT KUMAR, SUBHRA MOHANTY, VIRENDRA KUMAR GUPTA\*

POLYMER SYNTHESIS AND CATALYSIS GROUP, RELIANCE INDUSTRIES LIMITED, NAVI MUMBAI, MAHARASHTRA, INDIA

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**ABSTRACT**

Butadiene rubber (BR) is one of the most useful and second most produced rubber worldwide. Polymerization of 1,3-butadiene (BD) is a highly stereospecific reaction that offers a wide variety of BR with different microstructures and influences the fundamental properties of the rubber. Since the first successful polymerization of conjugated diene using the Ziegler–Natta–based catalyst ( $\text{TiCl}_4$  or  $\text{TiCl}_3$  with aluminum alkyls) in 1954, the research on producing synthetic rubber with an appropriate catalyst system has been accelerated. Subsequently, various research groups are actively engaged in designing active catalyst systems based on a suitable combination of transition metal complexes with alkyl-aluminum and successfully using them in BD polymerization. Although various scientific inventions have proven their significance for the production of high-quality BR, with the rising demands in improving the quality of the product, research on developing new catalyst systems with enhanced catalytic activity and high stereoselectivity is still in progress. The present review focuses on the synthesis of BR using various transition metal catalysts and discusses their microstructures. The catalysts based on new-generation metal complexes with phosphorus, nitrogen, and oxygen donor ligands (e.g., phosphines, imines, 1,10-phenanthroline, and imino-pyridines) have been introduced. The role that catalysts play in the production of BR with different microstructures (i.e., high-*cis*, high-*trans* or low-*cis*, low-*trans* polybutadiene) has also been described. The combination of catalyst (transition metal complex) and suitable co-catalyst (alkyl-aluminum) is the major factor influencing the reaction and microstructure of the resulting polymer. This report focuses on the effect of transition metal catalysts (i.e., lithium [Li], titanium [Ti], zirconium [Zr], iron [Fe], cobalt [Co], nickel [Ni], and neodymium [Nd]) on the activity and stereoselectivity of polymers such as 1,4-*cis*-, 1,4-*trans*-, and 1,2-*vinyl*-polybutadiene. [doi:10.5254/rct.21.79948]

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**I. INTRODUCTION**

Polymerization of conjugated dienes has attracted immense interest in academic and industrial research in terms of both fundamental and practical perspectives.<sup>1,2</sup> The polymerization of conjugated dienes takes place naturally in plants as well as synthetically in laboratories. The tropical rubber tree (*Hevea brasiliensis*) provides a milky white-color fluid called *latex ensuing natural rubber*, which is mainly the polymer of isoprene (2-methyl-1,3-butadiene). The high elastomeric property of natural rubber is associated with the *Z*-(*cis*-) configuration of the double bond in the

\*Corresponding author. Email: virendrakumar.gupta@ril.com

isoprene unit present in polymer.<sup>3</sup> The elastic behavior in elastomers is caused by the interactions between double bonds present in multiple chains, leading cross-linkage.<sup>4</sup> Importantly, major synthetic rubbers are the polymer of various conjugated dienes (i.e., 1,3-butadiene [BD], isoprene, chloroprene [2-chloro-1,3-butadiene], etc.). Although research on the polymerization of conjugated dienes has consistently improved, there remains a need for better performance.

BR is the second most frequently produced synthetic rubber worldwide, after styrene-butadiene rubber. For multiple purposes, the universal consumption of BR is approximately 2.8 million metric tons per year.<sup>5,6</sup> The future demand of rubber worldwide has been estimated to be about 30 million tons, of which nearly 67% is synthetic rubber.<sup>7</sup> BR demonstrates excellent abrasion resistance, reduced tread wear, bend resistance, rebound resilience, and cold resistance behavior and is thus widely used in the manufacturing of tires, shoes, and golf balls.<sup>8</sup> Overall, about 70% of the total BR produced is used in the treads of tires and sidewalls.<sup>9,10</sup> Because of the high demand for good-quality BR, continuous improvement in synthetic procedures as well as catalysts is highly desirable. In other words, because of the excess demand and high-scale production, even a very small improvement in process can have a great benefit at the industrial scale. BR is a widely used synthetic rubber in the tire industries because its elastomeric properties can be easily modified by tuning the synthetic procedure and catalysts used, resulting in an improvement in performance via better wear resistance, wet/dry grip, and fuel efficiency, all of which effectively decrease the rolling resistance.<sup>9–13</sup>

BR is typically categorized based on the polymerization technology or catalyst/initiator used during synthesis. Polymerization of 1,3-dienes using the Ziegler–Natta (ZN)-based catalyst system was initiated in 1954, just after the first report on  $\alpha$ -olefin polymerization.<sup>14</sup> A combination of  $\text{TiCl}_4/\text{TiCl}_3$  with alkyl-aluminum was used for the first time as a catalyst for 1,3-dienes polymerization. Polymerization of 1,3-BD can produce polybutadiene with different isomeric structures, such as *cis*-1,4, *trans*-1,4, and *vinyl*-1,2 (Figure 1). 1,3-BD polymerization using a ZN-based catalyst system in solution technique results in a highly elastomeric *cis*-1,4-product. Catalysts based on metal ions, such as lithium (Li),<sup>15</sup> titanium (Ti),<sup>16</sup> iron (Fe),<sup>17</sup> cobalt (Co),<sup>17,18</sup> nickel (Ni),<sup>19</sup> chromium (Cr),<sup>20</sup> and neodymium (Nd),<sup>21</sup> have received much attention in BR synthesis and have been most intriguingly used in the presence of various alkyl-aluminum complexes as a co-catalyst.<sup>22,23</sup> In 1960, Phillips Petroleum Co. was the first to explore a Ti-based catalyst for high-*cis* BR production at the industrial scale.<sup>24</sup> Further, Goodrich–Gulf was the first to produce high-*cis* BR at the industrial scale using Co-based catalyst. Bridgestone Tire Co., together with Japan Synthetic Rubber Co., developed a Ni-based catalyst containing Ni carboxylate with boron trifluoride diethyl etherate ( $\text{BF}_3 \cdot \text{Et}_2\text{O}$ ) and triethyl aluminum (TEAL) for 1,3-BD polymerization, and the product was marketed by Japan Synthetic Rubber in 1964.<sup>25–27</sup> In 1980, Enichem successfully launched a Nd-based catalyst system to produce a high-*cis* product at commercial scale. Among all of the catalysts, Co-based catalysts have gained much attention and have been the most extensively studied because of their technological and commercial advantages over other catalysts.<sup>28,29</sup> The successful demonstration in 1980 of methyl aluminoxane (MAO) as a new alkylating agent caused a revolution in polymerization chemistry.<sup>30,31</sup> Moreover, the use of transition metal complexes with nitrogen, phosphorus, and oxygen ligands as next-generation catalysts for 1,3-BD polymerization in the 1990s has enhanced research in the polymer industries.<sup>32,33</sup> The Cr, Fe, and Co complexes composed of phosphorus and/or nitrogen donor ligands in the presence of MAO as an alkylating agent resulted in a breakthrough in the direction of 1,3-BD polymerization.<sup>33,34</sup> These complexes have been demonstrated to be highly active catalysts for 1,3-BD polymerization and systematically investigated in the synthesis of BR with different microstructures by simply varying the ligand and metal centers. In the current review, we summarize the recent progress on the polymerization of 1,3-BD using various catalytic systems

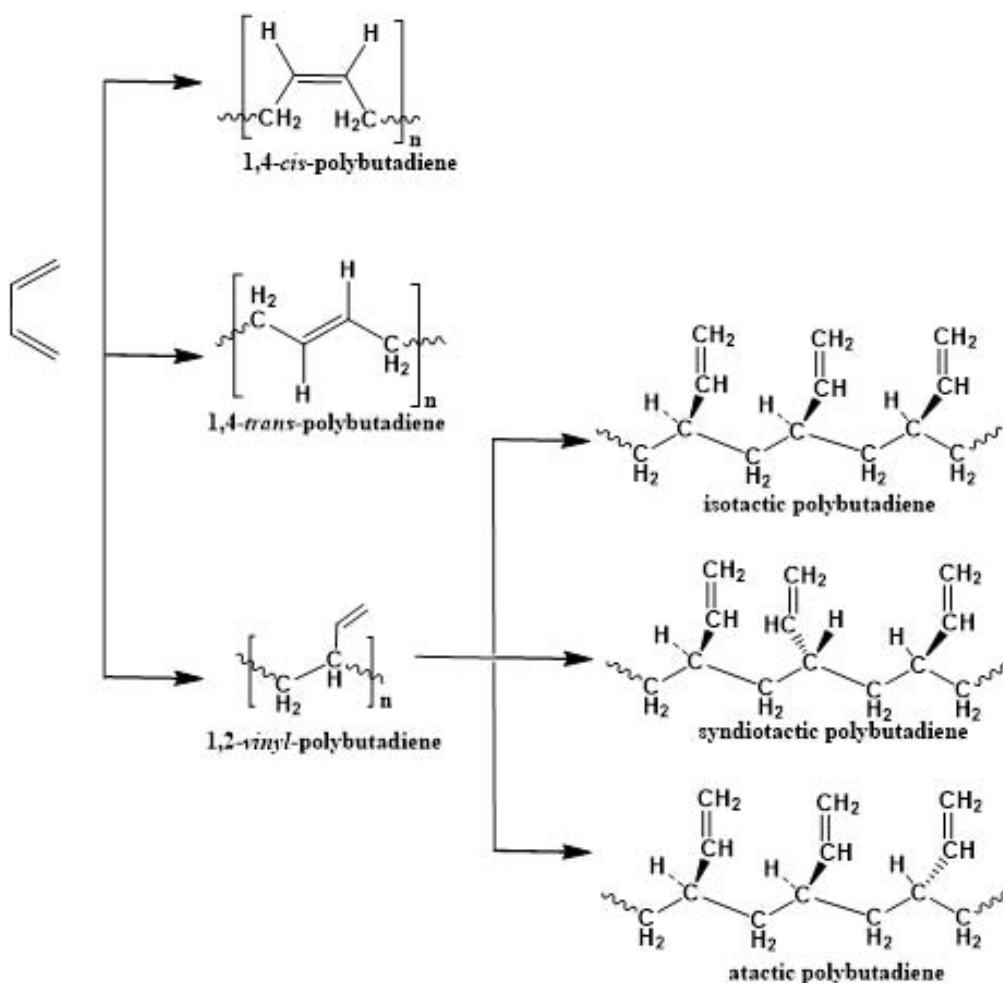


FIG. 1. — Schematic representation of 1,3-BD polymerization resulting in *cis*-1,4, *trans*-1,4, and *vinyl*-1,2 product. Structures for isotactic, syndiotactic, and atactic *vinyl*-1,2-polybutadiene.

based on transition metal complexes, and we discuss the effect of catalysts on the polymer microstructures.

## II. POLYMER MICROSTRUCTURE OF BR

The polymerization of 1,3-BD is a highly stereospecific reaction that produces structurally different products varying on the 1,2 or 1,4 positions, where the polymerization takes place (Figure 1).<sup>35-38</sup> The polymerization of BD at the 1,4 position offers either *cis*-1,4- or *trans*-1,4-polybutadiene or more possibly a combination of both. Because of the higher elastomeric nature, *cis*-1,4-polybutadiene is one of the most frequently used materials in the rubber industries and is commercially available in two main forms. The first, low *cis*-polybutadiene, contains less contribution (~40%) of the *cis*-1,4-repeating unit and can mainly be produced using alkyl-Li-based catalysts.<sup>39</sup> Besides the use of low *cis*-polybutadiene in tire manufacturing either in pure form or blended with other polymers, it can also be used as an additive in plastics because of the low gel

content. The other major form is high *cis*-polybutadiene containing 92% to 98% *cis*-1,4-repeating unit and is mainly produced by transition metal-based ZN catalyst systems.<sup>40</sup> The structure of *cis*-1,4-polybutadiene is almost similar to natural rubber, except for the methyl groups that are also present in natural rubber.<sup>41</sup> Because of their own distinct properties, both high *cis*- and the low *cis*-BR are highly consumed rubbers in the manufacturing of tires.<sup>42</sup>

High *cis*-1,4-polybutadiene leads to a very low glass-transition temperature (T<sub>g</sub>), with excellent abrasion resistance. However, the low wet skid resistance in high *cis*-1,4-polybutadiene is improved by increasing the vinyl content.<sup>43</sup> Further, high *trans*-polybutadiene, which is mainly plastic crystal and not an elastomer, refers to a product with more than 90% *trans*-1,4-polybutadiene.<sup>44–46</sup> High *trans*-1,4-polybutadiene shows high T<sub>g</sub> with high thermoplastic characteristics. On the other hand, 1,2-polymerization of BD instead of 1,4-polymerization offers a 1,2-*vinyl* product that has vinyl groups on a chiral carbon atom. The 1,2-*vinyl* polymer product has further been classified into three categories: (1) 1,2-syndiotactic polybutadienes, in which vinyl groups are attached to the backbone chiral carbon in an alternative manner; (2) 1,2-isotactic polybutadienes, which have all vinyl groups attached to the chiral carbon with the same spatial arrangements; and (3) 1,2-atactic polybutadienes, which show a random arrangement of vinyl groups to the backbone carbon atom. Importantly, a higher content of 1,2-*vinyl* polybutadiene leads to a better wet grip as well as low heat buildup properties, which can improve the quality of BR in tire applications.<sup>47</sup>

In *cis*-1,4- and *trans*-1,4-polybutadiene structures, all of the carbon atoms are arranged in a linear manner without the formation of any side chains; hence, the resulting double bonds are part of the internal backbone chain. On the contrary, the monomer in 1,2-*vinyl*-polybutadiene polymerizes at the 1,2 position rather than at 1,4, resulting in two carbon vinyl groups as a short side chain directly attached to the polybutadiene backbone.<sup>48</sup> The T<sub>g</sub> and the melting temperature (T<sub>m</sub>) of the crystalline phase of BR are harshly affected on altering the microstructures.<sup>49</sup> Because of the structural diversity, polybutadiene exhibits different properties and consequently shows diverse industrial applications. In practical applications, the nature of the actual polymer depends on the microstructures present in the polymer and are mainly affected by the polymerization technique, catalysts used, and reaction conditions employed.<sup>34–37</sup>

### III. CONTROLLED STEREOSELECTIVITY OF BR

The stereoselective polymerization of 1,3-BD is highly challenging but has been extensively investigated in academics as well as in industries. It is primarily governed by tuning the polymerization parameters (i.e., reaction temperature, solvents used, and special metal/ligand-based catalyst systems). Regulating stereo isomeric selectivity during the synthesis of *cis*-1,4- and *trans*-1,4-polybutadiene with unique elastomeric properties and long-standing industrial scalability is crucial. Gong et al. reported that metal-dependent controlled regio- and stereoselectivity for 1,3-BD polymerization probably occurs due to the diverse intrinsic behavior of the central metal.<sup>50</sup> Previous researchers have reported a series of Cr(III), Fe(III), Fe(II), Co(II), and Ni(II) chloride-based complexes, including 2,6-bis[1-(iminophenyl)ethyl]pyridine ligand. The controlled regio- and stereoselectivity and catalytic performance of synthesized complexes are strongly controlled by the transition metals used and methyl aluminum oxide (Al[CH<sub>3</sub>]<sub>x</sub>O<sub>y</sub>)<sub>n</sub>, MAO as a co-catalyst. The metal complexes with a Fe(III) and Cr(III) center in combination with MAO showed excellent catalytic performance, approaching 95% and 90% conversion of 1,3-BD to *trans*-1,4 polybutadiene, respectively, as shown in Table I, whereas Fe(II) showed significant lowering in *trans*-1,4 selectivity to ~55% (with ~35% of *cis*-1,4 product). On the other hand, Ni(II) complex yielded the highest *cis*-1,4 selective product. The catalytic activity of these complexes follows the order of Fe(III) > Co(II) > Cr(III) ≈ Ni(II), as shown in Table I.<sup>50</sup> In addition, high *cis*-

TABLE I  
1,3-BD POLYMERIZATION USING Fe(III), Cr(III), Fe(II), Co(II), AND Ni(II) METAL COMPLEXES WITH 2,6-BIS[1-(IMINOPHENYL)ETHYL] PYRIDINE LIGANDS<sup>50</sup>

Entry <sup>a</sup>	Precursor <sup>b</sup>	MAO/Mt <sup>c</sup>	Yield, %	M <sub>n</sub> (× 10 <sup>-4</sup> )	M <sub>w</sub> /M <sub>n</sub>	Microstructure, %			T <sub>m</sub> <sup>d</sup>
						<i>cis</i> -1,4	<i>trans</i> -1,4	1,2	
1	FeCl <sub>3</sub>	100	0	—	—	—	—	—	—
2	FeCl <sub>3</sub> L	50	100	2.9	2.9	0	95.3	4.7	101
3	FeCl <sub>3</sub> L	100	100	2.7	1.9	0	94.6	5.4	103
4	CrCl <sub>3</sub>	100	0	—	—	—	—	—	—
5	CrCl <sub>3</sub> L	50	38	4.9	2.0	9.5	90.2	0.3	87
6	CrCl <sub>3</sub> L	100	46	4.1	2.2	11.5	88.1	0.4	85
7	FeCl <sub>2</sub> L	100	0	—	—	—	—	—	—
8	FeCl <sub>2</sub> L	50	69	3.7	1.7	35.5	55.1	9.4	—
9	FeCl <sub>2</sub> L	100	82	3.5	1.7	34.8	54.9	10.3	—
10	CoCl <sub>2</sub>	100	24	2.6	1.8	98.1	1.6	0.3	—
11	CoCl <sub>2</sub> L	25	0	—	—	—	—	—	—
12	CoCl <sub>2</sub> L	50	39	1.0	1.7	0	94.4	5.6	96
13	CoCl <sub>2</sub> L	75	86	4.8	4.9	78.8	18.2	3.0	—
14	CoCl <sub>2</sub> L	100	100	5.2	7.0	79.2	18.0	2.8	—
15	NiCl <sub>2</sub>	100	24	2.4	3.9	90.1	6.1	4.1	—
16	NiCl <sub>2</sub> L	50	33	1.3	2.2	95.1	1.1	3.8	—
17	NiCl <sub>2</sub> L	100	42	1.4	2.9	96.2	2.1	1.7	—
18	NiCl <sub>2</sub> L	200	39	1.6	2.6	96.9	2.0	1.1	—

<sup>a</sup> Polymerization conditions: precursor, 0.01 mmol; butadiene, 0.01 mol; toluene, 5 mL; time, 4 h; temperature, 20 °C.

<sup>b</sup> FeCl<sub>3</sub>L, CrCl<sub>3</sub>L, FeCl<sub>2</sub>L, CoCl<sub>2</sub>L, and NiCl<sub>2</sub>L denote complexes.

<sup>c</sup> MAO/precursor molar ratio.

<sup>d</sup> Melting temperature, determined by differential scanning calorimetry.

polybutadiene can mainly be produced by reacting 1,3-BD using transition metals such as Co-, Ni-, Ti-, and Nd-based catalysts with alkyl-aluminum complexes as co-catalysts in organic solvents.<sup>51</sup> The *cis*-1,4 content in BR during polymerization can be controlled by varying the transition metals in the catalyst system. For example, Ti-based catalysts resulted in 90% to 93%, whereas Co- and Ni-based catalysts offered 96% to 98%, and Nd-based catalysts gave 97% to 99% *cis*-1,4 product.<sup>52</sup>

In contrast, 1,2-stereoselectivity of 1,3-BD is considered more difficult and challenging and is mainly influenced by the reaction parameters and catalysts used. In this regard, Behera et al. investigated the synthetic procedures for polybutadiene using a Co-based catalyst system to control 1,2-*vinyl* content in polymer followed by modification of vinyl functionality via a thiol-ene reaction.<sup>47</sup> The results revealed that Co octanoate (Co[oct]<sub>2</sub>) as a catalyst in combination with diethyl aluminum chloride (DEAC) and TEAL as co-catalysts in cyclohexane resulted in significant enhancement of the vinyl content (68%) on polymerization of 1,3-BD. The factors that affect the production of high-*vinyl* BR are the concentrations of catalyst, co-catalyst, and monomer as well as the reaction conditions, such as the reaction temperature and solvent. Furthermore, Hao and Zhang reported a syndiotactic 1,2-polybutadiene using an electrospinning technique in dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>).<sup>53</sup> They explained that CH<sub>2</sub>Cl<sub>2</sub> is the best solvent for producing nanofibers of syndiotactic 1,2-polybutadiene. O'driscoll and Yonezawa reported the 1,2-polymerization of 1,3-BD using *t*-butyl Li.<sup>54</sup>

#### IV. ROLE OF CATALYSTS IN BR SYNTHESIS

The metal-catalyzed polymerization of conjugated dienes is highly regio- and/or stereoselective and is considered to be a major polymerization technique with great industrial importance. The catalyst plays a substantial role in the polymerization of 1,3-BD. In practice, three different types of coordination catalysts are effective for the polymerization of conjugated dienes: (1) transition metal-based catalysts with alkyl aluminum, known as ZN catalysts, which have been extensively investigated in 1,3-BD polymerization; (2) allyl derivatives of transition metals; and (3) mono- and/or bimetallic transition metal catalysts. In this review, we discuss various metal ion-based catalysts, and they are summarized in Table II.

##### A. LITHIUM CATALYSTS

The conversion of conjugated diene monomers into a polymer occurs in several ways using a Li-based catalyst. The development of novel materials that behave like initiators is one of the best techniques for extending the productivity of the materials. Amongst these materials, alkyl Li-based initiators are a popular direction, in which the associated alkyl Li is the active center. Firestone Tire & Rubber Company reported that rubber productivity can be improved using alkyl Li compounds, such as methyl Li, ethyl Li, butyl Li, pentyl Li, hexyl Li, 2-ethylhexyl Li, n-dodecyl Li, and n-hexadecyl Li.<sup>74</sup> The higher the concentration (>1 mmol) of alkyl Li, the greater the increase in the number of associated alkyl Li centers that directly influence the catalytic activity toward polymerization.<sup>75</sup> In this way, O'driscoll and Yonezawa reported sevenfold enhancement (7% to 47%) in the 1,2-polymerization product of 1,3-BD by increased concentration of *t*-butyl Li.<sup>54</sup> Tapia et al. developed high *trans*-1,4-polybutadiene through anionic polymerization using an initiator system including alkyl aluminum, n-butyl Li, and barium alkoxide.<sup>55</sup> The solubility, reproducibility, and commercial availability of the initiator systems are the key factors affecting the use of catalyst and also influence catalytic performance and productivity. Therefore, the initiator system with solubility in nonpolar hydrocarbons was chosen, incorporating barium alkoxide with n-butyl Li and trioctyl aluminum fitting all the requirements for *trans*-1,4-polybutadiene synthesis. Min et al. synthesized hydroxyl-terminated polybutadiene using a novel alkyl Li-based initiator *t*-butyl dimethylsiloxy dimethylpropyl Li (TBDMSODPrLi) with relatively large steric hindrance, resulting from the anionic polymerization technique (Figure 2).<sup>39</sup> Furthermore, researchers have investigated the combination of an organic acid salt of lanthanum compound with an organo Li compound and found it to be a catalytically effective system for the chemical synthesis of 1,4-*trans* polybutadiene.<sup>56</sup>

##### B. TITANIUM AND ZIRCONIUM CATALYSTS

Ti was first used as a catalyst in combination with  $\text{TiCl}_4$  or  $\text{TiCl}_3$  with alkyl aluminum in 1954 for the stereospecific polymerization of conjugated dienes. Ti catalysts are frequently used in the production of high *cis*-polybutadiene at a commercial level in Europe and United States. A 1,4-stereoselective polymerization of 1,3-BD in the presence of a cationic ( $\text{TiCp}[\text{polybutadienyl}][\text{butadiene}]^+$ ) active catalyst system has been investigated by a comprehensive theoretical study.<sup>76</sup> Zakharov et al. investigated a micro-heterogeneous Ti catalyst  $\text{TiCl}_4\text{-Al}(i\text{-C}_4\text{H}_9)_3$  with different sizes of active species that influences the concentration of polymerization centers.<sup>57</sup>

Further, many research groups have investigated other metal catalysts of group IV and found that Zr also showed significant activity toward the polymerization of 1,3-BD. Annunziata et al. reported Zr-based catalysts showing superior activity over Ti-based catalysts. In this investigation, a series of group IV metal (Zr and Ti) complexes, including anilidomethylpyridine ligands, were

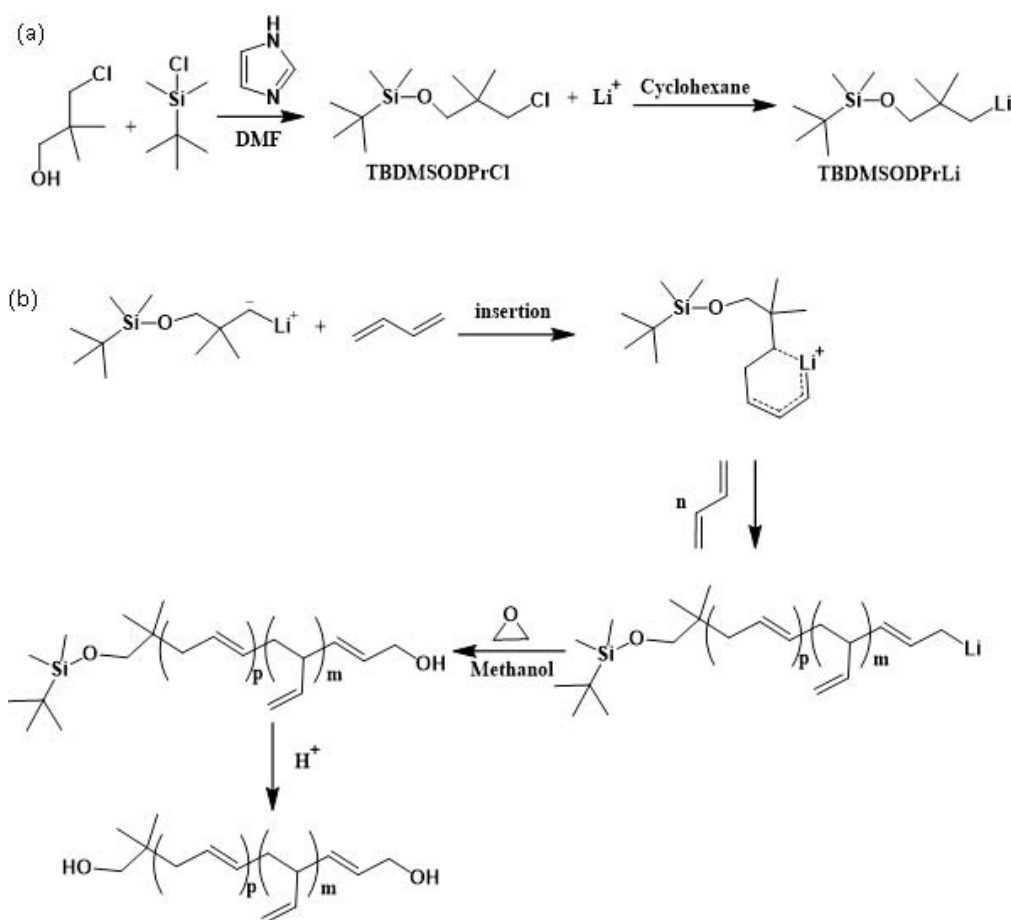


FIG. 2. — (a) Synthetic strategy for the preparation of alkyl lithium-based initiator (*t*-butyldimethyl-siloxydimethylpropyl-lithium; TBDMSODPrLi) from *t*-butyldimethylsiloxy-dimethylpropyl chloride (TBDMSODPrCl) and (b) polymer initiation mechanism.<sup>39</sup>

synthesized (Figure 3)<sup>58</sup> and characterized using various spectral techniques and demonstrated activity toward 1,3-BD polymerization after activation by  $\text{Al}i\text{Bu}_2\text{H}$  and MAO. The results revealed that Zr complexes showed superior activity over homologous Ti. In the case of Zr catalyst, the resulting polymer contained ~99.9% *cis*-1,4 polybutadiene, which was reduced in Ti complexes with increasing *trans*-content.

### C. IRON CATALYSTS

Fe complexes have not been extensively investigated for 1,3-BD polymerization as compared with other transition metal complexes. However, few complexes derived from Fe with various ligands have been explored for polymerization of 1,3-BD, resulting in BR with a mixed *cis*-1,4/vinyl-1,2 structure. Bazzini et al. reported a series of Fe-based complexes composed of 1,10-phenanthroline ligand in the presence of alkyl aluminum (i.e.,  $\text{Al}i\text{Bu}_3$ ,  $\text{AlEt}_3$ ), and MAO showed the formation of syndiotactic 1,2-polybutadiene (Figure 4).<sup>77,78</sup> The results revealed that the formation of 1,2-content (67.5–91%) and syndiotactic degree (rrrr, 36.9–52.5%) increased as the

TABLE II  
BRIEF SUMMARY OF DIFFERENT CATALYSTS IN BUTADIENE POLYMERIZATION

Catalyst	Ligand	Co-catalyst	Microstructure, %	References
n-Butyl-lithium ( <i>t</i> -Butyldimethyl- siloxydimethylpropyl) lithium	n-Butyl anion <i>t</i> -Butyldimethyl- siloxydimethylpropyl	Al(C <sub>8</sub> H <sub>17</sub> ) <sub>3</sub> /(RO) <sub>2</sub> Ba	<i>trans</i> -1,4; 60–90 <i>cis</i> -1,4; 35.2, <i>trans</i> -1,4; 56.3, <i>vinyl</i> -1,2; 8.5	55 39
La[Li] <sub>3</sub> and n-BuLi	L= bis(2-ethylhexyl) phosphate, dodecylbenzene- sulfonate, and nonylphenoxide	—	<i>trans</i> -1,4; 88–92, <i>vinyl</i> - 1,2; 4–6	56
TiCl <sub>4</sub> /Al( <i>i</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>		Al( <i>i</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	<i>cis</i> -1,4; 75–80, <i>trans</i> -1,4; 18–23, <i>vinyl</i> -1,2; 1–2	57
Ti(IV) [anilidomethyl- pyridine]	Anilidomethyl-pyridine	AliBu <sub>2</sub> H/MAO	<i>cis</i> -1,4; 89.3, <i>trans</i> -1,4; 4.2, <i>vinyl</i> -1,2; 6.5	58
Zr (IV) [anilidomethyl- pyridine]	Anilidomethyl-pyridine	AliBu <sub>2</sub> H/MAO	<i>cis</i> -1,4; 99.9	59
(Fe[2-EHA] <sub>3</sub> )	2-EHA = 2-ethylhexanoic acid	AliBu <sub>3</sub> /diethyl phosphite	<i>cis</i> -1,4; 51.0, <i>trans</i> -1,4; 5.0, <i>vinyl</i> -1,2; 44.0	60
(Fe[2-EHA] <sub>3</sub> )	2-EHA = 2-ethylhexanoic acid	AliBu <sub>3</sub> /substituted triphenyl phosphates	<i>vinyl</i> -1,2; 80–97 <i>I,4</i> -content; 5–20	61
2-(3-Methylpyrazol-1-yl)- 1,10-phenanthroline Fe(acac) <sub>3</sub>	2-(3-Methylpyrazol-1-yl)- 1,10-phenanthroline Acetyl acetone	AliBu <sub>3</sub>	<i>trans</i> -1,4; 96.2	62
Co(II)-bis(benzimidazolyl) amine.Cl <sub>2</sub>	Bis(benzimidazolyl)amine	AliBu <sub>3</sub> /phosphate additives MAO	<i>vinyl</i> -1,2; 80–95, <i>I,4</i> - content; 5–20 <i>cis</i> -1,4; 94–97, <i>trans</i> -1,4; 0–5, <i>vinyl</i> -1,2; 0–2	18
		MAO/PPh <sub>3</sub>	<i>cis</i> -1,4; 30–38, <i>trans</i> -1,4; 0–2, <i>vinyl</i> -1,2; 61–68	



TABLE II  
CONTINUED

Catalyst	Ligand	Co-catalyst	Microstructure, %	References
2,6-Bis(imino)pyridyl Co(II) complex	2,6-Bis(imino)pyridine	MAO	<i>cis</i> -1,4; 77.5–97, <i>trans</i> -1,4; 2.5–21.4, 1,2-vinyl; 0.6–3.1	63
Co(II).bis(N-arylcarboximidoyl)chloride pyridine	Bis(N-arylcarboximidoyl)chloride pyridine	EASC	<i>cis</i> -1,4; 92–96, <i>trans</i> -1,4; 0.6–4.0, 1,2-vinyl; 2.4–4.0	64
Co(II)pyridine(bisoxazoline)	Pyridine(bisoxazoline)	EASC	<i>cis</i> -1,4; 95–97, <i>trans</i> -1,4; 1.5–4.0, 1,2-vinyl; 0.8–3.2	65
[Co(Phen) <sub>3</sub> ][TfO] <sub>2</sub>	1,10-Phenanthroline	EASC	<i>cis</i> -1,4; 97, <i>trans</i> -1,4; 1.1, 1,2-vinyl; 1.9	66
[LCoCl <sub>2</sub> ]	L = 2-pyrazolyl-substituted 1,10-phenanthroline	MAO	<i>cis</i> -1,4; 91–95.1, <i>trans</i> -1,4; 2.7–6.7, 1,2-vinyl; 2.0–2.9	67
Bis-diphenylphosphine cobalt complex	Bis-diphenylphosphine	MAO	1,2-vinyl; 94.5	68
Nickel naphthenate	Naphthenic acid	TEA/BF <sub>3</sub> -OEt <sub>2</sub>	<i>cis</i> -1,4; 97.6, <i>trans</i> -1,4; 1.7, 1,2-vinyl; 0.7	69
Ni(COD) <sub>2</sub>	COD = cyclo-octadiene	Borate salt [CPh <sub>3</sub> ][B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ]	<i>cis</i> -1,4; 91, <i>trans</i> -1,4; 5.0, 1,2-vinyl; 4.0	70
Nd(neodecanoate) <sub>3</sub>	Neodecanoic acid	AlEt <sub>2</sub> Cl/Al( <i>i</i> Bu) <sub>3</sub>	<i>cis</i> -1,4; 97.1, <i>trans</i> -1,4; 2.3, 1,2-vinyl; 0.6	71
Nd(neodecanoate) <sub>3</sub>	Neodecanoic acid	AlEt <sub>2</sub> Cl/Al( <i>i</i> Bu) <sub>3</sub> /tri-p-fluorophenyl phosphine	<i>cis</i> -1,4; 99.7, <i>trans</i> -1,4; 0.1, 1,2-vinyl; 0.2	72
Nd(octanoate) <sub>3</sub>	Octanoic acid	DEAC/TEAL	<i>cis</i> -1,4; 81–92	73
Ni/Nd-based Ziegler–Natta catalyst		DEAC/TEAL	<i>cis</i> -1,4; 95–96, <i>trans</i> -1,4; 3.07–4.44, 1,2-vinyl; 0.13–0.26	

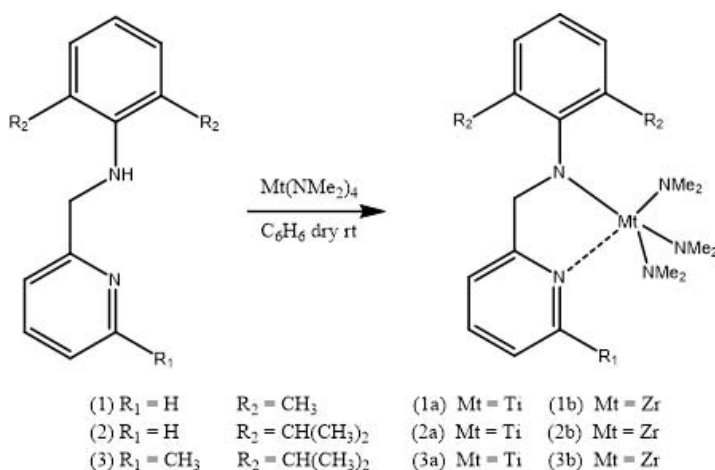


FIG. 3. — Synthetic strategy for the preparation of Ti and Zr complexes using anilidomethylpyridine ligands.<sup>58</sup>

reaction temperature was decreased. Zhang et al. reported Fe complexes composed of ethylhexanoate (EHA) and diethyl phosphite (DEP) as catalysts for the polymerization of 1,3-BD in hexane at 40 °C.<sup>59</sup> More importantly, Fe-based catalysts can be generated in situ for the polymerization of 1,3-BD. Gong et al. reported the in situ generation of Fe catalyst via mixing Fe(III) 2-ethylhexanoate and  $\text{Al}i\text{Bu}_3$  in hexane in the presence of phosphate donors for BR synthesis.<sup>60</sup> These type of catalysts showed extremely high selectivity toward syndiotactic 1,2-polybutadiene. Furthermore, a series of Fe(II) complexes containing tridentate 2-pyrazolyl substituted 1,10-phenanthroline ligand have been reported and demonstrated to be an efficient catalyst for 1,3-BD polymerization in the presence of alkyl aluminum.<sup>61</sup> The complexes showed significant activity (73.5–94.3%) at 20 °C, which increases on increasing the reaction temperature with *trans*-selectivity. Further, highly stereo- and 1,2-regioselective polymerization of 1,3-BD has been reported by using Fe-based catalysts with newly synthesized phosphate and phosphite compounds as additives.<sup>62</sup> The role of additives on the catalytic performances by varying the nature of phosphate and the mechanism by which the phosphate assists the Fe catalyst has been explained.

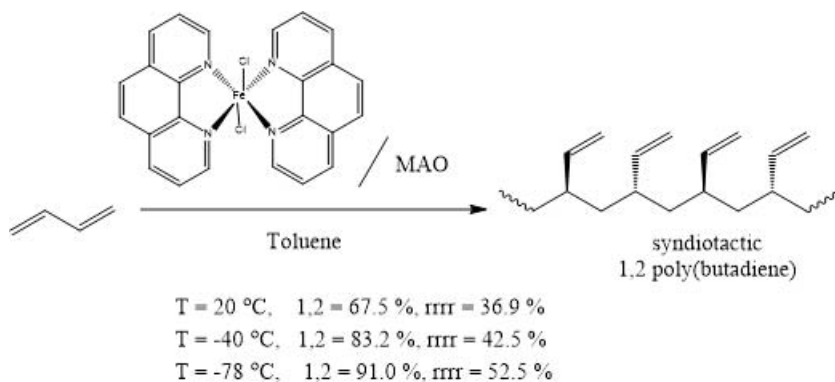


FIG. 4. — 1,3-BD polymerization using  $\text{Fe}(\text{Phen})_2\text{Cl}_2$  catalysts with MAO in toluene (where T = reaction temperature, rrrr = degree of syndiotacticity).<sup>77</sup>

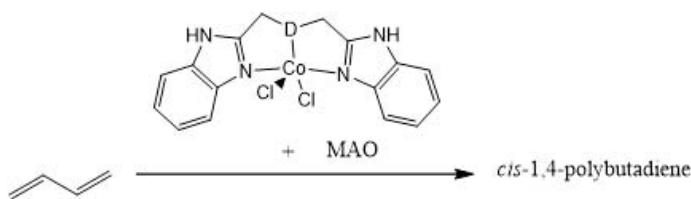


FIG. 5. — 1,3-BD polymerization using cobalt(II) benzimidazole complex.<sup>18</sup>

#### D. COBALT CATALYSTS

Co-based catalysts play a crucial role in 1,3-BD polymerization, mainly producing BR with a high *cis*-1,4 content (up to 96–97%). The catalytic activity of these complexes has mainly been influenced by the catalyst design, co-catalyst used, and reaction conditions that affect the microstructure and the properties of the resultant polymer. Several Co-based catalytic systems in the presence of a suitable co-catalyst have been investigated for 1,3-BD polymerization that resulted in high *cis*-1,4-polymer. Co(acetylacetonate) complex in the presence of AlEt<sub>2</sub>Cl–H<sub>2</sub>O (Co[acac]<sub>3</sub>–AlEt<sub>2</sub>Cl–H<sub>2</sub>O) resulted in high *cis*-BR, whereas changing the catalyst system Co(acac)<sub>3</sub>–AlEt<sub>3</sub>–H<sub>2</sub>O resulted in equibinary *cis*-1,4/1,2-BR. Shiono et al. reported 1,3-BD polymerization in the presence of CoCl<sub>2</sub> catalyst combined with MAO as a co-catalyst.<sup>79</sup> Further, the addition of PPh<sub>3</sub> in combination with CoCl<sub>2</sub> and MAO resulted in slowly initiated living polymerization with a high *cis*-1,4 content (about 99%) at 0 °C. The role of additives such as triphenylphosphine (PPh<sub>3</sub>) on catalytic performance has also been investigated. PPh<sub>3</sub> was found to interact with multiple propagation centers, resulting in regioblock polybutadiene. An increasing amount of PPh<sub>3</sub> resulted in an increase in 1,2-content. Cariou et al. reported a series of Co(II) complexes with benzimidazole and chloride ligands and demonstrated that the behavior of the donor atoms may affect the binding affinity of the ligand metal center.<sup>18</sup> These complexes, upon activation with MAO as co-catalyst, showed catalytic activity toward 1,3-BD polymerization, resulting in a highly selective *cis*-1,4-product (Figure 5). Further, the addition of PPh<sub>3</sub> increases the activity of catalysts, significantly enhancing the 1,2-*vinyl*-product (60–70%).

Co(II) complexes derived from 2,6-bis(imino)pyridyl ligand in the presence of MAO showed moderate to high conversion (42–99%) toward 1,3-BD polymerization in toluene producing a *cis*-1,4 structure (77.5–97%) with control molecular weight.<sup>63</sup> Liu et al. reported a series of Co(II) complexes comprising bis(*N*-arylcarboximidoyl-chloride)pyridine ligands that exhibited high catalytic activity toward 1,3-BD polymerization in combination with ethyl aluminum sesquichloride (EASC) as co-catalyst, affording predominant *cis*-1,4 content (up to 96%) in polybutadiene.<sup>64</sup> The results revealed that the incorporation of chlorine atoms into the ligand improves the performance of the catalyst. Guo et al. reported a series of ion-pair Co complexes bearing pyridine bisoxazoline ligands, in which the Co center was coordinated by six nitrogen atoms from two ligands with a distorted octahedral geometry (Figure 6).<sup>65</sup> These complexes in combination with EASC showed high catalytic activity and *cis*-1,4-selectivity toward 1,3-BD polymerization. Further, the selectivity of the catalyst can be improved by the addition of PPh<sub>3</sub> as additive. The authors have also performed a controlled experiment using both the Co complex/CoCl<sub>2</sub> and EASC individually and found that none can initiate the reaction. In addition, it has been found that the catalytic activities of the complexes depends on the structure of substituent on oxazoline ring of the ligand.

Singh et al. studied the role of solvents (i.e., aliphatic [cyclohexane] and aromatic solvents [toluene, *o*-xylene, ethylbenzene {EB}, and *p*-diethylbenzene {PDEB}]) with different  $\pi$ -electron densities on 1,3-BD polymerization catalyzed by Co(II) octanoate/DEAC solution resulting in high

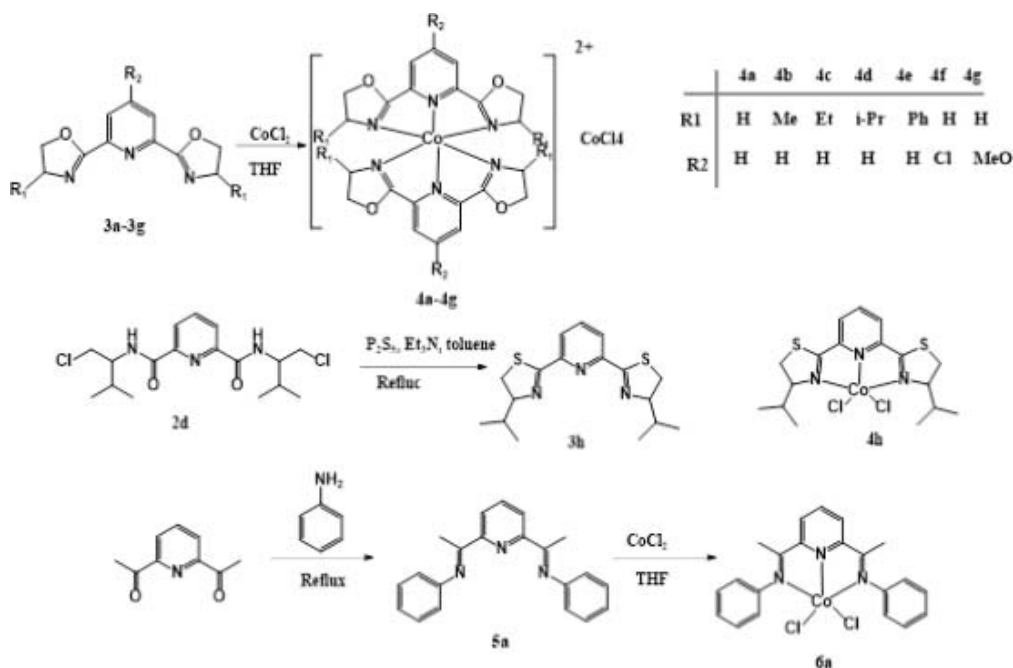


FIG. 6. — Synthesis of the cobalt complexes bearing pyridine bisoxazoline ligands.<sup>65</sup>

*cis*-BR.<sup>6</sup> Those authors observed that the blue color of the catalyst disappears on addition of DEAC and BD in the reaction mixture, indicating that DEAC ( $\text{Et}_2\text{AlCl}$ ) reacts with butadiene, generating a butadienyl ion, which forms a complex with Co, replacing one octanoate molecule. The resulting intermediate binds with another monomer of the butadiene, initiating the polymerization reactions, which offer high *cis*-BR product. Further, the mechanism of the formation of high *cis*-BR using the Co catalyst system can be explained by  $\eta^3$  bonding of 1,3-BD to the metal center.<sup>49</sup> The Co center binds to the  $\pi$ -allylic end group of the growing polymer chain, leading to two different reactive sites (C1 and C3) for the incoming monomer unit, which results in 1,4-(*trans*- or *cis*-) and 1,2-(*vinyl*) products, respectively.<sup>80</sup> The metal center coordinates with the terminal allyl group of the polymer chain that can appear in either in *anti*- or *syn*-conformation, which plays a crucial role in determining the microstructure of BR. The selectivity of the 1,4-*cis*- and 1,4-*trans*-product mainly depends on the addition of the new monomeric unit to the *anti*- and *syn*-conformation of the terminal allyl unit of the polymer chain, respectively (Figure 7).<sup>80</sup>

Liu et al. synthesized a series of cationic Co complexes including neutral N,N-chelating ligands (i.e., 1,10-phenanthroline, bipyridine, benzimidazole, terpyridine), and a positive charge of complexes has been compensated with trifluoromethanesulfonate and methane sulfonate as counter anions.<sup>66</sup> Upon activation with EASC, these Co(II) complexes showed high catalytic activities toward 1,3-BD polymerization. Further, Co(II) complexes containing tridentate ligands obtained by the substitution of 2-pyrazole on 1,10-phenanthroline ( $\text{LCoCl}_2$ ) have been successfully synthesized and demonstrated to be efficient catalysts for high *cis*-1,4-selective polymerization of 1,3-BD.<sup>67</sup> The results revealed that the bulky substituent on the pyrazole ring decreases the activity of the catalysts, whereas the electron-withdrawing substituents increase the performance of the catalyst. Recently, Ricci et al. reported novel Co complexes containing diphenyl phosphine ligand (Figure 8).<sup>68</sup> These complexes in combination with MAO have been demonstrated to be efficient

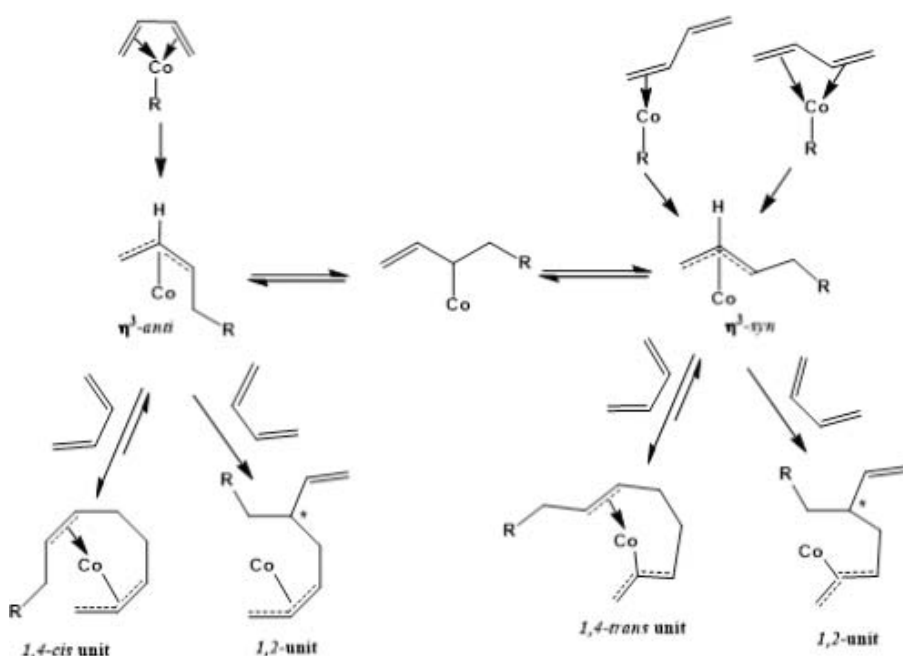
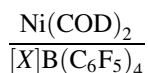


FIG. 7. — Reaction mechanism for 1,3-bD polymerization using cobalt catalyst.<sup>80</sup>

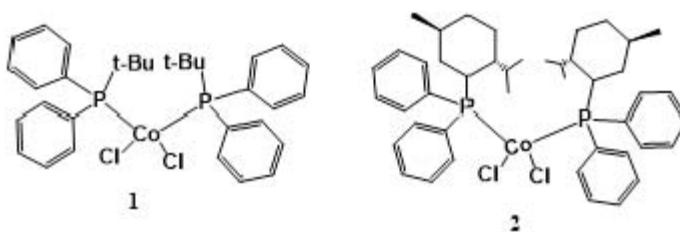
catalysts for 1,3-BD polymerization. The catalyst resulted in high syndiotactic 1,2-polybutadiene, with a syndiotactic index ( $rr\%$ ) up to 95% and 85%, respectively.

#### E. NICKEL CATALYSTS

Ni-based catalysts have been investigated extensively as active catalysts toward the polymerization of 1,3-BD. They demonstrated good activity and stereoselectivity and hence have reached the level of industrial interest. A catalyst system based on Ni(octanoate)<sub>2</sub> with triethyl aluminum and boron trifluoride etherate (BF<sub>3</sub>·OEt<sub>2</sub>) is mainly used for the industrial production of high cis-polybutadiene (96–97%).<sup>81</sup> Singh et al. demonstrated 1,3-BD polymerization in aliphatic and aromatic solvents using a catalyst system containing Ni naphthenate, BF<sub>3</sub>·Et<sub>2</sub>O, and triethylaluminum.<sup>69</sup> In addition, the effect of the catalyst concentration, BF<sub>3</sub>·Et<sub>2</sub>O/alkyl aluminum ratio, catalyst aging temperature, and reaction temperature have been investigated. The results revealed that a lower catalyst concentration with a smaller number of active sites leads to a higher molecular weight, with a reverse trend in polydispersity index. Vaultier et al. developed a series of Ni-based catalysts in the presence of borate as co-catalyst



where X = CPh<sub>3</sub> or HNMe<sub>2</sub>Ph, toward the stereospecific polymerization of butadiene (Figure 9).<sup>70</sup> The results showed that highly active catalytic species for stereospecific polymerization was obtained using a stoichiometry between Ni and borane as 1:1, with the mechanism of the formation of active catalytic species shown in Figure 9. In addition, research has been conducted on the design of Ni(II) complexes with nitrogen donor ligands imino- or amino-pyridyl alcohol ligands.<sup>82</sup>

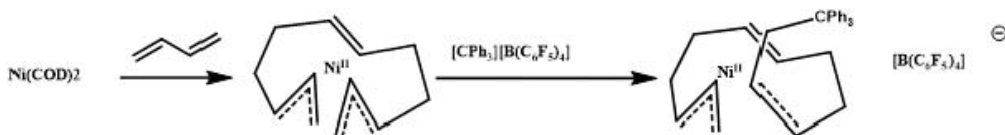
FIG. 8. — Bis-diphenylphosphine cobalt complexes.<sup>68</sup>

## F. LANTHANIDE CATALYSTS

Taube and coworkers reported that the lanthanide metal-based catalysts can be efficient for 1,3-BD polymerization, with the highest *cis*-1,4-product.<sup>83</sup> The synthesis of polybutadiene with a controlled microstructure is crucial for the production of synthetic rubber that directs the characteristic polymer properties.<sup>84</sup> Nd-based catalysts are well known to produce the highest *cis*-1,4-polybutadiene.<sup>85</sup> Rao et al. introduced an Nd-tripentanolate-based catalyst system in the presence of TEA as co-catalyst, which showed *cis*-1,4 polybutadiene with 99% of *cis*-BR content.<sup>86</sup> Kwag et al. demonstrated a monomeric Nd catalyst based on Nd(neodecanoate)<sub>3</sub>/(neodecanoic acid)(NdV4)/AlEt<sub>2</sub>Cl/Al(*i*Bu)<sub>3</sub> toward 1,3-BD polymerization and investigated their physical and spectroscopic properties. Further, the microstructure of polybutadiene has been controlled using phosphine ligands that lead to ultrahigh *cis*-1,4-polybutadiene with >99% content in the presence of tri-*p*-fluorophenyl phosphine.<sup>71</sup>

Masuda et al. demonstrated a significant improvement in *cis*-1,4 stereospecificity from 90%–95% by using chlorinated co-catalysts such as DEAC in the catalyst system, comprising Nd isopropoxide (Nd(O*i*-Pr)<sub>3</sub> with MAO.<sup>87</sup> Maiti et al. reported a Nd-based catalyst composed of Nd-octanoate, DEAC, and TEAL toward polymerization of 1,3-BD.<sup>72</sup> Dai et al. reported a ternary catalyst containing Nd(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>·H<sub>2</sub>O·3(tributyl phosphate)/Mg(*n*-Bu)<sub>2</sub>/(modified MAO {MMAO}) resulting in a copolymer via chain shuttling polymerization.<sup>88</sup> The molar ratio of [MMAO]/Nd and [Mg]/[Nd] and delayed feeding time of MMAO regulate the stereo-selectivity of monomers units in *cis*-1,4 and *trans*-1,4 polybutadiene copolymers. The *trans*-1,4 content can be significantly increased from 8.4% to 95.3% by increasing the [MMAO]/[Nd] ratio and the delayed feeding time of MMAO as well as the reduced [Mg]/[Nd] ratio. Chatarsa et al. reported that Nd-based ZN catalyst with a combination of transition metals (i.e., Ni- [Ni/Nd]) using DEAC and TEAL as co-catalysts influenced the polymerization of 1,3-BD.<sup>73</sup> The results revealed that both the *vinyl*-1,2 and *trans*-1,4 content in high *cis*-1,4 polybutadiene (95–96%) is significantly reduced with an increase in the Ni/Nd molar ratio.

Mecking et al. reported on functionalized aluminum alkyls, which are capable of selective polymerization via coordinative chain transfer.<sup>89</sup> In this regard, functionalized and easily accessible mixed ( $\omega$ -aminoalkyl)diisobutyl aluminum reagents with a suitable combination of Nd- and gadolinium-based complexes and [PhNMe<sub>2</sub>H<sup>+</sup>]/[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>] were demonstrated for highly efficient and selective coordinative chain transfer polymerizations of 1,3-BD. The results revealed

FIG. 9. — Mechanism of formation of the active species with Ni(COD)<sub>2</sub>/[CPh<sub>3</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in the presence of butadiene.<sup>77</sup>

that a large number ( $\sim 90\%$ ) of aluminum-bound carbazole groups are able to initiate polymerization while retaining high (90–95%) *cis*-1,4 butadiene.

## V. CONCLUSION

Polymerization of conjugated dienes using the ZN-based catalyst system (transition metal complexes with alkyl aluminum) began in 1954. Subsequently, the research on butadiene polymerization has been stimulated for developing various catalytic systems based on transition metals and lanthanides toward improving the catalytic performance and stereoselectivity of the catalysts. In the current review, we summarized various transition metal- and lanthanide-based complexes with nitrogen, oxygen, and phosphorus donor ligands for 1,3-BD polymerization and discussed the microstructures based on regio- and stereoselectivity of the catalysts. The stereoisomeric selectivity based on catalysts has been explained for the synthesis of *cis*-1,4-, *trans*-1,4-, and *vinyl*-1,2-polybutadiene, resulting in unique elastomeric properties and long-standing industrial scalability. The Co(II), Ni(II), and Nd(III) complexes in the presence of appropriate co-catalysts offer high *cis*-1,4-polybutadiene (95–98%), whereas the Li-based catalysts result in high *trans*-product.

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