

## Role of catalysis in sustainable production of synthetic elastomers

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**Abstract.** Elastomer business plays a significant role in the transportation industry. In fact, elastomers make the world move. Due to limited availability of natural rubber, synthetic elastomers bridge the gap between demand and supply in today's growing tyre and automobile industry. With more than ~10000 KTA total world productions, the impact of synthetic elastomer business cannot be overlooked. The need of synthetic elastomers for tyre and automobile industries is stringently specific. Catalysis plays an inevitable role in achieving the growing demand of specific synthetic elastomers. The present study will describe how catalysis plays a significant role in the sustainable development of elastomers with special reference to polybutadiene rubber.

**Keywords.** Elastomers; catalysis; tyres and automobiles; mechanism; manufacturing process.

### 1. Historical glimpse of rubbers/elastomers

Elastomer/rubber by definition is a polymeric material that can stretch and then return to its original shape without permanent deformation. Technically, elastomer/rubber can be defined as a polymeric material with the following typical characteristics: (i) the glass transition temperature ( $T_g$ ) should be lower than room temperature; (ii) amorphous in unstrained conditions and (iii) low Young modulus and high failure strain. Historically, rubber is the most ancient natural polymer known to mankind and its first use was as an eraser.<sup>1</sup> Apparently, the name 'rubber' originated for the substance having ability to rubbing or erasing the pencil mark on paper. The story started with the use of graphite as a writing device by the 1560s. It was observed by the French Academy of Sciences in 1752 that undesirable pencil (graphite) marks could be rubbed off by condensed latex (kautschuk) obtained from the rubber tree (*Hevea brasiliensis*). Hence, erasers are called as rubbers in most parts of the world.<sup>1</sup> Generally, elastomers are obtained from two sources:

- Naturally known as 'Natural Rubber'.
- Synthetically, i.e., man-made known as 'synthetic elastomers/rubbers'.

Major drawbacks of ancient time rubbers were the unstable physical behaviour, e.g., softening, hardening,

and sticky depending upon the environmental conditions. Charles Goodyear,<sup>1</sup> developed a vulcanization procedure to cure rubber in 1839. As per Goodyear's vulcanization process, addition of sulphur facilitates cross-linking between the rubber's polymer chains which increases strength, stability, and elasticity of the rubber. Goodyear's discovery became the breakthrough in broader application of rubber for many common items apart from erasers, for e.g., tyre sector. Before the rubber era, wheels were made of wood and steel.

Use of the rubbers played a crucial role during World-War II,<sup>1</sup> for example, each Sherman tank contained 20 tons of steel and half a ton of rubber. Each warship contained 20,000 rubber parts. Rubber was used to coat every centimetre of wire, used in every factory, home, office and military facilities throughout the USA. After the attack on Pearl Harbor, the Japanese invaded Malaysia, one of the major producers of natural rubber, to take over natural rubber production from the allies. This gave the Axis control over 95% of world rubber supplies, plunging the USA into a crisis, which forced USA to initiate the following steps:

- Use of rubber in non-essential products was banned.
- Speed limits were reduced to 35 miles/hour on US highways.
- The USA underwent largest rubber recycling campaign.
- Rubber chips were sold at a penny. Chemists and engineers were asked to develop the synthetic rubber industry.

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Development of varied catalysts for polymerization of butadiene helped to produce synthetic polybutadiene rubber (BR) and the advent of Ziegler–Natta (Z–N) catalysis later played a key role in sustenance of PBR production.

The names of top five natural rubber producers in the world are given in table 1.<sup>2</sup> Thailand is the world's largest producer of natural rubber. It produced 3,394 thousand MT in 2011. Indonesia is the second largest producer contributing around 27% of the world's total natural rubber production. Malaysia produced 996 thousand MT and occupies the third place in terms of production. India is the fourth largest producer of natural rubber in the world. In the year 2011, India produced 890 thousand MT of natural rubber. India contributes 8% of the world natural rubber.

Major application of elastomer/rubbers is in the manufacture of tyre/automobile industries.<sup>2</sup> Demand for elastomers has been constantly increasing particularly due to rapid growth rate of automobile industries, the supply from only rubber industries was not sufficient. Hence, an expedition for alternative of natural rubber was started. Eventually, catalysis has played a significant role in finding a substitute for natural rubber. Automobile ownership ratio in the US is at one automobile for every 1.2 people, and Japan's is one for every 1.7 people. If the ownership ratio of India and China in 2030 will reach one for every 3.4 people, the total number of automobiles in use from both the countries would be almost the same as the current number of automobiles in use in the world. About 5% of automotive parts are made from rubber. World-wide rubber consumption is shown in table 2. Tyres account for 2/3 of the mass of rubber parts used in an automobile. However, the nomenclature and various applications of different types of synthetic rubbers are given in table 3. Indian tyre industry (Dunlop Rubber Limited) set up the first tyre company in 1926 followed by MRF in 1946. Today, the Indian tyre industry produces the complete range of tyres demanded by the Indian automotive industry, except for aero and specialty tyres.

Conjugated dienes, namely 1,3-butadiene and isoprene, have represented and are still the most widely

used standard feedstocks for the production of synthetic elastomers. Methods for polymerization of conjugated dienes have been known for a long time. In the 1930s, polybutadiene rubber was synthesized by polymerization of butadiene by use of metallic sodium, (the first synthetic rubber made for general purpose).<sup>3</sup> However, due to presence of various isomeric units in the polymer chains; polybutadiene rubber had inferior low-temperature resistance. Before 1954, no polymerization methods were available to obtain a polymer with high regularity of the structure from the readily available conjugated dienes. A true breakthrough in the development of conjugated dienes rubber took place after the discovery of stereospecific polymerization with Z–N catalysis. After the discovery, catalysis of stereospecific polymerization of conjugated dienes namely, 1,3-butadiene and isoprene, has been of commercial interest from both the scientific and industrial viewpoints.<sup>4</sup>

## 2. Polymer microstructures of polybutadiene

A variety of structurally different polymers can be obtained by stereospecific catalytic polymerization of dienes,<sup>4,5</sup> as shown in scheme 1.

By 1,4-polymerization of each of these dienes, a *cis*-, a *trans*-isomer or a combination of both can be obtained. On the other hand, if the dienes are 1,2-polymerized, a chiral carbon atom with the vinyl group arises. A total of three vinyl structures is possible; isotactic, in which all the vinyl groups are attached to a backbone carbon with same spatial arrangements; syndiotactic, in which the vinyl groups are attached to backbone carbons with alternating and atactic with random arrangements. In the actual polymer, it is possible to have any or all the several forms in a single chain depending on the type of polymerization catalyst and conditions employed.<sup>4,5</sup> In the case of isoprene, 3,4-polymerization can additionally take place with the probability of isotactic or syndiotactic chiral carbon atom. The different microstructures of polybutadienes can be determined by infrared and Raman spectroscopy.<sup>5</sup> The glass-transition temperature

**Table 1.** Top 5 natural rubber producing countries.

	Country	Production 2011	Production 2010	Production 2004
1	Thailand	3,394,000 mt	3,166,910 mt	3,007,612 mt
2	Indonesia	2,982,000 mt	2,921,872 mt	2,065,820 mt
3	Malaysia	996,000 mt	1,072,400 mt	1,168,700 mt
4	India	890,000 mt	819,000 mt	749,665 mt
5	Vietnam	812,000 mt	659,600 mt	419,000 mt

**Table 2.** Worldwide rubber consumption.

	KTA	%
SBR	4100	43
BR	2600	27
EPDM	1050	11
NBR	420	4
CR	300	3
Other synthetics	1250	12
Total SR – CIS	700	
Total synthetics	10420	
NR	9000	
Total (SR + NR)	19420	

( $T_g$ ) and the melting point ( $T_m$ ) of polybutadienes are microstructure-dependent (table 4).

Among different isomeric polybutadienes, 1,4-*cis*-polybutadiene has gained much industrial importance,<sup>1,2</sup> especially in tyre production, due to its natural rubber-like characteristics. *cis*-Polybutadiene rubber is the second-largest group of synthetic elastomers used worldwide after styrene-butadiene rubber (SBR) and the total world production capacity of 1,4-*cis*-BR is ~2.2 MT/year with a trend to increase further.<sup>2</sup> At commercial level, 1,4-*cis*-polybutadiene was being produced using solution polymerization with Z–N type catalysts<sup>6</sup> (table 5).

The 1,2-polybutadiene is also being produced in much smaller quantities, which is a thermoplastic polymer of high tensile strength used as a high permeability film and can be transformed into strings and fibre.<sup>7</sup>

Among different polyisoprenes, the 1,4-*cis* isomer also has characteristics to an identical to that of natural rubber, which can also be produced by Z–N-type catalytic system. However, due to difficulty of synthesis and poor availability of isoprene monomer, synthetic 1,4-*cis*-polyisoprene cannot compete economically with natural rubber.<sup>1,2</sup>

### 3. Polymerization catalysts

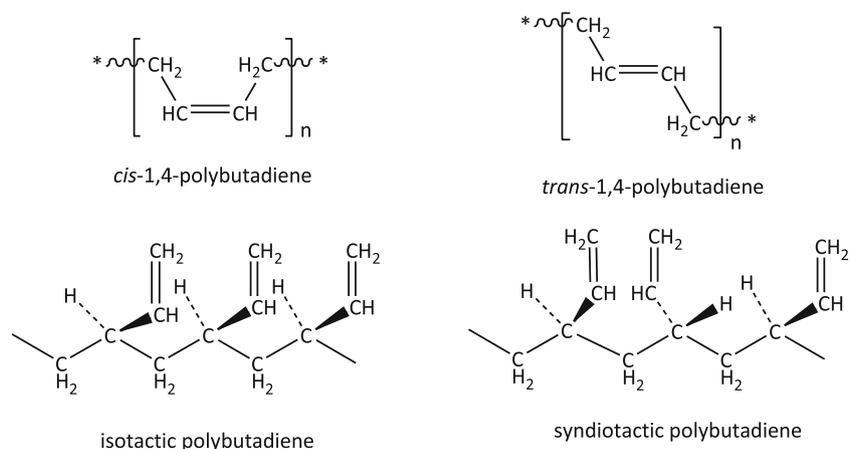
Generally, three classes of the coordination catalysts are effective in the polymerization of conjugated dienes.<sup>4</sup>

- Catalyst system based on Z–N-type derived from alkyl aluminium and transition metal compounds.
- Catalyst system based on allyl derivatives of transition metals.
- Catalyst system based on mono- and/or bimetallic transition metal salts.

Coordination polymerization of conjugated dienes started in 1954, soon after the low pressure polymerization of ethylene has been published by Ziegler and co-workers.<sup>6</sup> The titanium-catalysed first stereo-regular 1,4-*cis*- and 1,4-*trans*-polyisoprene along with stereo-regular polymers of butadiene were derived.<sup>4,6</sup> Thereafter catalysts containing cobalt,<sup>8</sup> nickel<sup>9</sup> for synthesizing 1,4-*cis*-polybutadiene were obtained, and in the early 1960s, the polymers were already being produced commercially using typically Z–N-based catalytic system. With advancement in industrial technology, neodymium-containing catalyst in aliphatic solvents was introduced in early 1980s.<sup>10</sup>

**Table 3.** Nomenclature and various applications of different types of synthetic rubbers.

Name of synthetic rubbers	Tyre	Asphalt modification	Footwear	Adhesive	Technical goods
Emulsion styrene-butadiene rubber (e-SBR)	Yes	No	Yes	Yes	Yes
Solution styrene-butadiene rubber (s-SBR)	Yes	Yes	Yes	Yes	Yes
Polybutadiene rubber (BR)	Yes	No	Yes	No	Yes
Nitril rubber (NBR)	No	No	Yes	No	Yes
Ethylene-propylene diene monomer (EPDM)	Yes	Yes	No	No	Yes
Butyl rubber (IIR)	Yes	No	No	Yes	Yes
Polychloroprene rubber (CR)	No	Yes	Yes	Yes	Yes
Plastics (TR)	No	Yes	Yes		No



### 3.1 Ziegler–Natta type catalyst

Conjugated dienes can undergo polymerization with several types of Z–N catalyst.<sup>4,6</sup> Effectiveness of Z–N catalyst regarding their stereoregulation ability in the polymerization of conjugated dienes depends on the type of: transition metal, ligand, activators and monomer.

Typically, early transition metals are less likely to participate in metal-hydride elimination chain-transfer reactions than the more electron-rich late transition metals. This phenomenon allows early metal systems such as titanium to catalyse the formation of polymers with narrow molecular weight distributions and low branching. Conversely, nickel systems are dominated by chain-transfer reactions and therefore generate polybutadienes with very large molecular weight distributions. Cobalt, also a late transition metal, catalyses the formation of branched polybutadiene presumably by reinsertion of a terminated conjugated diene end group. Another factor controlling the macrostructure of Ziegler–Natta polybutadiene is the propensity of the catalyst to chain-transfer to the aluminium co-catalyst. This type of chain-transfer reaction is dominant in neodymium systems leading to linear polymers but with broad molecular weight distributions.<sup>11</sup>

**3.1a Titanium-based Z–N catalysts:** Polymerization of conjugated dienes is usually carried out using  $\text{TiCl}_4$ ,  $\text{TiCl}_3$ ,  $\text{TiI}_4$ , or  $\text{Ti}(\text{OR})_4$  as catalyst precursors. However, the  $\text{TiCl}_4\text{--AlR}_3$  and  $\text{TiCl}_4\text{--AlH}_x\text{Cl}_{3-x}$  catalysts are of interest as they have been successfully applied in synthesis of 1,4-*cis*-polydienes. The titanium catalyst was the first system to be commercialized in the 1950s by Phillips Petroleum for the synthesis of 1,4-*cis*-polybutadiene.<sup>12</sup> The first commercial catalyst was made from a  $\text{TiI}_4$  precursor and an aluminium alkyl co-catalyst. The metal precursor,  $\text{TiI}_4$  has poor solubility in hydrocarbon solvents, therefore alternative catalysts based on soluble iodine-containing precursors such as  $\text{TiCl}_2\text{I}_2$  or iodine containing activators, e.g.,  $\text{AlEt}_2\text{I}_2$  have been developed. The catalysts of  $\text{Ti}(\text{OR})_4\text{--AlR}_3$  type are readily soluble in hydrocarbon solvents and polymerize butadiene and isoprene into polymers having predominantly 1,2-vinyl- and 3,4-structure, respectively. Generally, titanium-catalysed polybutadiene is known for low branch content and narrow molecular weight distribution leading to good tensile properties and fatigue resistance but poor processibility.<sup>13</sup> The *cis*-content of polybutadiene is very sensitive to the type of halogen derivative employed during the polymerization (table 6). The dependence of microstructure on halide is ostensible for all the *cis*-specific transition metal catalysts except neodymium.<sup>14</sup>

**Table 4.** Glass transition and melting temperature of selected polybutadienes.

Polybutadiene	$T_g$ , °C	$T_m$ , °C
1,4- <i>cis</i> -	–106	2
1,4- <i>trans</i> -	–107	–
1,2-Syndiotactic	–28	156
1,2-Isotactic	–	126
1,2-Atactic	–4	–

**Table 5.** Various catalyst systems used to produce 1,4-*cis*-polybutadiene.

Catalytic system	Metal (mg/L)	1,4- <i>cis</i> -PBD (kg/gM)	Cis (%)
TiCl <sub>4</sub> /I <sub>2</sub> /Al( <i>i</i> -Bu) <sub>3</sub>	50	4–10	93
Co(O <sub>2</sub> CR) <sub>2</sub> /H <sub>2</sub> O/AlEt <sub>2</sub> Cl	1–2	40–160	96
Ni(O <sub>2</sub> CR) <sub>2</sub> /BF <sub>3</sub> .OEt <sub>2</sub> /AlEt <sub>3</sub>	5	30–90	97
Nd(O <sub>2</sub> CR) <sub>2</sub> /Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub> /Al( <i>i</i> -Bu) <sub>2</sub> H	10	7–15	98

3.1b *Cobalt-based Z-N catalysts:* Application of cobalt catalysts in the production of 1,4-*cis*-polybutadiene has been known since 1955 and further research and development is being carried out at commercial and academic levels.<sup>15</sup> Catalysts based on cobalt compounds and alkyl aluminium chlorides readily dissolve in hydrocarbon solvents and are very effective in 1,4-*cis*-polymerization. A variety of cobalt compounds such as CoCl<sub>2</sub>, Co(acac)<sub>2</sub>, cobalt carboxylate, etc. have been used as catalyst precursors. However, only soluble compounds such as cobalt octanoate or cobalt naphthenate have commercial applications. Moreover, maximum activity appears to be linked to the Lewis acidity of the co-catalyst. Alkyl aluminium halides such as diethyl aluminium chloride (DEAC) or ethyl aluminium sesquichloride are used as co-catalysts. Maximum activity is achieved only when a small amount of water or other donor is added with the diethyl aluminium chloride.<sup>8</sup> An alkylaluminumoxane is formed in the reaction of DEAC with water; this turns out to be an effective activator for the 1,4-*cis*-polymerization of butadiene. Above this concentration, water begins to act as a catalyst poison retarding the rate of polymerization. Molecular weight must also be regulated in these systems through the use of a chain-transfer agent. Suitable chain-transfer agents are those that regulate molecular weight without adversely affecting the rate of chain propagation and polymer microstructure. For the cobalt systems, hydrogen, ethylene, propylene, and allenes such as 1,2-butadiene and 1,5-cyclooctadiene are effective regulators.<sup>16</sup> Cobalt-based polybutadiene is characterized by a high degree of branching and hence good processability. A two-level fractional factorial design model was also developed to study the solution polymerization of butadiene in a batch reactor using a commercially used

catalytic system (Co octoate/Et<sub>2</sub>AlCl/water).<sup>10</sup> The supported cobalt-based catalyst was also reported to be highly active in the high *cis*-1,4-polymerization of butadiene.<sup>17</sup>

3.1c *Nickel-based Z-N catalysts:* Nickel-catalysed 1,4-*cis*-polybutadiene, first developed by Bridgestone,<sup>9</sup> is typically less branched than commercial cobalt polybutadiene but exhibits an equally high *cis*-content up to 98%. The polymer is also characterized by a large molecular weight distribution of 4–5 giving the material good processability. The commercial catalyst system comprises nickel naphthenate/BF<sub>3</sub>.O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>/Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> which is as useful as cobalt-based catalyst for 1,4-*cis*-polymerization of butadiene. Catalytic activity is influenced by reaction conditions such as temperature, etc. Many mechanistic studies of this system have been undertaken due to the unique ability of nickel to readily form stable metal-allyl complexes.<sup>18</sup>

3.1d *Other transition metal-based Z-N catalyst:* Stereospecific polymerization of conjugated dienes using transition metals such as rhodium, ruthenium, iron, chromium, molybdenum and vanadium are also known in the literature.<sup>19</sup> Cr and Mo-based catalysts provide mainly 1,2-vinyl polybutadienes. Cr-compounds such as Cr(acac)<sub>3</sub> along with alkyl aluminium give apparently hydrocarbon-soluble active catalyst system for conjugated dienes. Soluble catalysts are formed from Mo-compounds such as Mo(acac)<sub>3</sub> or MoO<sub>2</sub>(acac)<sub>2</sub> on reaction with alkyl aluminium in the presence of ethyl acetate or sulphides. Heterogeneous vanadium-based catalysts derived from VCl<sub>3</sub>, VOCl<sub>3</sub> or VCl<sub>4</sub> and AlR<sub>3</sub> or AlR<sub>2</sub>Cl have been developed

**Table 6.** Dependence of *cis*-content (%) on the different types of metal halide.

Metal	Iodine	Bromine	Chlorine	Fluorine
Titanium	93	87	75	35
Cobalt	50	91	98	93
Nickel	10	80	85	98
Neodymium	97	97	96	96

for the polymerization of conjugated dienes affording polymers with predominant 1,4-*trans* monomeric units.<sup>20</sup>

### 3.1e Lanthanide and actinide based Z-N catalysts:

The most recent catalyst system developed for the commercial production of high *cis*-polybutadiene is based on the rare earth metal neodymium. In the 1980s, Bayer and Enichem developed a manufacturing process based on neodymium catalyst.<sup>10</sup> The catalyst derived from compounds of lanthanide and actinide metals is used in the preparation of conjugated dienes polymers with high 1,4-*cis* content. The catalyst based on cerium, neodymium and uranium derivatives is especially effective in conjugated dienes polymerization.<sup>21</sup> In the early 1960s, catalysts based on uranium such as  $U(Al)_4-AlEt_2Cl$  and  $U(OR)_4-AlEt_2Cl_2$  were studied.<sup>21</sup> Uranium-based catalysts were found to be highly effective and afforded polymer with 1,4-*cis* content as high as 99%. However, despite excellent activity, uranium-based catalysts have not attained commercial utilization because of residual radioactivity in the polymer. On the other hand, cerium-based catalysts also have some disadvantage owing to the fact that cerium residue remaining in the polymer may catalyse the oxidation of polymers. Therefore, the interest was focused on neodymium-based catalysts which do not present the disadvantages of uranium and cerium.

Major advantages of Nd-catalyst over other catalyst systems lie in the aliphatic solvents that can be used with Nd, the wide range of temperature ( $-70^\circ$  to  $130^\circ C$ ) and the properties of the resulting polybutadiene. In contrast to d-electron transition metal (Ti, Co, Ni, etc.) catalyst system, the Nd-based catalyst systems operate in aliphatic solvents. Aliphatic solvents are cheaper, less toxic and easier to remove in the solvent-stripping process.<sup>10</sup> The Nd-catalysts are stable to higher temperature without affecting the *cis*-content of the polymer. The polymer produced from Nd-based catalyst is characterized by a linear macrostructure and a very high *cis*-content of greater than 98% giving the rubber excellent abrasion and fatigue performance. However, the high, linearity and higher molecular weight, make this rubber more difficult to process than the other high *cis*-polymers. New versions of neodymium polybutadiene are now available, which contain long chain branches reducing cold flow and improving processability while maintaining a high *cis* microstructure.<sup>10,21</sup>

### 3.1f Single-site metallocene based Z-N catalysts:

The use of single-site metallocene-based catalysts has

provided better information on the relationship of monomer structure and polymerization chemoselectivity and stereospecificity. The homogeneous single-site Z-N-based catalysts consist of half-sandwich metallocenes such as  $CpTiCl_3$ ,  $CpTi(OR)_3$ ,  $[CpTiCl_2]_x$  in combination with methylaluminoxane, etc.<sup>22</sup> The Ti-based catalyst affords polymers with better 1,4-*cis* monomeric units for 1,3-butadiene. Apart from homogeneous catalysts, conjugated dienes have been polymerized using supported half-sandwich metallocene-based catalysts. In contrast to monoolefin polymerization where the conjugate dienes act as donors of two electrons, polymerization of conjugated dienes catalysed by half-sandwich metallocene-based catalysts may occur because the conjugate dienes can act as a donor of four electrons. Isoprene polymerization was reported by supported  $CpTiCl_3$  on alumina-silica gels.<sup>23</sup> Stereo-specificity of the polymer was reported to be dependent upon the type of the support used during the polymerization reaction.

### 3.2 Allyl derivatives of transition metals as catalysts

Activity and stereospecificity of  $\pi$ -allylic metal catalysts for conjugated dienes polymerization depend both on the type of metal and on the nature of the ligand attached to the metals. Although some catalysts of the  $\pi$ -allylic type exhibit activity and stereospecificity comparable with those of Z-N-based catalysts, they have not been used at commercial level. One of the possible reasons may be that well-defined  $\pi$ -allylic type polymerization catalysts produce low molar mass *cis*-1,4-polybutadienes in contrast to the multi-component industrial catalyst system. Development of nickel-allyl complexes commences investigation on the stereochemistry of butadiene and other conjugated dienes polymerization reactions.<sup>24</sup> A wide range of cationic nickel allyl complexes by varying ligands and counter-anions was reported for stereospecific butadiene polymerization.<sup>25</sup> Polymer microstructure depends strongly on the nature of X ligand.<sup>24,25</sup> Presence of electron-withdrawing groups with allylic metals complexes such as Cl or anionic ligands such as  $F_3CCOO^-$ , etc. yields a polymer with high 1,4-*cis* contents. On the other hand, addition of electron donors or Lewis bases to allylic metal complexes yields a drop in the 1,4-*cis* content of the polymer.<sup>26</sup> The 1,4-*cis* polybutadiene-specific allylnickel trifluoroacetate catalyst alters the stereospecificity of the polymer to equibinary eb-1,4-*cis*/1,4-*trans*-polybutadiene on addition of an electron donor such as benzene during the polymerization.<sup>25,26</sup> Supported heterogeneous  $\pi$ -allylic

metal catalysts have also been studied and have shown improved performance compared to their unsupported counterparts.<sup>27</sup>

Polymerization of 1,3-butadiene using various important Z-N-based catalyst systems is summarized in table 7.

### 3.3 Transition metal salts as catalysts

In contrast to monoolefins, conjugated dienes can undergo stereospecific polymerization using transition metal salts without any activators such as alkyl aluminiums, etc. Such types of catalyst include both monometallic and bimetallic precursors, e.g.,  $\text{RhCl}_3$ ,  $\text{Rh}(\text{NO}_3)_3$  and  $\text{CoCl}_2\text{-AlCl}_3$ , etc.<sup>28</sup> The Rh-metal-based salts exhibit better activity during polymerization of butadiene with predominantly 1,4-*trans*-monomeric unit in the protic solvents. Bimetallic catalysts such as  $\text{TiCl}_4\text{-Ni}(\text{PCl}_3)_4$ ,  $\text{CoCl}_2\text{-AlCl}_3$ ,  $\text{Ni}(\text{CO})_4\text{-VCl}_4$ ,  $\text{Ni}(\text{CO})_4\text{-WCl}_6$ , etc. afford polymers with better 1,4-*cis* monomeric unit for butadiene polymerization.<sup>28</sup>

## 4. General mechanistic principles

General mechanism of stereospecific polymerization of conjugated dienes with metal-complex-based catalyst follows insertion-type polymerization.<sup>3,6</sup> After the insertion of the coordinated monomer, the growing chain end being in the form of an  $\eta^3$ -allylic ligand is attached to the metal centre. Then, polymer growth occurs by repetitive insertion of the monomer into the metal-carbon bond, alternatively changing its nature from  $\pi$ -allylic to  $\sigma$ -allylic species and vice versa in each prorogation steps.

The initial step of polymerization of conjugated dienes is the insertion of the first monomer molecule which occurs on the metal-allyl bond with the reformation of a new  $\eta^3$ -butenyl group. Growth of the polymer molecule occurs by insertion of the monomer into the  $\eta^3$ -butenyl bond between the transition metal and the last polymerized unit.<sup>3</sup> Finally, the chain termination step of the growing chain can be done by following various methods.

- Transfer with aluminium alkyls.
- Transfer to monomer.
- Using chain transfer agents.
- Mono and bimetallic terminations.

Due to the commercial interest, such termination processes have been studied in detail for *cis*-polymerization of the conjugated dienes. In the case of

living polymerization of conjugated dienes, the degree of polymerization  $n$  increases linearly with the conversion  $C$  of the monomer and can be calculated by the following equation since every metal  $M$  of the catalyst initiates the formation of only one growing chain.

$$n = \{[\text{Monomer}]_0 \cdot C\} / [M].$$

Termination reaction of the growing chain with alkyl aluminium compounds, used as an activator, has been observed in neodymium-catalysed polymerization of 1,3-butadiene. Molecular weight of 1,4-*cis*-polybutadiene was found to decrease by increasing ratio of alkyl aluminium to Nd-catalyst. Commercially, transfer reaction using alkyl aluminium is an effective practical tool in regulating the molecular weight of the 1,4-*cis* polymers. Transfer to monomer type occurs usually in the Co-catalyzed *cis*-polymerization reactions. In such a polymerization, molecular weight of the polymer initially increases with monomer concentration and then remains constant.

Another approach to control the molecular weight of the *cis*-polymer is the deliberate addition of foreign chemicals such as alkenes or non-conjugated dienes along with polymerization catalyst, which are known as a chain transfer agents (CTA), regulators or modifiers. A variety of alkenes, non-conjugated dienes have been used as CTA and among them, allene, 1, 2-butadiene and 1,5-cyclooctadiene were found to be most effective.<sup>16</sup> However, Gippin reported that the cobalt-amine complexes are also effective in reducing molecular weight of the polymer.<sup>15</sup> Commercially, in cobalt-based processes, 1,2-butadiene is used as a CTA to control the molecular weight of the BR. Industrial utilization of 1,2-butadiene and/or allene as a CTA has some serious concerns, such as being expensive and having an impact on the price of final product; and being an extremely flammable compressed gas it can lead to handling and dosing difficulties. The CTA are particularly effective even at very low concentrations.

For mono- and bimetallic termination, principally, two types of chain termination reactions can occur. In the first type, a mononuclear termination can take place by abstracting hydrogen from the growing chain with the formation of M-H bond (scheme 2). The second type, bimetallic termination which involves haemolytic cleavage of the metal-allyl bond leading to polymer chain bearing free radicals and metal, undergoes the lower oxidation state (scheme 3). The radical chain will form a terminated polymer either by coupling with another free radical or by disproportionation or by hydrogen abstraction from the polymer solvent.

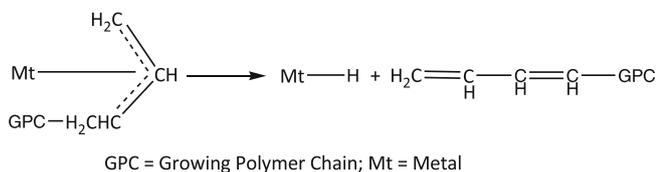
**Table 7.** Polymerization of 1,3-butadiene using various Z-N-based catalyst system.

Catalyst system	1,4- <i>cis</i> (%)	1,4- <i>trans</i> (%)	1,2-vinyl (%)
<b>Titanium-based Z-N catalysts</b>			
TiCl <sub>4</sub> -AlI <sub>3</sub> -AlHCl <sub>2</sub> .OEt <sub>2</sub>	93	2.5	4.5
Ti(OBu) <sub>4</sub> -AlEtCl <sub>2</sub>	–	93–94	–
Ti(OR) <sub>4</sub> -AlR <sub>3</sub>	–	–	95
<b>Cobalt-based Z-N catalysts</b>			
Co(OCOR) <sub>2</sub> -AlEt <sub>2</sub> Cl-H <sub>2</sub> O	98	1	1
Co(acac) <sub>2</sub> -CS <sub>2</sub> -AlR <sub>3</sub>	–	–	99–100
Co(acac) <sub>2</sub> -AlEt <sub>3</sub>	–	–	90–95
<b>Nickel-based Z-N catalyst</b>			
Ni(OCOR) <sub>2</sub> -BF <sub>3</sub> .OEt <sub>2</sub> -AlEt <sub>3</sub>	97	–	–
Ni(acac) <sub>2</sub> -AlEt <sub>2</sub> Cl	90	–	–
<b>Other transition metal-based Z-N catalysts</b>			
VCl <sub>3</sub> -AlEt <sub>3</sub>	–	98–99	–
V(acac) <sub>3</sub> -AlEt <sub>3</sub>	–	–	90–95
Cr(acac) <sub>3</sub> -AlEt <sub>3</sub>	–	–	95–97
Cr(PhCN) <sub>6</sub> -AlEt <sub>3</sub>	–	–	100
Mo(acac) <sub>3</sub> -AlR <sub>3</sub>	–	–	80
Mo(OR) <sub>2</sub> Cl <sub>2</sub> -AlR <sub>3</sub>	49	2	49
Rh(acac) <sub>3</sub> -AlR <sub>3</sub>	–	98	–
<b>Lanthanide and actinide-based Z-N catalysts</b>			
Ce(OCOR) <sub>3</sub> -AlEt <sub>2</sub> Cl-AlR <sub>3</sub>	97	–	–
Pr(OCCl <sub>3</sub> ) <sub>3</sub> -AlEt <sub>2</sub> Cl-Al( <i>i</i> -Bu) <sub>3</sub>	98	–	–
Nd(OCCl <sub>3</sub> ) <sub>3</sub> -AlEt <sub>2</sub> Cl-Al( <i>i</i> -Bu) <sub>3</sub>	97–99	–	–
Nd(OCOR) <sub>3</sub> - <i>t</i> -BuCl-Al( <i>i</i> -Bu) <sub>2</sub> H	98	–	–
U(OR) <sub>4</sub> -AlEtCl <sub>2</sub>	99	–	–
<b>Single-site metallocene-based Z-N catalysts</b>			
CpTi(OBu) <sub>3</sub> -[Al(Me)O] <sub>x</sub>	82	2	16
CpTiCl <sub>3</sub> -[Al(Me)O] <sub>x</sub>	80	2	18
<b>Allyl-derivatives of transition metals as a catalyst</b>			
Ni( $\eta^3$ -C <sub>3</sub> H <sub>5</sub> )OCOCF <sub>3</sub>	96	2	2
Ni( $\eta^3$ -C <sub>3</sub> H <sub>5</sub> )OC <sub>6</sub> H <sub>2</sub> Br <sub>3</sub>	–	96	4
Ni( $\eta^3$ -C <sub>3</sub> H <sub>5</sub> )OCOCF <sub>3</sub> -EtOH	–	96	4
[Ni( $\eta^3$ -C <sub>3</sub> H <sub>5</sub> )SbPPh <sub>3</sub> ]PF <sub>6</sub>	88	9	3
[Ni( $\eta^3$ -C <sub>3</sub> H <sub>5</sub> )P(OPh) <sub>3</sub> ]PF <sub>6</sub>	5	94	1
Ni( $\eta^3$ -C <sub>4</sub> H <sub>7</sub> )OCOCF <sub>3</sub> -F <sub>3</sub> CCOOH	50	50	–
Ni( $\eta^3$ -C <sub>3</sub> H <sub>5</sub> )OCOCF <sub>3</sub> -PhNO <sub>2</sub>	50	50	–
Ni( $\eta^3$ -C <sub>3</sub> H <sub>5</sub> )OCOCF <sub>3</sub> -C <sub>6</sub> H <sub>6</sub>	49	50	1
Ni( $\eta^3$ -C <sub>3</sub> H <sub>5</sub> ) <sub>2</sub> -SnCl <sub>2</sub>	52	47	1
Ni( $\eta^3$ -C <sub>3</sub> H <sub>5</sub> ) <sub>2</sub> -SnI <sub>4</sub>	–	95	5
Nb( $\eta^3$ -C <sub>4</sub> H <sub>7</sub> ) <sub>2</sub> Cl	91	5	4
Nb( $\eta^3$ -C <sub>4</sub> H <sub>7</sub> ) <sub>3</sub>	–	–	100
Cr( $\eta^3$ -C <sub>3</sub> H <sub>5</sub> ) <sub>2</sub> Cl	90	6	4
Cr( $\eta^3$ -C <sub>3</sub> H <sub>5</sub> ) <sub>3</sub>	1	9	90
Cr( $\eta^3$ -C <sub>3</sub> H <sub>5</sub> ) <sub>3</sub> -0.5O <sub>2</sub>	–	93	7
Mo( $\eta^3$ -C <sub>3</sub> H <sub>5</sub> ) <sub>4</sub>	–	2	98
Co( $\eta^3$ -C <sub>4</sub> H <sub>7</sub> ) <sub>3</sub> .2HCl	91	1	8
Co( $\eta^3$ -C <sub>8</sub> H <sub>13</sub> )C <sub>4</sub> H <sub>6</sub>	1	1	98
U( $\eta^3$ -C <sub>3</sub> H <sub>5</sub> ) <sub>3</sub> X (X = Cl, Br, I)	98	1	1

#### 4.1 Chemo- and stereo-selectivity of polymerization reactions

Chemoselectivity of the polymerization of conjugated dienes, i.e., the predominant formation of 1,4-monomeric unit against 1,2-monomeric unit in the

resulting polymer mostly depends on the mode of addition of incoming monomer to  $\eta^3$ -butenyl bond between the transition metal and the last polymerized unit (scheme 4). A  $\eta^3$ -butenyl group has two reactive points; C(1) and C(3). Addition of incoming monomer *vis.* Mt-C(1) bond gives rise of a 1,4-monomeric unit (*cis*- or



**Scheme 2.** Mechanism of mononuclear termination.

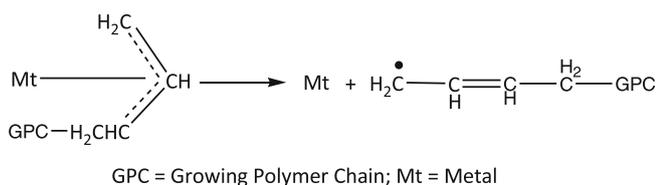
*trans*-, respectively), whereas on the other hand, addition via Mt-C(3) bond gives rise to a 1,2-monomeric unit. The factors, which determine the type of such addition reaction for various catalysts, are mostly electronic and steric in nature.

Formation of a 1,4-*cis* or 1,4-*trans*-monomeric unit is related to the structure, *anti*- or *syn*- of the last polymerized unit. In the coordination polymerization of butadiene, the last inserted monomeric unit, i.e., the butenyl group as an  $\eta^3$ -ligand to the metal, may exist in one of the two forms, *anti*- and *syn*- forms. The situation becomes more complex in the case of non-symmetrically substituted conjugated dienes as many structures and *syn*- as well as *anti*- forms can exist (scheme 5). A plausible scheme for the formation of 1,4-*cis* and 1,4-*trans* monomeric units for butadiene polymerization is shown below in scheme 6.

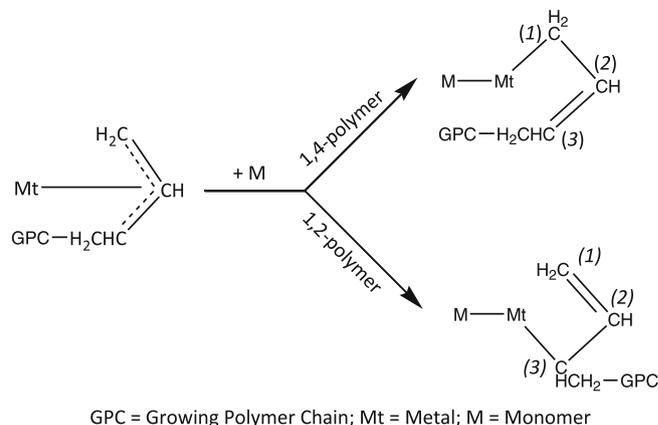
As depicted in scheme 6, the *anti* form gives rise to the formation of 1,4-*cis*-monomeric unit, whereas the *syn* form leads to 1,4-*trans* unit. A conjugated diene can coordinate to a transition metal by only one double bond, as an *s-trans*- $\eta^2$  ligand or with two double bonds as a *s-cis*- $\eta^4$  or as *s-trans*- $\eta^4$  ligand.<sup>29</sup> The *anti*- and *syn*-forms of the  $\pi$ -allylic ligand are in equilibrium. If the rate of *anti*- to *syn*- isomerization is greater than that of rate of monomer insertion, the 1,4-*trans*- monomeric unit can be generated either involving a pathway (1)-(4) and (2)-(4) or involving a pathway (6)-(5)-(4). On the other hand, when the rate of isomerization is lower than the rate of insertion, the 1,4-*cis*-monomeric units can be obtained by involving a pathway (6)-(7).

## 5. 1,4-*cis*-Polybutadiene manufacturing processes

Polybutadiene can be manufactured by a number of processes, including bulk, solution, suspension, emulsion,



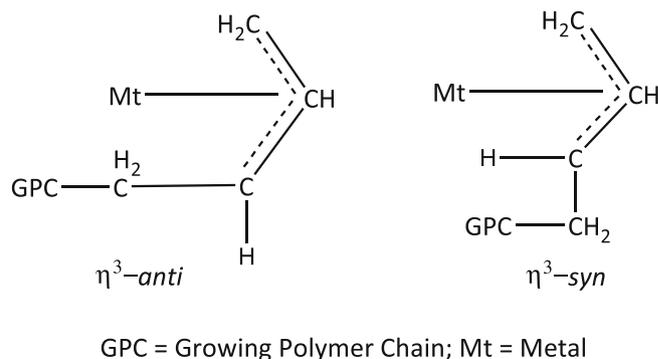
**Scheme 3.** Mechanism of bimetallic termination.



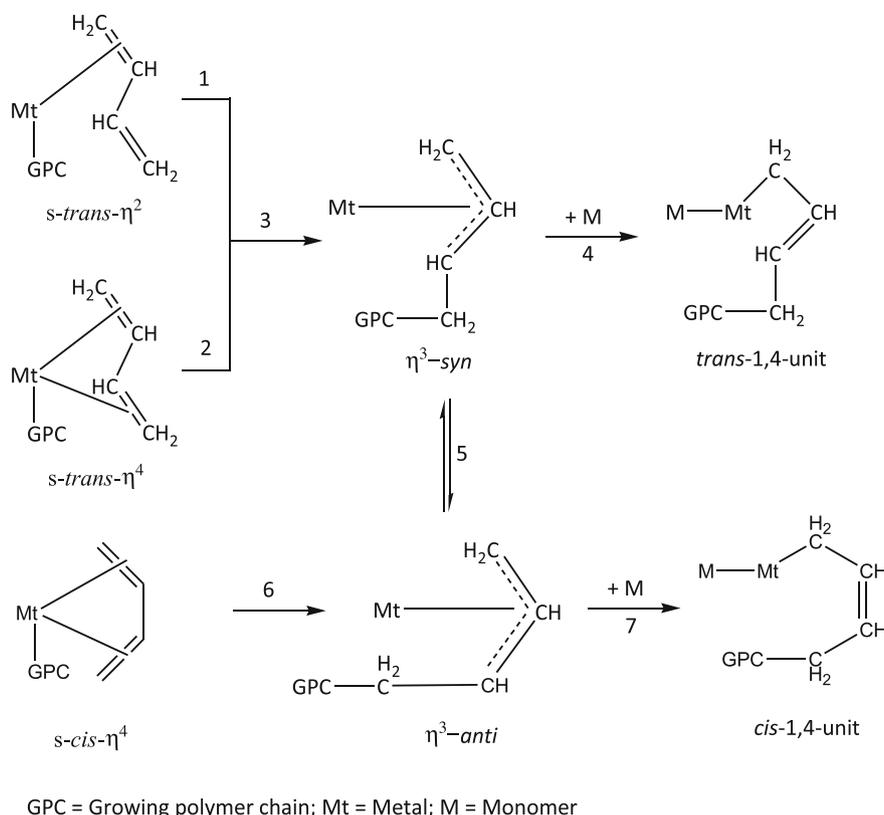
**Scheme 4.** Pathway of chemo-selective 1,4- and 1,2-polymer formation.

and gas-phase polymerizations.<sup>3,30</sup> Production of 1,4-*cis*-polybutadiene (BR) technologies are the most predominant, which is carried out mainly in solution processes using Z-N-type catalysts. Feed requirements for the Z-N-based solution polymerization is very stringent because various materials such as water, oxygen, etc. are known to be destructive to these catalysts. Major global manufacturers are listed in table 8.

In general, at higher temperatures, the rate of polymerization increases and the solution viscosity decreases, resulting in better heat transfer in such exothermic solution polymerization reactions.<sup>6</sup> However, higher temperature may have impact on the earlier deactivation of the catalyst and stereo-selectivity of the resulting polymer. Polymerization is carried out at pressure sufficient to maintain the monomer butadiene substantially in the liquid phase. Aspects of different technologies and resultant products are depicted in table 9.



**Scheme 5.** *Anti*- and *syn*- forms of coordination polymerization.



**Scheme 6.** Plausible mechanism of *cis*- and *trans*-monomeric unit formation during polybutadiene polymerization.

### 5.1 Titanium-polybutadiene (Ti-BR)

The first commercial use of Ti-based catalyst made from  $\text{TiI}_4$  and  $\text{AlR}_3$  was developed by Phillips.<sup>12,30</sup> Rate of polymerization increases with increasing amount of catalyst, while the molecular weight and the 1,4-*cis*-content of the resulting polymer decrease. Catalyst requirement has been measured to be 2–5 mmol  $\text{TiI}_4/\text{kg}$  of BR and the turnover number of about  $(2-5) \times 10^3$  mol of butadiene/(mol.Ti.h). The exact amount of active catalyst was difficult to determine due to poor solubility of  $\text{TiI}_4$  in hydrocarbon solvents. Other soluble commercial catalysts e.g.,  $\text{TiCl}_4/\text{I}_2/\text{AlR}_3$  and  $\text{Ti}(\text{OEt})_3/\text{TiCl}_4/\text{AlEt}_3$  were also developed and utilized at commercial level.<sup>12,13,30</sup>

### 5.2 Cobalt-polybutadiene (Co-BR)

Use of cobalt catalyst in the production of high *cis*-1,4-polybutadiene has been known since 1955. Only soluble compounds such as cobalt-octanoate or cobalt-naphthenate have practical use at commercial level.<sup>8,30</sup> As co-catalyst, alkyl aluminium halides such as diethyl aluminium chloride or ethyl sesquichloride are used. The catalyst attains its highest activity only in the

presence of small amount of water or other donors. Requirement of the catalyst has been measured as 0.1–4 mmol/kg of butadiene. A change in the monomer concentration has an effect on the product quality. High butadiene content causes the formation of gel that can coat the walls of the reaction vessels and pipelines; consequently smooth operation is disrupted. Aromatic compounds (especially benzene) are used as a solvent. During the course of polymerization, branching of polymer grows with increasing conversions and the final rubber properties are strongly influenced by final monomer conversion.

### 5.3 Nickel-polybutadiene

This process was developed by Bridgestone Tyre Co. in 1959, using catalyst components comprising nickel carboxylate, boron trifluoride-diethyl ether complex and trialkyl aluminium.<sup>9,30</sup> On a commercial level, BR is produced by using nickel naphthenate/ $\text{BF}_3 \cdot \text{OEt}_2/\text{Al}(\text{C}_2\text{H}_5)_3$ . Use of  $\text{BF}_3 \cdot \text{OEt}_2$  increases the catalyst activity as well as the molecular weight of the resulting polymer. Requirement of the nickel catalyst has been measured as 0.2–0.6 mmol/kg

**Table 8.** Major global producers of 1,4-*cis*-polybutadiene rubber.

Manufacturer	Country
JSR	Japan
Karbochem Division of Sentrachem	South Africa
Kumho Petrochemical Co. Ltd.	Korea
LG Chemical	Korea
Michelin et CIE	France
Nippon Zeon	Japan
Petrobras Energia S.A.	Argentina
Petkim	Turkey
PETROFLEX-Industria e Comercio	Brazil
Petro China	China
Eferemov Synthetic Rubber Enterprise	Russia
Nizhnekamskneftekhim	Russia
Voronezh Syntezkauchuk	Russia
SINOPEC	China
TSRC Corporation	Taiwan
Thai Synthetic Rubber	Thailand
UBE Industries	Japan
Asahi Chemicals	Japan
Qenos	Australia
Lanxess (Bayer AG)	Germany, USA, France
Chi Mei Corporation	Taiwan
Dow Chemical (Buna GMBH)	Germany, France
Dynasol Elastomers	Mexico, Spain
Polimeri	UK, Italy, France
Firestone Polymers	USA
Goodyear	USA
Reliance Industries Limited	India

of butadiene. Catalyst activity as well as the microstructure of the polymer is influenced by the reaction temperature. Aromatic hydrocarbons mixed with aliphatic hydrocarbons are used as solvents. Apart from the Z–N-based catalyst used industrially, till date, only the structure of nickel catalyst has been demonstrated.<sup>30</sup>

#### 5.4 Neodymium–polybutadiene

In the 1980s Bayer and Enichem developed a manufacturing process based on Nd-based Z–N catalyst.<sup>10,21,30</sup> The catalyst system consists of three components; a carboxylate of Nd-, an alkyl aluminium and a

**Table 9.** Technological and the obtained product features of the existing solution processes for the production of high *cis*-BR.

Technology	Cobalt-based	Nickel-based	Titanium-based	Neodymium-based
Solvent	Benzene, Cyclohexane	Aliphatic solvents, Toluene, Benzene	Benzene, Toluene	Hexane, Cyclohexane
Total solids (wt%)	14–22	15–16	11–12	18–22
Monomer conversion (%)	55–80	<85	<95	~ 100
Maximum polymerization Temperature (°C)	80	80	50	120
<i>cis</i> -1,4-Content (%)	96	97	93	98
T <sub>g</sub> (°C)	–106	–107	–103	–109
Linearity of products	Adjustable	Branched	Linear	Highly linear
Distribution of molar mass	Medium	Low	High	High
Cold flow	Adjustable	Low	High	High
Gel content	Variable	Medium	Medium	Extremely low
Color	Colourless	Colourless	Coloured	Colourless
Availability of tyre grades	Yes	Yes	Yes	Yes
Availability of HIPS grades	Yes	No	No	Yes
Availability of ABS grades	Yes	No	No	No

Lewis acid containing halide. A typical catalyst system is neodymium (II)neodecanoate/diisobutyl aluminium/butyl chloride. Nd-based catalyst systems allow independent control of the main structural parameters such as molecular weight and their distributions, etc. Molecular weight can be controlled via the polymerization temperature, catalyst concentration and ratio of alkyl aluminium/Nd-compounds.

## 6. Concluding remarks and path forward

Polymerization catalysis plays an inevitable role in the sustenance of the ever-growing synthetic elastomer business. Since the discovery of synthetic elastomer, a variety of polymerization catalysts such as homogenous and heterogeneous Z-N-based, single-site metallocene-based, allyl-derivatives of transition metal-based, have been attempted and commercially utilized. Research and development is focused mainly upon the investigation of polymer properties obtained while using various transition metals, ligands and activators during polymerization reaction. On the other hand, many polymerization catalysts were investigated to understand the mechanism for the polymerization reaction of conjugated dienes such as 1,3-butadiene, etc. The chemo- and stereo-selectivity during polymerization reaction depend mostly upon the type of the transition metal, ligands and activators employed.

Further advancement of polymerization catalysts for the production of synthetic elastomers is being carried out to meet stringent demands such as low rolling resistance, fuel economy in target application areas such as tyres and automobile industries. For tyres and automobiles industries, the choice of micro- and macro-structure of synthetic elastomers is too strict and critical. Such intrinsic properties of synthetic elastomers can be very well-controlled by the type of polymerization catalyst employed during polymerization reaction. Development of commercial catalysts and process from titanium-based to the latest neodymium-based are a strong evidence of the promising future of catalysis in the synthetic elastomer business. Globally, the demand for elastomers is estimated as ~30 MT/annum by 2020 with ~67% share of synthetic rubber. Demand for synthetic elastomers depends mainly upon the rapid growth of the tyre and automobile industries. Utilization of classical Z-N-based catalyst systems at the commercial level is an unambiguous evidence of the most feasible and economical catalytic pathway for the large-scale production of synthetic elastomers. On the other hand, the single-site metallocene-based and allyl-derivatives of transition metal based

catalysts systems have also shown promising potential. However, research and development of such novel polymerization catalysts, apart from the classical Z-N-based catalyst system, is being carried out to obtain tyre-grade high molecular weight polymers with precise control upon chemo- and stereo-selectivity.

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