

# Catalysts for Synthesis of Ethylene-Propylene-Diene Rubbers

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Ethylene-propylene-diene rubbers (EPDM) are one of the most important polyolefin materials widely commercialized and used in various industries in recent years. The production of EPDM is based solely on catalytic coordination polymerization processes. The development of new catalysts and processes for the synthesis of EPDM has expanded the range of products and their manufacturing in terms of energy efficiency, processability, and environmental safety.

Keywords: single-site catalyst ; ethylene ; propylene ; diene ; EPDM ; rubber

## 1. Introduction

Ethylene-propylene-diene rubbers (EPDM) are ternary copolymers of ethylene, propylene, and non-conjugated dienes, 5-ethylidene-2-norbornene (ENB), dicyclopentadiene (DCPD), and 5-vinyl-2-norbornene (VNB). These elastomeric materials are used as materials showing excellent resistance to heat, air, ozone, and steam <sup>[1][2][3][4]</sup>.

EPDM is produced using Ziegler-type ion-coordination polymerization catalysts. Homogeneous catalytic systems developed in the early 1960s and widely used up to now include a combination of a vanadium precatalyst ( $\text{VCl}_4$ ,  $\text{V}(\text{acac})_3$ , more often  $\text{VOCl}_3$ ) and an organoaluminum cocatalyst ( $\text{AlEt}_2\text{Cl}$ ,  $\text{AlEt}_3$ ,  $\text{Al}_2\text{Et}_3\text{Cl}_3$ ) in slight excess to the precatalyst ( $\text{Al}/\text{V} \sim 10$  mol/mol), as well as chlorine-containing promoters such as ethyltrichloroacetate, *n*-butylperchlorocrotonate, etc. <sup>[3][5][6][7]</sup>. These catalytic systems provide the formation of random, fully amorphous terpolymers with a high ratio of comonomers incorporation showing very good elastomeric properties and operating in a wide temperature range ( $-50$ – $+130$  °C). However, these systems show low activity ( $80$ – $120$  kg of copolymer/mol<sub>V</sub>) and poor catalytic stability even at  $20$ – $60$  °C. The consequence of low activity is the high residual content of a catalyst and promoters in the polymer, which is highly toxic and has a negative effect on the properties of the copolymer. The presence of undesirable impurities requires additional technological operations to remove them.

New opportunities in the synthesis of EPDM are opened by single-site catalytic systems based on metallocene, constrained geometry, half-sandwich, and post-metallocene chelate complexes of Group IVB transition metals. As compared to vanadium ones, these systems have a number of advantages such as high activity, stability at elevated temperatures, single-site nature of active sites, which ensures uniformity of molecular weight characteristics, the microstructure of terpolymers, and, hence, the possibility of creating EPDM with desired properties. It is worth emphasizing that in recent years, there has been a surge of interest in the world's main elastomer manufacturers (ARLANXEO, Dow Elastomers, ExxonMobil, Mitsui Chemicals, etc.) to new-generation single-site catalytic systems, likely caused by more stringent requirements for the environmental safety of production and properties of products. A wide range of EPDM properties produced on these systems by the world's leading manufacturers can be illustrated in **Table 1**.

**Table 1.** EPDM characteristics of leading manufacturers.

EPDM Manufacturer	Polymer Grade	Ethylene Content, wt%	Diene (ENB) Content, wt%	Mooney Viscosity ML1+4(125 °C) <sup>1</sup>	Polymer Structures	Ref.
ARLANXEO	Keltan <sup>®</sup>	44–71	0–11.0	22–92	LCB <sup>2</sup> , ND <sup>3</sup> , MD <sup>4</sup> , BD <sup>5</sup>	<sup>[8]</sup>
DOW Elastomers	Nordel <sup>™</sup>	50–85	0–8.5	18–85	ND, MD, BD	<sup>[9]</sup>
ExxonMobil	Vistalon <sup>™</sup>	54–77	0–10.0	16–82	LCB, ND, MD, BD	<sup>[10]</sup>

EPDM Manufacturer	Polymer Grade	Ethylene Content, wt%	Diene (ENB) Content, wt%	Mooney Viscosity ML1+4(125 °C) <sup>1</sup>	Polymer Structures	Ref.
Mitsui Chemical	Mitsui EPT™	41–72	0–14.0	40–78	LCB, ND, MD, BD	[11]
KumhoPolychem	KEP®	55–71	0–10.0	23–95	No data	[12]

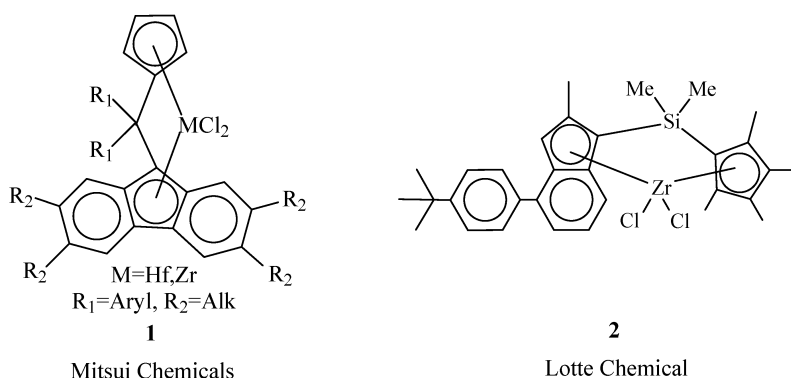
<sup>1</sup> Mooney viscosity is the routine industry standard correlated with molecular weight of EPDM. High Mooney viscosities are preferred. Abbreviation according to ASTM D1646 is ML 1+4 (125 °C), where M—Mooney units, L—large rotor, 1—the sample preheat time (min), 4—the sample test time (min) at 125 °C. <sup>2</sup> Long Chain Branching. <sup>3</sup> Narrow molecular weight distribution. <sup>4</sup> Medium molecular weight distribution. <sup>5</sup> Broad molecular weight distribution.

## 2. Single-Site Catalysts

### 2.1. Metallocene Catalysts

Metallocene catalysts (MC) are a broad class of Group IVB complexes in which a transition metal is bounded by  $\pi$ -bonds to two cyclopentadienyl rings of substituted or unsubstituted ligands: Cyclopentadienyl (Cp), indenyl (Ind), and fluorenyl (Flu) [13][14].

Promising for producing EPDM are two types of complexes: metallocenes of Cs symmetry [4][5][6][7][8] and zirconocenes of C1 symmetry [9]. The capabilities of Cs symmetry catalysts in the synthesis of EPDM can be demonstrated by the patent data of Mitsui Chemicals [16][17][18][19][20]. They claim a new effective class of hafnocene and zirconocene complexes of type **1** (Figure 1) containing different substituents in both the bridging group and the peripheral positions of the Flu ligand. When activated with  $\text{CPh}_3\text{B}(\text{C}_6\text{F}_5)_4$  (4 and 10 equiv.), the complexes effectively provide ternary copolymerization of E/P/ENB at 80–120 °C. Hafnocenes **1** ensure the incorporation of ENB at a level of 7–11 wt% and form elastomers with high molecular weights ( $M_w = 1000\text{--}2000$  kDa) [16][17][18]. The compounds with  $R_1 = 4\text{-MePh}$ ,  $4\text{-MeOPh}$ ,  $4\text{-Me}_2\text{NPh}$  and  $R_2 = \text{Me}$  show the highest activity up to a 10,000–20,000 kg copolymer/(mol<sub>Hf</sub> h atm)). Zirconocenes **1** show high efficiency in the synthesis of well-vulcanizing VNB terpolymers with a low degree of branching [19]. Such copolymers cannot be obtained by using conventional vanadium and other metallocene systems. The content of VNB in this EPDM reaches 10 wt%. The molecular weights range from 50 to 600 kDa.



**Figure 1.** Chemical structures of MCs **1** and **2**.

Another promising type of MC catalysts for the synthesis of EPDM is a new group of complexes of type **2** (Figure 1) developed by Lotte Chemical [20]. Their activity upon activation with MAO in the ternary copolymerization of ethylene, propylene, and ENB reaches 155,000–190,000 kg copolymer/(mol<sub>Zr</sub> h) at 80 °C. Terpolymers with  $M_w = 163\text{--}209$  kDa,  $M_w/M_n = 5.6\text{--}9.3$ , and ENB content up to 7.1–8.5 wt% have been obtained.

In the vast majority of publications, MAO (or modified MAO) and perfluoroaryl borates are reported to be used to activate metallocene precatalysts in the synthesis of polyolefins [13][14][21][22][23], including EPDM [4][15][16][17][18][19][24][25][26]. However, MAO is too expensive, unstable during storage, and is used in large molar excess to the precatalyst. The borates are extremely sensitive to impurities and demonstrate unstable polymerization kinetics. Thus, the development of new effective inexpensive activators of MC is an actual task that should also be noted.

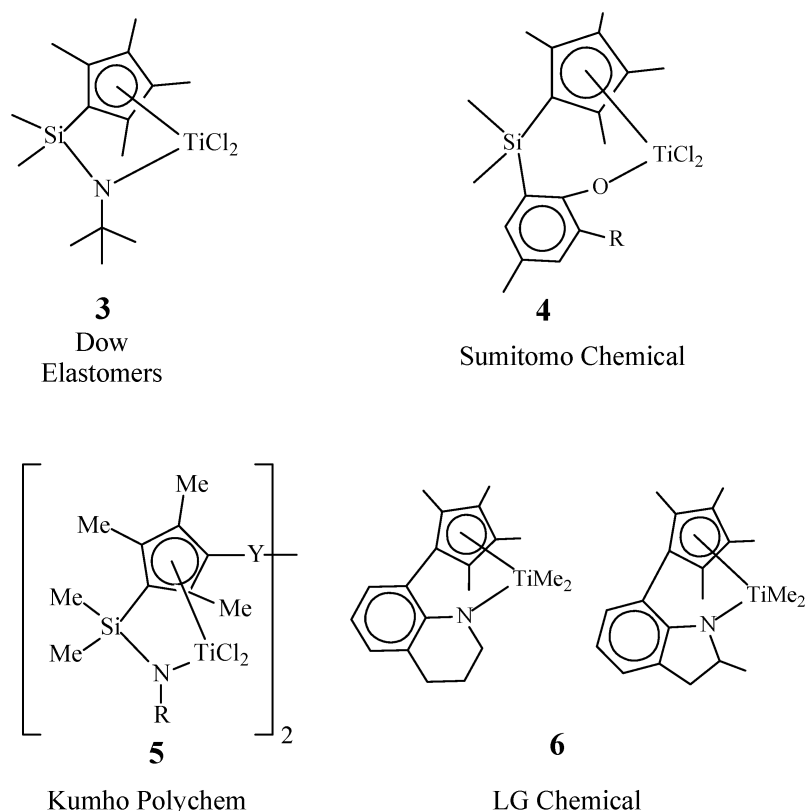
Among promising alternative activators, the following can be noted. Thus, researchers from the Uniroyal Chemical Comp successfully employ a mixture of boraryl compounds  $\text{LiB}(\text{C}_6\text{F}_5)_4$  and  $\text{B}(\text{C}_6\text{F}_5)_3$ , which provide higher process stability even at elevated temperatures [15]. Other new effective activators for the synthesis of EPDM based on isobutylaluminumoxanes

$(-O-Al(Bu^i)_3)_n$  and isobutylaluminum aryl oxides  $(Al(Bu^i)_3)_3-kOAr_k$  have been proposed [27][28][29][30][31][32]. These compounds effectively activate MC precatalysts at low molar excess (200–300 molar equiv.) and, unlike conventional MAO-based systems, allow the production of copolymers with a low content of propylene blocks, which determines their good elastomeric properties.

## 2.2. “Constrained” Geometry Complexes

Special attention in the synthesis of EPDM is paid to bridged monocyclopentadienyl complexes, the so-called “constrained” geometry complexes (CGCs). CGCs contain  $h^5$ -Cp-ligand linked by a bridging group with a donor ligand (Don). The bridging group reduces the Cp–M–Don angle by approximately 20–30° as compared to Cp–M–Cp, which ensures high availability of a transition metal in the active site and, thus, a high degree of comonomer incorporation [24][22][23]. The donor is linked to the transition metal by a  $\sigma$ -bond and ensures high stability of catalysts of this type at elevated temperatures (up to 160–180 °C). Variations in any part of the CGC ligands as well as the type of transition metal affect catalytic properties of the complexes, such as activity, the ability to insert comonomer(s), and molecular weight characteristics of the resulting polymers.

CGCs **3** (Figure 2) were commercialized by DOW in the mid of the 1990s for homogeneous polymerization processes used for production of linear low-density polyethylene [23][24][25][26]. Complexes of this type are also effective for the synthesis of EPDM [25][26], which allowed DOW to launch a wide range of elastomers (Nordel™ IP). CGCs provide production of EPDM with a wide range of  $M_w$  (up to 500 kDa), composition (up to 50 wt% of propylene and 7.5 wt% of ENB), and the Mooney viscosity ( $ML1+4(125^\circ C)=18-85$ ).



**Figure 2.** Chemical structures of CGCs **3-6**.

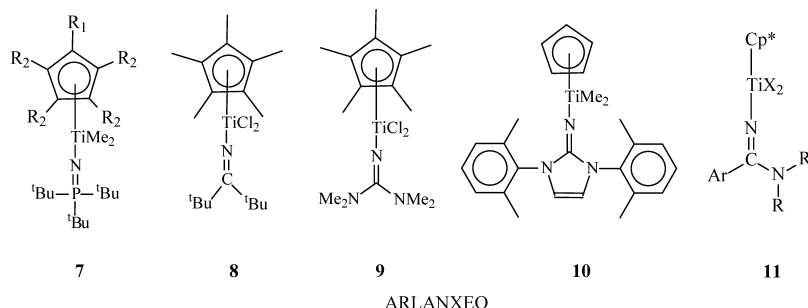
In recent years, one can note increasing interest to catalysts of this type from several leading EPDM manufacturers. From the late 1990s to the present, active developments in the field of CGC molecular design have been carried out at Sumitomo Chemical, KumhoPolychem, and LG Chem, which have made it possible to significantly expand the range of promising catalysts for the synthesis of EPDM [27][28][29][30][31][32][33][34].

## 2.3. Half-Sandwich Titanium Complexes

Another promising class of catalysts for the synthesis of EPDM are half-sandwich titanocenes **7–11** (Figure 3) containing N-donor ligands [35][36][37][38][39][40][41][42][43][44][45][46][47][48][49][50][51][52]. Catalysts are included in the new technology was called Keltan Advanced Catalyst Elastomer (Keltan ACE™)

Keltan ACE™ catalysts are characterized by high catalytic activity (up to 1200 tons copolymer/(mol<sub>Ti</sub> h)) in ternary copolymerization of olefins and dienes and make it possible to obtain copolymers with a high content of dienes (up to 15 wt% of ENB, 5 wt% of VNB and 20 wt% of DCPD). Most of these catalysts are stable in copolymerization processes at temperatures up to 120°C and form copolymers with high M<sub>w</sub> values up to 2000 kDa. A variety of developed complexes of this type makes it possible to obtain EPDM with a wide range of properties [40][41][42][43][44][45][46][47][48][49][50][51][52].

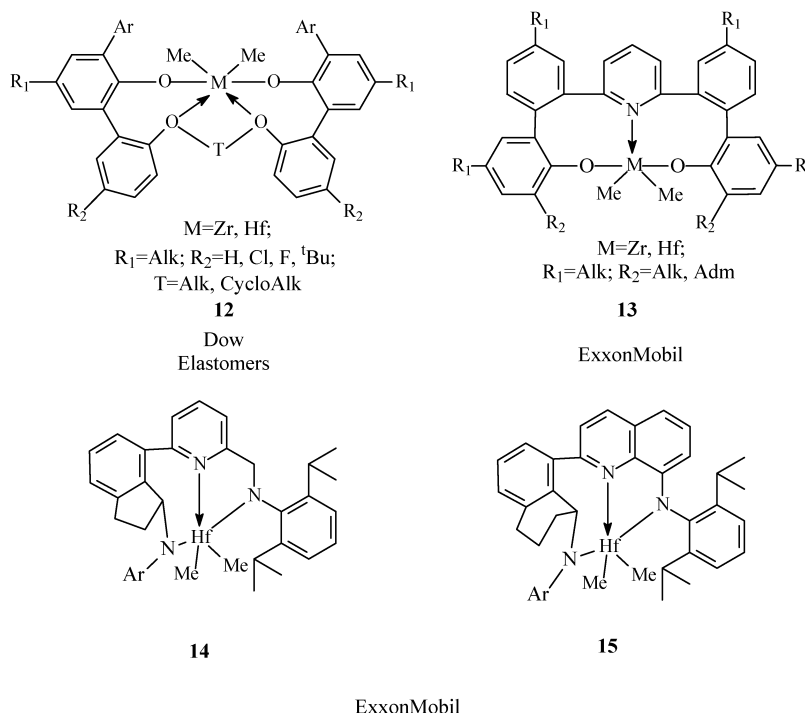
On the basis of Keltan ACE™ technology, large-scale production of EPDM has been organized at the plants in Geleen, Netherlands, and Changzhou, China, each with listed annual capacity of 160000 tons, along with 40000 tons per year in Triunfo, Brazil [39][54][55].



**Figure 3.** Chemical structures of half-sandwich titanium complexes 7-11.

## 2.4. Post-MetalloceneChelate Catalysts

The most promising catalysts of this class for the synthesis of EPDM are aryloxyether<sup>12</sup> complexes of hafnium and zirconium (**Figure 4**). The compounds were discovered using the approaches of Combinatorial Chemistry and High-Throughput Screening [56][57][58][59][60] and have been actively developed by Dow Elastomers for the last 15 years [25][61][62][63][64][65][66][67][68][69][70][71][72][73][74][75].



**Figure 4.** Chemical structures of aryloxyether<sup>12</sup> complexes.

Aryloxyether complexes **12** have the most unique catalytic characteristics and by sum of properties surpass many known classes of catalysts for the production of EPDM [25][61][62][63][64][65][66][67][68]. The advantages of the catalysts are the ability to be effectively activated by low molar amounts of the activator (Al<sub>MAO</sub>/M=10-200, B<sub>borate</sub>/M up to 5 mol/mol), and high activity in copolymerization processes in high-temperature solution polymerization conditions (120-180°C). The advantage of a high-temperature process carried out in the solution polymerization (the polymer is soluble in the reaction medium) is the formation of amorphous copolymers with broad molecular weight distribution. A feature of these systems is also their ability to form copolymers with high molecular weights (M<sub>w</sub>=100-1000 kDa) and low content of gel fraction [25]. Such catalysts were used to obtain rubbers with a high content of propylene (up to 50 wt%) and diene comonomers of various types (ENB, VNB, DCPD, etc., up to 16 wt%). Aryloxyether complexes are the basis of highly efficient Advanced

Molecular Catalyst technology (AMC) developed in 2015 for obtaining new Nordel™ rubber grades with improved properties [25]. Based on this technology, a plant with annual capacity of 200 thousand tons of EPDM was launched in Plakimin (USA) in 2018 [69].

### 3. Conclusions

In conclusion, it should be noted that despite the fact that EPDM have being produced by the industry for more than 50 years, there is a high potential in both improving the technologies for the synthesis of EPDM and expanding the range of their grades. This potential is ensured by the development of new-generation catalytic systems based on Group IVB complexes, which are alternatives to low-activity, unstable, and toxic vanadium catalysts. In particular, this is evidenced by high research activity over the past 10–15 years of the world's leading manufacturers of EPDM in the development of new systems and their active commercialization. The main advantage of modern systems compared to vanadium ones is their environmental safety, higher activity, and thermal stability, with the possibility of producing EPDM with different contents of comonomers and microstructures, including highly branched and bimodal terpolymers. The use of these catalytic systems has already made it possible to bring to market new grades of EPDM with a wide range of properties (for example, Keltan® (ARLANXEO), Nordel™ IP (Dow Elastomers), Vistalon™ (Exxon), Mitsui EPT™ (Mitsui), etc.).

The huge potential for tuning the structures of catalytic systems allows researchers to count on the further creation of new efficient systems for the synthesis of EPDM and, accordingly, the production of elastomers with a high content of diene(s) and the creation of new polymer microstructures with an even wider range of properties.

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