

# Catalysts for Synthesis of Ethylene-Propylene-Diene Rubbers

Subjects: [Chemistry, Applied](#) | [Polymer Science](#) | [Others](#)

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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.

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 [\[1\]\[2\]\[3\]\[4\]](#).

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 ( $\text{Al/V} \sim 10$  mol/mol), as well as chlorine-containing promoters such as ethyltrichloroacetate, *n*-butylperchlorocrotonate, etc. [\[3\]\[5\]\[6\]\[7\]](#). 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®	44–71	0–11.0	22–92	LCB <sup>2</sup> , ND <sup>3</sup> , MD <sup>4</sup> , BD <sup>5</sup>	[8]
DOW Elastomers	Nordel™	50–85	0–8.5	18–85	ND, MD, BD	[9]
ExxonMobil	Vistalon™	54–77	0–10.0	16–82	LCB, ND, MD, BD	[10]
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—new 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.

1. Noordermeer, J.W. Ethylene-Propylene Elastomers. In Encyclopedia of Polymer Science and Technology, John Wiley & Sons: New York, NY, USA, 2002; pp. 178–196.

2. Single-Site Catalysts

2. Ravishankar, P.S. Treatise on EPDM. Rubber Chem. Technol.2012, 85, 327–349.

2.1. Metallocene Catalysts

3. Van Duin, M.; van Doremale, G.; van der Aar, N. Defining EPDM for the past and the next 50 years. KGC2017, 11–12, 14–23.

Metallocene catalysts (MC) are a broad class of Group IVB complexes in which a transition metal is bounded by π-bonds to two cyclopentadienyl rings of substituted or unsubstituted ligands. Cyclopentadienyl (Cp), indenyl (Ind), and fluorenyl (Flu) [13][14]. ethylene-propylene-diene elas-tomers by ion-coordination polymerization on single-site catalytic systems of new generation. Polym. Sci. Ser. C2020, 62, 1–16.

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 [10][11][12]. 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 CpPh<sub>2</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (4 and 10 equiv), the complexes

6. Kapteles, R.; Cross, A.V. EPDM rubber technology. In Handbook of Elastomers, 2nd ed., Bhownick, A.R., Stephens, H.L., Eds, Marcel Dekker: New York, NY, USA, 2001, pp. 845–876.

effectively; Reardon, D.; Combariza, S. Y. P.; En, B.; Zahed, H.; Lemay, C. Vanadium-catalyzed ethylene-propylene copolymerization: the question of the metal oxidation state in Ziegler-Natta polymerization promoted by (3-alkoxy) silyl organometallics. *Organometallics* 1999, 18, 2773–2781. 10,000–20,000 kg copolymer/(mol<sub>Zr</sub>·h·atm)). Zirconocenes **1** show high efficiency in the synthesis of well-vulcanizing VNB

8. ARLANXEOWebsite/Find Products/Ethylene Propylene Diene Rubber. Available online: <https://www.arlanxeo.com/en/products/finder?q=%3aname-asc%3abrandCategory%3akeltan>

terpolymers with a low degree of branching <sup>[19]</sup>. 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.

9. NORDEL™ EPDM Product Selection Guide—265-11001-01-nordel-epdm-product-selection-guide.pdf. Available online: <https://www.dow.com/content/dam/dcc/documents/en-us/catalog-selguide/265/265-11001-01-nordel-epdm-product-selection-guide.pdf> (accessed on 21 June 2022).

10. ExxonMobil/Home/Resources/Technical Data Sheets/EPDM Rubber. Available online: <https://www.exxonmobilchemical.com/en/resources/product-data-sheets/epdm-rubber> (accessed on 21 June 2022).

11. MITSUI EPT™/EPDM Rubber. Available online:

<https://us.mitsui-chemical.com/service/product/mitsui-ept.htm> (accessed on 21 June 2022).

12. KUMHO POLYCHEM Website/EPDM/Overview. Available online:

<https://www.polychem.co.kr/eng/product/epdm?seq=1> (accessed on 21 June 2022).

13. Resconi, L.; Cavallo, L.; Fagnoli, L.; Giannini, F. Selectivity of MCs in propylene polymerization with metallocene catalysts. *Chem. Rev.* 2000, 100, 1253–1346.

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 <sup>[20]</sup>. 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<sub>w</sub> =

153,000 kg/mol, M<sub>w</sub>/M<sub>n</sub> = 1.3. Process for Producing Polyolefin Elastomer Employing a Metallocene Catalyst. Patent US 6225426 B1, 1 May 2001.

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 <sup>[13/14/21/22/23]</sup>, including EPDM <sup>[4/15/16/17/18/19/24/25/26]</sup>. 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. A1, 1 December 2016.

Thus, the development of new effective inexpensive activators of MC is an actual task that should also be noted.

17. Ichino, K.; Kikuchi, Yo.; Tohi, Ya.; Matsugi, T.; Yanagimoto, Ya.; Arino, M.; Shishido, K.; Hosoya, M. Ethylene/α-Olefin/Non-Conjugated Polyene Copolymer, and Production Process and Use Thereof. Patent US 10435494 B2, 08 November 2018.

18. Ichino, K.; Yamaguchi, T.; Aita, Yu.; Noguchi, Yu. Thermoplastic Elastomer Composition, Use Thereof, Method for Producing Same, Ethylene/α-Olefin/Unconjugated Polyene Copolymer and Use Thereof. Patent US 2018/0072877 A1, 15 March 2018.

and, unlike conventional MAO-based systems, allow the production of copolymers with a low content of propylene blocks, which determines their good elastomeric properties.

## 12.2. “Constrained” Geometry Complexes

Chen, H.S.; Xpe, Marks, T.D. Copolymers for metal-catalyzed olefin polymerization. Activators, as well as activation processes, and their catalytic activity relationships. *Chem. Rev.* 2000, 100, 1891–1934. insert comonomer(s), and molecular weight characteristics of the resulting polymers.

20. Hong, Y.J.; Shin, E.H.; Jung, S.W.; Woo, H.Y.; Lee, R.H.; Min, J.K.; Chae, B.H. Process for Ethylene/Propylene/Dieneterpolymer Using New Transition Metal Compound, Patent KR 101792956 B1, 11 March 2017.

21. Chen, H.S.; Xpe, Marks, T.D. Copolymers for metal-catalyzed olefin polymerization. Activators, as well as activation processes, and their catalytic activity relationships. *Chem. Rev.* 2000, 100, 1891–1934. insert comonomer(s), and molecular weight characteristics of the resulting polymers.

22. Zijlstra, H.S.; Harder, S. Methylalumoxane—History, production, properties, and applications. *Eur. J. Inorg. Chem.* 2015, 2015, 19–43.

CGCs **3** (Figure 2) were commercialized by DOW in the mid of the 1990s for homogeneous polymerization of ethylene and propylene. The chemistry of catalyst activation. The case of group 4 polymerization catalysts is effective for the synthesis of EPDM, *Polym. Bull.* 2016, 73, 473–491.

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 ( $ML1+4(125^\circ\text{C})=18-85$ ).

Comparative analysis of ethylene/diene copolymerization and ethylene/propylene/diene terpolymerization using ansa-zirconocene catalyst with alkyl-aluminum/borate activator: The effect of conjugated and nonconjugated dienes on catalytic behavior and polymer micro-structure. *Molecules* 2021, 26, 2037.

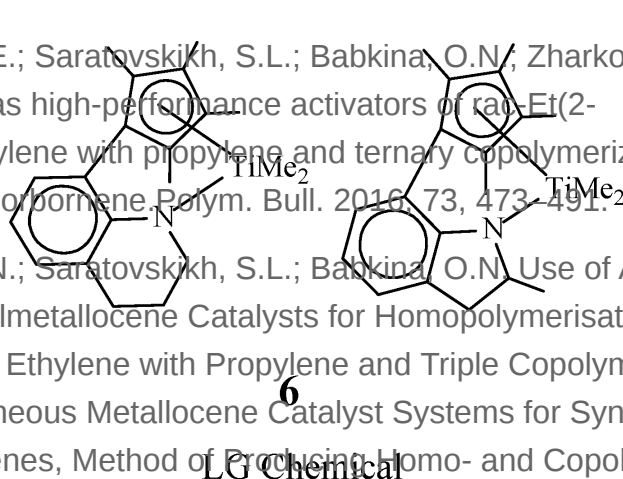
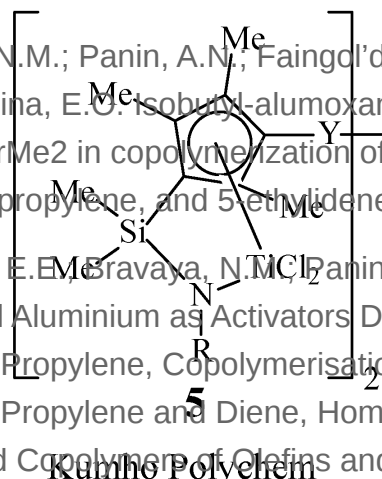
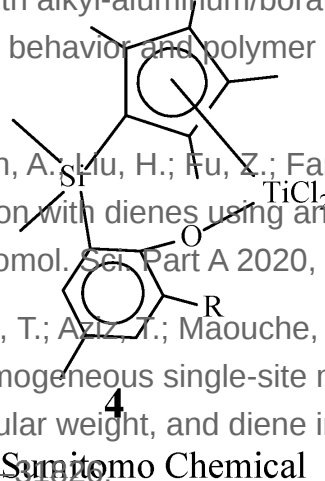
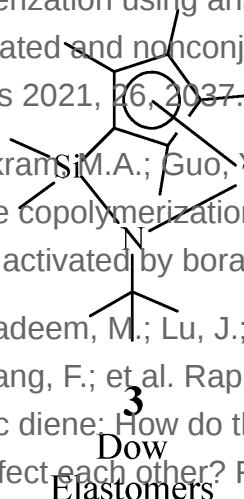
25. Ali, A.; Akram, M.A.; Guo, Y.; Wu, H.-L.; Liu, W.; Khan, A.; Liu, H.; Fu, Z.; Fan, Z. Ethylene-propylene copolymerization and their terpolymerization with dienes using ansa-zirconocene catalysts activated by borate/alkylaluminum. *J. Macromol. Sci. Part A* 2020, 57, 156–164.

26. Ali, A.; Nadeem, M.; Lu, J.; Moradian, J.M.; Rasheed, T.; Aziz, T.; Maouche, C.; Guo, Y.; Awais, M.; Zhiqiang, F.; et al. Rapid kinetic evaluation of homogeneous single-site metallocene catalysts and cyclic diene: How do the catalytic activity, molecular weight, and diene incorporation rate of olefins affect each other? *RSC Adv.* 2021, 11, 31817–31826.

27. Bravaya, N.M.; Panin, A.N. Method of Producing Copolymers of Olefin Monomers with Cyclic or Linear Dienes. Patent RU 2477289 C1, 10 March 2013.

28. Bravaya, N.M.; Panin, A.N.; Faingol'd, E.E.; Saratovskikh, S.L.; Babkina, O.N.; Zharkov, I.V.; Perepelitsina, E.G. Isobutyl-alumoxanes as high-performance activators of  $\text{rac-Et(2-MeInd)}_2\text{ZrMe}_2$  in copolymerization of ethylene with propylene and ternary copolymerization of ethylene, propylene, and 5-ethylidene-2-norbornene. *Polym. Bull.* 2016, 73, 473–491.

29. Faingol'd, E.E.; Bravaya, N.M.; Panin, A.N.; Saratovskikh, S.L.; Babkina, O.N. Use of Aryl Oxides of Isobutyl Aluminium as Activators Dialkylmetallocene Catalysts for Homopolymerisation Ethylene, Propylene, Copolymerisation of Ethylene with Propylene and Triple Copolymerisation of Ethylene, Propylene and Diene, Homogeneous Metallocene Catalyst Systems for Synthesis of Homo- and Copolymers of Olefins and Dienes, Method of Producing Homo- and Copolymers of





Olefins and Dienes, Method for Stabilization of Homo- and Copolymers of Olefins and Dienes. Patent RU 2588496 C2, 27 June 2016.

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, Kumho Polychem, 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].

31. Faingol'd, E.E.; Zharkov, I.V.; Bravaya, N.M.; Panin, A.N.; Saratovskikh, S.L.; Babkina, O.N.;

### 2.3. Half-Sandwich Titanium Complexes

Shilov, G.V. Sterically crowded dimethylisobutylaluminumaryloxides: Synthesis, characteristics, and application as activators in homo- and copolymerization of olefins. J. Organomet. Chem.

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

32. Faingol'd, E.E.; Saratovskikh, S.L.; Panin, A.N.; Babkina, O.N.; Zharkov, I.V.; Garifullin, N.O.;

Shilov, G.V.; Bravaya, N.M. Ethylene/propylene and ethylene/propylene/5-ethylidene-2-

Keltan ACE™ technology was called Keltan Advanced Catalyst Elastomer (Keltan ACE™). The catalysts are based on a metallocene (2,6-di-*i*-Bu-2PhO-120Buz) catalyst system, which is a primary copolymerization of ethylene 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

33. Baier, M.C.; Zuideveld, M.A.; Mecking, S. Post-metallocenes in the industrial production of polyolefins. Angew. Chem. Int. Edit. 2014, 53, 9722–9744.

developed complexes of this type makes it possible to obtain EPDM with a wide range of properties [40][41][42][43][44]

34. Braunschweig, M.; Breitling, F.M. Constrained geometry complexes—synthesis and applications.

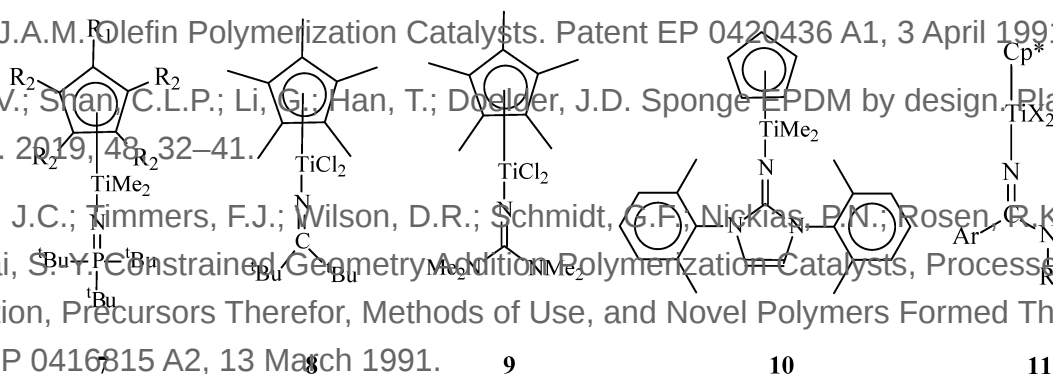
Coord. Chem. Rev. 2006, 250, 2691–2720.

On the basis of Keltan ACE™ technology, large-scale production of EPDM has been organized at the plants in 35. Klosin, J.; Fontaine, P.P.; Figueroa, R. Development of group IV molecular catalysts for high temperature ethylene- $\alpha$ -olefin copolymerization reactions. Account Chem. Res. 2015, 48, 2004–2016.

36. Canich, J.A.M. Olefin Polymerization Catalysts. Patent EP 0420436 A1, 3 April 1991.

37. Thakur, V.; Shan, C.L.P.; Li, G.; Han, T.; Doelder, J.D. Sponge EPDM by design. Plast. Rubber Compos. 2019, 48, 32–41.

38. Stevens, J.C.; Timmers, F.J.; Wilson, D.R.; Schmidt, G.F.; Nicklas, P.N.; Rosen, C.K.; Knight, G.W.; Lai, S.-Y. Constrained Geometry Addition Polymerization Catalysts, Processes for Their Preparation, Precursors Therefor, Methods of Use, and Novel Polymers Formed Therewith. Patent EP 0416815 A2, 13 March 1991.



39. Katayama, H.; Nabika, M.; Imai, A.; Miyashita, A.; Watanabe, T.; Johohji, H.; Oda, Y.; Hanaoka, H.

Transition Metal Complex, Process for Producing the Same, Olefin Polymerization Catalyst

Containing the Transition Metal Complex and Process for Producing Olefin Polymers. Patent US

### 2.4. Post-Metallocene Chelate Catalysts

40. Kim, S.-B.; Goo, H.-R.; Hong, Y.-J.; Lee, M.-H.; Do, Y.-G.; Park, M.-H.; Park, J.-H. Dinuclear Metalocene Catalysts and Process for the Manufacture of EP and EPDM Polymers Using Them. The most promising catalysts of this class for the synthesis of EPDM are aryloxyether zirconium (Figure 4). The compounds were discovered using the approaches of Combinatorial Chemistry and Patent KR 101216691 B1, 28 December 2012.

41. Kim, H.; Hwang, K.; Borden, S.G.; Kim, S.K.; Yoon, S.-C.; Ko, J.S.; Choi, S.-Y. **A Catalyst Composition for preparing 1,5-ethynyl-1,3-butadiene copolymer, and method for preparing elastic copolymer, which comprises ethylene and alpha-olefin or ethylene, alpha-olefin and unconjugated diene, by using same.** Patent US 11220566 B2, 11 January 2022.

42. Park, S.H.; Yoon, S.C.; Kim, M.K.; Ko, J.S.; Park, S.E.; Choi, S.Y. **Elastic Diene Terpolymer and Preparation Method Thereof.** Patent US 9428600 B2, 30 June 2016.

43. Kim, S.K.; Park, S.H.; Yoon, S.C.; Ko, J.S.; Choi, S.Y. **Elastic Diene Terpolymer and Preparation Method Thereof.** Patent US 9493593 B2, 15 November 2016.

44. Yoon, S.-C.; Park, S.-H.; Ko, J.-S.; Choi, S.-Y. **Elastic Terpolymer Including Diene Group and Preparation Method Thereof.** Patent US 9410008 B2, 9 August 2016.

45. Park, S.H.; Yoon, S.C.; Kim, S.K.; Ko, J.S.; Park, S.E.; Choi, S.Y. **Elastic Diene Terpolymer and Preparation Method Thereof.** Patent US 9650460 B2, 16 May 2017.

46. Wang, Q.; Brown, S.J. **Process to Prepare Ethylene Propylene Elastomer.** Patent EP 1162214 A1, 12 December 2001.

47. Windmuller, P.J.H.; van Doremale, G.H.J. **Process for the Production of a Polymer Comprising Monomeric Units of Ethylene, an  $\alpha$ -Olefin and a Vinyl Norbornene.** Patent WO 2005/005496 A2, 20 January 2005.

48. Ijpeij, E.G.; Arts, H.J.; van Doremale, G.H.J.; Beijer, F.H.; van Der Burgt, F.; Zuideveld, M.A. **Process for the Preparation of a Polyolefin.** Patent WO 2005/014601 A2, 17 February 2005.

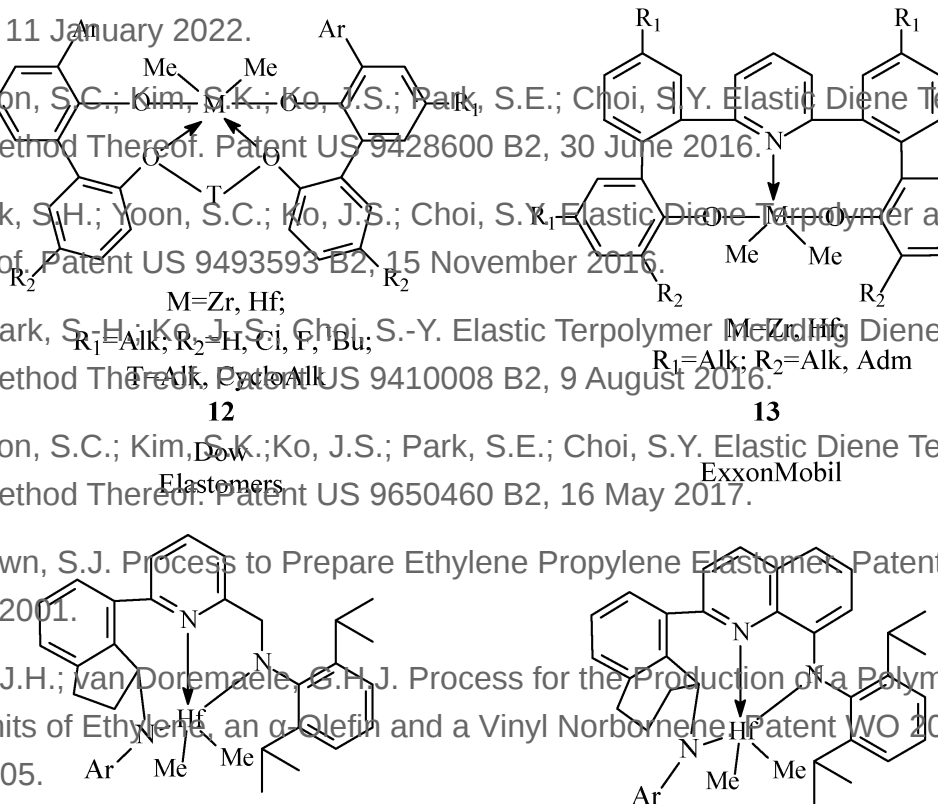
49. Windmuller, P.; Doremale, G. **Process for the Production of a Polymer Comprising Monomeric Units of Ethylene, an  $\alpha$ -Olefin and a Vinyl Norbornene.** Patent US 2006/0205900 A1, 14 September 2006.

50. Windmuller, P.; Doremale, G. **Process for the Production of a Polymer Comprising Monomeric Units of Ethylene, an  $\alpha$ -Olefin and a Vinyl Norbornene.** Patent US 7829645 B2, 9 November 2010.

51. Van Doremale, G.; van Duin, M.; Valla, M.; Berthoud, A. **On the development of titanium K1- (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 ( $M_w$ =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 comonomers of various types (ENB, VNB, DCPD, etc), up to 16 wt%.

52. Van Doremale, G.H.J.; Zuideveld, M.A.; Leblanc, A.; Norambuena, V.F.O. **Catalyst Component for the Polymerization of Olefins Having a Guanidinate Ligand.** Patent US 8987393 B2, 24 March 2015.

53. Ijpeij, E.; Arts, H.; van Doremale, G.; Windmuller, P.; van der Burgt, F.; Zuideveld, M.A. **Polymerization Catalyst Comprising Amidine Ligand.** Patent US 7956140 B2, 7 June 2011.



**Figure 4.** Chemical structures of aryloxyether complexes.

**3. Conclusions**

54. Van Doremaele, G.H.J.; Berthoud, A.; Norambuena, V.Q.; Rupnicki, L.; Karbaum, P. Metal Complex with a Cyclic Amidine Ligand. Patent WO 2015113957 A1, 6 August 2015.

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 polymerization catalysts. Organometallics 2017, 36, 2167–2181.

55. Collins, R.A.; Russell, A.F.; Scott, R.T.W.; Bernardo, R.; van Doremaele, G.H.J.; Berthoud, A.; Mountford, P. Monometallic and bimetallic titanium  $\kappa^1$ -amidinate complexes as olefin polymerization catalysts. Organometallics 2017, 36, 2167–2181.

56. Berthoud, A.; van Doremaele, G.H.J.; Norambuena, V.Q.; Scott, R.; Zuideveld, M.A.; Arts, J.D. Bimetallic Complex Comprising Cyclopentadienyl and Amidine Ligands. Patent US 9862736 B2, 9 January 2018.

One of the main advantages 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.).

57. Van Doremaele, G.H.J.; Zuideveld, M.A.; Mountford, P.; Heath, A.; Scott, R.T.W. Ti Catalyst System Comprising Substituted Cyclopentadienyl, Amidine and Diene Ligand. Patent WO 2011076775 A1, 30 June 2011.

58. Van Doremaele, G.H.J.; Zuideveld, M.A. Borane Activated ti Catalyst System Comprising Amidine and Diene Ligand. Patent WO 20141076772 A1, 30 June 2014.

The high demand for new generations of catalytic systems has led 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.

59. Karbaum, P.; Scott, R.T.W.; van De Moosdijk, J. Metal Complex Comprising Amidine and Substituted Cyclopentadienyl Ligands. Patent US 10472431 B2, 12 November 2019.

60. Berthoud, A.; Van Doremaele, G.H.J.; Scott, R.T.W.; Perez, F.; Bernardo, R. Catalyst System. Patent WO 2017/029141 A1, 23 February 2017.

61. Scott, R.T.W.; Zuideveld, M.A.; Mountford, P. Metal Complex with a Lewis Base Ligand. Patent WO 2014180913 A1, 13 November 2014.

62. Scott, R.T.W.; Bernardo, R.; van de Moosdijk, J.; Berthoud, A. Metall Complex Comprising Amidine and Substituted Cyclo-pentadienyl Ligands. Patent EP 3272761 A1, 24 January 2018.

63. Goryunov, G.P.; Samsonov, O.V.; Uborsky, D.V.; Voskoboynikov, A.Z.; Berthoud, A.; Valla, M. Metal Complex Comprising Amidine and Indole Fused Cyclopentadienyl Ligands. Patent US 20210269465 A1, 2 September 2021.

64. Bernardo, R.; van Doremaele, G.; van Meerendonk, W.; Windmuller, P. Catalyst Mixture. Patent US 20220056162 A1, 24 February 2022.

65. DSM continues to invest in innovative growth in performance materials cluster. Available online: <https://www.pressreleasefinder.com/pr/DSMELPR005/en/> (accessed on 19 May 2022).

66. History | ARLANXEO Website/Customer Portal. Available online: <https://www.arlanxeo.com/en/company/history> (accessed on 19 May 2022).

67. Arlanxeo to close Texas Keltan EPDM plant | Rubber News. Available online: <https://www.rubbernews.com/suppliers/arlanxeo-close-texas-keltan-epdm-plant> (accessed on 19 May 2022).

68. Boussie, T.R.; Bruemmer, O.; Diamond, G.; Goh, C.; Lapointe, A.M.; Leclerc, M.K.; Shoemaker, J.A. Bridged bi-Aromatic Lig-ands, Complexes, Catalysts and Processes for Polymerizing and Polymers Therefrom. Patent WO 03/091262A1, 6 November 2003.
69. Boussie, T.; Bruemmer, O.; Diamond, G.; LaPointe, A.; Leclerc, M.; Micklatcher, C.; Sun, P.; Bei, X. Bridged bi-Aromatic Cat-alysts, Complexes, and Methods of Using the Same. Patent US 20060025548 A1, 2 February 2006.
70. Boussie, T.; Diamond, G.; LaPointe, A.; Leclerc, M.; Micklatcher, C.; Sun, P.; Bei, X. Bridged bi-Aromatic Catalysts, Complexes, and Methods of Using the Same. Patent US 20060052554 A1, 9 March 2006.
71. Boussie, T.R.; Diamond, G.M.; Goh, C.; Hall, K.A.; LaPointe, A.M.; Leclerc, M.; Lund, C.; Murphy, V.; Shoemaker, J.A.W.; Tracht, U.; et al. A fully integrated high-throughput screening methodology for the discovery of new polyolefin catalysts: discovery of a new class of high temperature single-site group (IV) copolymerization catalysts. *J. Am. Chem. Soc.* 2003, 125, 4306–4317.
72. Boussie, T.R.; Diamond, G.M.; Goh, C.; Hall, K.A.; LaPointe, A.M.; Leclerc, M.; Murphy, V.; Shoemaker, J.A.W.; Turner, H.; Rosen, R.K.; et al. Nonconventional catalysts for isotactic propene polymerization in solution developed by using high-throughput-screening technologies. *Angew. Chem. Int. Ed.* 2006, 45, 3278–3283.
73. Konze, W.V.; Vanderlende, D.D. Polyolefin Solution Polymerization Process and Polymer. Patent US 8349984 B2, 8 January 2013.
74. Boone, H.W.; Iverson, C.N.; Konze, W.V.; Vanderlende, D.D. Ethylene/Alpha-Olefin/Diene Solution Polymerization Process and Polymer. Patent US 8299189 B2, 30 October 2012.
75. Konze, W.V.; Stevens, J.C.; Vanderlende, D.D. High Efficiency Solution Polymerization Process. Patent WO 2007/136495 A3, 17 January 2008.

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