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Russ. Chem. Rev., 2025, **94** (9) RCR5184

https://doi.org/10.59761/RCR5184

Coordination copolymerization of α-olefins with non-conjugated polar vinyl monomers: current catalytic approaches and prospects for practical applications

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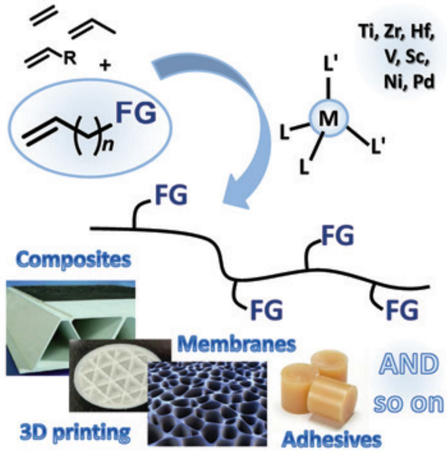
The reactivity of polar vinyl monomers, unsaturated compounds containing functional groups, depends on the presence or absence of conjugation between the C=C bond and the neighbouring unsaturated moieties or donor heteroatoms. Conjugated polar vinyl monomers (acrylates, vinyl ethers, *etc.*) (co)polymerize upon free-radical initiation. The reaction is widely used to produce numerous polymer materials that qualitatively differ from polyolefins in their characteristics. Copolymerization of ethylene, propylene, and higher α-olefins with non-conjugated vinyl monomers containing polar or reactive functional groups gives so-called 'functional polyolefins', that is, polymer materials with unique mechanical and rheological characteristics, increased thermal and oxidative stability, and controlled hydrophilicity. In the synthesis of functional polyolefins, only coordination polymerization, catalyzed by complex compounds of Group 4 metals, V, Sc, Ni, and Pd is effective. This review summarizes for the first time data on the (co)polymerization of polar vinyl monomers catalyzed by early transition metal complexes, discusses the current results achieved in the catalysis of copolymerization of polar vinyl monomers by Group 10 metal complexes, and considers the prospects for practical application of functional polyolefins and for organization of their industrial production. The bibliography includes 272 references.



Keywords: functional polyolefins, polar vinyl monomers, Ziegler–Natta catalysts, metallocene catalysts, post-metallocene catalysts

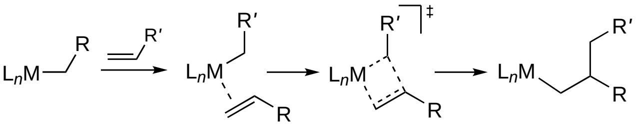
Contents

Received 5 May 2025

1. Introduction

Polyolefins are large-scale products of the modern petrochemical industry, with the annual production output exceeding 200 million tons.[1] Modern polyolefin production processes are based on the coordination (co)polymerization of ethylene, propylene, 1-butene, and higher α-olefins catalyzed by transition metal compounds.[2–6] The large-scale production of popular polyolefin brands makes use of heterogeneous titanium chloride-based Ziegler–Natta catalysts (ZNC)[7] and chromium oxide catalysts.[8] In the production of so-called advanced polyolefins, single-site catalysts based on Group 4 and, more rarely, Group 3, 5, and 6 metal complexes are widely utilized.[2,3,5,6] The mechanism of polymerization in the presence of single-site catalysts (Scheme 1) includes the formation of (L_nM-Alkyl) active species followed by coordination and insertion of an α-olefin molecule *via* a four-center transition state.[6]

Scheme 1

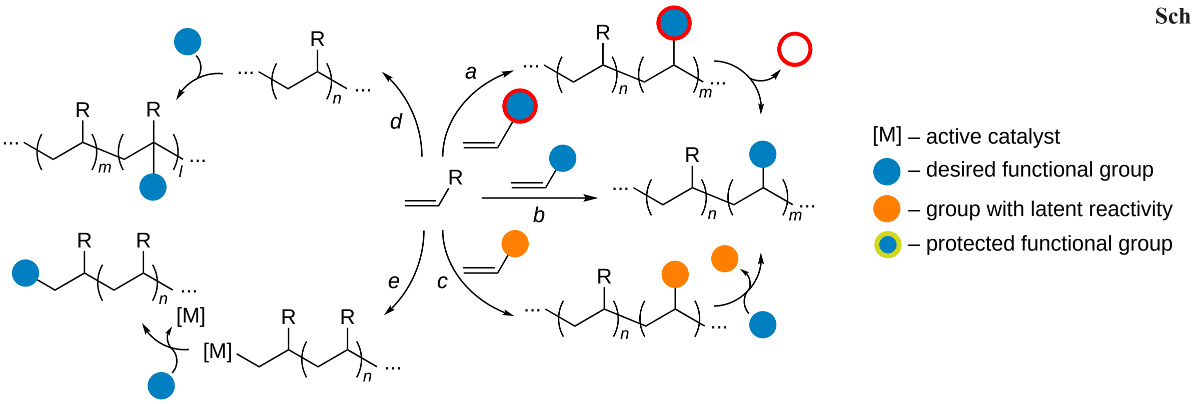


Ethylene and α-olefins are far from being the only type of unsaturated compounds that can (co)polymerize. A broad range of high-demand materials is produced by free-radical (co)-polymerization of conjugated vinyl monomers such as vinyl ethers, acrylates, acrylonitrile, maleic anhydride, and other compounds in which the C=C bond is located near an sp^2-hybridized carbon atom or donor heteroatom. If the C=C bond adjoins to a saturated >CH– group (*i.e.*, it is isolated), free-radical polymerization is complicated by chain termination giving allyl radicals. The synthesis of macromolecular (co)polymers of polar olefins with isolated C=C bonds requires the use of coordination polymerization.

Copolymers of ethylene or α-olefins with non-conjugated polar vinyl monomers of this type, so-called functional polyolefins,[9–11] are promising advanced materials. The presence of polar functional groups expands the range of polyolefin characteristics: increases the hydrophilicity and adhesive properties and qualitatively changes the dielectric constant and mechanical characteristics. Meanwhile, the presence of electron-donating functional groups in the polar comonomer molecules often leads to a critical loss of catalyst activity of early transition metal complexes in the copolymerization, since the donor heteroatom of the functional group is preferably bound to the catalyst active site.[6,12]

The general synthetic approaches to functional polyolefins, as discussed by O'Hare and co-workers[10] and supplemented by our data, are depicted in Scheme 2. The synthesis of functional polyolefins by pathway (**a**) is based on coordination copolymerization of monomers with protected polar groups. Usually, direct copolymerization with polar comonomers (pathway **b**) can be accomplished in the presence of Pd and Ni complexes; the complexes of early transition metals are effective towards copolymerization of monomers that have bulky substituents near the donor heteroatom or have latent reactivity (*e.g.*, ω-halo- or ω-R_2B-substituted α-olefins in which the functional groups are less prone to coordination to the active site), which is followed by post-modification involving introduction of the desired functional groups (pathway **c**). Functionalization of polyolefins (preparation of graft copolymers, pathway **d**) does not allow full control of the copolymer microstructure, while the chain termination with the introduction of a functional group (pathway **e**) does not provide a sufficiently high degree of functionalization.

Scheme 2



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Translation: Z.P.Svitanko

The reviews devoted to copolymerization of α-olefins with polar vinyl monomers address, first of all, actually on copolymerization, with the attention being focused on the catalysts used in this reaction. The results of early studies considering the synthesis of functional polyolefins are summarized in a number of publications.[13–15] Classification according to the type of catalyst is also retained in more recent reviews, most of which supplement the above-mentioned studies[13–15] by new references.[9,16–18] A relevant review is devoted to the stereoselectivity issues in α-olefin copolymerization with polar vinyl monomers in the presence of various types of catalysts.[19] A few reviews published in the 2020s address copolymerization catalyzed by the complexes of Group 10 metals: Ni,[20–22] Pd,[23] or Ni and Pd.[24–26] The α-olefin copolymerization with polar comonomers catalyzed by early transition metal complexes was addressed in a review by Marks and co-workers[27] published in 2020. Copolymerization catalysts based on Group 4 metal complexes are also considered in a recent (2024) review,[28] which focuses on the type of catalysts and comonomers used. Other reviews published in 2024 are devoted to the prospects of application of various types of catalytic systems for the synthesis of functional polyolefins[12] and DFT modelling of polymerization involving polar monomers.[29]

The properties of copolymers prepared using early transition metal-based catalysts and the existing and potential practical applications of the copolymers are barely touched upon in the above publications. Actually, the *properties* of functional polyolefins are addressed only in one review,[30] which considers possible applications of ethylene copolymers with polar monomers, giving vivid, but few examples.

In view of the ability of Group 10 metal-based catalysts to initiate isomerization of the polymer chain to give short-chain branches, particularly early transition metal complexes appear to be the most promising platform for the development of production processes of advanced functional polyolefins with improved mechanical characteristics and novel properties. The present review considers in detail the use of Group 4 metal, Sc, and V complexes (over all years of research) and Ni and Pd complexes (2021–2025) for the copolymerization of ethylene, propylene, and higher olefins with polar and functionalizable vinyl monomers containing no conjugated groups or donor heteroatoms adjacent to the C=C bond, discusses the effect of comonomers of this type on the characteristics of the obtained materials, and evaluates the prospects for practical use of these materials.

The topicality of the subject matter of this review is clearly demonstrated by Fig. 1, which shows the number and rating of publications of 2020–2025 devoted to (co)polymerization of non-conjugated polar olefins.

2. Copolymers of ethylene with polar vinyl monomers

2.1. Copolymerization of ethylene catalyzed by Group 4 metal complexes

The ethylene copolymerization with polar vinyl monomers has been studied since the second half of the 1980s using classic Ziegler–Natta catalysts (such as $3\,TiCl_3 \cdot AlCl_3$) in the early period[31,32] and much more active single-site catalysts, zirconocenes, half-sandwich Ti(IV) complexes (**Ti01**–**Ti12**, **Zr01**–**Zr26**), and post-metallocene Ti, Zr, and Hf complexes (**Ti13**–**Ti59**, **Zr27**–**Zr38**, **Hf01**) activated with methylaluminoxane (MAO), perfluoroarylborane $B(C_6F_5)_3$ (B^F), or perfluoroarylborates $[Ph_3C][B(C_6F_5)_4]$ (TB^F), $[PhNMe_2H][B(C_6F_5)_4]$ (NB^F) in the later period of research.[11,28,31,33–108]

The copolymerization of ethylene catalyzed by Group 4 metal complexes was investigated for a broad range of polar vinyl comonomers **C001**–**C090**.[11,31,33–108] This Section addresses some key patterns identified in the studies of ethylene copolymerization with comonomers of various structural types.

2.1.1. Copolymerization of ethylene with ω-alken-1-ols, hydroxyalkyl norbonenes, and unsaturated alcohol derivatives

The results of studies of ethylene copolymerization with unsaturated alcohols and their derivatives (ethers, silyl ethers) are summarized in Table 1.

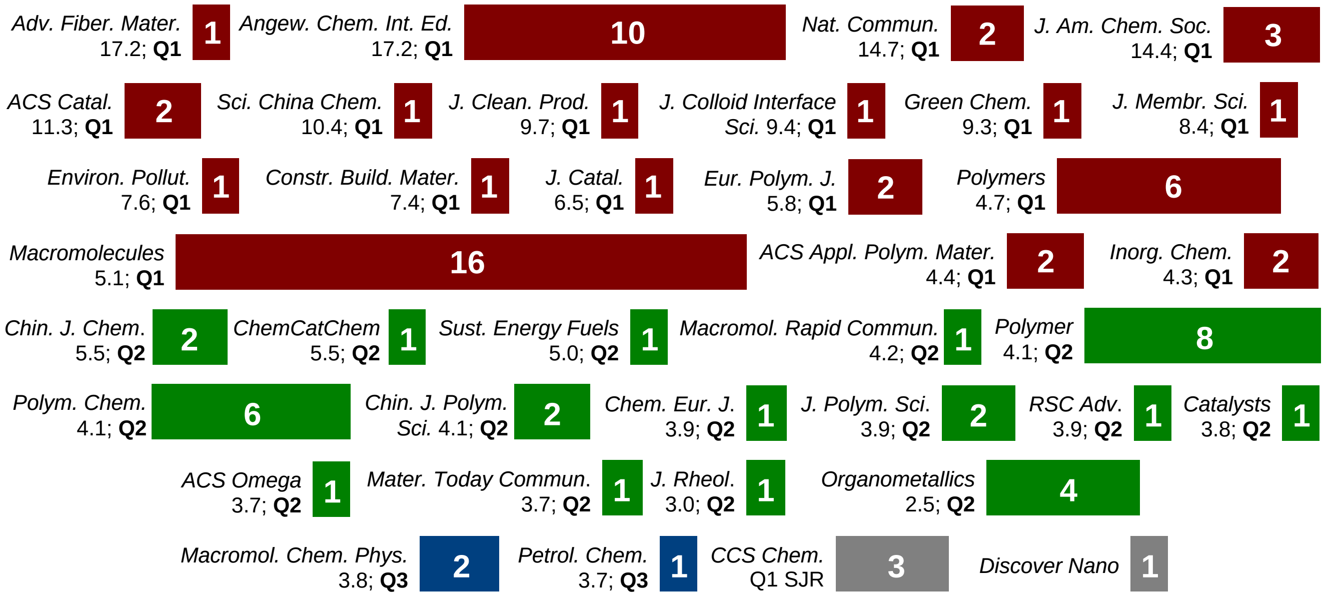
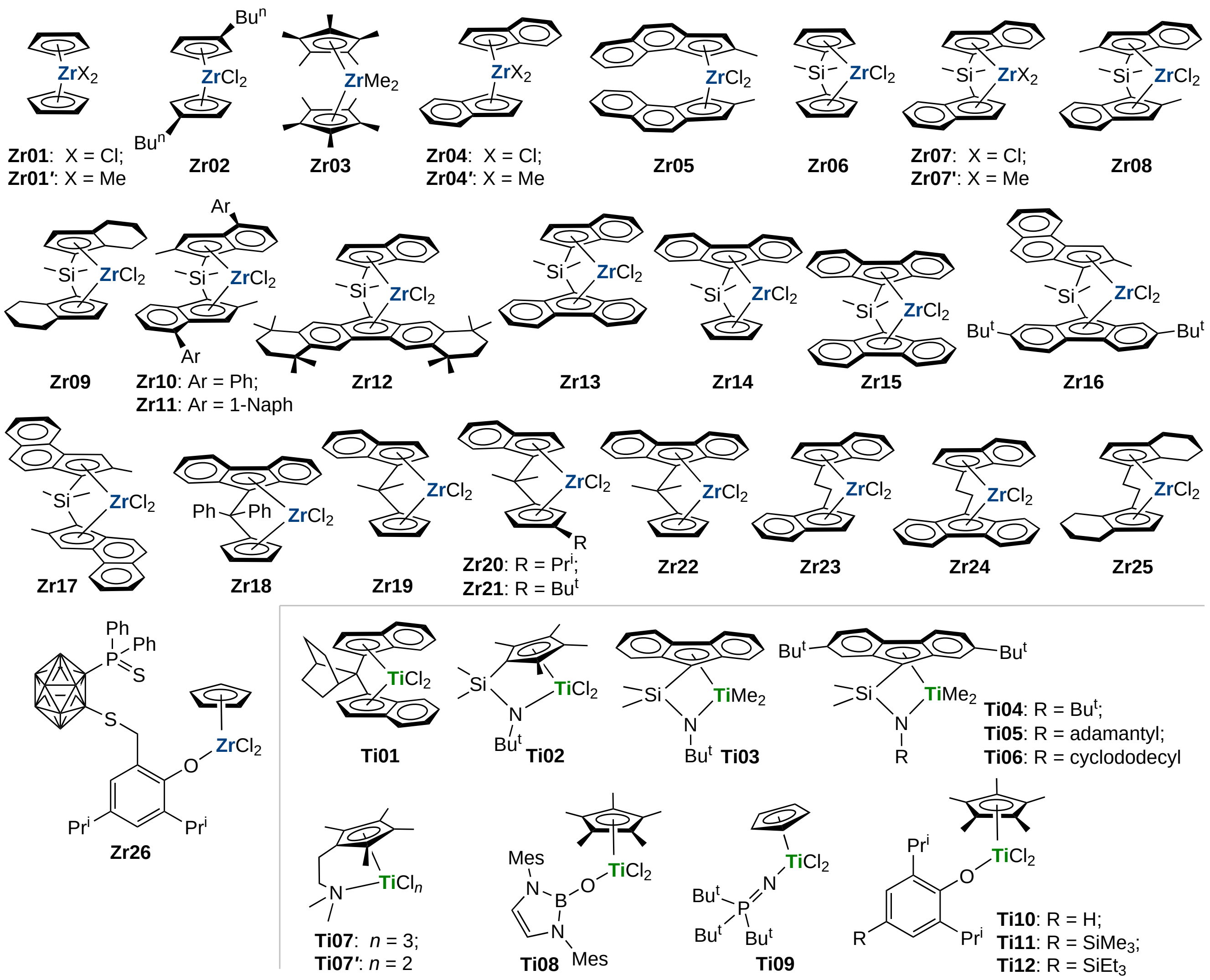


Figure 1. Number and rating of the relevant publications devoted to (co)polymerization of non-conjugated polar olefins.

Structures of metallocene precatalysts Zr01 – Zr26 and Ti01 – Ti12



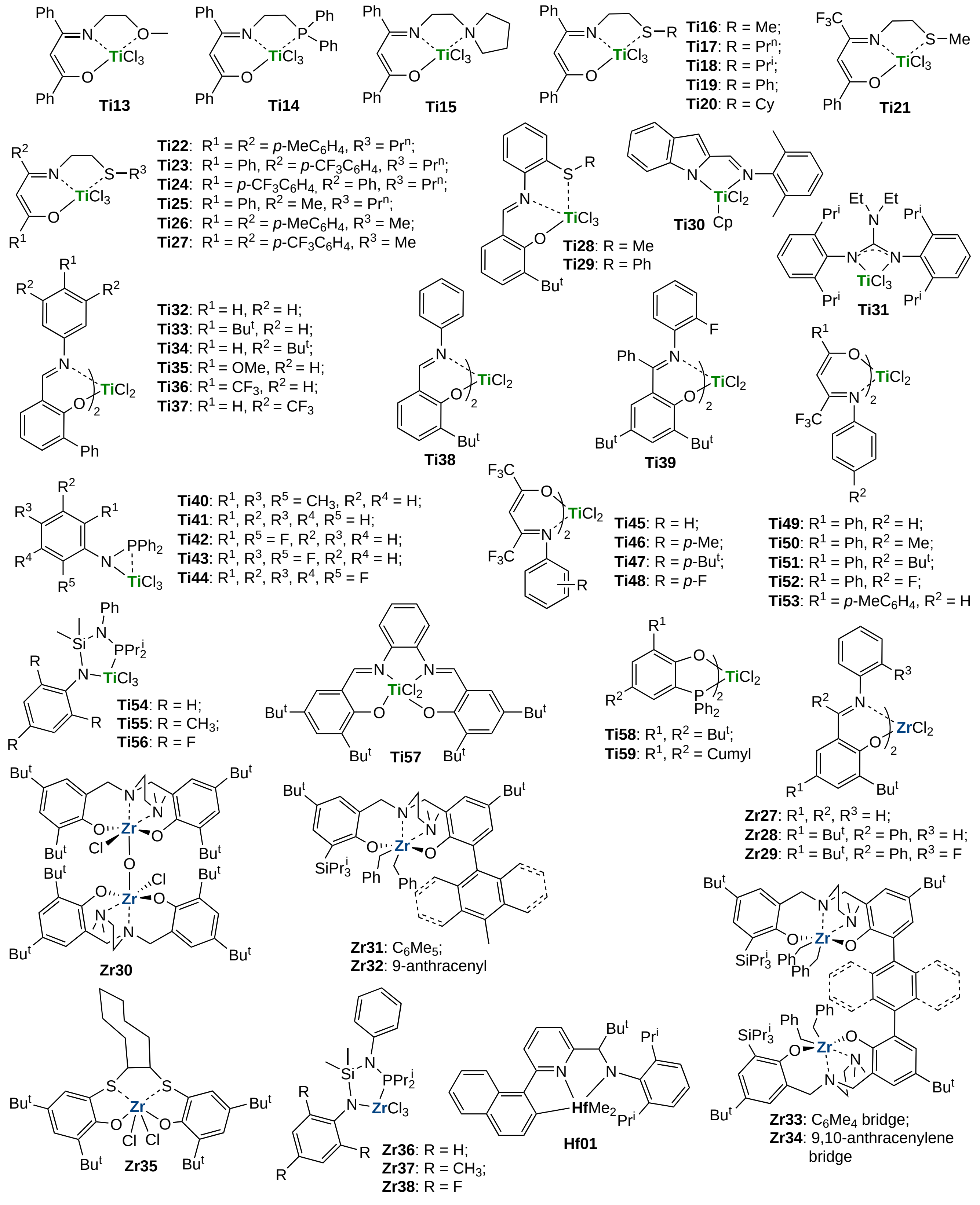
Copolymerization of ω-alken-1-ols catalyzed by Group 4 metal complexes becomes possible after treatment with organoaluminium compounds (OAC) R_3Al, resulting in the formation of aluminum ω-alkenyloxy complexes, as shown in Scheme 3 in relation to the reaction with $^{i}Bu_3Al$. In the subsequent text, adducts of this type are designated by **C###-**AlR_2, indicating the initial polar comonomer and the organoaluminum moiety in the product of reaction between the comonomer and OAC. The alkoxides $CH_2{=}CH(CH_2)_nOAlR_2$ dimerize in non-polar medium,[37,39,76,77] which may complicate copolymerization due to the cross-linking of polymer chains (Scheme 3) giving a gel.[78–80] According to the results of DFT modelling, $CH_2{=}CH(CH_2)_4OAlEt_2$ exists in non-polar media as a trimer (>90%) at 20°C and as a dimer at 130°C.[77]

A study of the reaction of methyl 10-undecenoate **C018**, prepared from commercially available 10-undecenoic acid, with various OAC showed that the reaction with 2 equiv. of Bu^i_2AlH gives alkoxide **C006** in a quantitative yield (Scheme 4).[81]

According to the generally accepted point of view, the slowing of copolymerization with increasing concentration of $CH_2{=}CH(CH_2)_nOAlR_2$ is caused by competitive inhibition: coordination of O atom to the metal prevents π-coordination of the olefin (Scheme 5 *a*). According to some studies devoted to the copolymerization of ethylene with ω-alken-1-ols **C001** – **C006**, for equal loadings of the polar comonomer an increase in the distance between the oxygen atom and the C=C bond leads to increasing activity and increasing comonomer incorporation ratio X_M, that is, the molar percentage of polar comonomer units in the resulting copolymer: in the case of copolymerization of **C004** or **C006** with ethylene, the highest X_M were 0.9 and 1.6 mol.% for **Zr02**,[34] 1.0 and 4.0 mol.% for **Zr05**,[37] 5.0 and 10.0 mol.% for **Zr23**,[37] 0 and 2.3 mol.% for **Zr25**,[45] and 0.25 and 1.08 mol.% for **Ti39**,[62] respectively. Initially, this effect was attributed to decreasing stability of the complex resulting from the simultaneous coordination of the C=C group and O atom to the active site.[34,35,37,45,61,62] In 2022, O'Hare and co-workers[10] suggested that deactivation may be due to the *intramolecular* coordination of the already incorporated polar comonomer (Scheme 5 *b*).

Sterically hindered **C009** and **C012** could not be involved into **Zr02**/MAO-catalyzed copolymerization without preliminary treatment with OAC, even for [Al]/[Zr] = 5000;[34,35] copolymerization was initiated at $[Al_{MAO}]/[Zr] > 10^4$.[34–36,45,46,57,65] Most likely, high $[Al_{MAO}]/[Zr]$ ratios ensured that the residual Me_3Al concentration in MAO was sufficient for the formation of Al alkoxides.[34–36] When the $[R_3Al]:[$ω-alken-1-ol$]$ was > 1, the catalyst activity increased,[37,39,48,51] and the efficiency of R_3Al increased in the raw $Me_3Al < Et_2AlCl < Et_3Al < Bu^i_3Al$.[39,41,62,82] The difference between the R_3Al efficiency was demonstrated in a study of the

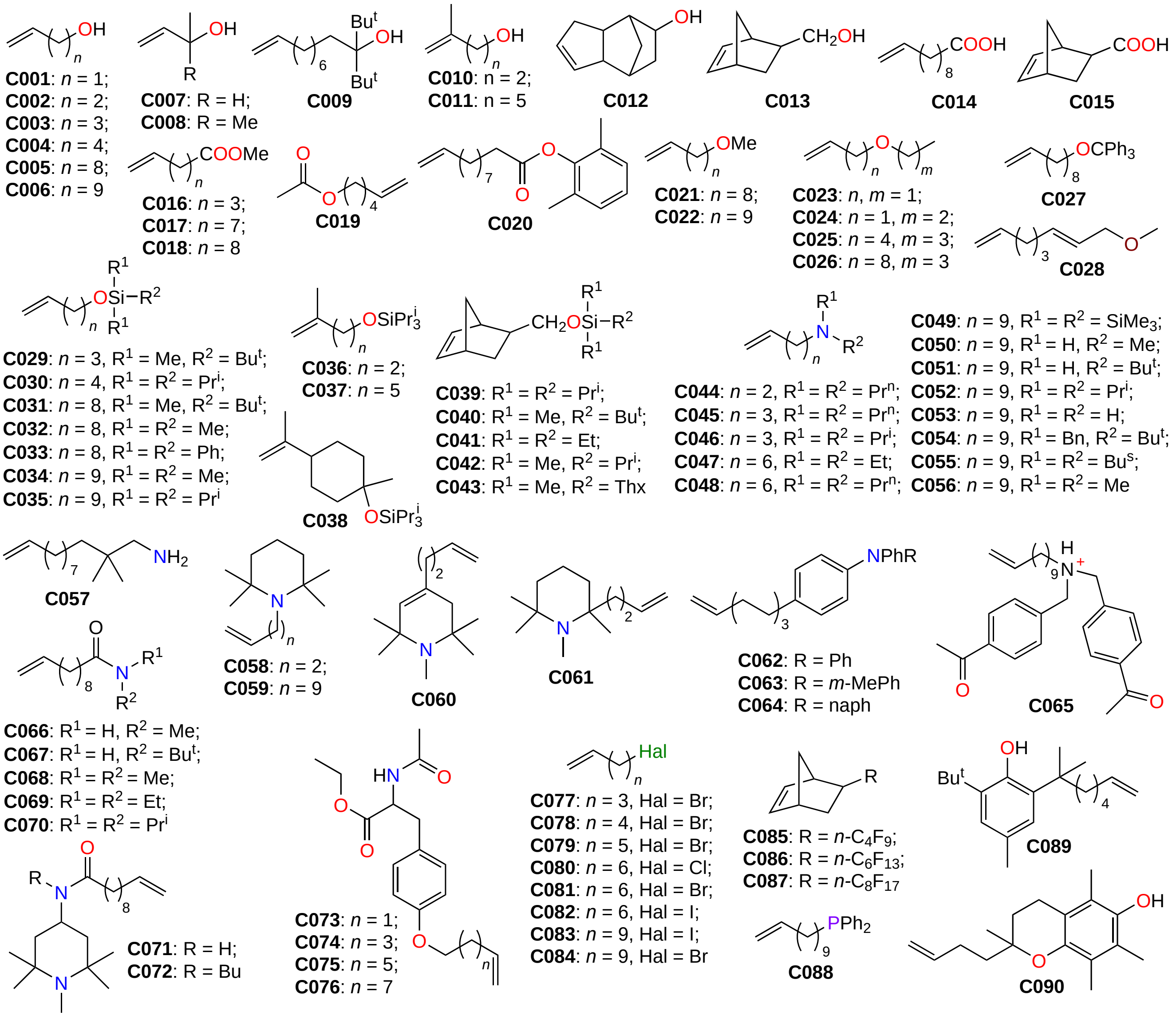
Structures of post-metallocene precatalysts Ti13–Ti59, Zr27–Zr38, and Hf01



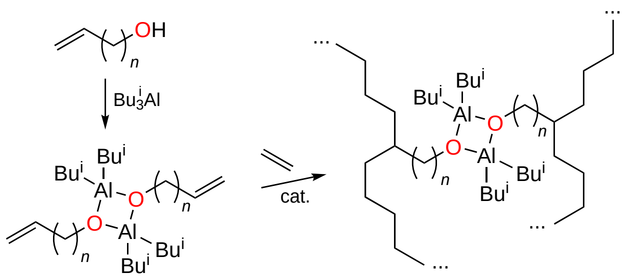
Zr16/MAO-catalyzed copolymerization of ethylene with allyl alcohol **C001**: in the presence of Bu^i_3Al, X_M was 10 mol.%; the use of $(^nC_8H_{17})_3Al$ afforded a copolymer containing 0.1 mol.% hydroxyl groups; and the products of the reaction of **C001** with Me_3Al and Et_3Al did not undergo copolymerization.[40]

Meanwhile, high [Al]/[M] ratios increased the probability of the formation of bridged alkyl complexes, intermediates of chain termination *via* chain transfer to aluminum;[51] this transfer was facilitated by the use of sterically less hindered Me_3Al and Et_3Al.[39–41]

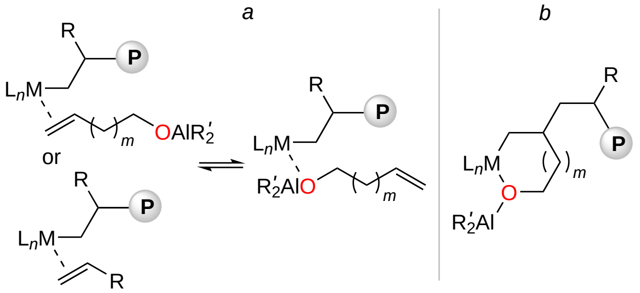
Structures of polar vinyl comonomers C001 – C090



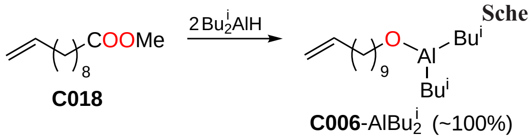
Scheme 3



Scheme 5



Scheme 4



Recently, Wang *et al.*[44] demonstrated that copolymerization of ethylene with poorly reactive comonomer **C003**-$AlBu^i_2$ catalyzed by **Zr18**/MAO or **Zr18**/TB^F, can be considerably accelerated by adding a third reaction component, a sterically hindered phenol (Scheme 6*a*); this was also accompanied by increasing X_M. The putative reaction mechanism is shown in Scheme 6*b*. The possible role of phenol is to form the mixed-ligand complex **C003**-Al(OAr)Bu^i. The less electron-donating oxygen atom of the OAr moiety in this complex is coordinated to the active site less efficiently than the oxygen atom in **C003**-$AlBu^i_2$ (Scheme 6*b*). The most pronounced effect was observed for phenol **6**, which can be attributed to additional Cl coordination to Zr or Al.

Table 1. Main characteristics of the copolymerization of ethylene with unsaturated alcohols and their derivatives catalyzed by Group 4 metal complexes.

Precatalyst /activator	Al/M	Comonomer	OAC	P_{E}, atm[a]	T, °C	Activity, kg mol^{-1} h^{-1}	X_{M} (mol.%)	Comments	Ref.
Alcohols									
Zr01/MAO	1.5	**C013**	$\mathrm{Me_3Al}$	1	35	173	0		33
Zr02/MAO	2000–5000	**C004**	none	2.5	60–80	100–2900	0–0.9		34, 35
		C006				200–7227	0.2–1.8		
		C008				1600–1700	0		
		C009				3500	0		
		C012				3250	0		
Zr04/MAO	n.d.	**C006**	none	n.d.	70	n.d.	0.14–0.3	M_{n} = 43.8–260.5 kDa, $Đ_{\mathrm{M}}$ = 2.2–2.9	36
Zr05/MAO	2000–5000	**C004**	$\mathrm{Me_3Al}$	0.34–0.36 M	25	80–9500	0.65–1.1	M_{n} = 116.7–234.1 kDa, $Đ_{\mathrm{M}}$ = 2.1–2.5	37
		C006				310–5440	2.2–4.0	M_{n} = 116.7–340.0 kDa, $Đ_{\mathrm{M}}$ = 2.1–2.8	
Zr06/MAO	1.5–5	**C013**	$\mathrm{Me_3Al}$	1	35	64–182	4.8–6.2		33
Zr07/MAO	4000	**C006**	none	2.5	60	~2500–4000	n.d.		35
	n.d.	**C006**	none	n.d.	70	n.d.	0.06–1.3	M_{n} = 64.6–168.3 kDa, $Đ_{\mathrm{M}}$ = 2.4–2.9	36
			$\mathrm{Bu^i_3Al}$	2.5	40	~1900	n.d.		11
	360	**C006**	$\mathrm{Bu^i_3Al}$	0.25	40	83	7.8	Heterogeneous catalysis, M_{n} = 20.8 kDa, $Đ_{\mathrm{M}}$ = 2.6	38
Zr08/MAO	n.d.	**C006**	none	n.d.	70	n.d.	0.1–1.4	M_{n} = 92.3–169.6 kDa, $Đ_{\mathrm{M}}$ = 2.2–2.4	36
Zr10/MAO	n.d.	**C006**	$\mathrm{Bu^i_3Al}$	2.5	40	~1000	n.d.		11
Zr13/MAO	640	**C004**	$\mathrm{Me_3Al}$	0.1	RT	1.03	n.d.	M_{n} = 1.0 kDa, $Đ_{\mathrm{M}}$ = 1.37	39
Zr15/MAO	640	**C004**	$\mathrm{Me_3Al}$	0.1	RT	0–0.5	n.d.	M_{n} = 9.4 kDa, $Đ_{\mathrm{M}}$ = 1.57	39
			$\mathrm{Bu^i_3Al}$			2.5–21.4	n.d.	M_{n} = 4.8–8.9 kDa, $Đ_{\mathrm{M}}$ = 1.32–1.44	39
Zr16/MAO	630	**C001**	$\mathrm{Me_3Al}$	1	50	n.d.	0	M_{n} = 13.4 kDa, $Đ_{\mathrm{M}}$ = 2.42	40
			$\mathrm{Et_3Al}$				0	M_{n} = 4.5 kDa, $Đ_{\mathrm{M}}$ = 2.38	
			$\mathrm{Bu^i_3Al}$				10	M_{n} = 23.4 kDa, $Đ_{\mathrm{M}}$ = 2.59	
			$\mathrm{Oct^n_3Al}$				0.1	M_{n} = 12.8 kDa, $Đ_{\mathrm{M}}$ = 2.54	
	n.d.	**C006**	none	1	80	730	0.2	M_{w} = 289.5 kDa	41
			$\mathrm{Bu^i_3Al}$		50–80	200–42 300	0.25–36.7	M_{w} = 121.0–388.1 kDa	
			$\mathrm{Et_3Al}$		80	100	16.5	M_{n} = 4.7 kDa, $Đ_{\mathrm{M}}$ = 1.63	
Zr18/MAO	1000	**C013**	$\mathrm{Bu^i_3Al}$	n.d.	70	384–486	2.4–19.4	M_{n} = 0.6–4.8 kDa, $Đ_{\mathrm{M}}$ = 3.0–10.2	42
Zr19/MAO	2000	**C013**	$\mathrm{Bu^i_3Al}$	0.5–1	25	32–72	12–23.5		38
	2200	**C013**	$\mathrm{Bu^i_3Al}$	1.5	40	2300–5200	4.6–15.3	M_{n} = 3.7–4.3 kDa, $Đ_{\mathrm{M}}$ = 2.4–3.1	43
Zr20/MAO	2200	**C013**	$\mathrm{Bu^i_3Al}$	1.5	40	6000–12 700	2.5–11.1	M_{n} = 8.8–10.8 kDa, $Đ_{\mathrm{M}}$ = 2.0–2.8	43
Zr21/MAO	2200	**C013**	$\mathrm{Bu^i_3Al}$	1.5	40	13 300–21 200	2.5–7.1	M_{n} = 8.2–10.3 kDa, $Đ_{\mathrm{M}}$ = 2.1–2.7	43
Zr23/MAO	1000	**C003**	$\mathrm{Bu^i_3Al}$	n.d.	70	420	4.2	M_{n} = 8.5 kDa, $Đ_{\mathrm{M}}$ = 2.4	44
						510–744	4.2–6.3	TC1–TC6	
	2500–3500	**C004**	$\mathrm{Me_3Al}$	0.36M	25	30–320	0.1–5.0	M_{n} = 33.6 kDa, $Đ_{\mathrm{M}}$ = 1.9	37
	n.d.		MAO	1.6	60	13 312–36 747	0.1–1.2		45
	1000	**C005**	$\mathrm{Bu^i_3Al}$	n.d.	40	1000–14000	1.4–2.2	M_{n} = 32.5–63.3 kDa, $Đ_{\mathrm{M}}$ = 1.8–4.4	46
	5000		none	n.d.	40	n.d.	1.0	Modified with caprolactone	47
	n.d.	**C006**	none	n.d.	70	n.d.	0.5–0.9	M_{n} = 53.9–76.6 kDa, $Đ_{\mathrm{M}}$ = 2.3–2.4	36

Table 1 (continued).

Precatalyst /activator	Al/M	Comonomer	OAC	P_{E}, atm[a]	T, °C	Activity, kg mol^{-1} h^{-1}	X_{M} (mol.%)	Comments	Ref.
				Alcohols					
Zr23/MAO	n.d.	**C006**	MAO	1.6	60	23 273 – 104 852	0.5 – 5.4	M_{n} = 30.8 – 46.5 kDa, $Đ_{\mathrm{M}}$ = 4.0 – 5.3	45
	4000			1.5 – 3	60	1200 – 2700	0.7 – 3.6	M_{n} = 18.9 – 29.2 kDa, $Đ_{\mathrm{M}}$ = 1.9 – 2.4	48
	$2.4 - 12 \times 10^{3}$			1.5 – 3	60 – 80	2600 – 9400	0.2 – 1.1	M_{n} = 22 – 47.5 kDa, $Đ_{\mathrm{M}}$ = 2.0 – 2.9	49
	2140		$\mathrm{Me_3Al}$	0.36 M	25	40 – 1400	4.5 – 10	M_{n} = 106 kDa, $Đ_{\mathrm{M}}$ = 2.0	37
	770		$\mathrm{Bu^{i}_{3}Al}$	1	60	504 – 8280	n.d.		50
	1.5	**C013**	$\mathrm{Me_3Al}$	1	35	109	3.1		33
Zr23/$\mathrm{Bu^{i}_{3}Al}$/TB$^{\mathrm{F}}$	800	**C003**	$\mathrm{Bu^{i}_{3}Al}$	n.d.	70	378	5.9	M_{n} = 3.0 kDa, $Đ_{\mathrm{M}}$ = 2.2	44
						288 – 498	6.0 – 7.3	TC1 – TC6	
Zr24/MAO	n.d.	**C004**	$\mathrm{Me_3Al}$	0.1 – 1	20 – 40	n.d.	8 – 50	M_{n} = 1.0 – 14 kDa, $Đ_{\mathrm{M}}$ = 1.34 – 1.96	51
Zr25/MAO	n.d.	**C004**	MAO	1.6	60	46 820 – 53 379	0		45
		C006				35 712 – 59 563	0.3 – 2.3		
Zr26/MAO	3000	**C005**	$\mathrm{Bu^{i}_{3}Al}$	1	30	530	0.6	M_{n} = 38.7 kDa, $Đ_{\mathrm{M}}$ = 3.1	52
Ti01/MAO	n.d.	**C006**	MAO	1.6	35 – 60	2796 – 11 728	1.0		45
Ti02/MAO	800	**C001**	$\mathrm{Bu^{i}_{3}Al}$	2.5	40	0	0		53
	n.d.					~250 – 1000	n.d.		11
	800	**C002**				0	0		53
	800	**C004**				0	0		53
	2600		$\mathrm{Me_3Al}$	0.32M	70	1 – 510	1.6 – 3.8	M_{n} = 17.5 kDa, $Đ_{\mathrm{M}}$ = 2.1	37
	$1.2 - 3 \times 10^{5}$	**C005**	$\mathrm{Bu^{i}_{3}Al}$	6	25 – 50	110 160 – 525 600	0.9 – 1.7	M_{n} = 70 – 89.7 kDa, $Đ_{\mathrm{M}}$ = 1.8 – 2.0	54
	500			1	25 – 80	129 – 798	0.8 – 12.4	M_{n} = 3.7 – 36.6 kDa, $Đ_{\mathrm{M}}$ = 2.2 – 3.9	55
	800	**C006**		2.5	40	670	0		53
	2000		$\mathrm{Me_3Al}$	0.32 – 0.33M	70	510 – 670	1.0 – 4.0		37
	n.d.		$\mathrm{Bu^{i}_{3}Al}$	2.5	40	~750 – 1000	n.d.		11
Ti02/MAO	400	**C006**	$\mathrm{Bu^{i}_{3}Al}$	15	20	840 – 1480	0.2 – 4.9	Heterogeneous catalysis	56
Ti05/MAO/BHT	1000	**C006**	$\mathrm{Bu^{i}_{3}Al}$	1 – 11	0	1180 – 9050	0.5 – 1.6	M_{n} = 458.9 – 1108.5 kDa, $Đ_{\mathrm{M}}$ = 1.4 – 1.9	57
Ti06/MAO/BHT	400/15	**C010**	none	1	25	n.d.	n.d.	M_{n} = 500 kDa, $Đ_{\mathrm{M}}$ = 1.8	58
		C011					1.8	M_{n} = 480 kDa, $Đ_{\mathrm{M}}$ = 2.0	
Ti07/MAO	1100	**C006**	n.d.	n.d.	n.d.	1800 – 2350	0.6 – 1.4	M_{n} = 13.3 – 21.4 kDa, $Đ_{\mathrm{M}}$ = 3.6 – 5.8	53
	n.d.					~2000 – 2250	n.d.		11
Ti07′/MAO	800	**C001**	$\mathrm{Bu^{i}_{3}Al}$	2.5	40	1310 – 2150	0.06 – 3.0	M_{n} = 2.6 – 4.2 kDa, $Đ_{\mathrm{M}}$ = 2.4 – 3.6	53
	n.d.					~1000 – 2000	~ 1.1		11
	n.d.	**C002**				~1000 – 1800	~ 1.0		11
	800					1330 – 1980	< 0.04 – 1.7	M_{n} = 3.8 – 6.2 kDa, $Đ_{\mathrm{M}}$ = 2.4 – 3.6	53
	800	**C004**				1210 – 1700	0.2 – 1.3	M_{n} = 4.1 – 6.2 kDa, $Đ_{\mathrm{M}}$ = 2.4 – 3.6	53
	n.d.					~1000 – 1600	~ 1.2		11
	800	**C006**				1160 – 2210	0.2 – 2.1	M_{n} = 0.7 – 2.5 kDa, $Đ_{\mathrm{M}}$ = 1.4 – 9.6	53
	n.d.					~1000 – 1700	~ 1.4		11
	n.d.	**C007**				~1000 – 1250	~ 0.8		11
	800					1180 – 1330	0.04 – 1.0	M_{n} = 3.5 – 6.0 kDa, $Đ_{\mathrm{M}}$ = 3.1 – 5.1	53
Ti08/MAO	6000	**C006**		4	20	95 300 – 304 000	4 – 32.1	M_{n} = 37 – 99 kDa, $Đ_{\mathrm{M}}$ = 2.2 – 3.8	59

Table 1 (continued).

Precatalyst /activator	Al/M	Comonomer	OAC	P_E, atm[a]	*T*, °C	Activity, kg mol^{-1} h^{-1}	X_M (mol.%)	Comments	Ref.
Alcohols									
Ti07′/MAO/BHT	700	**C006**	Bu^i_3Al	2.5	40	950, 420	2.7, 5.4	MAO/BHT = 0.9, 2.0	53
Ti09/MAO	800	**C001**				240	< 0.04	M_n = 18.0 kDa, $Đ_M$ = 5.3	53
		C002				0	0		
		C004				0	0		
		C006				460–740	0.2–0.6	M_n = 5.9–18.4 kDa, $Đ_M$ = 2.3–3.3	
	n.d.					~500–800	n.d.		11
	800	**C007**				0	0		53
Ti10/MAO	500	**C003**		1	30	156–183	4.5–10.5 (5.7–8.8)		60
	1.2–3 × 10^5	**C005**		6	25–50	31 800–37 000	0.8–1.2	M_n = 72.9–138 kDa, $Đ_M$ = 1.81–1.83	54
	500			1		144–417	1.6–13.6	M_n = 3.8–101 kDa, $Đ_M$ = 2.4–5.5	55
Ti11/MAO	1.2–3 × 10^5	**C005**		6	25–50	53 300–183 000	1.2–1.8	M_n = 71–130 kDa, $Đ_M$ = 1.67–1.72	54
Ti12/MAO	3 × 10^5	**C004**		6–8	50	45 400–381 000	0.3–2.4	M_n = 53.2–105 kDa, $Đ_M$ = 1.5–2.1	54
	1.2–3 × 10^5	**C005**		6	25–50	23 600–111 000	1.3–3.6	M_n = 65.5–100 kDa, $Đ_M$ = 1.5–2.1	54
Zr27/MAO	770	**C006**		1	25	17600–23200	0.1–0.2	M_n = 3.0–6.1 kDa, $Đ_M$ = 1.6–1.8	50
Zr28/MAO	770	**C006**		1	25	14 600–20 600	0.1–0.2	M_n = 7.6–28.2 kDa, $Đ_M$ = 2.0–2.3	50
Zr29/MAO	1000	**C004**		1	25	6840–11 600	0.03–0.1		61
	770–3000	**C006**		1	0–75	7260–22 900	0.2–1.0	M_n = 20.9–68.4 kDa, $Đ_M$ = 1.9–2.4	50, 61
Zr30/Bu^i_3Al/TB^F	15/1.5	**C004**		3	60	13.7	n.d.		62
		C005		n.d.	n.d.	n.d.	3.0–16.5	M_n = 1.8–2.5 kDa, $Đ_M$ = 1.6–2.1	63
				1–5	60	45.3–790	2.9–5.6	M_n = 1.8–6.8 kDa, $Đ_M$ = 1.6–2.1	62
			Et_3Al	3		61.5	5.5	M_n = 3.3 kDa, $Đ_M$ = 3.6	
			Et_2AlCl			0	0		
		C006	Bu^i_3Al	3–5		119.4–1042.2	2.1–5.9	M_n = 2.3–11.1 kDa, $Đ_M$ = 1.9–4.5	
				n.d.	n.d.	n.d.	2.1–5.6	M_n = 2.3–5.8 kDa, $Đ_M$ = 1.9–2.0	63
Zr31/MAO	1000	**C004**		5	80	1190	0.3	M_n = 1.2 kDa, $Đ_M$ = 2.9	64
		C006				1230–1580	0.2–1.4	M_n = 1.1–1.5 kDa, $Đ_M$ = 5.9–7.3	
Zr32/MAO	1000	**C004**				1390	0.1	M_n = 2.1 kDa, $Đ_M$ = 2.3	
		C006				1030	1.7	M_n = 1.4–1.7 kDa, $Đ_M$ = 7.4–9.7	
Zr33/MAO	1000	**C004**				1680	0.1	M_n = 5.9 kDa, $Đ_M$ = 30	
		C006				1080–1780	0.1–0.8	M_n = 4.3–8.9 kDa, $Đ_M$ = 13–26	
Zr34/MAO	1000	**C004**				1750	0.04	M_n = 8.2 kDa, $Đ_M$ = 16.5	
		C006				1520–1790	0.2–0.8	M_n = 5.6–7.2 kDa, $Đ_M$ = 12–17	
Ti13/MAO	n.d.	**C005**	Bu^i_3Al	n.d.	40	300	6.2	M_n = 55.3 kDa, $Đ_M$ = 3.2	46
Ti14/MAO					40	2100	4.1	M_n = 19.3 kDa, $Đ_M$ = 1.5	
Ti15/MAO					40	n.d.	n.d.		

Table 1 (continued).

Precatalyst /activator	Al/M	Comonomer	OAC	P_E, atm[a]	T, °C	Activity, kg mol^{-1} h^{-1}	X_M (mol.%)	Comments	Ref.
				Alcohols					
Ti16/MAO	1000	**C003**			40	2800	1.4	M_n = 9.8 kDa, $Đ_\mathrm{M}$ = 4.8	46
	3000		none	1	25	74	0.6	M_n = 42 kDa, $Đ_\mathrm{M}$ = 2.0	65
	200 – 2000	**C005**	$\mathrm{Bu^i_3Al}$	n.d.	0 – 40	600 – 3300	5.8 – 11.2	M_n = 35 – 80.9 kDa, $Đ_\mathrm{M}$ = 1.6 – 2.8	46, 65
	3000		none	1	25	120	3.7	M_n = 45.5 kDa, $Đ_\mathrm{M}$ = 1.8	65
Ti17/MAO	1000		$\mathrm{Bu^i_3Al}$	n.d.	40	4400	4.8	M_n = 7.4 kDa, $Đ_\mathrm{M}$ = 3.4	46
Ti18/MAO						4400	3.6	M_n = 21.6 kDa, $Đ_\mathrm{M}$ = 3.0	
Ti19/MAO						1400	4.1	M_n = 19.3 kDa, $Đ_\mathrm{M}$ = 2.9	
Ti20/MAO						5200	3.5	M_n = 23.3 kDa, $Đ_\mathrm{M}$ = 2.4	
Ti21/MAO						2000	2.3	M_n = 26 kDa, $Đ_\mathrm{M}$ = 2.5	
Ti22/MAO						5600 – 16 000	2.2 – 4.8	M_n = 6.6 – 33.9 kDa, $Đ_\mathrm{M}$ = 2.3 – 3.8	
Ti23/MAO						3300	2.7	M_n = 10 kDa, $Đ_\mathrm{M}$ = 2.6	
Ti24/MAO						5100	4.1	M_n = 28 kDa, $Đ_\mathrm{M}$ = 2.5	
Ti25/MAO						2400	3.5	M_n = 4.5 kDa, $Đ_\mathrm{M}$ = 3.1	
Ti28/MAO				1	25	70	3.4	M_n = 52.3 kDa, $Đ_\mathrm{M}$ = 2.2	65
Ti29/MAO						60	3.5	M_n = 324.1 kDa, $Đ_\mathrm{M}$ = 2.9	
Ti31/MAO	800	**C001**		2.5	40	0	0		53
		C002				0	0		
		C004				0	0		
		C006				1480	1.4	M_n = 16.4 – 1.72 kDa, $Đ_\mathrm{M}$ = 2.3 – 2.5	
	n.d.					~1500	n.d.		11
	800	**C007**				0	0		53
Ti39/MAO	1000	**C004**		1	25	1820 – 2150	0.11 – 0.25		61
		C006			0 – 75	732 – 2230	0.23 – 1.08		
Ti45/MAO	2500	**C013**	none	1	25	53	5.5	M_n = 12 kDa, $Đ_\mathrm{M}$ = 1.9	66
Ti46/MAO	1500 – 2500		none			120 – 300	2.8 – 10.0	M_n = 19.2 – 34.2 kDa, $Đ_\mathrm{M}$ = 1.9 – 2.6	
	n.d.		$\mathrm{Et_2AlCl}$			700 – 1900	7.0 – 22	M_n = 28.7 – 41.1 kDa, $Đ_\mathrm{M}$ = 1.8 – 1.9	
Ti47/MAO	1500 – 2500		none			150 – 337	1.6 – 6.0	M_n = 16.7 – 55.9 kDa, $Đ_\mathrm{M}$ = 1.7 – 2.2	
	n.d.		$\mathrm{Et_2AlCl}$			1350 – 2500	5.3 – 16	M_n = 31.3 – 58.4 kDa, $Đ_\mathrm{M}$ = 1.6 – 2.3	
Ti48/MAO	2500		none			30	6.8	M_n = 3.6 kDa, $Đ_\mathrm{M}$ = 2.1	
Ti49/MAO	2500					41	5.2	M_n = 9.8 kDa, $Đ_\mathrm{M}$ = 1.9	
Ti50/MAO	1500 – 2500					80 – 240	1.8 – 9.2	M_n = 15.5 – 49.7 kDa, $Đ_\mathrm{M}$ = 1.7 – 2.1	
Ti51/MAO	1500 – 2500					100 – 270	1.5 – 5.6	M_n = 21.3 – 63.8 kDa, $Đ_\mathrm{M}$ = 1.6 – 1.9	
Ti52/MAO	2500					15	6.5		
Ti53/MAO	2500					35	1.2	M_n = 18.1 kDa, $Đ_\mathrm{M}$ = 1.8	
Ti57/MAO	1500	**C006**	$\mathrm{Et_3Al}$	50	70	17.4 – 35.6	4.78 – 5.73	M_n = 20.8 – 47.1 kDa, $Đ_\mathrm{M}$ = 2.4 – 2.5	67
				Ethers					
Zr07/MAO	2500	**C023**	$\mathrm{Bu^i_3Al}$	4	45 – 60	1600 – 5000	1.1 – 3.2	M_w = 420 – 530 kDa	68
		C025				1400 – 54 600	0.1 – 0.6	M_w = 105 – 194 kDa	
		C026				540 – 79 300	0.1 – 0.6	M_w = 117 – 346 kDa	
		C028				9.1 – 26.5	0.3 – 1.5	M_w = 75 – 182 kDa	
Zr08/MAO	n.d.	**C025**	none	4	60	1400 – 54 600	0.1 – 0.6	M_w = 105 – 194 kDa	69
		C026				540 – 130 900		M_w = 117 – 346 kDa	
Zr11/MAO	n.d.	**C023**	none	n.d.	n.d.	n.d.	16		68

Table 1 (continued).

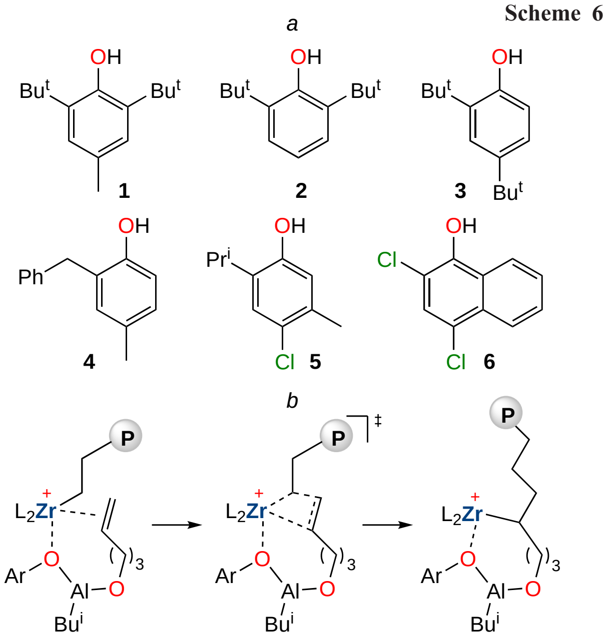
Precatalyst /activator	Al/M	Comonomer	OAC	P_E, atm[a]	T, °C	Activity, kg mol^{-1} h^{-1}	X_M (mol.%)	Comments	Ref.
Ethers									
Zr12/MAO	n.d.	**C024**	none	n.d.	n.d.	12000	8.2		68
		C028				n.d.	1.5		
Zr23/MAO	1000	**C021**	none	n.d.	n.d.	n.d.	0.1–0.9	M_n = 2.17–4.52 kDa	70
		C027					0.004–1.1	M_n = 2.87–25.4 kDa	
	4000	**C022**	MAO	1.5	60	1700–2600	0.9–2.3	M_n = 8.9–15 kDa, $Đ_M$ = 1.9–2.0	48
Silyl ethers of alcohols									
Zr07/MAO	4800	**C035**	none	2	25	n.d.	0.15–2.2	M_n = 87–121 kDa, $Đ_M$ = 2.3–2.9	71
	359		none	0.6–2	40	58 – 1190	0.3–14.4	Heterogeneous catalysis, M_n = 41.9–74.5 kDa, $Đ_M$ = 1.6–3.3	71
Zr19/MAO	2200, 6000	**C039**	none	1.5–2	25–60	2750–3700	2.5–13.3	M_n = 2.9–5.5 kDa, $Đ_M$ = 2.0–2.4	71, 72
	320			0.8–2	40	n.d.	0.09 – 15.9	Heterogeneous catalysis	71
	2200	**C040**		0.9–1.5	40–60	56–1636	2.2–11.4	M_n = 1.1–2.4 kDa, $Đ_M$ = 1.8–2.1	72, 73
		C041				95–988	0.7–8.8	M_n = 0.8–1.9 kDa, $Đ_M$ = 1.6–2.1	
		C042				30–1060	0.7–8.6	M_n = 1.2–2.6 kDa, $Đ_M$ = 1.3–2.1	
		C043				730–3090	1.5–13.9	M_n = 3.7–4.5 kDa, $Đ_M$ = 1.9–2.2	
Zr20/MAO	2200	**C039**	none	1.5	60	4620–14240	1.7–13.0	M_n = 4.8–13 kDa, $Đ_M$ = 1.8–2.4	72
		C040				960–2060	3.5–7.3	M_n = 1.9–2.4 kDa, $Đ_M$ = 1.8–1.9	
		C042				200–1030	0.7–9.8	M_n = 2.9–3.0 kDa, $Đ_M$ = 2.1–2.2	
		C043				800–5120	3.3–13.7	M_n = 5.4–8.3 kDa, $Đ_M$ = 2.0–2.5	
Zr21/MAO	2200	**C039**	none	1.5	60	8700–14100	3.3–7.5	M_n = 6.1–10.7 kDa, $Đ_M$ = 1.8–2.2	72
		C042				190–470	1.2–6.1	M_n = 3.6–4.9 kDa, $Đ_M$ = 2.0–2.1	
		C043				2020–6470	2.3–8.8	M_n = 5.5–10.5 kDa, $Đ_M$ = 1.8–2.3	
Zr23/MAO	2000	**C032**	none	1	25	600	4.6	M_n = 25.5 kDa, $Đ_M$ = 2.7	65
	1000	**C032**	none	n.d.	n.d.	n.d.	0.1–0.2	M_n = 5.36–6.82 kDa	70
		C033					0.4–1.2	M_n = 8.66–51.0 kDa	
	4000	**C034**	MAO	1.5	60	1500–2500	1.4–3.0	M_n = 17–25.8 kDa, $Đ_M$ = 1.9–2.0	48
	4800	**C035**	none	2	25	n.d.	0.15–2.18	M_n = 87–121 kDa, $Đ_M$ = 2.3–2.9	71
	359		none	0.6–2	40	58–1190	0.31–14.4	Heterogeneous catalysis	71
Ti03/MAO	400	**C036**	none	13.9 mmol	25	n.d.	n.d.	M_n = 19 kDa, $Đ_M$ = 9.9	58
Ti04/MAO	400	**C036**	none	13.9 mmol	25	n.d.	1.1	M_n = 28 kDa, $Đ_M$ = 6.0	58
Ti06/MAO/BHT	200/15	**C036**	none	1	25–80	n.d.	0.9–2.4	M_n = 6–990 kDa, $Đ_M$ = 1.4–14.6	58
		C037					6.0		
Ti06/MAO	400	**C038**	none	13.9 mmol	25	n.d.	1.5	M_n = 41 kDa, $Đ_M$ = 4.8	58
Zr35/MAO	250–2000	**C030**	none	1	25	77–470	7.5–21.4	M_n = 1.4–4.9 kDa, $Đ_M$ = 1.9–2.5	74
Ti16/MAO	3000	**C029**	none	–	40	900	1.8	M_n = 35.6 kDa, $Đ_M$ = 2.5	46
	1000–3000	**C031**	none	–	40	1500–4200	2.9–5.6	M_n = 34.2 kDa, $Đ_M$ = 2.6	46
	2000		none	1	25	100–290	3.9–5.1	M_n = 81.3–480 kDa, $Đ_M$ = 2.0–2.5	65

Table 1 (continued).

Precatalyst /activator	Al/M	Como-nomer	OAC	P_E, atm[a]	T, °C	Activity, kg mol^{-1} h^{-1}	X_M (mol.%)	Comments	Ref.
Silyl ethers of alcohols									
Ti40/MAO	550	**C032**	none	0.5	60	790	1.31	M_n = 115.9 kDa, $Đ_M$ = 4.4	75
Ti41/MAO						860	1.23	M_n = 124.5 kDa, $Đ_M$ = 4.9	
Ti42/MAO						930	1.73	M_n = 200 kDa, $Đ_M$ = 5.1	
Ti43/MAO						960	1.79	M_n = 205.5 kDa, $Đ_M$ = 5.5	
Ti44/MAO						1040	1.70	M_n = 240.4 kDa, $Đ_M$ = 5.7	

Note. OAC is organoaluminum compound that was used as a cocatalyst (masking reagent) for polar comonomer. PE is ethylene pressure. XM is the content of the polar comonomer in the copolymer, mol.%. BHT is 2,6-di-tert-butyl-4-methylphenol; n.d. means no data. [a] M is the molar concentration of ethylene.

Scheme 6



Analysis of scientific periodicals (see Table 1) indicates that *ansa*-complexes with –SiMe$_2$– and –CH$_2$CH$_2$– bridges are most active in the series of zirconocenes. It is noteworthy that the use of **Zr16**/MAO catalyst resulted in the formation of **C006**-AlBu$^i_2$ or **C006**-AlEt$_2$ copolymers containing 36.7 and 16.5 mol.% comonomer with M_w = 121.0 and 7.7 kDa, respectively.[41] This result clearly demonstrates that Bu$^i_3$Al is the preferable masking reagent that reacts with **C006** according to general Scheme 3. The activity of the –CH$_2$CH$_2$– bridged bis-indenyl complex **Zr23**/MAO in the copolymerization of **C006**-MAO reached 104 850 kg mol^{-1} h^{-1} (X_M up to 5.4 mol.%).[45] In the copolymerization of **C004**-AlMe$^i_2$, the activity of **Zr23**/MAO decreased by three orders of magnitude (30 kg mol^{-1} h^{-1}).[37] When the tetrahydroindenyl analog **Zr25**/MAO and **C004**-MAO were used, ethylene homopolymerization took place without incorporation of the comonomer.[45] The record-high X_M value (~50 mol.%) was achieved in the copolymerization of ethylene with **C004**-AlMe$^i_2$ catalyzed by **Zr24**/MAO; the resulting low-molecular-weight (M_n = 1.0 kDa) polymer was characterized by an almost alternating microstructure.[51] Thus, zirconocene catalysts make it possible to prepare ethylene copolymers with variable contents of ω-alken-1-ols. At low X_M values, the resulting copolymers have mechanical characteristics similar to those of linear low-density polyethylene (LLDPE) with a low surface hydrophobicity, while at high X_M, copolymers exhibit elastomeric behavior and improved adhesive properties (see Section 2.4).

Among post-metallocene zirconium complexes, high activities in the copolymerization of **C006**-AlBu$^i_2$ were observed for bis(phenoxy imine) complexes **Zr27**–**Zr29**, with X_M not exceeding 1.4 mol.%.[50,61] Higher X_M values, 16.5 mol.% for **C005** and 5.9 mol.% for **C006**, were achieved by using a less active (45.3 and 436.2 kg mol^{-1} h^{-1}) binuclear complex **Zr30**.[62] Complex **Ti39** isostructural to **Zr29** exhibited a much lower activity in the copolymerization with **C006**-AlBu$^i_2$.[61] In a comparative study of mononuclear (**Zr31**, **Zr32**) and binuclear (**Zr33**, **Zr34**) post-metallocene complexes in ethylene copolymerization with **C004**-AlBu$^i_2$ and **C006**-AlBu$^i_2$, mononuclear complexes showed higher performance and provided higher incorporation of comonomers.[64]

Norbornene derivative **C013** is a promising polar comonomer. In the copolymerization of ethylene with **C013**-AlBu$^i_2$, high activity was found for complexes **Zr19**, **Zr20**, and **Zr21** (see Table 1). The introduction of bulky substituents (Pr^i, Bu^t) into the cyclopentadienyl ring of metal complexes resulted in a higher activity towards ethylene copolymerization with **C013**, but lower X_M.[43,73] As the concentration of the polar comonomer increased, the catalyst activity decreased: a 23.5 mol.% incorporation of **C013** was attained for **Zr19**/MAO activity of 32 kg mol^{-1} h^{-1}.[38] Post-metallocene complexes **Ti45**–**Ti53** had a moderate catalytic activity towards ethylene copolymerization with unprotected **C013** (15–270 kg mol^{-1} h^{-1}); the activity increased in the presence of Me/Bu^t electron-donating group in the catalyst molecule (**Ti46**, **Ti47**). The use of the Et$_2$AlCl cocatalyst in the copolymerization with **C013** furnished a copolymer with 22.0 mol.% comonomer content and M_n = 28.8 kDa.[66]

In the series of half-sandwich titanium complexes, high activity in the copolymerization with **C004**-AlBu$^i_2$ and **C005**-AlBu$^i_2$ (up to 111000 and 381 000 kg mol^{-1} h^{-1}, respectively, X_M = 2.2–2.4 mol.%) was found for **Ti12**/MAO.[54] The high activity of **Ti12** was attributed in this study to stabilization of the catalytic site by the SiEt$_3$ electron-donating group in the *para*-position of the aryloxy ligand. Higher incorporation ratios in the ethylene copolymerization with **C005**-AlBu$^i_2$ were achieved by using **Ti02**/MAO and **Ti10**/MAO.[55]

In a study of post-metallocene titanium complexes **Ti13**–**Ti29**/MAO in the copolymerization with **C005**-AlBu$^i_2$, the complexes **Ti16** (~10 000 kg mol^{-1} h^{-1}, 11.2 mol.% comonomer)[65] and **Ti22** (5600–16 000 kg mol^{-1} h^{-1}, 2.2–4.8 mol.% comonomer) were identified as the most active.[46] It is noteworthy that the most active catalysts contained a Ti atom coordinated to ligands characterized by enhanced electron-donating capacity. The increase in the electron-donating capacity of ligands that form the active site is an effective approach to the design of single-site catalysts for polymerization of ethylene and propylene.[†] In all probability, the concept of catalyst 'coordination readiness' developed as applied to ethylene and propylene copolymers is also applicable to copolymerization of polar comonomers with ethylene.

Recently, Wei *et al*.[59] reported the development of a catalyst for copolymerization of **C005**-$\mathrm{AlBu^i_2}$ that was superior in the performance and X_M to all currently known Group 4 metal complexes. Owing to the presence of electron-donating *N*-heterocyclic boryloxy ligand, the half-sandwich complex **Ti08** exhibited an activity of up to 300 000 kg mol^{-1} h^{-1} (6.9 mol.% comonomer) at 20°C and 4 atm of ethylene; the highest X_M of 32.1 mol.% (2 atm of ethylene) corresponded to the activity of 26500 kg mol^{-1} h^{-1}.

In some cases, the use of silyl ethers of unsaturated alcohols makes it possible to markedly decrease the content of OAC in the reaction mixture, while X_M increases. A study of ethylene copolymerization with $\mathrm{CH_2{=}CH(CH_2)_9OSiPr^i_3}$ (**C035**) catalyzed by **Zr07**/MAO gave products with comonomer contents of up to 14.4 mol.% (M_n = 41.9 kDa);[71] under the same conditions, **C006**-$\mathrm{AlBu^i_2}$ afforded a copolymer with X_M ~8 mol.% (M_n = 20.8 kDa).[38] The increase in the substituent bulk in the $\mathrm{OSiR_3}$ moiety in the presence of the **Zr23**/MAO catalyst provided a higher X_M (up to 0.2 mol.% for **C032** with the $\mathrm{SiMe_3}$ group and up to 1.2 mol.% for **C033** with the $\mathrm{SiPh_3}$ group) and prevented the interaction of $\mathrm{OSiR_3}$ with OAC, resulting in the formation of aluminum alkoxides, and the hydrolysis of silyl ethers during isolation of the copolymer.[70]

In the copolymerization of ethylene with 5-hydroxymethylnorbornene silyl ethers catalyzed by zirconium *ansa*-complexes **Zr19** – **Zr21**, the highest X_M was observed for (2,2,3-trimethylbutyl)dimethylsilyl ether (**C043**), and the highest catalyst activity was achieved in the copolymerization of triisopropylsilyl ether (**C039**).[71–73] Copolymerization of **C039** was also carried out using the supported **Zr19**/MAO@$\mathrm{SiO_2}$ catalyst, which gave copolymers with a bimodal molecular weight distribution (MWD).[71] The synthesis of bimodal polyethylenes (PE) characterized by high tensile strength and good molding properties is a relevant trend in modern polyolefin industry. Therefore, preparation of these materials using a one-component catalyst is of obvious practical interest.

There are relatively few papers in scientific literature that address copolymerization of ω-alken-1-ol ethers. Copolymerization experiments were carried out using considerable excess of MAO, and the reaction rate increased with increasing [Al]/[Zr] ratio, which suggests that electrophilic centers of MAO served as masking reagents for the alkoxy groups. Complexes **Zr11** and **Zr12** provided incorporation ratios of up to 16.0 and 8.2 mol.% for **C023** and **C024**, respectively.[68] The use of ethylene-bridged zirconium bis-indenyl complex **Zr23** as a catalyst resulted in the synthesis of copolymers containing 0.9 mol.% **C021**, 2.3 mol.% **C022**, and 1.1 mol.% **C027**.[48,70] As the concentration of comonomer **C022** increased from 16.7 to 50 mM, the catalyst activity increased from 1700 to 2600 kg mol^{-1} h^{-1}.[48] Copolymers of ethylene with ω-alken-1-ol ethers have not found any practical use, apparently, this accounts for the absence of recent studies on the copolymerization of ethers using new metallocene and post-metallocene catalysts.

2.1.2. Copolymerization of ethylene with ω-alkenoic acids and esters

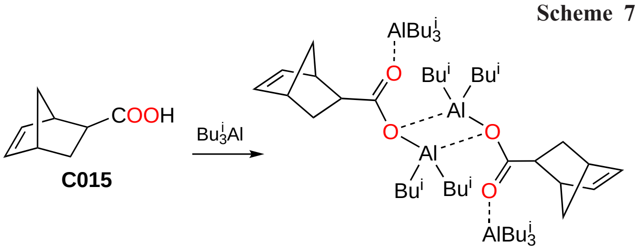
The results of experiments on the copolymerization of ethylene with unsaturated carboxylic acids and their derivatives catalyzed by Group 4 metal complexes are summarized in Table 2.

10-Undecenoic acid (**C014**) and 5-norbornene-2-carboxylic acid (**C015**) were tested in the copolymerization with ethylene. In the copolymerization with **C014**-MAO, the **Zr23**/MAO catalyst showed activity of 12 200 kg mol^{-1} h^{-1} and X_M = 0.5 mol.%.[49] The use of **Zr23**/MAO and **C014**-$\mathrm{AlMe_2}$ afforded a copolymer containing 7.4 mol.% **C014**. Post-metallocene complex **Zr29** possessing a high activity (up to 12 400 kg mol^{-1} h^{-1}) catalyzed the formation of a low-molecular-weight (M_n = 2.2 kDa) copolymer containing 0.5 mol.% **C014**.[61] Among the post-metallocene titanium complexes, the highest activity in the copolymerization of ethylene with **C014** was found for **Ti16** (X_M = 2.5 mol.%, M_n = 1.5 kDa).[46] The titanium–magnesium $\mathrm{TiCl_4@MgCl_2}$/diisobutyl phthalate catalyst had low activity (18 kg mol^{-1} h^{-1}) and produced a high-molecular-weight (M_n = 1428 kDa) copolymer containing 0.3 mol.% **C014**.[88] The study by Tan *et al*.[88] is of particular interest, as the authors implemented the advanced strategy of 'ionic clusters', that is, self-organization of the product of reaction between **C014** and $\mathrm{Et_2AlCl}$, $\mathrm{(CH_2{=}CH(CH_2)_8COO)_2AlCl}$, to give polynuclear species, which then underwent copolymerization. The **Ti33**/MAO catalyst exhibited an activity of 200 kg mol^{-1} h^{-1} in the homogeneous copolymerization, resulting in the formation of copolymer particles with a microsphere morphology.[88] The formation of microspherical polymer particles in the homogeneous reaction considerably facilitates scaling up and industrial use of the catalytic system, owing to the reduced risk of reactor fouling.

The **Zr19** – **Zr21**/MAO-catalyzed copolymerization of ethylene with **C015** was carried out using $\mathrm{Bu^i_3Al}$ as a cocatalyst.[43,73] An activity of up to 3400 kg mol^{-1} h^{-1} and X_M of up to 8.9 mol.% were achieved. The reaction of carboxylic acids with OAC is similar to the reaction of ω-alkenols, but a pronounced masking effect of OAC is manifested at [Al]/[**C015**] > 2, owing to formation of the complex that is depicted in Scheme 7, which shows the reaction of **C015** with $\mathrm{Bu^i_3Al}$. A possible function of the second equivalent of $\mathrm{Bu^i_3Al}$ is coordination to the carbonyl oxygen atom, which prevents inhibition of the catalytic site.

Copolymerization of ω-alkenoic acid esters with ethylene is addressed in a small number of studies. Most likely, this is due to the lower masking efficiency of OAC for esters. An early study describes copolymerization of ethylene, propylene, and sterically hindered 2,6-dimethylphenyl 10-undecenoate **C020** initiated by $\mathrm{AlTi_3Cl_{12}/Et_2AlCl}$ and the subsequent hydrolysis of the reaction product to polycarboxylic acid.[32]

Scheme 7



[†] See P.V.Ivchenko. Design and synthesis of Group 4 metallocenes, effective precatalysts of the homo- and copolymerization of alkanes. Doctoral Thesis. Moscow, 2014

Table 2. Main characteristics of the copolymerization of ethylene with unsaturated carboxylic acids and their derivatives catalyzed by Group 4 metal complexes.

Catalyst/ activator	Al/M	Comonomer	OAC	P_E, atm	T, °C	Activity, kg mol^{-1} h^{-1}	X_M (mol.%)	Comments	Ref.
Carboxylic acids									
Zr01/MAO	2200–4000	**C014**	MAO	0.6	23–71	600–12 000 kg mol$_{Zr}^{-1}$ · [Et]$^{-1}$	0.2–2.2	M_n = 3.8–98.2 kDa, $Đ_M$ = 3.3–6.7	83
	2200		MAO	1	60	104–2520	0.3–2.2	M_n = 10.5–155 kDa, $Đ_M$ = 3.0–5.2	84
	1000		Bu^i_3Al	1.2	25	390–10700	0.7–2.2	MCM-41	85–87
Zr02/MAO	4000		MAO	2.5	60	800–2500	~0–0.3	M_n = 39.1–40.9 kDa, $Đ_M$ = 3.2–4.4	34, 35
Zr14/MAO	1000		MAO	1	60	53–231	0.4–2.1	M_n = 26.6–97.5 kDa, $Đ_M$ = 3.2–4.8	84
Zr18/MAO	1000		MAO	1.5	60	53–151	1.4–7.3		84
Zr23/MAO	8–16 × 10^3		MAO	1.5–3	60	1200–12 200	0.3–0.5	M_n = 30.5–44 kDa, $Đ_M$ = 2.0–2.5	49
	4000		MAO	2.5	60	~2000–4000	–		35
	1900		Me_3Al	0.36M	25	340–820	5.5–7.4		37
Ti02/MAO	2000		Me_3Al	0.33M	70	330	–		37
Zr29/MAO	1000		Bu^i_3Al	1	25	8640–12 400	0.1–0.3	M_n = 2.2–3.28 kDa, $Đ_M$ = 2.3–2.7	61
Ti16/MAO	1000		MAO	n.d.	40	5700	2.5	M_n = 1.5 kDa, $Đ_M$ = 2.0	46
			Bu^i_3Al	1	25	1120	1.6	M_n = 30.7 kDa, $Đ_M$ = 2.8	65
	3000		MAO	1	25	100	1.5	M_n = 149 kDa, $Đ_M$ = 2.0	65
Ti33/MAO	300		Et_2AlCl	2	50	200	0.3	M_n = 1471.3 kDa, $Đ_M$ = 1.9	88
Ti39/MAO	1000		Bu^i_3Al	1	25	1970–2300	0.25–0.5	M_n = 28.9–29.5 kDa, $Đ_M$ = 2.3	61
$TiCl_4$/DIBP/$MgCl_2$/ Et_2AlCl	150		Et_2AlCl	2	50	18	0.3	M_n = 1428.1 kDa, $Đ_M$ = 2.3	88
Zr19/MAO	2200	**C015**	Bu^i_3Al	0.9–1.5	40	325–1436	4.0–5.4	M_n = 1.8–3.7 kDa, $Đ_M$ = 2.2–2.5	73
Zr19/MAO	2200		Bu^i_3Al	0.9–1.5	40	400–1400	3.0–8.9	M_n = 1.2–2.7 kDa, $Đ_M$ = 2.2–2.5	43
Zr20/MAO	2200		Bu^i_3Al	0.9–1.5	40	1500–3400	0.9–3.8	M_n = 4.4–5.8 kDa, $Đ_M$ = 2.7–3.4	43
Zr21/MAO	2200		Bu^i_3Al	0.9	40	2800–3300	1.1	M_n = 4.4–5.0 kDa, $Đ_M$ = 2.6–3.3	43
Esters									
$TiCl_3$/Et_2AlCl	10	**C020**	none	1	25	4.4	3	η = 5.61 dL g^{-1}	31
Zr02/MAO	4000	**C017**	MAO	2.5	60	850–2940	0.2	M_n = 33.6–58.4 kDa, $Đ_M$ = 3.2–3.9	35 34
Zr26/MAO	3000	**C016**, **C018**	MAO	1	30	84, 108	~0, 0.6	M_n = 25.6 kDa, $Đ_M$ = 3.4, M_n = 28.4 kDa, $Đ_M$ = 3.2	52
Ti16/MAO	1000	**C018**	MAO	n.d.	40	400	1.3	M_n = 12.1 kDa, $Đ_M$ = 2.4	46
Ti30/MAO	50	**C018**	MAO	1	n.d.	3.5	About 1%	M_n = 40.6 kDa, $Đ_M$ = 2.5	82
			Et_3Al			4.0		M_n = 48.6 kDa, $Đ_M$ = 3.4	
			Me_3Al			0			
			Et_2AlCl			3.0		M_n = 34.4 kDa, $Đ_M$ = 2.3	
			MMAO			4.5		M_n = 34.3 kDa, $Đ_M$ = 2.4	
			Bu^i_3Al	1–10		1.5–69		M_n = 31.0–695.8 kDa, $Đ_M$ = 2.0–6.9	
Ti33/dMAO	300	**C018**	none	2	50	0	0		88
$TiCl_4$/DIBP/ $MgCl_2$/Et_2AlCl	150	**C018**	none	2	50	0	0		88
Ti58/MAO	2000–4000	**C018**	MAO	1	25–50	90–234	0.5–1	M_n = 9.1–19.0 kDa, $Đ_M$ = 2.1–2.8	89
Ti59/MAO	3000	**C018**	MAO	1	25	114	0.8	M_n = 12.4 kDa, $Đ_M$ = 3.3	89

Table 2 (continued).

Catalyst/ activator	Al/M	Comonomer	OAC	P_E, atm	T, °C	Activity, kg mol^{-1} h^{-1}	X_M (mol.%)	Comments	Ref.
Esters									
Ti32/dMAO	250–300	**C019**	none	1	25	11–337	0.8–2.45	M_n = 11.1–122.3 kDa, $Đ_M$ = 1.8–2.2	90
Ti33/dMAO						15–341	0.9–3.2	M_n = 14.4–124.1 kDa, $Đ_M$ = 1.6–2.2	
Ti34/MAO						61–515	0.7–1.8	M_n = 30.5–161.2 kDa, $Đ_M$ = 2.2–2.4	
Ti35/MAO						56–353	0.7–2	M_n = 30.5–114.5 kDa, $Đ_M$ = 1.8–2.2	
Ti36/MAO						17–178	0–0.5	M_n = 79.2 kDa, $Đ_M$ = 2.4	
Ti37/MAO						28	n.d.		
Ti38/MAO						86	0.13	M_n = 236.6 kDa, $Đ_M$ = 2.1	
Amides									
Zr23/MAO	4000	**C066**, **C067**, **C068**, **C069**, **C070**	none	1.5	60	330–3800, 2900, <30, 40–190, 130	0.2–0.6, 0.3, 0, 0.4–1.3, 0.6	M_n = 16.1–33.4 kDa, $Đ_M$ = 3.2–3.3, M_n = 25.5 kDa, $Đ_M$ = 2.7, M_n = 2.3–6 kDa, $Đ_M$ = 2.5–3.0, M_n = 4.2 kDa, $Đ_M$ = 2.4	91

Note. DIBP is diisobutyl phthalate, dMAO is dried MAO (containing no Me_3Al).

In most studies, precatalysts have been activated using MAO, the masking efficiency of which is questionable.[92] Zuo *et al.*[82] investigated the effect of various cocatalysts (MAO, Me_3Al, Et_3Al, Et_2AlCl, Bu^i_3Al) in the copolymerization of **C018** on the performance of the **Ti30**/MAO catalyst and the molecular weight of the obtained copolymers; the best result was obtained by using Bu^i_3Al (69 kg mol^{-1} h^{-1}, M_n = 340.4 kDa).[82] In the **Zr02**/MAO-catalyzed copolymerization of **C017** and **C018**, the catalyst activity was up to 2940 kg mol^{-1} h^{-1} (~0.2 mol.% comonomer).[34,35] The highest X_M value (1.3 mol.%) was achieved for Bu^i_3Al-treated **C018** in the presence of **Ti16**/MAO (400 kg mol^{-1} h^{-1}).[46] Post-metallocene complexes **Ti58** and **Ti59** showed lower activity (234 and 114 kg mol^{-1} h^{-1}, respectively);[89] the titanium/magnesium Ziegler–Natta catalyst proved to be inert towards the copolymerization involving **C018**.[88] Among the post-metallocene Ti complexes, higher performance in the ethylene copolymerization with 5-hexen-1-yl acetate **C019** was found for phenoxyimine complexes with electron-donating substituents **Ti33**–**Ti35**. The beneficial effect of the electron-donating groups on the catalytic activity was confirmed by the results of DFT modelling that estimated the energy difference between the C=C group and the carbonyl oxygen atom coordinated to the titanium atom (8.8–14.3 kcal mol^{-1}).[90] The modelling did not take into account the possible effect of the cocatalyst (OAC) on the coordination.

2.1.3. Copolymerization of ethylene with ω-alkenamines

ω-Alkenamines represent a fairly specific group of polar comonomers the ability of which to copolymerize with ethylene considerably depends on the type of amine (the presence of N–H bonds capable of reacting with OAC) and the nature of substituents on the nitrogen atom. The results of experimental studies of the copolymerization of ethylene with unsaturated amines are summarized in Table 3.

As in the case of $CH_2{=}CH(CH_2)_nOAlR_2$, copolymerization of ω-alkenamines may be accompanied by the intramolecular coordination of the N atom to the catalytic site after the comonomer incorporation. Marks and co-workers[94] carried out an experimental and theoretical study of the effect of the length of the $(CH_2)_n$ sequence on the activity of **Zr04′**/TB$^{\mathrm{F}}$ and **Zr07′**/TB$^{\mathrm{F}}$ in the reactions involving **C044** and **C048**. An increase in the $(CH_2)_n$ length hampered the coordination, which is consistent with experimental data (**Zr04′**: 39 kg mol^{-1} h^{-1} for **C044**, 2600 kg mol^{-1} h^{-1} for **C048**; **Zr07′**: 14 kg mol^{-1} h^{-1} for **C044**, 3400 kg mol^{-1} h^{-1} for **C048**).[94] An increase in the bulk of the substituent at the nitrogen atom did not have a pronounced effect on the activity and X_M (**Zr04**: 1.8 mol.% for **C047** and 1.5 mol.% for **C048**; **Zr07′**: 5.0 mol.% for **C047** and 5.0 mol.% for **C048**).[94] These data contradict the results of earlier studies by Löfgren and co-workers,[91] who showed that in the **Zr08**/MAO- and **Zr23**/MAO-catalyzed copolymerization the presence of more bulky substituents (Bu$^{\mathrm{t}}$, Bu$^{\mathrm{s}}$, Bn) on the N atom in unsaturated amines increases the catalyst activity (simultaneously, X_M decreases). The **Zr22**/MAO-catalyzed copolymerization of ethylene with ω-alkenamines containing aryl substituents on the N atom (**C062**–**C064**) yielded copolymers containing up to 12.6 mol.% comonomer.[93] This result is attributable to the lower nucleophilicity of the nitrogen atom in arylamines compared to alkylamines.

Of particular interest are early studies of the copolymerization of ethylene with **C045** catalyzed by **Zr07**/MAO[38] and with cyclic amines (**C058**–**C061**, **C071**, **C072**) catalyzed by **Zr09**/MAO.[95] The cited publications describe the preparation of functional polyethylenes in the presence of metallocene catalysts supported on MAO-activated silica, which opens up the possibility of using modern techniques for the production of metallocene LLDPE and for the synthesis of functional polyethylenes.

2.1.4. Copolymerization of ethylene with ω-halogenated α-olefins and other polar comonomers

The results of investigation of ethylene copolymerization with halogenated olefins and polar comonomers other than those mentioned in Sections 2.1.1–2.1.3 are summarized in Table 4.

Table 3. Main characteristics of the copolymerization of ethylene with ω-alkenamines catalyzed by Group 4 metal complexes.

Catalyst/ activator	Al/M	Comonomer	OAC	P_E, atm	T, °C	Activity, kg mol^{-1} h^{-1}	X_M (mol.%)	Comments	Ref.
Zr01/MAO	1000	**C062**	none	1	75	29 500	0.9	M_n = 2.0 kDa, $Đ_M$ = 21.9	93
Zr01′/TB^F	n.d.	**C047**	none	1	25	840	1.4		94
Zr03/B^F	n.d.	**C047**	none	1	25	1800	0.3		94
Zr03/TB^F	n.d.	**C047**	none	1	25	1700–3400	0.2 – 0.3		94
		C044				39	<0.1		
		C045				520	0.4		
		C047				3100	1.8		
Zr04′/TB^F	n.d.	**C048**	none	1	25	2600	1.5		94
Zr07/MAO	1000	**C062**	none	1	75	22 800	2.4	M_n = 68.1 kDa, $Đ_M$ = 2.6	93
Zr07′/TB^F	n.d.	**C044**	none	1	25	39	<0.1		94
		C045				520	0.4		
		C047				3100	1.8		
Zr09/MAO	3000	**C058**	none	2	40–80	4200–7800	0.06–0.8	M_n = 7.1–12.2 kDa, $Đ_M$ = 2.2–2.6	95
		C059				6600–8200	0.07–1.5	M_n = 5.7–12.2 kDa, $Đ_M$ = 1.9–2.6	
		C060				3000–4600	0.1–0.3	M_n = 14.1–15.3 kDa, $Đ_M$ = 2.0–2.1	
		C061				5800	0.03	M_n = 18.1 kDa, $Đ_M$ = 2.0	
		C071				240–9600	0.04–0.3	M_n = 8.4–62.3 kDa, $Đ_M$ = 1.9–2.4	
		C072				760–10 800	0.04–0.62	M_n = 1.5–44.9 kDa, $Đ_M$ = 2.3–2.5	
	100	**C059**	none	5	80	9730	0.01		95
		C071				1400	0		
		C072				1500	0		
Zr17/MAO	16 000	**C049**	none	2	n.d.	n.d.	1.01–3.7	T_m = 100.9–115.6°C	96
Zr22/MAO	1000–2000	**C062**	none	1	75	5500–10 000	4.0–11.6	M_n = 50.6–82.2 kDa, $Đ_M$ = 1.7–2.3	93
		C063				9900–21 000	5.1–12.6	M_n = 66.6–66.1 kDa, $Đ_M$ = 1.8–2.5	
		C064				7000–14 400	3.5–11.3	M_n = 81.5–84.5 kDa, $Đ_M$ = 1.5–1.9	
Zr23/MAO	8000	**C050**	MAO	1.5	60	1500	1.24	M_n = 6.5 kDa, $Đ_M$ = 1.7	49
	4000	**C050**	none	1.5	60	1500–1700	0.8–1.2	M_n = 6.5–8.8 kDa, $Đ_M$ = 1.6–1.7	91
		C051				1400	0.65	M_n = 13.5 kDa, $Đ_M$ = 1.7	
		C052				1400–1900	0.4–0.7	M_n = 6.0–9.6 kDa, $Đ_M$ = 2.0–2.3	
		C053				950	0.9	M_n = 6.2 kDa, $Đ_M$ = 2.1	
		C054				2500–2700	0.3–0.5	M_n = 11.0–14.0 kDa, $Đ_M$ = 2.0–2.1	
		C055				1500–2200	0.3–0.6	M_n = 9.1–17.1 kDa, $Đ_M$ = 2.3–3.8	
		C056				2100–3000	0.4–0.9	M_n = 7.7–13.5 kDa, $Đ_M$ = 1.7–2.2	
		C057				2200	0.3	M_n = 10.8 kDa, $Đ_M$ = 2.4	
	2000	**C062**	none	1	75	5800–25 700	1.2–6.1	M_n = 49.3–54.6 kDa, $Đ_M$ = 1.5–2.0	97
	1000	**C062**	none	1	75	30 200	1.8	M_n = 54.8 kDa, $Đ_M$ = 2.2	93
Zr25/MAO	n.d.	**C065**	none	1	60	71–84	0.25–1.37	M_n = 37.5–73.6 kDa, $Đ_M$ = 2.8–3.2	98
Ti02/MAO	1000	**C062**	none	1	75	300–1700	5.4–6.8	M_n = 104.1–145.4 kDa, $Đ_M$ = 1.7–2.3	93
Ti16/MAO	3000	**C046**	none	n.d.	40	2800	1.9		46

Table 4. Main characteristics of the copolymerization of ethylene with halogenated olefins and other polar comonomers catalyzed by Group 4 metal complexes.

Catalyst/ activator	Al/M	Comonomer	OAC	P_E, atm	T, °C	Activity, kg mol^{-1} h^{-1}	X_M (mol.%)	Comments	Ref.
Halo derivatives									
Zr23/MAO	1000	**C077**	Bu^i_3Al	2	70	5268	1.7	$M_n = 11.9$, $Đ_M = 4.5$	99
		C078				1104	1.1	$M_n = 5.7$, $Đ_M = 5.3$	
		C079				6334	2.9	$M_n = 8.7$, $Đ_M = 6.0$	
		C084				1112–8644	0.5–6.1	$M_n = 1.4–7.4$, $Đ_M = 3.4–8.2$	
		C083	none	1	25	1020 – 2120	2.9–16.6	$M_n = 48.3–111.6$ kDa, $Đ_M = 2.2–2.5$	100
Zr23/TB^F	n.d.	**C083**	Bu^i_3Al	–	25	1810 – 2940	9.5–19.8	$M_n = 20.5–22.7$ kDa, $Đ_M = 2.2–2.6$	101
Zr25/MAO	2300	**C084**	none	1	25	29–1087	1.0–25.2	Degree of crystallinity 22–27%	102
Hf01/Bu^i_3Al/TB^F	100	**C081**	none	10	80	1500	1.1		103
		C082				3700	2.3		
		C083				4800	6.3		
Ti17/MAO	3000	**C086**	none	1	30	680–1360	2.5–4.3	$M_n = 2.9–4.5$ kDa, $Đ_M = 3.0–3.2$	104
Ti22/MAO	3000	**C086**	none	1	30	1150–1360	2.9–5.2	$M_n = 3.1–4.4$ kDa, $Đ_M = 2.2–3.0$	104
Ti26/MAO	3000	**C085**	none	1	30	80–990	5.2–9.7	$M_n = 2.2–2.6$ kDa, $Đ_M = 3.9–4.2$	104
		C086				50–1600	3.0–15.8	$M_n = 0.8–4.2$ kDa, $Đ_M = 2.8–4.4$	
		C087				220–1090	5.6–8.2	$M_n = 3.7–3.8$ kDa, $Đ_M = 3.1–4.2$	
Ti27/MAO	3000	**C086**	none	1	30	400 – 1090	2.8–4.5	$M_n = 3.1–3.7$ kDa, $Đ_M = 2.7–4.2$	104
Other polar comonomers									
Zr01/MAO	3000	**C089**	none	1.6	20–80	3445–7728	0.07–0.3	$M_n = 20.2$ kDa, $Đ_M = 2.4$	105
Zr09/MAO	3000	**C089**	none	1.6–2	20–80	3965–10620	0.3–0.7	$M_n = 22.4$ kDa, $Đ_M = 2.4$	105, 106
		C090				2500	0.25	$M_n = 20.5$ kDa, $Đ_M = 2.0$	
Zr25/MAO	3000	**C089**	none	1.6	20–80	2873–10260	0.3–0.8	$M_n = 28.3$ kDa, $Đ_M = 2.2$	105
Zr36/MAO	600	**C076**	none	2	60	16.1	0.41	$M_n = 46.6$ kDa, $Đ_M = 2.9$	107
Zr37/MAO	600	**C076**	none	2	60	20.6	0.56	$M_n = 50.7$ kDa, $Đ_M = 2.8$	107
Zr38/MAO	600	**C076**	none	2	60	24.5	0.91	$M_n = 56.7$ kDa, $Đ_M = 2.7$	107
Ti29/MAO	n.d.	**C088**	none	n.d.	n.d.	370	3.9		65
Ti54/MAO	600	**C076**	none	2	60	36.8	1.31	$M_n = 60.8$ kDa, $Đ_M = 2.6$	107
Ti55/MAO	600	**C076**	none	2	60	57.6	1.78	$M_n = 52.9$ kDa, $Đ_M = 2.8$	107
Ti56/MAO	600	**C073**	none	2	60	57.3–68.6	1.2–2.65	$M_n = 95.4–97.9$ kDa, $Đ_M = 2.9$	108
		C074				56.1–67.1	1.1–2.6	$M_n = 95.4–99.3$ kDa, $Đ_M = 2.9$	
		C075				55.3–66.7	1.1–2.6	$M_n = 96.2–99.7$ kDa, $Đ_M = 2.9$	
	300–1000	**C076**	none	2	25–70	24.4–66.3	0.8–2.6	$M_n = 59.7$ kDa, $Đ_M = 2.9$ $M_n = 96.8–97.9$ kDa, $Đ_M = 2.9$	107, 108

Halogen derivatives of olefins are conventionally considered as a polar comonomers with latent reactivity, as halogen atoms are less prone to coordination to the metal atom in the active site than O and N atoms. However, ethylene copolymers with ω-haloalkenes can be subjected to subsequent organochemical post-modification to introduce a large variety of functional groups.

Ethylene copolymers with ω-bromo- and ω-iodoalkenes (**C077**–**C079**, **C083**, **C084**) containing 1.7 mol.% **C077**, 1.1 mol.% **C078**, 2.9 mol.% **C079**, up to 19.8 mol.% **C083**, and up to 6.1 mol.% **C084** were prepared using **Zr23**/MAO catalyst.[99,100] Catalysis by post-metallocene hafnium complex **Hf01** was used to prepare ethylene copolymers containing 1.1 mol.% **C080**, 2.3 mol.% **C081**, and 6.3 mol.% **C082**.[103] The reactivity of $CH_2=CH(CH_2)_nHal$ depended on the nature of the halogen (Cl < Br < I) and increased with increasing length of the $(CH_2)_n$ sequence.

Polyolefins with side-chain perfluoroalkyl groups were synthesized by Tang and co-workers;[104] in the copolymerization of ethylene with 5-(perfluoro-n-alkyl)norbornenes (**C085**–**C087**), the highest catalytic activity was found for [ONS]-complex **Ti26** (up to 1600 kg mol^{-1} h^{-1}), with incorporation ratios of comonomers being 9.7 mol.% (**C085**), 15.8 mol.% (**C086**), and 8.2 mol.% (**C087**).[104]

Post-metallocene titanium and zirconium complexes **Ti54**–**Ti56** and **Zr36**–**Zr38** were tested in the copolymerization of ethylene with *N*-acetyl-*O*-(ω-alkenyl)-*L*-tyrosine esters (**C073**–**C076**).[107,108] Titanium complexes showed a higher activity (up to 68.6 kg mol^{-1} h^{-1}) than zirconium complexes (up to 24.5 kg mol^{-1} h^{-1}), and the resulting copolymers contained up to 2.6 mol.% comonomers. Ethylene copolymers containing up to 0.7 mol.% 6-*tert*-butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol (**C089**) were synthesized using **Zr25**/MAO (activity of up to 10620 kg mol^{-1} h^{-1}).[105] This same catalyst was also successfully used in the synthesis of copolymers containing ~0.25 mol.% 6-hydroxy-2,5,7,8-tetramethyl-2-(but-3-enyl) chromane (**C090**).[106] Comonomers **C089** and **C090** are of special interest, as they increase the thermo-oxidative stability of polyethylenes.

Thus, some comonomers require the use of cocatalysts (masking agents), while copolymerization of sterically hindered ω-alkenamines can be accomplished without the use of additional amounts of OAC. The problem of active site deactivation can be solved by designing the ligand environment of the metal atom. Meanwhile, of particular interest are the results obtained by Duchateau and co-workers,[53] who revealed the tolerance of the half-sandwich Ti(III) complex **Ti07′** to the comonomer concentration while studying copolymerization of ethylene with **C006**-Al^{i}Bu$_2$. Titanium(III) complexes have been barely investigated in the synthesis of functional polyolefins, and good prospects of further research in this direction are quite probable.

2.2. Copolymerization catalyzed by Sc and V complexes

The active site of catalysts based on Sc and V complexes can also be deactivated due to the coordination with a nucleophilic heteroatom of the polar comonomer. Meanwhile, this trend is less pronounced for V complexes than for Sc or Group 4 metal complexes, since in the case of V, the catalytic species are neutral complexes $L_nV(III)R$,[109] the products of the reaction of precatalysts with R_3Al or R_2AlCl,[110] which form less strong complexes with the functional groups of polar olefins.

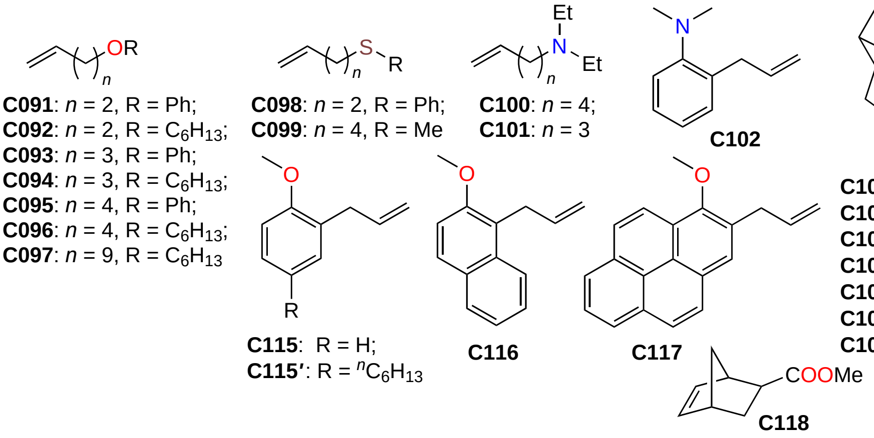
Apart from the comonomers mentioned above, that is, **C001**, **C004**–**C006**, **C013**, **C015**, **C018**, **C044**, **C045**, **C048**, and **C090**, which were tested in the copolymerization of ethylene catalyzed by Group 4 metal complexes, comonomers **C091**–**C118** were also investigated in the copolymerization of ethylene initiated by Sc and V complexes.[88,111–126]

2.2.1. Copolymerization of ethylene with polar vinyl monomers catalyzed by Sc complexes

A recent review by Marks and co-workers[27] considers examples of using Sc complexes in ethylene copolymerization with functional α-olefins and norbornene derivatives. Copolymerization with polar vinyl monomers, which are the subject of this review, was conducted using complexes **Sc01**–**Sc15** as catalysts. The results of these studies are summarized in Table 5.

Rare earth metal complexes were widely investigated in the polymerization of conjugated polar vinyl monomers (acrylates, phosphonates, *etc.*);[127,128] however, copolymerization of ethylene with non-conjugated polar comonomers has been addressed in relatively few publications.[111–120] Hou and co-workers[112] studied copolymerization of ethylene with polar comonomers containing OPh (**C091**, **C093**), SPh (**C098**), or PPh_2 (**C110**) groups using half-sandwich mononuclear complexes **Sc01**, **Sc12**, and **Sc15** as catalysts. The resulting copolymers contained up to 24.8 mol.% **C093**, 73.5 mol.% **C098**, and 9.5 mol.% **C110**.[112] Cui and co-workers[116] investigated copolymerization of ethylene with OPh-containing polar comonomer **C095** in more detail using half-sandwich complexes **Sc05**, **Sc09**, **Sc10**, and **Sc14** as catalysts. Complexes

Structures of C091–C118


C091: $n = 2$, R = Ph;
C092: $n = 2$, R = C_6H_{13};
C093: $n = 3$, R = Ph;
C094: $n = 3$, R = C_6H_{13};
C095: $n = 4$, R = Ph;
C096: $n = 4$, R = C_6H_{13};
C097: $n = 9$, R = C_6H_{13}

C098: $n = 2$, R = Ph;
C099: $n = 4$, R = Me

C100: $n = 4$;
C101: $n = 3$

C102

C110

C111: $n = 2$, Hal = Br;
C112: $n = 4$, Hal = Cl;
C113: $n = 4$, Hal = I;
C114: $n = 8$, Hal = Br

C103: R = Ph;
C104: R = p-MeC_6H_4;
C105: R = p-FC_6H_4;
C106: R = o-MeC_6H_4;
C107: R = o-FC_6H_4;
C108: R = Hex;
C109: R = Pr^i

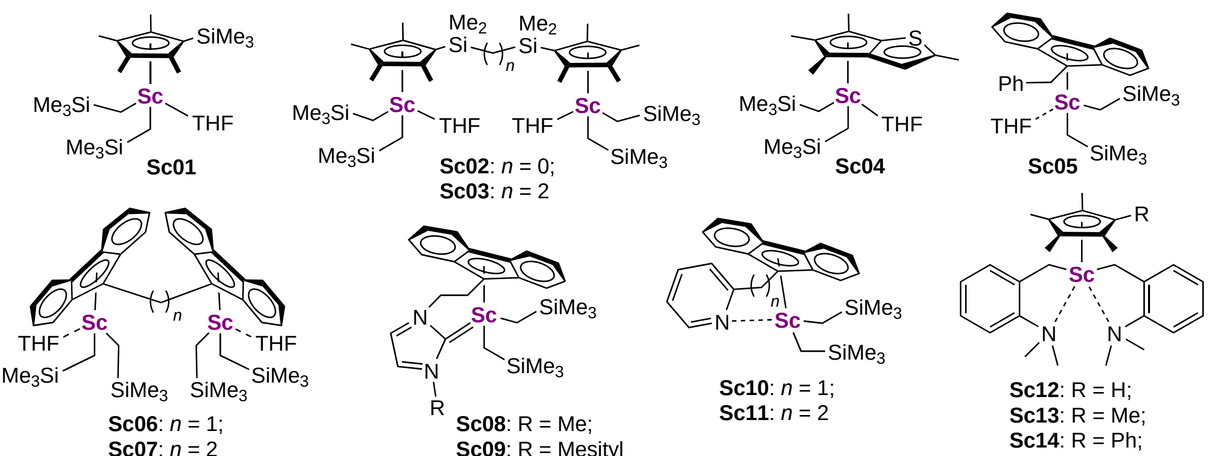
C115: R = H;
C115′: R = $^nC_6H_{13}$

C116

C117

C118

Structures Sc01–Sc15


Sc01

Sc02: $n = 0$;
Sc03: $n = 2$

Sc04

Sc05

Sc06: $n = 1$;
Sc07: $n = 2$

Sc08: R = Me;
Sc09: R = Mesityl

Sc10: $n = 1$;
Sc11: $n = 2$

Sc12: R = H;
Sc13: R = Me;
Sc14: R = Ph;
Sc15: R = $SiMe_3$

Table 5. Main characteristics of the copolymerization of ethylene with polar vinyl monomers catalyzed by Sc complexes.

Catalyst/ activator	Al/M	Como- nomer	OAC	P_E, atm	T, °C	Activity, kg mol^{-1} h^{-1}	X_M (mol.%)	Comments	Ref.
Sc01/TB^F	–	**C013**	Bu^i_3Al	1	20	160–2190	1.4–13	M_n = 74–162 kDa, Đ$_M$ = 2.2–5.7	111
	n.d.	**C093**	none	1	20	2.0–11.8	3.3–11.8	M_n = 83–154.2 kDa, Đ$_M$ = 2.2–2.7	112
		C045			25	100–420	0.3–1.5	T_m = 124.4–128.7°C	113
		C101				91	1.4	T_m = 124.5°C	
		C044				100–200	2.0–12.5	T_m = 122.9–125.9°C	
		C048				290	< 0.1	T_m = 103.7°C	
		C114				201–240	5–12	M_n = 57.0–86.7 kDa, Đ$_M$ = 1.4–1.9	114
		C098			20	5.8–7.4	2.6–38.9	M_n = 17–82.4 kDa, Đ$_M$ = 1.7–2.4	112
Sc02/TB^F	n.d.	**C045**	none	1	25	71–110	0.3–0.9	T_m = 125.3–129.0°C	113
		C101				53	0.5	T_m = 126.1°C	
		C044				75	1.9	T_m = 125.5°C	
		C048				130	0.2	T_m = 131.6°C	
Sc03/TB^F	n.d.	**C045**	none	1	25	150–240	0.3–1.0	T_m = 124.1–128.5°C	113
		C101				120	0.4	T_m = 126.0°C	
		C044				77–170	1.1–8.6	T_m = 121.9–125.4°C	
		C048				210	0.2	T_m = 130.6°C	
Sc04/TB^F/Bu^i_3Al	10	**C103**	none	1	20	106–150	0	M_n = 622–654 kDa, Đ$_M$ = 2.8–3.2	115
Sc05/TB^F/Bu^i_3Al	10	**C095**	none	2	60	810	7.0	M_n = 35.9 kDa, Đ$_M$ = 2.3	116
Sc05/TB^F	n.d.	**C092**	none	4	80	0	0		117
		C094				150	7.4	M_n = 51.8 kDa, Đ$_M$ = 2.0/1.9	
		C096				50	11.5	M_n = 11 kDa, Đ$_M$ = 1.3	
		C097				80	0.5	M_n = 12 kDa, Đ$_M$ = 1.1	
		C099				110	1.1	M_n = 11 kDa, Đ$_M$ = 3.8	
		C100				110	0.9		
Sc06/TB^F	n.d.	**C092**	none	4	80	0	0		117
		C094				80	4.4	M_n = 281 kDa, Đ$_M$ = 1.6	
		C096				180	1.3	M_n = 750 kDa, Đ$_M$ = 1.6	
		C097				260	0.7	M_n = 535 kDa, Đ$_M$ = 2.1	
		C099				420	0.5	M_n = 156 kDa, Đ$_M$ = 3.1	
		C100				220	0.8		
Sc07/TB^F	n.d.	**C092**	none	4	80	40	19.2	M_n = 127.7 kDa, Đ$_M$ = 1.4/1.2	117
		C094				260	0.6	M_n = 718 kDa, Đ$_M$ = 2.4	
		C096				130	0.8	M_n = 519 kDa, Đ$_M$ = 2.0	
		C097				300	1.0	M_n = 434 kDa, Đ$_M$ = 2.1	
		C099				140	0.6	M_n = 76 kDa, Đ$_M$ = 5.8	
		C100				140	0.7		
Sc08/TB^F/Bu^i_3Al	10	**C103**	none	1	20	75	21.1	M_n = 55 kDa, Đ$_M$ = 1.5	115
Sc09/TB^F/Bu^i_3Al	10	**C095**	none	2	60	140	0.7	M_n = 34.6 kDa, Đ$_M$ = 1.3	116
		C103	none	1	20	1110–3330	5.0–31.6	M_n = 21–210 kDa, Đ$_M$ = 1.2–4.3	115
		C104				2970	21.1	M_n = 164 kDa, Đ$_M$ = 1.8	
		C105				1980	16.3	M_n = 110 kDa, Đ$_M$ = 1.6	
		C106				780	13.4	M_n = 22 kDa, Đ$_M$ = 2.1	
		C107				570	15.3	M_n = 47 kDa, Đ$_M$ = 1.2	
		C108				0	0		
	10–20	**C109**	none	1	20	22–24	10.7–19.3	M_n = 40–62 kDa, Đ$_M$ = 1.7–2.0	115
Sc10/TB^F/Bu^i_3Al	10	**C095**	none	2	60	10	1.5	M_n = 1.1 kDa, Đ$_M$ = 1.5	116
		C103		1	20	3	15.1	M_n = 4 kDa, Đ$_M$ = 1.6	115
Sc11/TB^F/Bu^i_3Al	10	**C103**	none	1	20	5	25.9	M_n = 45 kDa, Đ$_M$ = 1.8	115
Sc12/TB^F	n.d.	**C098**	none	1	20	2.7	73.5	M_n = 14.7 kDa, Đ$_M$ = 1.8	112
	n.d.	**C102**	none	1	RT	n.d.	25	M_n = 35 kDa, Đ$_M$ = 1.8	118
Sc13/TB^F	n.d.	**C102**	none	1	RT	n.d.	23	M_n = 57 kDa, Đ$_M$ = 1.9	118

Table 5 (continued).

Catalyst/ activator	Al/M	Comonomer	OAC	P_E, atm	T, °C	Activity, kg mol^{-1} h^{-1}	X_M (mol.%)	Comments	Ref.
Sc14/TB^F/Bu$^i_3$Al	10	**C095**	none	1–4	20–100	150–2730	3.0–16.0	M_n = 160–470 kDa, $Đ_M$ = 1.4–2.7	116
Sc15/TB^F	n.d.	**C091**	none	1	20	0	0		112
		C093			20	20.5–90.4	8.7–24.8	M_n = 89.6–125 kDa, $Đ_M$ = 2.0–2.3	112
		C098			20	3.3–10.6	29.0–44.9	M_n = 20.6–57.7 kDa, $Đ_M$ = 1.4–1.9	112
		C110			20	64.4–103.2	9.5–32.5	M_n = 54 kDa, $Đ_M$ = 2.2	112
		C102			n.d.	n.d.	11–21	Terpolymerization, M_n = 66–131 kDa, $Đ_M$ = 1.6–1.9	118
							14	Terpolymerization, M_n = 68 kDa, $Đ_M$ = 2.0	
							14–17	Terpolymerization, M_n = 60–124 kDa, $Đ_M$ = 2.0–2.4	
		C115′		n.d.			36	M_n = 164 kDa, $Đ_M$ = 1.5	119
		C116					41	M_n = 115 kDa, $Đ_M$ = 2.0	
		C115′+C116					11–31 10–28	M_n = 41–355 kDa, $Đ_M$ = 1.5–1.9	
		C117					48	M_n = 656 kDa, $Đ_M$ = 3.0	
		C115′+C117					20–27 10–22	M_n = 48–206 kDa, $Đ_M$ = 1.7–2.3	
		C115		1	20	51–1100	39–46	M_n = 41–552 kDa, $Đ_M$ = 1.58–1.98	120

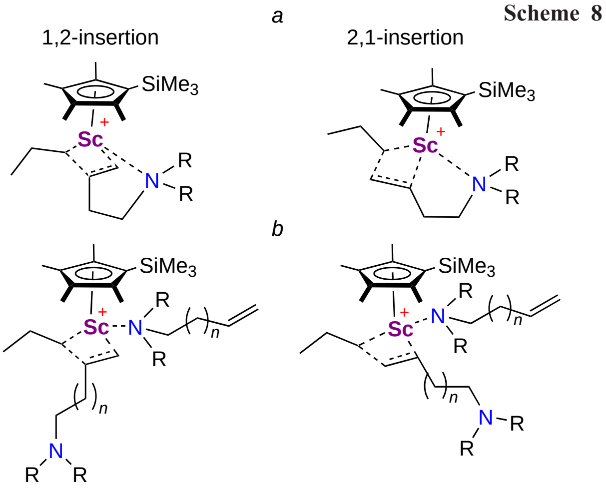
with strained rings (**Sc09**, **Sc10**) showed a lower activity (140 and 10 kg mol^{-1} h^{-1}, respectively) and lower X_M than complexes **Sc05** and **Sc14** (810 and 150–2730 kg mol^{-1} h^{-1}, respectively). The copolymers containing up to 16 mol.% **C095** were allowed to react with BBr$_3$ to be converted to bromo derivatives, which were subjected to quaternization by the reaction with *N*-methylimidazole and pyridine to give polyethylene ionomers.

Methylene- and ethylene-bridged binuclear complexes **Sc06** and **Sc07** showed a higher activity and provided lower X_M in the copolymerization of ethylene with oxygen- (**C092**, **C094**, **C096**, **C097**), nitrogen- (**C100**), and sulfur-containing (**C099**) comonomers compared to mononuclear complexes **Sc05**.[117]

The research group headed by T.Marks made the most significant contribution to the study of ethylene copolymerization with ω-alkenamines catalyzed by Sc complexes.[113,129] It was established that the length of the (CH$_2$)$_n$ sequence between the double bond and the amino group has a minor effect on the activity of complexes **Sc01**, **Sc02**, and **Sc03** activated by TB^F (**Sc01**: 200, 290, and 290 kg mol^{-1} h^{-1}; **Sc02**: 75, 110, and 130 kg mol^{-1} h^{-1}; **Sc03**: 170, 240, and 210 kg mol^{-1} h^{-1} for **C044**, **C045**, and **C048**, respectively). In this series, X_M increased with decreasing (CH$_2$)$_n$ length. The DFT modelling of the **Sc01**/TB^F-catalyzed copolymerization of ethylene with CH$_2$=CH(CH$_2$)$_n$NPr$^n_2$ (n = 2, **C044**; n = 6, **C048**)[129] revealed a qualitative difference between the mechanisms of incorporation of comonomers: in the case of **C044**, the preferable mechanism includes simultaneous coordination of the C=C bond and nitrogen atom followed by 1,2- or 2,1-insertion (Scheme 8*a*), whereas in the case of **C048**, the insertion at the catalytic site containing the Sc···N bond with a second comonomer molecule is preferred (Scheme 8*b*).[129]

In an early study by Marks and co-workers,[113] in which they actually first hypothesized that the heteroatom directly participates in the active site formation,[113] a specific behavior of binuclear complexes **Sc02** and **Sc03** was found, in particular, these complexes provided a higher X_M in the copolymerization with comonomer **C048** with a long (CH$_2$)$_n$ chain between the C=C group and the nitrogen atom than complex **Sc01**. In order to explain this fact, it was hypothesized that –CH=CH$_2$ and the N atom may be coordinated to different atoms of the binuclear catalyst, which facilitates the insertion of the polar comonomer.[113]

Scheme 8



Complex **Sc01**/TB^F was also studied in the copolymerization of **C013**-AlBu$^i_2$ (activity of up to 2190 kg mol^{-1} h^{-1}).[111] Ethylene copolymers with *N*-(R)-*cis*-5-norbornene-*endo*-2,3-dimethylenes (**C103**–**C109**) were synthesized in the presence of half-sandwich strained complexes **Sc03** and **Sc08**–**Sc11** activated by TB^F and Bu$^i_3$Al. Complex **Sc09** showed the highest activity (up to 3330 kg mol^{-1} h^{-1}), with the maximum X_M value (**C103**) being 31.6 mol.%.[115]

In the copolymerization of ethylene with 2-allylanisole **C115** (1 atm, 20°C), the activity of **Sc15**/TB^F reached 1100 kg mol^{-1} h^{-1}.[120] Ethylene terpolymers with 2-allylanisole analogs **C115′**–**C117** were also prepared in the presence of **Sc15**/TB^F.[119] The **Sc15**/TB^F catalyst was used to synthesize terpolymers of ethylene, 2-allyl-*N*,*N*-dimethylaniline **C102**, and styrenes with a controlled sequence of comonomers.[118]

The **Sc01**/TB^F catalyst was used to prepare copolymers of ethylene with 10-bromo-1-decene (**C114**), with the highest X_M

for **C114** being 12 mol.%.[114] Of considerable interest are copolymers of ethylene, propylene, and diene monomers (EPDM) involving **C114**, that is EPDM with side-chain bromoalkyl groups; however, Hou and co-workers[114] restricted themselves only to the synthesis of this type of copolymers, without subsequent functionalization.

Comparison of the performance of catalysts based on Group 4 metals and Sc is difficult, because a relatively small number of polar comonomers have been studied using both types of catalysts. In the copolymerization of ω-alkenamines (**C044**, **C045**, **C048**), Sc complexes were inferior to zirconocenes in the activity; in the copolymerization with unsaturated ethers, both types of catalysts showed low activity. The examples of processes in which the activity of Sc-based catalysts exceeded 1000 kg mol^{-1} h^{-1} are few and are mainly limited to functional derivatives of norbornene. Meanwhile, studies of ethylene copolymerization with polar vinyl monomers catalyzed by Sc complexes made it possible to reveal the mechanism of comonomer insertion with additional coordination of the donor atom of the functional group, which is of general importance for the synthesis of functional polyolefins.[27]

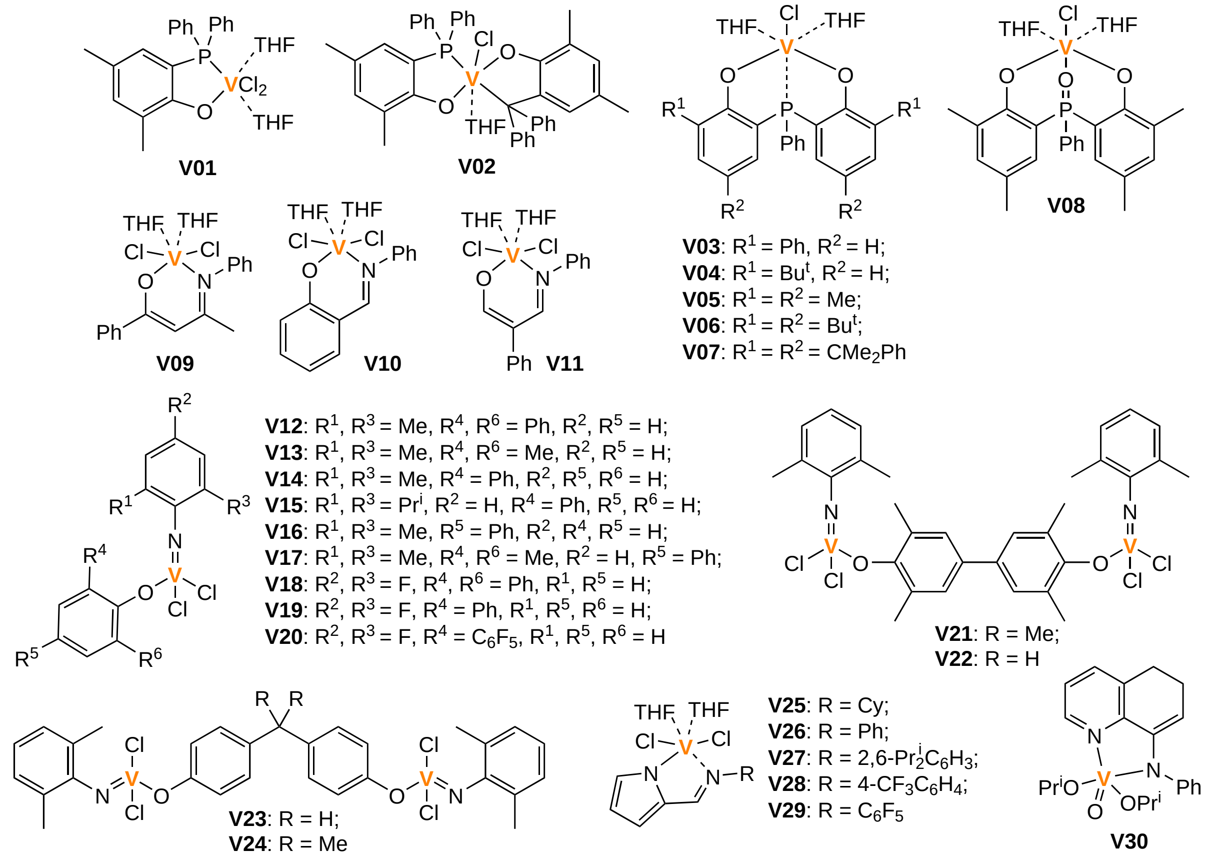
2.2.2. Copolymerization of ethylene with polar vinyl monomers catalyzed by V complexes

A promising alternative to the complexes based on Group 4 metals for copolymerization of ethylene with polar vinyl monomers are probably vanadium complexes, which are less susceptible to deactivation caused by binding to a nucleophilic atom of the comonomer. Vanadium complexes usually do not require the use of expensive activators (MAO, perfluoroarylborates), which is an additional advantage over Group 4 metal complexes and Sc. However, V-catalyzed processes are often complicated by the reduction of the active V^{3+} centers to V^{2+}; in some cases, this problem can be solved by adding oxidants, *e.g.*, CCl_3COOEt (ETA). Complexes **V01**–**V30** were tested in the copolymerization of polar monomers with ethylene; the experimental results are summarized in Table 6.

Copolymerization of ethylene with ω-alken-1-ols (**C001**, **C004**, **C006**) catalyzed by vanadium(III) complexes with [N,O]-bidentate ligands (**V09**, **V10**, **V11**) was studied in 2009 by Mu *et al.*[122] The efficiency of masking reagents in the copolymerization involving **C006** and the activity of **V09**/Et_2AlCl in the presence of ETA as a reactivating agent increased in the series $Bu^i_3Al < Et_3Al < Me_3Al < Et_2AlCl$. In the presence of **V09**/Et_2AlCl, the highest X_M for **C001**, **C004**, and **C006** were 0.4, 2.7, and 13.9 mol.%, respectively. The complexes with [O,P,O]- and [O,P=O,O]-tridentate ligands **V03**–**V08** and complexes with [O,P] type ligands **V01** and **V02** were also investigated in the copolymerization of ethylene with 10-undecen-1-ol (**C006**) protected by Et_2AlCl.[121] The highest X_M for **C006**-AlEtCl amounted to 14.6 mol.% when **V05** catalyst was used. A comparative study of complexes **V25**–**V29** with [N,N] type ligands in the copolymerization with **C006**-AlEtCl demonstrated high catalytic activity (up to 10 000 kg mol^{-1} h^{-1}), which depended only slightly on the substituent nature.[125]

Binuclear vanadium complexes (**V21**–**V24**) proved to be more active than mononuclear analogs **V12**–**V15**, **V17**–**V20** and provided higher X_M in the copolymerization of ethylene with **C006**-AlEtCl, **C018**, and **C112**.[124,123] This result can be attributed to the cooperative effect of the two catalytic centers discovered previously by Marks and co-workers, who studied binuclear scandium complexes.[113] However, mononuclear

Structures V01–V30



V01 **V02** **V08**

V03: R^1 = Ph, R^2 = H;
V04: R^1 = Bu^t, R^2 = H;
V05: R^1 = R^2 = Me;
V06: R^1 = R^2 = Bu^t;
V07: R^1 = R^2 = CMe$_2$Ph

V09 **V10** **V11**

V12: R^1, R^3 = Me, R^4, R^6 = Ph, R^2, R^5 = H;
V13: R^1, R^3 = Me, R^4, R^6 = Me, R^2, R^5 = H;
V14: R^1, R^3 = Me, R^4 = Ph, R^2, R^5, R^6 = H;
V15: R^1, R^3 = Pr^i, R^2 = H, R^4 = Ph, R^5, R^6 = H;
V16: R^1, R^3 = Me, R^5 = Ph, R^2, R^4, R^5 = H;
V17: R^1, R^3 = Me, R^4, R^6 = Me, R^2 = H, R^5 = Ph;
V18: R^2, R^3 = F, R^4, R^6 = Ph, R^1, R^5 = H;
V19: R^2, R^3 = F, R^4 = Ph, R^1, R^5, R^6 = H;
V20: R^2, R^3 = F, R^4 = C$_6$F$_5$, R^1, R^5, R^6 = H

V21: R = Me;
V22: R = H

V23: R = H;
V24: R = Me

V25: R = Cy;
V26: R = Ph;
V27: R = 2,6-Pr$^i_2$C$_6$H$_3$;
V28: R = 4-CF$_3$C$_6$H$_4$;
V29: R = C$_6$F$_5$

V30

Table 6. Main characteristics of the copolymerization of ethylene with polar vinyl monomers catalyzed by V complexes.

Catalyst/ activator	Al/M	Comonomer	OAC	P_E, atm	T, °C	Activity, kg mol^{-1} h^{-1}	X_M (mol.%)	Comments	Ref.
V01/Et_2AlCl/ETA	300	**C006**	Et_2AlCl	1	50	4200	3.8	M_n = 4.2 kDa, Đ_M = 1.7	121
V02/Et_2AlCl/ETA						3120	2.1	M_n = 9.2 kDa, Đ_M = 2.4	
V03/Et_2AlCl/ETA						6240	2.94	M_n = 9.6 kDa, Đ_M = 2.2	
V04/Et_2AlCl/ETA						6600	3.1	M_n = 8.0 kDa, Đ_M = 2.4	
V05/Et_2AlCl/ETA	300–4000				25–70	2160–9480	2.6–14.6	M_n = 1.6–39.0 kDa, Đ_M = 2.0–2.6	
V06/Et_2AlCl/ETA	300				50	10100	2.8	M_n = 8.0 kDa, Đ_M = 1.8	
V07/Et_2AlCl/ETA						4080	2.3	M_n = 5.3 kDa, Đ_M = 2.1	
V08/Et_2AlCl/ETA						7320	3.1	M_n = 7.7 kDa, Đ_M = 1.9	
V09/Et_2AlCl/ETA	4000/500	**C001**	Et_2AlCl	1	50	3900	0.4	M_n = 8.9 kDa, Đ_M = 1.9	122
		C004	Et_2AlCl			8500	2.7	M_n = 6.9 kDa, Đ_M = 2.1	
		C006	Bu^i_3Al			1980	2.2	M_n = 8.3 kDa, Đ_M = 1.8	
			Et_3Al			3240	2.3	M_n = 4.7 kDa, Đ_M = 1.9	
			Me_3Al			8340	2.5	M_n = 4.5 kDa, Đ_M = 2.0	
	500–4000	**C006**	Et_2AlCl		20–60	720–12 800	1.4–13.9	M_n = 2.3–32.8 kDa, Đ_M = 1.8–5.4	
V10/Et_2AlCl	4000	**C006**	Et_2AlCl		50	8700	4.0	M_n = 4.5 kDa, Đ_M = 2.0	
V11/Et_2AlCl		**C006**	Et_2AlCl		50	11 200	3.4	M_n = 5.9 kDa, Đ_M = 2.0	
V12/Et_2AlCl	2500	**C018**	none	4	0	1000	0.7	M_n = 240 kDa, Đ_M = 2.3	123
V13/Et_2AlCl	1500	**C006**	Et_2AlCl			114	0.8	M_n = 260 kDa, Đ_M = 2.1	124
	2500	**C018**	none			720	0.9	M_n = 130 kDa, Đ_M = 2.4	123
	1500		none			72	0.5	M_n = 170 kDa, Đ_M = 2.7	124
		C112	none			1740	n.d.	M_n = 756 kDa, Đ_M = 2.0	124
V14/Et_2AlCl	2500	**C018**	none			1200	1.2	M_n = 72 kDa, Đ_M = 2.1	123
V15/Et_2AlCl		**C018**	none			940	0.6	M_n = 96 kDa, Đ_M = 2.1	123
V16/Et_2AlCl		**C018**	none			230–1700	1.2–4.1	M_n = 100–160 kDa, Đ_M = 2.1–2.3	123
V17/Et_2AlCl		**C018**	none			340	0.6	M_n = 110 kDa, Đ_M = 2.2	123
V18/Et_2AlCl		**C006**	Et_2AlCl			460–1070	0.6	M_n = 240 kDa, Đ_M = 2.6	123
		C018	none			650–2160	0.4	M_n = 220–230 kDa, Đ_M = 2.3–2.5	123
		C112	none			790–1080	0.3	M_n = 300 kDa, Đ_M = 1.8	123
V19/Et_2AlCl		**C018**	none			1470	0.6	M_n = 100 kDa, Đ_M = 2.6	123
V20/Et_2AlCl		**C018**	none			2250	1.7	M_n = 170 kDa, Đ_M = 2.5	123
V21/Et_2AlCl	1500	**C006**	Et_2AlCl			258–654	0.6	M_n = 3240–3650 kDa, Đ_M = 2.1–2.2	124
		C018	none			84–277	1.4	M_n = 1880–2580 kDa, Đ_M = 2.9–3.1	124
		C112	none			1980–2290	n.d.	M_n = 4260 kDa, Đ_M = 2.4	124
V22/Et_2AlCl		**C006**	Et_2AlCl			192	1.1	M_n = 950 kDa, Đ_M = 2.7	124
		C018	none			19	0.5	M_n = 280 kDa, Đ_M = 2.2	124
V23/Et_2AlCl		**C006**	Et_2AlCl			216	2.4	M_n = 670 kDa, Đ_M = 2.3	124
		C018	none			34	0.9	M_n = 240 kDa, Đ_M = 2.1	124
V24/Et_2AlCl		**C006**	Et_2AlCl			279	5.2	M_n = 740 kDa, Đ_M = 2.5	124
		C018	none			42	1.2	M_n = 370 kDa, Đ_M = 2.3	124
V25/Et_2AlCl/ETA	2000	**C006**	Et_2AlCl	1	50	1300–8600	3.4–14.7	M_n = 1.9–8.3 kDa, Đ_M = 1.8–1.9	125
V26/Et_2AlCl/ETA	2000	**C006**	Et_2AlCl			1400–11 100	2.4–15.8	M_n = 1.7–9.0 kDa, Đ_M = 1.8–2.1	125
V27/Et_2AlCl/ETA	2000	**C006**	Et_2AlCl			1700–10 100	3.7–14.2	M_n = 1.8–6.7 kDa, Đ_M = 1.9–2.0	125
V28/Et_2AlCl/ETA	2000	**C006**	Et_2AlCl			4500–6800	3.9–11.1	M_n = 2.8–6.2 kDa, Đ_M = 1.8–2.0	125
V29/Et_2AlCl/ETA	2000	**C006**	Et_2AlCl			1900–11 200	3.3–14.6	M_n = 1.7–7.2 kDa, Đ_M = 1.9–2.2	125
V30/Et_2AlCl/ETA	1000	**C006**	Et_2AlCl	4	20	62–249	1.0–3.2	Terpolymer (16–28.5 mol.% propylene)	126
$VCl_3(THF)_3$	Et_2AlCl	**C015**	Et_2AlCl	2	30	210	2.1	M_n = 34.9 kDa, Đ_M = 3.1	88
	Et_2AlCl	**C118**	none	2	30	77	1.5	M_n = 17.4 kDa, Đ_M = 2.5	88

complexes **V16** and **V20** made it possible to incorporate a large amount of **C018** (up to 4.1 mol.%).[123]

Ethylene copolymers with norbornene derivatives (**C015**-AlEtCl, **C118**) were prepared using $VCl_3(THF)_3$; the activity of this catalytic system did not exceed 210 kg mol^{-1} h^{-1} and X_M values were 2.1 and 1.5 mol.%, respectively.[88]

2.3. Copolymerization of ethylene catalyzed by Group 10 metal complexes

Copolymerization of ethylene with polar olefins catalyzed by Ni and Pd complexes is addressed in a number of early[9,13–16,130] and recent[12,17,18,20–22,24,25,131,132] reviews. For this reason, we decided to restrict ourselves to a brief account of recent results on this subject reported in 2021–2025.[133–162]

Characteristic features of ethylene polymerization catalysts based on Group 10 metal complexes include lower 'oxophilicity' of the catalytic site compared to the catalytic sites formed by early transition metal complexes as well as the migration of the metal–alkyl bond and isomerization of the macromolecular backbone during polymerization (chain-walking polymerization).[163] Group 10 metal complexes are usually inferior in activity to Group 4 metal complexes; however, lower oxophilicity of the reaction center makes it possible to perform masking reagent-free copolymerization with functional comonomers, in particular, in polar solvents. In recent years, polar comonomers **C001**–**C006**, **C014**, **C018**, **C019**, and **C112** and comonomers **C119**–**C147** were investigated in the copolymerization with ethylene catalyzed by Group 10 metal complexes.

2.3.1. Copolymerization of ethylene catalyzed by Ni complexes

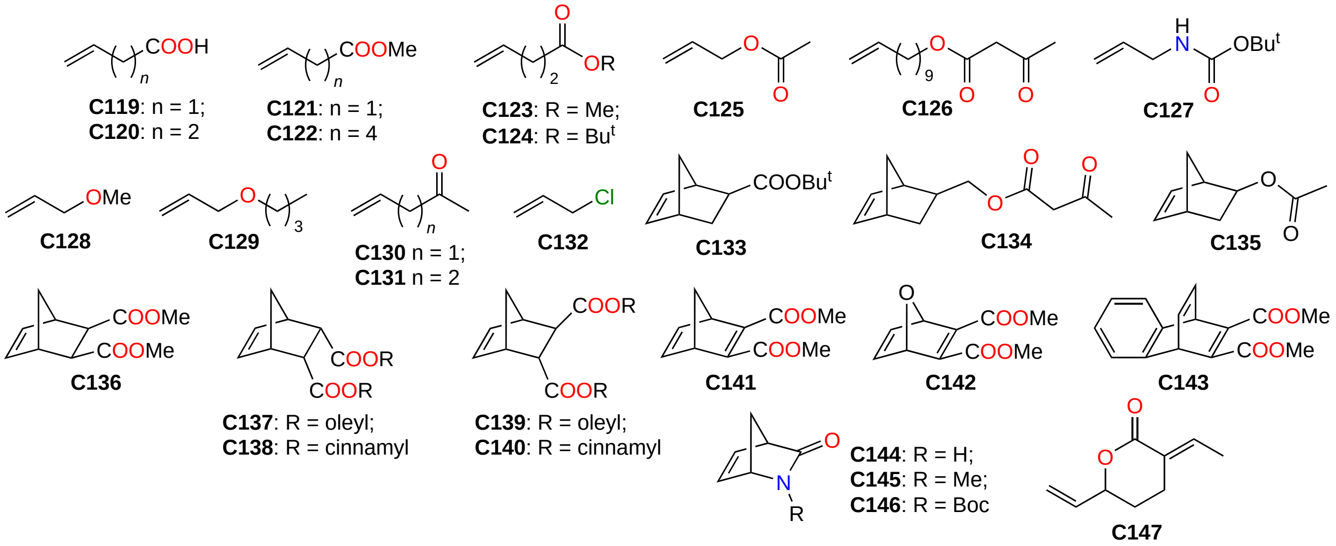
In 2021–2025, nickel complexes with [N,N], [N,O], and [P,O] type ligands **Ni01**–**Ni59** were investigated in the copolymerization of ethylene with non-conjugated polar vinyl monomers. The results of these studies are summarized in Table 7.

A comparative study of [N,N]-complexes **Ni19**–**Ni24**, analogs of the Brookhart catalyst, showed that the introduction of F into the *ortho*-position of the aryl moiety at the ligand N atom considerably influences the catalytic activity and properties of the resulting PE: the presence of F in the *para*- and *meta*-positions (**Ni20**–**Ni22**) decreases the activity and the PE molecular weight and increases the branching density, while the presence of F in the *ortho*-positions (**Ni23**, **Ni24**) has a beneficial effect (increase in the activity and M_n and formation of more linear polymer).[140] Meanwhile, copolymerization with methyl 10-undecenoate **C018** catalyzed by complexes **Ni23** and **Ni24** resulted in the lowest X_M, while the relatively high activity and M_n were retained. The comparative study of the behavior of [N,N]-complexes **Ni16** and **Ni17** in the copolymerization of ethylene (30°C, 8 atm, activation with Et_2AlCl) with **C006**, **C014**, and **C018** published in 2025 showed that *ortho*-MeO substituents in the aryl moieties of the ligand are preferable over *ortho*-Me groups (activity of up to 1400 kg mol^{-1} h^{-1} and X_M of up to 1.2 mol.%).[139]

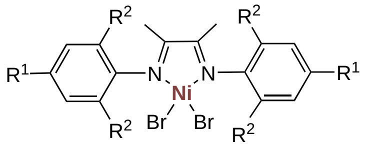
The introduction of additional aryl (Ph, 1-naphthyl, 9-anthracenyl) moieties into the [N,N]-complex **Ni06** induced a qualitative change in the catalytic properties: after activation with modified methylaluminoxane (MMAO), **Ni06** was no longer able to catalyze the copolymerization of ethylene with **C018**, while the substituted analogs **Ni07**–**Ni10** provided the incorporation of 0.18–0.44 mol.% comonomer, and the resulting copolymers contained 9.8–13.9 branches per 1000 C atoms.[135] Upon the introduction of additional CH_xPh_{3-x} substituents ($x = 0-2$) into the *para*-position of the phenyl groups in complex **Ni07** (complexes **Ni03**–**Ni05**), the catalytic activity towards copolymerization with **C018** somewhat increased (**Ni03**, **Ni04** in the presence of 1000 equiv. of MAO), while X_M decreased twofold, and M_n of the copolymer reached 1140 kDa; complex **Ni05**/MAO catalyzed homopolymerization in the presence of 0.2 M of the comonomer.[134] The Et_2AlCl-activated unsymmetrically substituted [N,N]-complexes **Ni11** and **Ni12** catalyzed copolymerization of ethylene (20°C, 8 atm) with polar comonomers **C006**, **C014**, and **C112**, exhibiting an activity of 200–560 kg mol^{-1} h^{-1} and providing $X_M = 0.2-4.3$ mol.%.[136] Copolymers with **C014** had abnormally high M_n values (~2000 kDa according to GPC data). This may be due to cross-linking involving carboxyl groups and residual Al ions: a single precipitation of the polymer in HCl/MeOH is apparently insufficient for complete removal of aluminum.

The polymerization catalysts based on Ni complexes are most often designed using bidentate ligands. However, the possibility of additional intramolecular coordination upon the

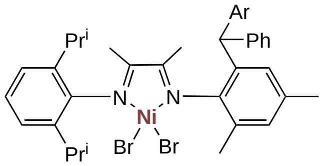
Structures C119–C147



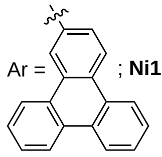
Structures Ni01–Ni59



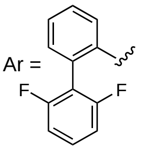
Ni01: R^1 = H, R^2 = Pr^i;
Ni02: R^1 = Me, R^2 = 4-Me–C_6H_4;
Ni03: R^1 = Me, R^2 = 4-CH_2Ph–C_6H_4;
Ni04: R^1 = Me, R^2 = 4-$CHPh_2$–C_6H_4;
Ni05: R^1 = Me, R^2 = 4-CPh_3–C_6H_4;
Ni06: R^1 = Me, R^2 = H;
Ni07: R^1 = Me, R^2 = Ph;
Ni08: R^1 = Me, R^2 = 4-Ph–C_6H_4;
Ni09: R^1 = Me, R^2 = 4-naph–C_6H_4;
Ni10: R^1 = Me, R^2 = 4-anth–C_6H_4

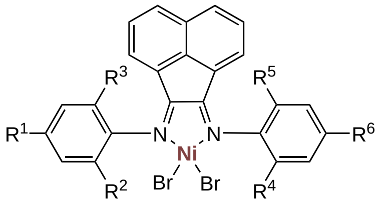


Ni11: Ar =

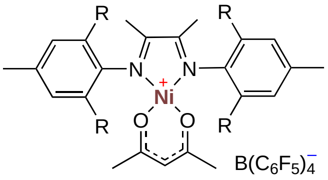


; **Ni12**: Ar =

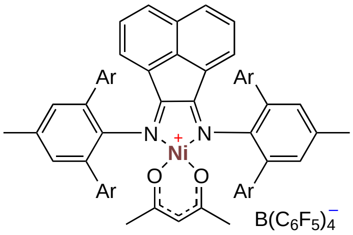




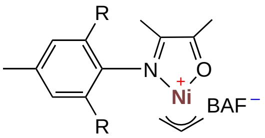
Ni13: R^1 = R^6 = H, R^2 = R^3 = R^4 = R^5 = Pr^i;
Ni14: R^1 = R^2 = R^3 = R^4 = R^5 = R^6 = Me;
Ni15: R^1 = R^2 = R^4 = R^6 = Me, R^3 = R^5 = $CHPh_2$;
Ni16: R^1 = H, R^2 = R^3 = Me, R^4 = R^5 = $CHPh_2$, R^6 = Me;
Ni17: R^1 = H, R^2 = R^3 = OMe, R^4 = R^5 = $CHPh_2$, R^6 = Me



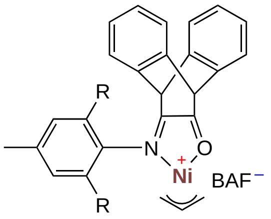
Ni18: R = 4-anth–C_6H_4



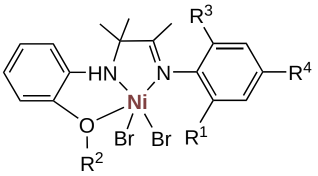
Ni19: Ar = Ph;
Ni20: Ar = 4-F-C_6H_4;
Ni21: Ar = 3,5-F-C_6H_3;
Ni22: Ar = 3,4,5-F-C_6H_2;
Ni23: Ar = 2,4,6-F-C_6H_2;
Ni24: Ar = C_6F_5



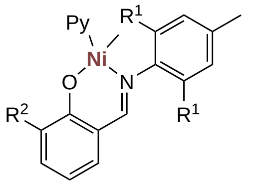
Ni25: R = 4-NPh_2–C_6H_4;
Ni26: R = 4-Bu^t–C_6H_4;
Ni27: R = 4-Cy–C_6H_4;
Ni28: R = 4-Ad–C_6H_4;
Ni29: R = 4-Ph–C_6H_4;
Ni30: R = 4-naph–C_6H_4
BAF^{-} = $[B(3,5-(CF_3-C_6H_3)_4]^{-}$



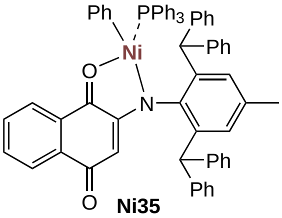
Ni31: R = 4-NPh_2-C_6H_4



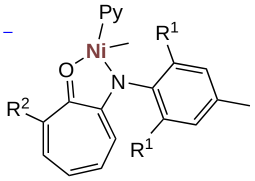
Ni32: R^1 = R^3 = Pr^i, R^2 = Me, R^4 = H;
Ni33: R^1 = $CHPh_2$, R^2 = R^3 = R^4 = Me



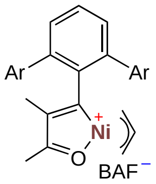
Ni34: R^1 = 3,5-$(CF_3)_2$–C_6H_3, R^2 = 9-anthracenyl



Ni35

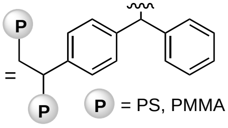


Ni36: R^1 = Ph, R^2 = H;
Ni37: R^1 = 4-Ph–C_6H_4, R^2 = H;
Ni38: R^1 = 4-[4′-Ph–C_6H_4]–C_6H_4, R^2 = H;
Ni39: R^1 = 4-NPh_2–C_6H_4, R^2 = H;
Ni40: R^1 = 3,5-$(CF_3)_2$–C_6H_3, R^2 = H;
Ni41: R^1 = 3,5-$(CF_3)_2$–C_6H_3, R^2 = anth

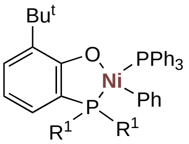


Ni42

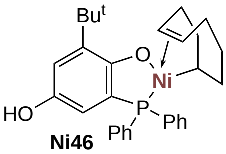
Ar =



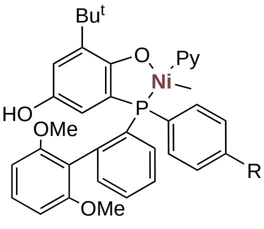
Ⓟ = PS, PMMA



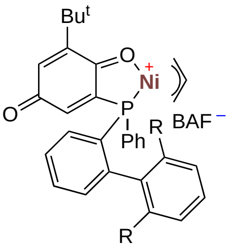
Ni43: R^1 = 2,6-$(OMe)_2$–C_6H_3;
Ni44: R^1 = 2,4,6-$(OMe)_3$–C_6H_2;
Ni45: R^1 = 2,6-$(OPr^i)_2$–C_6H_3



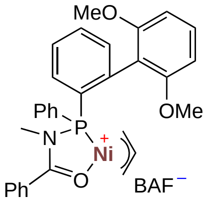
Ni46



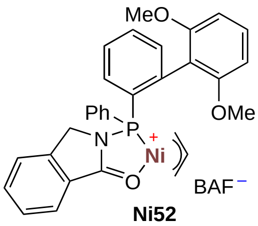
Ni47: R = H;
Ni48: R = OH



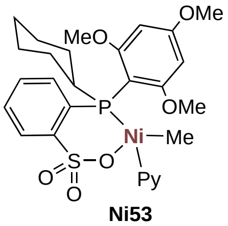
Ni49: R = OMe;
Ni50: R = F



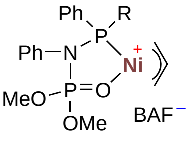
Ni51



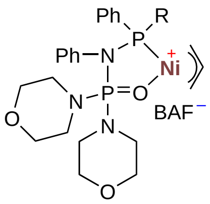
Ni52



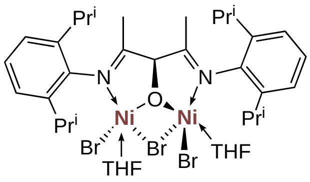
Ni53



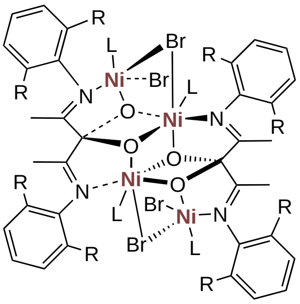
Ni54
R = 2-[2',6'-$(OMe)_2$–C_6H_3]–C_6H_4



Ni55
R = 2-[2',6'-$(OMe)_2$–C_6H_3]–C_6H_4



Ni56



Ni57: R = Pr^i, L = CH_3CN;
Ni58: R = Me, L = THF;
Ni59: R = Cl, L = THF

Table 7. Main characteristics of the copolymerization of ethylene with polar monomers catalyzed by Ni complexes.

Catalyst/ activator	Al/M	Comonomer	OAC	P_E, atm	T, °C	Activity, kg mol^{-1} h^{-1}	X_M (mol.%)	Comments	Ref.
Ni01/MAO	2250	**C119**	none	1	30	0	0		133
			Me_3Al			122	0.2	M_n = 31 kDa, $Đ_M$ = 2.0	
Ni02/MAO	1000	**C006**	none	1	30	429	0.3	M_n = 1100 kDa, $Đ_M$ = 1.5	134
		C014				140	0.2	M_n = 830 kDa, $Đ_M$ = 1.4	
	1000–3000	**C018**		1–2	30	18–336	0.1 – 0.4	M_n = 650–1080 kDa, $Đ_M$ = 1.1–1.7	134
Ni03/MAO	1000	**C018**	none	1	30	500	0.1	M_n = 780 kDa, $Đ_M$ = 1.1	134
Ni04/MAO	1000	**C018**	none	1	30	488	0.1	M_n = 840 kDa, $Đ_M$ = 1.1	134
Ni05/MAO	1000	**C018**	none	1	30	248	0		134
Ni06/MAO	1000	**C018**	none	2	60	188	0		135
Ni07/MAO	1000	**C018**	none	2–4	60	392–544	0.1–0.4	M_n = 166.7–215.7 kDa, $Đ_M$ = 1.2–1.3	135
Ni08/MAO	1000	**C018**	none	2	60	348	0.3	M_n = 165.6 kDa, $Đ_M$ = 1.3	135
Ni09/MAO	1000	**C018**	none	2	60	404	0.3	M_n = 160.0 kDa, $Đ_M$ = 1.6	135
Ni10/MAO	1000	**C018**	none	2	60	456	0.2	M_n = 198.5 kDa, $Đ_M$ = 1.4	135
Ni11/Et_2AlCl	2000	**C006**	none	8	20	500	0.2	M_n = 134 kDa, $Đ_M$ = 2.4	136
		C014				560	3.3	M_n = 2161 kDa, $Đ_M$ = 1.5	
		C112				200	1.2	M_n = 68 kDa, $Đ_M$ = 1.8	
Ni12/Et_2AlCl	2000	**C006**	none	8	20	320	0.7	M_n = 269 kDa, $Đ_M$ = 2.4	136
		C014				400	4.3	M_n = 2229 kDa, $Đ_M$ = 1.4	
		C112				320	3.7	M_n = 200 kDa, $Đ_M$ = 1.8	
Ni13/Et_2AlCl	500	**C014**	Et_2AlCl	8	0–20	5–18	n.d.	Ionic clusters, added fillers	137
Ni13/Et_2AlCl	500	**C014**	Et_2AlCl	8	5	2050	n.d.	Ionic clusters	138
Ni13/**Ni14**/ Et_2AlCl	500	**C014**	Et_2AlCl	8	5	290–2030	n.d.	Ionic clusters	138
Ni14/Et_2AlCl	500	**C014**	Et_2AlCl	8	20	12	n.d.	Ionic cluster, added filler (clay)	137
Ni14/Et_2AlCl	500	**C014**	Et_2AlCl	8	5	1400	n.d.	Ionic clusters	138
Ni14/**Ni13**/Et_2AlCl	500	**C014**	Et_2AlCl	8	5	1410	n.d.	Ionic clusters	138
Ni14/**Ni15**/Et_2AlCl	500	**C014**	Et_2AlCl	8	5	380	n.d.	Ionic clusters	138
Ni16/Et_2AlCl	2000	**C006**	none	8	30	800	0.4	M_n = 30.9 kDa, $Đ_M$ = 2.5	139
		C014				1100	Traces	M_n = 32.2 kDa, $Đ_M$ = 2.3	
		C018				200	0	M_n = 38.6 kDa, $Đ_M$ = 1.8	
Ni17/Et_2AlCl	2000	**C006**	none	8	30	1300	1.2	M_n = 1.3 kDa, $Đ_M$ = 3.5	139
		C014				1400	0.8	M_n = 3.7 kDa, $Đ_M$ = 2.7	
		C018				400	0.9	M_n = 5.0 kDa, $Đ_M$ = 2.2	
Ni18/MAO	1000	**C018**	none	2	60	528	0.2	M_n = 166.4 kDa, $Đ_M$ = 1.4	135
Ni19/TB^F/Et_2AlCl	1000	**C006**	none	4	30–60	884	0.4	M_n = 1.8 kDa, $Đ_M$ = 2.1	140
		C014				1270	0.7	M_n = 17.3 kDa, $Đ_M$ = 2.0	
		C018				256–898	0.3–0.6	M_n = 23.3–34.9 kDa, $Đ_M$ = 1.8–2.0	
Ni20/TB^F/Et_2AlCl	1000	**C018**	none	4	30	994	0.3	M_n = 26.6 kDa, $Đ_M$ = 1.9	140
Ni21/TB^F/Et_2AlCl	1000	**C018**	none	4	30	566	0.3	M_n = 39.1 kDa, $Đ_M$ = 1.8	140
Ni22/TB^F/Et_2AlCl	1000	**C018**	none	4	30	148	0.4	M_n = 46.6 kDa, $Đ_M$ = 1.7	140
Ni23/TB^F/Et_2AlCl	1000	**C018**	none	4	30	920	0.02	M_n = 414.3 kDa, $Đ_M$ = 1.2	140
Ni24/TB^F/Et_2AlCl	1000	**C018**	none	4	30	584	0.2	M_n = 260.9 kDa, $Đ_M$ = 1.3	140
Ni25/BAF	n.d.	**C006**	none	4–8	30	11.5	1.3	M_n = 1.1 kDa, $Đ_M$ = 1.8	141
		C018				20.8–175.3	2.9–3.9	M_n = 2.6–5.4 kDa, $Đ_M$ = 2.2–2.5	
		C112				40.5	1.3	M_n = 11.4 kDa, $Đ_M$ = 2.8	
Ni26/BAF	n.d.	**C018**	none	8	30	52.7	1.8	M_n = 3.3 kDa, $Đ_M$ = 3.0	141
Ni27/BAF	n.d.	**C018**	none	8	30	135.5	2.1	M_n = 3.5 kDa, $Đ_M$ = 2.9	141
Ni28/BAF	n.d.	**C018**	none	8	30	211	1.6	M_n = 2.8 kDa, $Đ_M$ = 2.9	141
Ni29/BAF	n.d.	**C018**	none	8	30	180.7	3.2	M_n = 2.6 kDa, $Đ_M$ = 2.9	141
Ni30/BAF	n.d.	**C018**	none	8	30	171.3	3.3	M_n = 2.1 kDa, $Đ_M$ = 2.8	141

Table 7 (continued).

Catalyst/ activator	Al/M	Como- nomer	OAC	P_E, atm	T, °C	Activity, kg mol^{-1} h^{-1}	X_M (mol.%)	Comments	Ref.
Ni31/BAF	n.d.	**C018**	none	8	30	113	2.5	M_n = 2.6 kDa, $Đ_\mathrm{M}$ = 2.6	141
Ni32/Et_2AlCl	300	**C006**	none	8	n.d.	249	0.1	M_n = 439 kDa, $Đ_\mathrm{M}$ = 2.7	142
		C119				32.8	0.2	M_n = 57.2 kDa, $Đ_\mathrm{M}$ = 2.8	
		C014				307	1.2	M_n = 354 kDa, $Đ_\mathrm{M}$ = 2.2	
		C018		2–8		245–471	0.9–2.6	M_n = 80.8–11.3 kDa, $Đ_\mathrm{M}$ = 2.2–2.4	
		C112		8		226	0.8	M_n = 26.1 kDa, $Đ_\mathrm{M}$ = 2.2	
Ni33/Et_2AlCl	300	**C119**	none	8	n.d.	53.5	0.3	M_n = 34.3 kDa, $Đ_\mathrm{M}$ = 1.9	142
		C018				466	0.6	M_n = 38.9 kDa, $Đ_\mathrm{M}$ = 3.1	
Ni34	n.d.	**C019**	none	8	65	1.3	0.2	M_n = 7 kDa, $Đ_\mathrm{M}$ = 2.0	143
Ni35	n.d.	**C125**	none	10	40	34	0.4	M_n = 16.5 kDa, $Đ_\mathrm{M}$ = 3.5	144
		C019				1152	1.0	M_n = 117 kDa, $Đ_\mathrm{M}$ = 4.6	
Ni35/SiO_2	n.d.	**C125**	none	10	40	18–36	0.3–0.5	M_n = 624–832 kDa, $Đ_\mathrm{M}$ = 2.8–3.0	144
		C018		3–10	40	356–996	0.4–0.7	M_n = 366–378 kDa, $Đ_\mathrm{M}$ = 2.5–2.6	
		C019		10–20	40–80	900–2650	1.1–2.8	M_n = 321–631 kDa, $Đ_\mathrm{M}$ = 2.6–3.0	
Ni35/$Bu^i_3Al@SiO_2$	40	**C019**	none	10	40	2560	0.15	M_n = 152 kDa, $Đ_\mathrm{M}$ = 5.04, T_m = 127 °C	145
Ni35/$Et_3Al@SiO_2$	40	**C019**	none	10	40	1360	0.16	M_n = 132 kDa, $Đ_\mathrm{M}$ = 5.77, T_m = 126 °C	145
Ni35/$Et_2AlCl@SiO_2$	40	**C019**	none	10	40	310	0.23	M_n = 127 kDa, $Đ_\mathrm{M}$ = 6.05, T_m = 126 °C	145
Ni35/$EtAlCl_2@SiO_2$	40	**C019**	none	10	40	60	0.28	M_n = 101 kDa, $Đ_\mathrm{M}$ = 8.06, T_m = 125 °C	145
Ni36	n.d.	**C019**	none	8	70	1.1[a]	0.2	M_n = 76 kDa, $Đ_\mathrm{M}$ = 1.5	143
Ni37	n.d.	**C019**	none	8	70	0.3[a]	0.3	M_n = 59 kDa, $Đ_\mathrm{M}$ = 1.5	143
Ni38	n.d.	**C019**	none	8	70	0.68[a]	0.2	M_n = 66 kDa, $Đ_\mathrm{M}$ = 1.7	143
Ni39	n.d.	**C019**	none	8	70	0.21[a]	0.3	M_n = 46 kDa, $Đ_\mathrm{M}$ = 1.7	143
Ni40	n.d.	**C019**	none	8	70	3.21[a]	0.1	M_n = 162 kDa, $Đ_\mathrm{M}$ = 1.3	143
Ni41	n.d.	**C019**	none	4–8	60–70	0.75–7.86[a]	0.1–1.8	M_n = 56–345 kDa, $Đ_\mathrm{M}$ = 1.6–2.6	143
Ni42/BAF	n.d.	**C018**	none	8	50	349	2.5	M_n = 49 kDa, $Đ_\mathrm{M}$ = 1.7	146
Ni42@PS	n.d.	**C018**	none	8	50	259–877	0.3–1.5	Ligands in various ratios supported on PS	146
Ni42@PMMA	n.d.	**C018**	none	8	50	203–1067	0.6–1.2	Ligands in various ratios supported on PMMA	146
Ni43	n.d.	**C003**	none	20	50	4.6[a]	0.3	M_n = 40.5 kDa, $Đ_\mathrm{M}$ = 2.3	147
		C004				9.6[a]	0.6	M_n = 53.7 kDa, $Đ_\mathrm{M}$ = 2.5	
		C005				11.8[a]	0.3	M_n = 73.3 kDa, $Đ_\mathrm{M}$ = 2.6	
		C019				7.5[a]	0.2	M_n = 39.0 kDa, $Đ_\mathrm{M}$ = 2.8	
		C131				1.8[a]	0.5	M_n = 38.2 kDa, $Đ_\mathrm{M}$ = 2.7	
		C112				7.1[a]	1.1	M_n = 41.9 kDa, $Đ_\mathrm{M}$ = 2.6	
Ni44	n.d.	**C004**	none	20	50	1.8[a]	0.3	M_n = 63.9 kDa, $Đ_\mathrm{M}$ = 2.0	147
		C005				1.4[a]	1.6	M_n = 33.2 kDa, $Đ_\mathrm{M}$ = 2.3	
		C019				2.5[a]	0.1	M_n = 80.6 kDa, $Đ_\mathrm{M}$ = 2.0	
		C131				2.5[a]	1.2	M_n = 30.4 kDa, $Đ_\mathrm{M}$ = 2.0	
		C112				2.5[a]	1.2	M_n = 62.8 kDa, $Đ_\mathrm{M}$ = 1.9	
Ni45	n.d.	**C003**	none	20	50	2.1–3.9[a]	0.4–0.8	M_n = 132.7–144.6 kDa, $Đ_\mathrm{M}$ = 2.2	147
		C004				1.8–5.4[a]	0.4–1.0	M_n = 261.5–259.1 kDa, $Đ_\mathrm{M}$ = 1.6–1.8	
		C005				4.6–8.2[a]	0.1–0.7	M_n = 242.0–298.4 kDa, $Đ_\mathrm{M}$ = 1.7–1.8	
		C019				2.9–5.7[a]	0.5–1.3	M_n = 140.6–146.0 kDa, $Đ_\mathrm{M}$ = 1.7–3.0	
		C131				1.4–8.2[a]	0.2–0.4	M_n = 151.8–240.3 kDa, $Đ_\mathrm{M}$ = 1.9	
		C112				4.3–9.3[a]	0.4–1.1	M_n = 137.7–250.8 kDa, $Đ_\mathrm{M}$ = 1.5–1.8	
Ni46@MgO	n.d.	**C018**	none	8	80	740	1.2	M_n = 6.1 kDa, $Đ_\mathrm{M}$ = 2.8	148
Ni47@MgO	n.d.	**C018**	none	8	80	2320	0.1	M_n = 598.1 kDa, $Đ_\mathrm{M}$ = 2.7	148
Ni48@MgO	n.d.	**C018**	none	8	80	1640	0.6	M_n = 303.0 kDa, $Đ_\mathrm{M}$ = 2.7	148

Table 7 (continued).

Catalyst/ activator	Al/M	Como- nomer	OAC	P_E, atm	*T*, °C	Activity, kg mol^{-1} h^{-1}	X_M (mol.%)	Comments	Ref.
Ni46/**Ni47** (1 : 1)@MgO	n.d.	**C018**	none	8–30	80–120	1160–3920	0.5–1.3	M_n = 47.0–88.1 kDa, $Đ_M$ = 3.7–13.3	148
Ni46/**Ni47** (1 : 5)@MgO	n.d.	**C018**	none	8	80	660	0.9	M_n = 39.5 kDa, $Đ_M$ = 13.3	148
Ni46/**Ni47**/**Ni48**/ (1 : 1 : 1)@MgO	n.d.	**C018**	none	8	80	1620	0.7	M_n = 17.3 kDa, $Đ_M$ = 53.9	148
Ni46/**Ni47** (1 : 1)@TiO_2	n.d.	**C018**	none	8	80	1500	0.2	M_n = 44.6 kDa, $Đ_M$ = 11.4	148
Ni46/**Ni47** (1 : 1)@GF	n.d.	**C018**	none	8	80	2420	0.2	M_n = 78.0 kDa, $Đ_M$ = 11.8	148
Ni46/**Ni47** (1 : 1)@APP	n.d.	**C018**	none	8	80	2600	1.1	M_n = 40.1 kDa, $Đ_M$ = 9.0	148
Ni46/**Ni47** (1 : 1)@ Lignin	n.d.	**C018**	none	8	80	1660	0.2	M_n = 39.7 kDa, $Đ_M$ = 10.2	148
Ni46@MgO/ **Ni47**@MgO	n.d.	**C018**	none	8	80	1200	0.5	M_n = 21.1 kDa, $Đ_M$ = 34.4	148
Ni49	n.d.	**C005**	none	8	60	26	0.4	M_n = 15.7 kDa, $Đ_M$ = 2.1	149
		C018				6	0.2	M_n = 20.1 kDa, $Đ_M$ = 7.3	
		C112				6.5	0.1	M_n = 17.2 kDa, $Đ_M$ = 7.1	
Ni50	n.d.	**C005**	none	8	60	9.5	0.5	M_n = 20.7 kDa, $Đ_M$ = 5.9	149
		C018				3	0.5	M_n = 20.8 kDa, $Đ_M$ = 4.0	
		C112				12	0.6	M_n = 21.5 kDa, $Đ_M$ = 3.9	
Ni50@SiO_2	n.d.	**C005**	none	8	60	69.5	0.8	M_n = 19.4 kDa, $Đ_M$ = 3.5	149
		C018				91	0.5	M_n = 60.4 kDa, $Đ_M$ = 2.6	
		C112				70	0.8	M_n = 58.2 kDa, $Đ_M$ = 2.2	
Ni51/BAF	n.d.	**C125**	none	8	80	1.5	1.1	M_n = 13.7 kDa, $Đ_M$ = 1.8	150
Ni52/BAF	n.d.	**C125**	none	8	80	2.0	0.7	M_n = 8.7 kDa, $Đ_M$ = 2.6	150
		C132				6.5	0.6	M_n = 12.9 kDa, $Đ_M$ = 2.4	
Ni53	n.d.	**C112**	none	8–20	50–70	55.5–152	0.8–5.0	M_n = 3.2–15.4 kDa, $Đ_M$ = 1.9–2.4	151
Ni54	n.d.	**C018**	none	8	80	180	2.9	M_n = 5.2 kDa, $Đ_M$ = 2.2	152
		C112				160	1.2	M_n = 7.2 kDa, $Đ_M$ = 2.0	
		C118				52	1.0	M_n = 8.7 kDa, $Đ_M$ = 1.8	
Ni55	n.d.	**C112**	none	8	80	40	1.4	M_n = 5.8 kDa, $Đ_M$ = 1.7	152
Ni56/Et_2AlCl	3000	**C119**	none	1	30	540	3.6	M_n = 4.8 kDa, $Đ_M$ = 2.7	133
		C119	Et_2AlCl			1044	1.4	M_n = 24.5 kDa, $Đ_M$ = 2.9	
		C119	Bu^i_3Al			468	0.5	M_n = 58.9 kDa, $Đ_M$ = 3.5	
		C121	none			312	0.4	M_n = 45.0 kDa, $Đ_M$ = 1.6	
Ni57/MAO	900	**C001**	none	1	30	24	1.8	M_n = 2.5 kDa, $Đ_M$ = 3.2	133
	2250	**C002**	none			148–252	2.7–5.3	M_n = 12.2–30.0 kDa, $Đ_M$ = 2.9–3.2	
		C002	Me_3Al			960	1.3	M_n = 65.3 kDa, $Đ_M$ = 4.0	
		C119	none			48–54	1.9–2.1	M_n = 7.3–10.0 kDa, $Đ_M$ = 3.0–3.3	
		C119	MAO			84	0.4	M_n = 28.3 kDa, $Đ_M$ = 3.6	
		C119	Me_3Al			72	0.6	M_n = 9.8 kDa, $Đ_M$ = 5.4	
		C119	Et_3Al			78	0.4	M_n = 7.7 kDa, $Đ_M$ = 6.1	
		C119	Bu^i_3Al			114	0.4	M_n = 9.2 kDa, $Đ_M$ = 3.6	
	3000	**C120**	none			408	5.8	M_n = 8.2 kDa, $Đ_M$ = 3.8	
		C120	Me_3Al			672	1.0	M_n = 46.9 kDa, $Đ_M$ = 2.6	
		C014	none			576–1344	13.9–21.5		
		C014	Bu^i_3Al			1440	2.7		
	2250	**C121**	none			66	1.1	M_n = 5.0 kDa, $Đ_M$ = 3.0	
	900	**C128**	none			24	0.04	M_n = 4.4 kDa, $Đ_M$ = 3.2	
Ni58/MAO	2250	**C119**	none	1	30	18	1.7	M_n = 9.3 kDa, $Đ_M$ = 2.7	133
Ni59/MAO	2250	**C119**	none	1	30	12	2.4	M_n = 9.0 kDa, $Đ_M$ = 2.7	133

Note. BAF is $Na[B(3,5\text{-}(CF_3\text{-}C_6H_3)_4]$, PS is polystyrene, PMMA is poly(methyl methacrylate), GF is glass fiber, APP is ammonium polyphosphate. [a] 10^3 mol(C_2H_4) mol^{-1} h^{-1}.

introduction of a third donor atom into the [N,N] type ligand can qualitatively affect the catalyst behavior, as shown in a recent study in relation to **Ni32** and **Ni33**.[142] In the copolymerization of ethylene with **C014**, **C018**, and **C112** (40°C, 8 atm), the **Ni32**/Et_2AlCl catalyst showed an activity of 226–471 kg mol^{-1} h^{-1} and $X_M = 0.13–1.15$ mol.%; even 3-butenoic acid **C119** was involved in the copolymerization (32.8 kg mol^{-1} h^{-1}, $X_M = 0.19$ mol.%). The activity of **Ni33**/Et_2AlCl in the reaction with **C018** was 466 kg mol^{-1} h^{-1}, and $X_M = 0.64$ mol.%.

In 2021, Tang and co-workers[133] reported a study of the copolymerization of ethylene with the proton-containing comonomer $CH_2{=}CHCH_2COOH$ (**C119**, 0.2 M, up to 1440 kg mol^{-1} h^{-1} activity at 30°C) and other unsaturated carboxylic acids and alcohols catalyzed by tetranuclear [N,O] type complexes **Ni57**–**Ni59**.[133] The DFT modelling of copolymerization indicated the preference of the binuclear mechanism (Fig. 2), which was confirmed experimentally by a study of the catalytic behavior of binuclear compound **Ni56**. According to the results of modelling, homopolymerization of ethylene takes place on one of the Ni atoms (Ni1) *via* the classic coordination insertion mechanism. The carboxylate anion $CH_2{=}CHCH_2COO^-$ is coordinated to the Ni2 atom, and the spatial proximity between Ni1 and Ni2 in complex **18** (see Fig. 2) creates conditions for the insertion of C=C group of the coordinated comonomer into the Ni1–alkyl bond to give adduct **20** (see Fig. 2); the activation energy for this exergonic step is 15.5 kcal mol^{-1}. The resulting metallacyclic adduct undergoes rather easily β-hydride elimination to form Ni1–H and alkenyl carboxylate coordinated to the Ni2 atom, which then recombines to form the isomeric metallacycle **27** or undergoes ethylene insertion to give adduct **23** (see Fig. 2). The subsequent chain propagation requires ligand exchange between the intramolecularly coordinated carboxylate and $CH_2{=}CHCH_2COO^-$, which is driven by the strain in the metallacycle of adduct **23**.

In the ethylene copolymerization with **C018** (1 M, 30°C, 8 atm), [N,O]-complexes **Ni25**–**Ni31** showed activities of 53–211 kg mol^{-1} h^{-1} ($X_M = 1.6–3.3$ mol.%) and afforded low-molecular-weight ($M_n = 2.1–5.3$ kDa) and branched (9.9–22.8 branches per 1000 C atoms) copolymers.[141]

Particular attention is drawn by the results of studies of the catalytic performance of [N,O] type complex **Ni35** supported on OAC-activated mesoporous silica in the copolymerization of ethylene with $MeCOO(CH_2)_4CH{=}CH_2$ (**C019**).[145] The efficiency of OAC as activators decreased in a series $^iBu_3Al > Et_3Al > Et_2AlCl > EtAlCl_2$, which was attributed to decreasing electron density on the active site, resulting in deactivation *via* Ni···O coordination after the comonomer insertion. The **Ni35**-based supported catalyst was also prepared by direct reaction of the metal complex with mesoporous SiO_2, without pretreatment with OAC. Binding of the metal complex to the support surface was due to the formation of the >C=O···H–OSi hydrogen bond.[144] The resulting catalyst initiated homopolymerization of ethylene (40°C, 10 atm) even

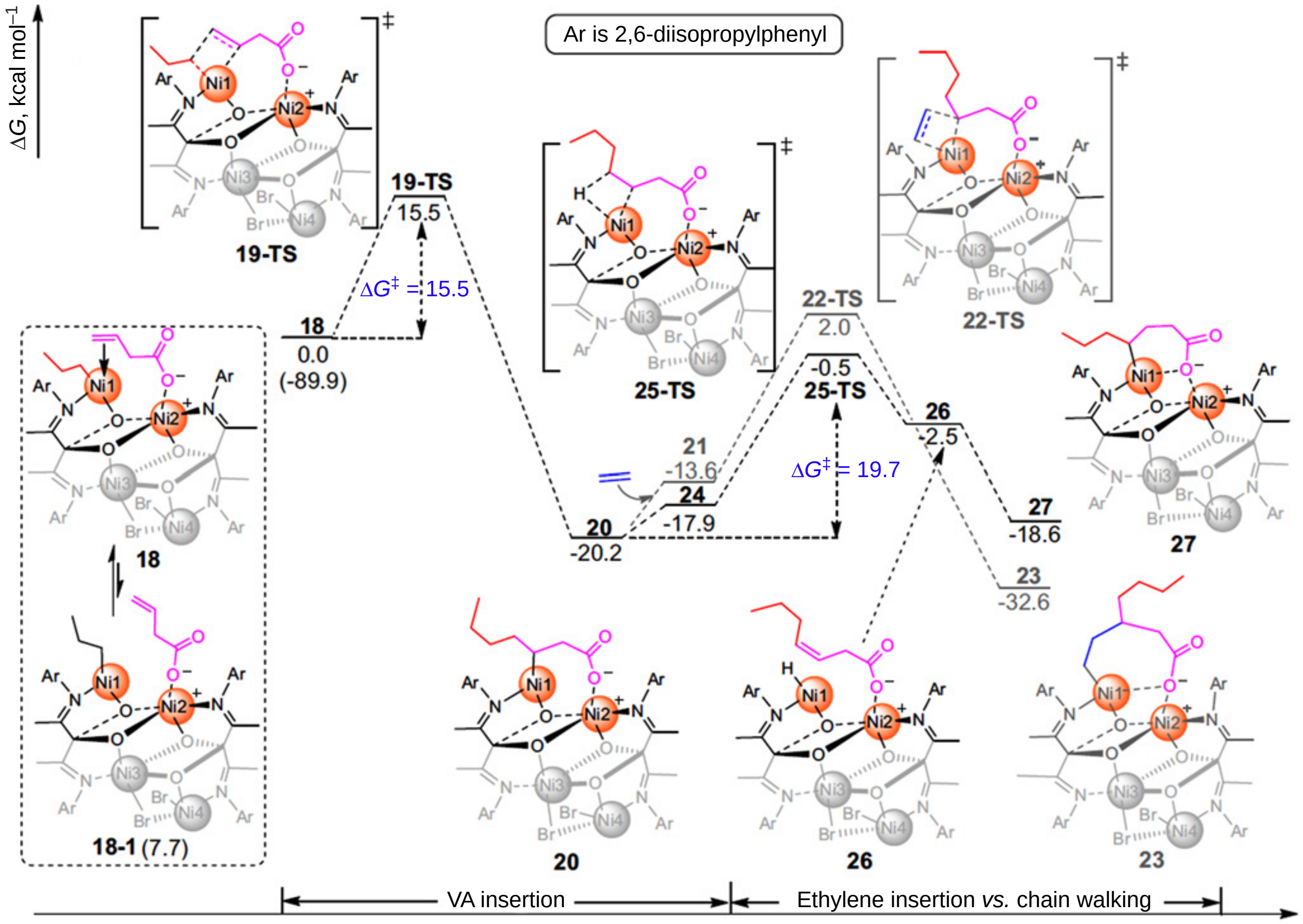


Figure 2. Energy profiles of the **Ni57**-catalyzed copolymerization of ethylene and **C119** anion.[133] Reproduced under the Creative Commons License CC-BY.

in the absence of OAC (activity of 720 kg mol^{-1} h^{-1}). The addition of 2 equiv. of ^{i}Bu$_3$Al resulted in increase in the activity to 4580 kg mol^{-1} h^{-1}. In the copolymerization with **C019** (1 M and 2 M in toluene) under the same conditions, the Bu$^i_3$Al-activated catalyst showed activities of 1270 and 1160 kg mol^{-1} h^{-1} with X_M of 2.1 and 2.8 mol.%, respectively.[144]

A comparative study of [N,O] type complexes with six-membered (**Ni34**) and five-membered (anilinotropone derivatives **Ni36**–**Ni41**) rings in the copolymerization of ethylene with **C019** (0.1 M, 60°C, 8 atm) revealed the highest activity for **Ni41** (TOF = 4320 h^{-1}, X_M = 0.3 mol.%).[143] At 65°C, **Ni41** and **Ni34** exhibited TOF = 5610 and 1250 h^{-1} and provided X_M = 0.25 and 0.16 mol.%, respectively; and the resulting copolymers had M_n = 225 and 7 kDa. The results of DFT modelling of the chain propagation and chain termination *via* β-hydride elimination confirmed the experimental results: the free energy differences between the transition states of the chain propagation and termination were 4.6 and 2 kcal mol^{-1} for **Ni41** and **Ni34**, respectively.[143]

A promising method for the preparation of a heterogeneous catalyst based on [N,O]-complex **Ni42** is based on emulsion copolymerization of styrene or methyl methacrylate (MMA) with the appropriate ligand followed by treatment with [Ni(allyl)Cl]$_2$.[146] The resulting heterogeneous catalysts with microspherical morphology exhibited activity of 259–1067 kg mol^{-1} h^{-1} and provided X_M = 0.3–1.5 mol.% in the copolymerization of ethylene with methyl 10-undecenoate **C018** (50°C, 8 atm).

Considering the results obtained for ethylene polymerization in an *aqueous* medium (H$_2$O/toluene/hexan-1-ol, 100 : 1 : 3 v/v/v) in the presence of [N,O] type Ni complexes, compounds **Ni43**–**Ni45** were chosen for studying copolymerization with polar monomers.[147] These complexes demonstrated fairly high activities (TOF = 1400–1180 h^{-1} at 50°C and 20 atm) towards comonomers of various natures (0.3–0.6 M): alcohols **C003**, **C004**, and **C006**, ester **C019**, ketone **C131**, and halo derivative **C112** (X_M = 0.12–1.63 mol.%).

Nickel allyl complexes containing [P,O]-ligands, **Ni54** and **Ni55**, showed a moderate activity (40–180 kg mol^{-1} h^{-1}) in the copolymerization of ethylene with ω-chloro-1-alkenes and unsaturated carboxylic acid esters.[152] In the copolymerization with 6-chloro-1-hexene (50°C, 20 atm), [P,O]-complex **Ni53** proved to be less active (below 152 kg mol^{-1} h^{-1}).[151] Complexes **Ni51** and **Ni52** also showed low activity in the copolymerization of ethylene with allyl acetate **C125** (80°C, 8 atm), namely, 1.5 and 2.0 kg mol^{-1} h^{-1}, X_M = 1.1 and 0.7 mol.%, respectively, M_n = 8.7–13.7 kDa.[150]

Complexes **Ni49** and **Ni50** of the [P,O] type had a low activity (9.5–26 kg mol^{-1} h^{-1}) in ethylene copolymerization with **C006**, **C018**, and **C112** (80°C, 8 atm); when **Ni50** was supported on mesoporous SiO$_2$, markedly more active catalysts were obtained (69.5, 91, and 70 kg mol^{-1} h^{-1}, respectively).[149]

Bimodal polyethylenes are a promising class of plastics possessing mechanical properties and molding behavior.[4] MgO-Supported catalysts based on [P,O] type complexes **Ni46** (formation of a low-molecular-weight fraction with higher X_M), **Ni47** and/or **Ni48** (formation of a high-molecular-weight fraction with lower X_M) were developed for the synthesis of polar bimodal PE, with **C018** being used as the comonomer.[148] In the case of copolymer with M_n = 17.3 kDa and $Đ_M$ = 53.9, the catalyst activity was 1620 kg mol^{-1} h^{-1} (80°C, 8 atm).

2.3.2. Copolymerization of ethylene catalyzed by Pd complexes

In the 2020s, palladium [N,N]-, [P,N]-, and [P,O]-complexes and [C,O]-carbene complexes **Pd01**–**Pd19**, were studied in ethylene copolymerization with non-conjugated polar monomers. The results of studies are summarized in Table 8.[153–162]

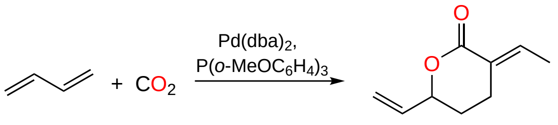
Palladium [N,N]-complexes have been intensively studied since the mid-1990s,[164] with the only study addressing complexes of this structural type in the copolymerization of ethylene with non-conjugated polar monomers being published in 2022.[153] The structurally rigid complex **Pd01** and reference catalyst **Pd02** proved to be inert in the copolymerization with ethylene and low-reactivity allyl acetate **C125** (0.5 M). Furthermore, in the case of **Pd01**, the addition of 100 and more equivalents of an additional donor (4-MeC$_6$H$_4$CN) triggered a very slow (1–4.7 kg mol^{-1} h^{-1}) reaction to give copolymers (M_n = 7.1–38.8 kDa, X_M = 0.1–0.7 mol.%) that contained 16 to 77 branches per 1000 carbon atoms; the reference catalyst had a negligibly low activity (0.1 kg mol^{-1} h^{-1}). A beneficial effect of the addition of an extra donor was also observed for other polar allyl comonomers (**C129**, **C132**) and **C124**; however, in all cases, the catalyst activity was lower than 10 kg mol^{-1} h^{-1}.[153] The results of this study are of certain theoretical interest, demonstrating the conceptual possibility of reactivation of the relatively stable metallacycles formed upon the insertion of allyl type comonomers and **C124**. However, the reactivation mechanism (competitive inhibition) causes exceptionally low catalyst activity.

In the presence of Na[B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$], [P,N]-complexes **Pd04**–**Pd06** catalyzed copolymerization of ethylene with **C019** (0.7 M, 60°C, 20 atm) with an activity of 4.2, 6, and 11.4 kg mol^{-1} h^{-1} (X_M = 1.19, 0.48, and 1.14 mol.%, respectively) to give low-molecular-weight products.[154]

In the copolymerization with comonomer **C127** (*N*-Boc-allylamine), [P,O]-complex **Pd12** showed a moderate activity (80 kg mol^{-1} h^{-1} at 8 atm).[161] In the copolymerization of ethylene with allyl acetate **C125** (80°C, 8 atm), complexes **Pd09** and **Pd10** proved to have low activities (2.5 and 4.5 kg mol^{-1} h^{-1}, X_M = 1.1 and 0.7 mol.%, respectively, M_n = 7.7 and 3.4 kDa). At equal X_M values, the products of Pd-catalyzed copolymerization had much lower T_m than the copolymers produced in the presence of isostructural Ni complexes.[150] Polar comonomers **C137** and **C138**, synthesized by the reaction of cyclopenta-1,3-diene — maleic anhydride adduct with oleyl or cinnamyl alcohol, respectively, and their *trans*-isomers **C139** and **C140** were tested in the copolymerization with ethylene catalyzed by [P,O]-complexes **Pd11** and **Pd12**.[156] *Trans*-isomers showed higher activity and X_M (up to 2040 kg mol^{-1} h^{-1} and 22.4 mol.% at 8 atm and 80°C).

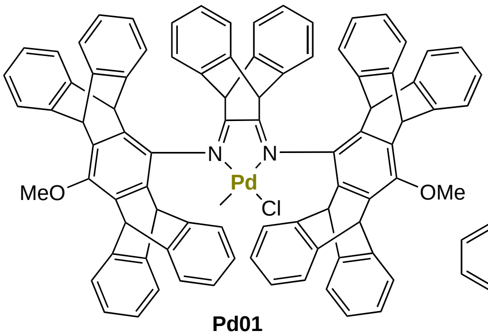
Comonomer **C147** deserves special attention as an example of non-conjugated polar monomer prepared by chemical fixation of CO$_2$, that is, by the reaction of butadiene with CO$_2$. This reaction, known since the late-1970s,[165] was recently optimized by Beller and coworkers[166] (Scheme 9). [P,O] type complexes **Pd11″**, **Pd13′**, **Pd14**, and **Pd18** were introduced into the

Scheme 9

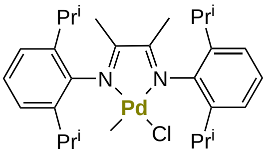


C147 (67%)

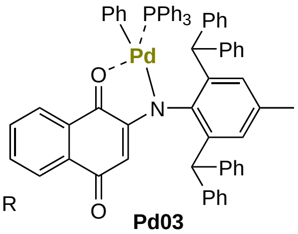
Structures Pd01 – Pd19



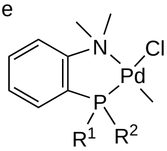
Pd01



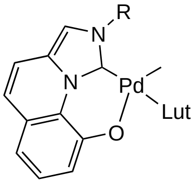
Pd02



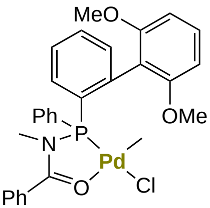
Pd03



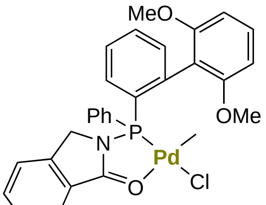
Pd04: $R^1 = R^2$ = 2-Pr^i–C_6H_4;
Pd05: $R^1 = R^2$ = 2-Ph–C_6H_4;
Pd06: R^1 = Ph;
R^2 = 2-[2,6-$(MeO)_2$–C_6H_3]–C_6H_4



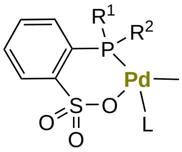
Pd07: R = Mes;
Pd08: R = Dip



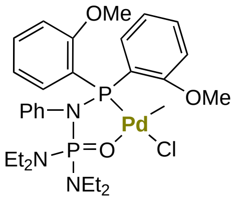
Pd09



Pd10



Pd11: $R^1 = R^2$ = 2-OMe–C_6H_4, L = DMSO;
Pd11′: $R^1 = R^2$ = 2-OMe–C_6H_4, L = Py;
Pd11″: $R^1 = R^2$ = 2-OMe–C_6H_4, L = 2,6-Me_2Py;
Pd12: R^1 = Ph, R^2 =2-[2′,6′-$(OMe)_2$–C_6H_3]–C_6H_4, L = DMSO;
Pd13: $R^1 = R^2$ = Cy, L = DMSO;
Pd13′: $R^1 = R^2$ = Cy, L = 2,6-Me_2Py;
Pd14: $R^1 = R^2$ = Men, L = 2,6-Me_2Py;
Pd15: $R^1 = Bu^t$, R^2 = 2,4,6-$(OMe)_3$–C_6H_2, L = DMSO;
Pd16: R^1 = Cy, R^2 = 2,4,6-$(OMe)_3$–C_6H_2, L = DMSO;
Pd17: $R^1 = R^2 = Bu^t$, L = DMSO;
Pd18: $R^1 = R^2 = Pr^i$, L = 2,6-Me_2Py



Pd19

Table 8. Main characteristics of the copolymerization of ethylene with polar monomers catalyzed by Pd complexes.

Catalyst/ activator	Al/M	Comonomer	OAC	P_E, atm	*T*, °C	Activity, kg mol^{-1} h^{-1}	X_M (mol.%)	Comments	Ref.
Pd01/BAF	n.d.	**C123**	none	n.d.	30–90	7.3	0.7	M_n = 24.6 kDa, $Đ_M$ = 1.7	153
		C125				1.0–4.7	<0.1–1.3	M_n = 7.1–38.8 kDa, $Đ_M$ = 1.1 – 1.9	
		C129				0.7	0.2	M_n = 5.3 kDa, $Đ_M$ = 2.1	
		C132				0.8	<0.1	M_n = 9.6 kDa, $Đ_M$ = 1.9	
Pd02/BAF	n.d.	**C125**	none	n.d.	50	0.1	0.2–0.3	M_n = 5.0–8.9 kDa, $Đ_M$ = 1.8	153
Pd03/MAO	200	**C135**	none	10	n.d.	198–290	42.3–48.8	M_n = 17–21.8 kDa, $Đ_M$ = 1.8–2.0	144
Pd03/SiO_2	n.d.	**C135**	none	10	n.d.	62–134	63.1–72.3	M_n = 89.7–97.4 kDa, $Đ_M$ = 2.3–2.6	144
Pd04/BAF	n.d.	**C019**	none	20	80	4.2	1.2		154
Pd05/BAF	n.d.	**C019**	none	20	60	6.0	0.5	M_n = 6.5 kDa, $Đ_M$ = 3.3	154
Pd06/BAF	n.d.	**C019**	none	20	60	11.4	1.9	M_n = 5.5 kDa, $Đ_M$ = 3.6	154
Pd07	n.d.	**C147**	none	30	80	0.6	3.7	M_n = 0.7 kDa, $Đ_M$ = 4.7	155
Pd08	n.d.	**C147**	none	30	60–100	2.0–9.5	0.5–2.2	M_n = 6.0–32 kDa, $Đ_M$ = 1.7–2.9	155
Pd09/BAF	n.d.	**C125**	none	8	80	2.5	1.1	M_n = 7.7 kDa, $Đ_M$ = 4.1	150
		C132				2.8	0.4	M_n = 7.5 kDa, $Đ_M$ = 3.2	
Pd10/BAF	n.d.	**C125**	none	8	80	4.5	0.7	M_n = 3.4 kDa, $Đ_M$ = 2.2	150
Pd11	n.d.	**C139**	none	8	80	2040	19.4	M_n = 74 kDa, $Đ_M$ = 1.7	156
		C140			80	1650	22.4	M_n = 68 kDa, $Đ_M$ = 1.5	
		C141			80–90	72–502	4.5–42.4	M_n = 29–134 kDa, $Đ_M$ = 1.8–2.5	157
		C142				0.3	38.0	M_n = 1.5 kDa, $Đ_M$ = 2.9	
		C144			90	0	0		158
		C145			90	45	3.5	M_n = 3.7 kDa, $Đ_M$ = 2.6	
		C146		4–8	90	57–269	1.3–30.1	M_n = 4.8–43.3 kDa, $Đ_M$ = 1.5–3.0	
Pd11′	n.d.	**C141**	none	4.8	80	93–200	0.2–23.4	M_n = 13.5–29.6 kDa, $Đ_M$ = 2.0–3.2	159
		C142		4.8		0	n.d.		
		C143		1.4		0.5	1.1	M_n = 1.8 kDa, $Đ_M$ = 2.0	
Pd11″	n.d.	**C147**	none	30	80	13	0.3	M_n = 6.4 kDa, $Đ_M$ = 3.1	155

Table 8 (continued).

Catalyst/ activator	Al/M	Como- nomer	OAC	P_E, atm	T, °C	Activity, kg mol^{-1} h^{-1}	X_M (mol.%)	Comments	Ref.
Pd12	n.d.	**C126**	none	8	80	150–240	1.0–2.3	M_n = 106–162 kDa, $Đ_M$ = 1.9–2.5	160
		C134				330–420	4.4–9.5	M_n = 88–102 kDa, $Đ_M$ = 2.1–3.2	
		C134 + 1-octene				270–350	3.8–6.5	M_n = 51–65 kDa, $Đ_M$ = 2.3–3.1	
		C137				330–930	1.9–3.6	M_n = 136–181 kDa, $Đ_M$ = 1.8–1.9	156
		C138				510–900	2.2–3.2	M_n = 124–139 kDa, $Đ_M$ = 1.7–1.9	
		C139				690–1380	2.7–4.9	M_n = 142–188 kDa, $Đ_M$ = 1.7–1.8	
		C140				900–1170	2.5–4.9	M_n = 130–156 kDa, $Đ_M$ = 1.6–1.8	
		C141			90	113	6.5	M_n = 157 kDa, $Đ_M$ = 2.1	157
		C142				0.1	15.2	M_n = 1.5 kDa, $Đ_M$ = 5.3	
		C145				41	1.4	M_n = 1.3 kDa, $Đ_M$ = 2.1	158
		C146				90	4.6	M_n = 57.6 kDa, $Đ_M$ = 1.6	
Pd12	none	**C127**	none	5, 8	80	65, 80	4.8, 2.7	M_n = 39 and 47 kDa, $Đ_M$ = 1.6 and 1.8	161
Pd13	n.d.	**C141**	none	8	90	82	16.4	M_n = 51 kDa, $Đ_M$ = 1.7	157
		C142				0.2	14.3	M_n = 2.8 kDa, $Đ_M$ = 6.2	157
		C146				55	9.7	M_n = 18.2 kDa, $Đ_M$ = 1.5	158
Pd13′	n.d.	**C142**	none	5.4	80	0.4–1.1	0.7–3.7	M_n = 13.5–18.8 kDa, $Đ_M$ = 1.9–3.0	159
		C147		30		48	0.1	M_n = 8.7 kDa, $Đ_M$ = 2.5	155
Pd14	n.d.	**C147**	none	30	80	17	0.04	M_n = 25.3 kDa, $Đ_M$ = 2.9	155
Pd15	n.d.	**C141**	none	8	90	141–380	15.7–16.2	M_n = 224–287 kDa, $Đ_M$ = 1.8–1.9	157
		C142				0.1	18.5	M_n = 1.0 kDa, $Đ_M$ = 1.6	
		C145				31	3.5	M_n = 2.1 kDa, $Đ_M$ = 2.6	158
		C146				134–142	9.9–11.2	M_n = 88.7–92.1 kDa, $Đ_M$ = 1.4–1.5	
Pd16	n.d.	**C125 + CO**	none	20	100	2	0.2	M_n = 3.3 kDa, $Đ_M$ = 3.0	162
	n.d.	**C129 + CO**	none	20	80–100	230–430	0.2–0.3	M_n = 30.7–33.2 kDa, $Đ_M$ = 1.7–1.8	162
Pd17	n.d.	**C146**	none	8	90	33	10.1	M_n = 7.6 kDa, $Đ_M$ = 1.5	158
Pd18	n.d.	**C147**	none	30	80	18	0.1	M_n = 6.5 kDa, $Đ_M$ = 2.7	155
Pd19	n.d.	**C132**	none	8	80	1	1.8	M_n = 4.4 kDa, $Đ_M$ = 2.5	152

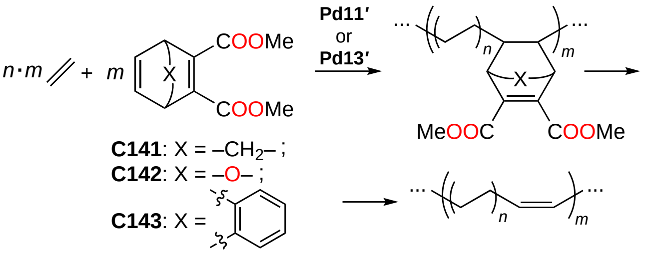
ethylene copolymerization with **C147** where they demonstrated moderate activities.[155] Complexes **Pd07** and **Pd08** with mixed type ligands (NCN-carbene–O) were found to be even less active; however, catalysis by these complexes resulted in an order of magnitude higher X_M.

Of certain interest are the results of the studies of ethylene copolymerization with allyl acetate **C125** or n-butyl allyl ether **C129** and CO catalyzed by [P,O]-complex **Pd16**. The catalyst activities were 2 and 43 kg mol^{-1} h^{-1}, respectively; X_M for CO and **C129** were 0.34 and 0.58 mol.%.[162]

The studies of [P,O] type complexes **Pd11**–**Pd13**, **Pd15**, and **Pd17** in the copolymerization of ethylene with polar comonomers, 2-azabicyclo[2.2.1]hept-5-en-3-one derivatives **C144**–**C146**, revealed low reactivity of **C144** and **C145**; in the case of **C146** (90°C, 8 atm), complexes **Pd11** and **Pd15** proved to be most active (up to 269 and 142 kg mol^{-1} h^{-1}, respectively).[158] In the copolymerization of 3-oxobutanoic acid derivatives **C126** and **C134** with ethylene (80°C, 8 atm), complex **Pd12** showed an activity of 150–420 kg mol^{-1} h^{-1}, providing X_M of up to 2.3 and 9.5 mol.%, respectively.[160] The resulting copolymers (M_n = 88–162 kDa) were subjected to post-modification by Michael addition [CH_2=CHC(O)$OCH_2CH_2S)_2$], amination [$N(CH_2CH_2NH_2)_3$], or metallation (Bu_2Mg or Et_2Zn) to give cross-linked polymers.

The introduction of CH=CH moieties into the polymer backbone is a method for 'programming' the chemical recycling of polyolefins using catalytic metathesis. Coates and co-workers[159] proposed an original approach to the synthesis of this type of polyolefins using polar comonomers **C141**–**C143**, which contain molecular groups that enable retro-Diels–Alder reaction in the copolymer (Scheme 10).[159] Complexes **Pd11′** or **Pd13′** were used in the copolymerization, and the best results were achieved for **Pd13′** and comonomer **C142**, which formed a copolymer that eliminated dimethyl furan-2,5-dicarboxylate at ~180°C. The unsaturated PE obtained in this way were used in the synthesis of polyethers (see Section 2.4). In 2024, Li and Jian,[157] who studied the **Pd11**–**Pd13**- and **Pd15**-catalyzed copolymerization of ethylene with **C141**, reported X_M of up to 42 mol.%.

Scheme 10



2.4. Properties of ethylene copolymers and prospects for their practical application

The introduction of polar comonomers into PE markedly affects the physical properties and mechanical characteristics of the polymer. The presence of long hydrocarbon chains between functional groups and the backbone naturally decreases the degree of crystallinity and related characteristics: melting point T_m and melting enthalpy ΔH_m (Refs 41, 44, 48, 50, 53, 57–59, 61, 62, 64, 68, 69, 75, 82–84, 96, 97, 102, 104, 105, 113, 121, 123, 144). However, in some experiments, the incorporation of a minor (<0.1 mol.%) amount of a comonomer with long $(CH_2)_n$ chain (*e.g.*, **C006**) resulted in a slight increase in T_m,[36] which was attributed to suppression of the formation of long-chain branches in the presence of the polar comonomer in the reaction mixture. Detailed information on the copolymer microstructure can be gained using the successive self-nucleation and annealing (SSA) method.[167] Figure 3 shows the thermograms obtained by this method and plots of the $(CH_2)_n$ sequence length distribution for ethylene copolymer with **C006**.[63] The differences in the number, positions, and areas of peaks attest to differences in the crystallite dimensions caused by the presence of $(CH_2)_n$ sequences of various lengths in copolymer macromolecules.

The presence of branches with terminal polar groups and the relative content of these branches affect the rheological behavior of copolymer melts. An important rheological characteristic of polymer melts is the relaxation time, which reflects the rate at which the system returns to equilibrium after deformation (shear). An increase in the relaxation time indicates the presence of interactions between macromolecules, while short relaxation times are characteristic of polymers with low M_n values (or, more generally, low lengths of interacting macromolecular sequences). A study of the ethylene copolymer with **C006** (M_n = 2.3–6 kDa) revealed a decrease in the relaxation time compared to that of PE (M_n = 3.7 kDa) for low comonomer content (~ 2 mol.%), caused by increasing molecular mobility of shorter $(CH_2)_n$ sequences in the copolymer. Meanwhile, an increase in the content of **C006** in the copolymer to 5.6 mol.% brought about an increase in the relaxation time due to the formation of hydrogen bonds between macromolecules.[63] In all probability, these interactions also account for the increase in complex viscosity and activation energy for viscous flow with increasing content of the comonomer.[63]

The introduction of polar groups into the PE side chain markedly affects the surface properties of the copolymer. For example, for the copolymer of ethylene with **C006**, the contact angle decreased from 105° (for parent PE) to 95 and 90° for copolymers containing 0.5 and 1.1 mol.% comonomer, respectively.[57] The copolymers of ethylene with isobutylene (10.9 mol.%) and **C011** (6 mol.%) had contacts angles of 111 and 81°, respectively.[58] For the copolymer with tyrosine derivative **C073** (2.65 mol.%), the contact angle was 48.5°.[108]

The effect of short-chain branches with polar functional groups on the mechanical properties of ethylene copolymers depends on the comonomer content, the nature of the substituent, and the length of the $(CH_2)_n$ sequence in the side chain. For relatively low comonomer contents (less than 1 mol.%) and equal M_n, the influence of the chemical nature of the comonomer is manifested as the appearance of additional chemical interactions (hydrogen bonds or Coulomb attraction forces giving ion clusters), which result in decreasing elasticity. For example, for equal M_n values (~40 kDa) and tensile strengths σ_t, ethylene copolymer with 5-hexen-1-ol **C004** (0.36 mol.%) had a substantially lower relative elongation at break ε than ethylene copolymer with 5-hexen-2-one **C131** (0.18 mol.%).[147] In relation to copolymers of ethylene and 9-decen-1-ol **C005** (M_n 74–99 kDa), it was shown that increase in the comonomer content from 6.9 to 20.4 mol.% leads to elastomeric behavior of the comonomers: σ_t decreases from 34 to 1.1 MPa and ε increases from 630 to 1200.[59] On further increase in the comonomer content to 32.1 mol.%, the copolymer becomes brittle.[59]

In some cases, the presence of bulky moieties in the side chain resulted in increasing elasticity and self-healing properties; this effect was demonstrated for ethylene copolymers with 2-allylanisole **C115** (M_n = 40–550 kDa, $Đ_M$ = 1.6–2.0),[120] terpolymers with substituted 2-allylanisole **C115′** and fused 2-allylanisole analogs (**C116**, **C117**),[119] (M_n = 110–355 kDa, $Đ_M$ = 1.5–1.9), and for terpolymers of ethylene, comonomer **C102**, and substituted styrenes (M_n = 66–130 kDa, $Đ_M$ = 1.6–1.9).[118] The content of ethylene in these copolymers was 50–70 mol.%.

A promising method for the synthesis of polymers possessing self-healing and shape memory properties is cross-linking of copolymers containing unsaturated alcohols (*e.g.*, **C006**) with the product of reaction of 4,4′-dithiodiphenylamine with isophorone diisocyanate (Scheme 11).[126] This line of research is new and has been little studied.

In some cases, the effect of charged polar groups can considerably change the mechanical properties of PE. Ethylene copolymer with **C004** containing 5.5 mol.% side-chain $(CH_2)_4OH$ groups had ε = 900% (σ_t = 13.7 MPa) and a yield strength of ~5 MPa (characteristics important for molding similar to the LLDPE properties), whereas copolymers with the $(CH_2)_4R^+$ Br^- groups [R = *N*-(*N′*-methyl)imidazolium, *N*-pyridyl] containing ~5 mol.% comonomer had ε = 500 and

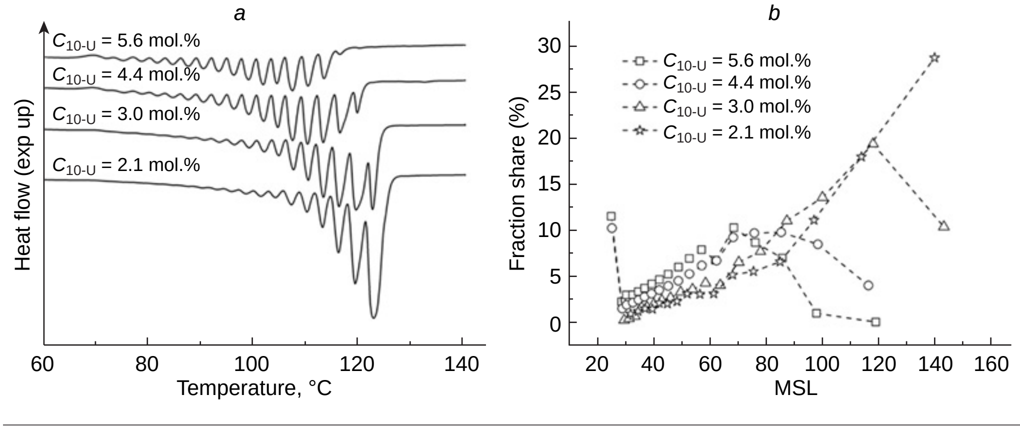
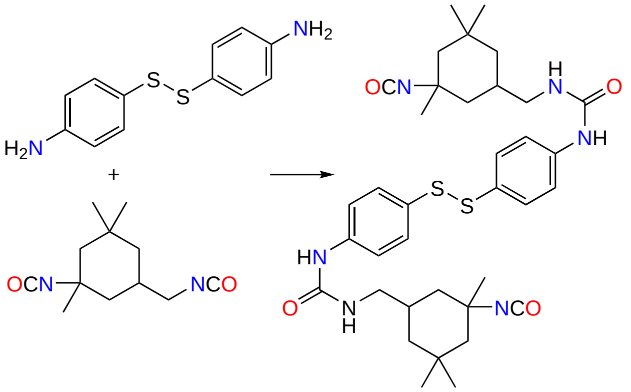


Figure 3. Melting curves obtained by SSA method (*a*) and $(CH_2)_n$ sequence length distribution curves (*b*) for copolymers of ethylene with various contents of 10-undecen-1-ol (**C006**).[63] Reproduced under the Creative Commons License CC-BY-NC-ND 4.0. MSL is the methylene sequence length. $C_{10\text{-}U}$ = **C006**.

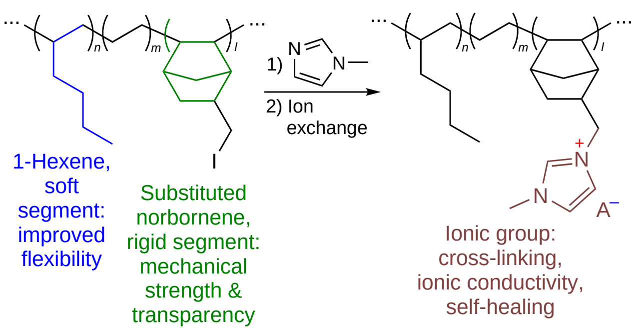
Scheme 11



573% at σ_t = 15.2 and 17.9 MPa, respectively; the yield strength for these copolymers was ~6.5 MPa. At higher contents of $(CH_2)_4R^+ Br^-$ groups (16 mol.%), the copolymers behaved as elastomers.[116]

Terpolymers composed of ethylene, hexene, and *N*-methylimidazolium-functionalized norbornene were obtained from the appropriate copolymers containing 5-iodomethyl-2-norbornene **C149**.[168] As shown in Scheme 12, the physicochemical properties of the copolymer depend on the backbone structure and the nature of substituents: the introduction of 1-hexene increases the elasticity, the norbornane moieties increase the strength, and ionic groups enable binding between the macromolecules. This study resulted in the preparation of a new type of elastomers characterized by high tensile strength (up to 13.7 MPa) and elastic recovery (up to 96%).[168]

Scheme 12



Polyethylene molding is usually accomplished by extrusion or die casting. 3D Printing is barely applicable to standard types of PE due to fast and non-uniform crystallization of the polymer, resulting in shrinkage and deformation of the product on cooling, which restricts diffusion and decreases the binding strength between the layers. The nonpolar nature of PE also reduces the adhesion between the product and the support.[169] Figure 4 vividly shows the results of a study aimed at solving this problem: the manufacture of high-quality filaments suitable for 3D printing is made possible by using the product of copolymerization of ethylene with **C018** in the presence of two-component supported catalysts based on **Ni46** and **Ni48**; the copolymer has a bimodal MWD with various comonomer contents in the low- and high-molecular-weight fractions.

Ultrahigh molecular weight polyethylenes (M_n up to 726.7 kDa) containing 0.2–4.9 mol.% OH groups were obtained by the copolymerization of ethylene with **C006**-$AlBu^i_2$ catalyzed by supported **Ti02**/MMAO/SiO_2.[56] The morphology of polymer particles was suitable for the subsequent fabrication of fibers by gel spinning followed by heat drawing. The resulting fibers were not inferior in their characteristics to fibers made of commercial ultrahigh molecular weight polyethylene (UHMWPE) and markedly exceeded them in terms of creep resistance (Table 9).

Copolymers of ethylene with **C014** prepared using ionic cluster strategy (prepolymerization of **C014**-AlEtCl followed by ethylene polymerization) substantially improved the mechanical properties of PE and poly(ethylene terephthalate) (PETP) blends, resulting from recycled packaging waste.[88]

The introduction of nitrogen-containing heterocycles into the PE side chain led to an increase in the photo-oxidative stability of polymers.[95]

In order to produce polyolefins possessing enhanced thermo-oxidative stability, O'Hare and co-workers[99] proposed introduction of phosphonate groups into the side chain. The introduction of $OP(OPr^i)_2$ (130°C, 48 h) and $OP(OPh)_2$ (180°C, 72 h) side groups into ethylene copolymers with ω-bromo-1-undecene **C084** (up to 6.1 mol.% comonomer) by the Michaelis–Arbuzov reaction gave materials with $T_{50\%}$ = 492 and 506°C, respectively (Fig. 5, for LLDPE, $T_{50\%}$ = 355°C). The composites consisting of 80 mass% LLDPE, 10 mass% $Al(OH)_3$, and 10 mass% copolymers containing side-chain phosphonate groups had $T_{50\%}$ = 473–475°C.

To increase the thermo-oxidative stability, side chains containing phenolic moieties were also introduced into PE macromolecules. The oxidation induction time at 200°C for the copolymer of ethylene with **C089** was 18–72 min (1 min for PE).[105] The ethylene copolymer with alkenyl tocopherol derivative **C090** (0.2 mol.%) had an oxidation induction temperature of 244°C (210°C for PE).[106]

A possible (although controversial, considering the issue of microplastics[170]) way for solving the problem of environmental pollution by PE waste is to decrease the photo-oxidative stability of the polymer. The incorporation of keto groups into the PE backbone and polar groups into side chains (copolymerization with CO and functional olefins) substantially decreases the stability and increases the hydrophilicity of PE.[162]

A promising practical application of cationic PE ionomers prepared by copolymerization of ethylene with ω-haloalkanes

Figure 4. (*a*) Filaments produced by the extrusion at 200°C using PE (homopolymer, **Ni46**/MgO catalyst, upper image) and copolymers with 0.5 mol.% **C018** (**Ni46**/MgO catalyst + **Ni48**/MgO, middle image; and **Ni46**+**Ni48**/MgO, lower image). 3D Printed samples made of (*b*) LLDPE, (*c*) copolymer with 1.1 mol.% **C018**, and composites (3 : 7 by weight) based on (*d*) PLA/HDPE and (*e*) PLA/copolymer with 1.1 mol.% **C018** [PLA is poly(*L*-lactide), HDPE is linear high-density polyethylene].[148] Reproduced with permission from Nature (CC-BY).

Table 9. Characteristics of ethylene copolymers with C006 in comparison with commercial UHMWPE.[56]

No.	X_M	M_n, kDa	T_m, °C	Draw ratio	Filament linear density, den [a]	Tensile strength, cN den^{-1}	Strain at break (%)	Tensile creep (%)	X_C,[b] (%)
1	0.2	726.7	141.6	31	62	19.1	2.58	0.32	80
2	0.4	603.8	141.7	32	67	19.8	2.27	0.31	82
3	0.8	558.3	142.4	36	53	21.5	2.56	0.26	89
4	1.9	513.2	140.8	33	58	20.1	1.91	0.17	88
5	2.8	504.6	142.5	30	75	17.6	3.12	0.25	79
C [c]	–		140.3	33	57	14.2	2.35	1.01	95

[a] Filament linear density (denier) is the weight of 9000 m of the filament in g. [b] Degree of crystallinity. [c] Commercial UHMWPE.

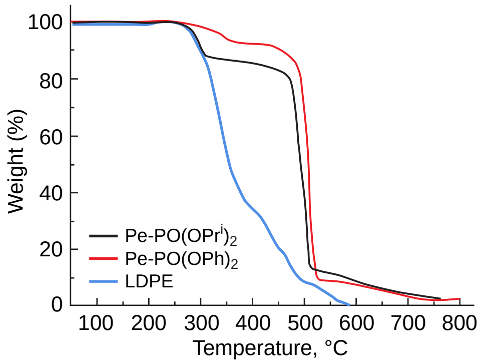


Figure 5. TGA curves (in air) for LLDPE and PE containing side-chain phosphonate groups.[99] Reproduced under the Creative Commons License CC-BY.

followed by post-modification is based on the bactericidal effect of ammonium salts against *S. aureus* and *E. coli*, which was recently demonstrated [100,161] in relation to copolymers containing *N*-methylimidazolium moieties. A much lower antimicrobial activity was inherent in the copolymers of ethylene with *N*-Boc-allylamine [161] and in copolymers of ethylene with **C146** treated with HCl and containing ammonium and carboxylate moieties.[158] An alternative approach to PE with antibacterial properties is based on the reactions of ethylene copolymers with **C014** with Ag^+, Zn^{2+}, or Cu^{2+} salts; materials containing Ag^+ ions regularly exhibited the greatest effect.[161]

A promising application for polyethylene ionomers is the development of ion exchange membranes. In 2011, Professor Chung's research team developed membranes of this type based on $CH_2{=}CH(CH_2)_nN(SiMe_3)_2$ copolymers ($n = 4, 9$; **C148** and **C049**).[171] A film sample (50 μm-thick) composed of the copolymerization product of ethylene with **C148** and 4-butenylstyrene (0.2 mol.%) after thermal cross-linking, hydrolysis, and exhaustive quaternization contained 28 mol.% $[(CH_2)_4NMe_3]^+Cl^-$ groups and showed a Cl^- ion conductivity of $\sim 10^2$ mS cm^{-1}.[171] Polyethylene ionomers are also promising for the manufacture of membranes for alkaline anion exchange fuel cells, which have been intensively studied in recent years,[172] as was shown by Cao *et al.*,[101] who considered membranes fabricated from the products of reaction of the copolymer of ethylene and **C083** with $Me_2N(CH_2)_6NMe_2$ and Me_3N.[101] The resulting membranes proved to be resistant to alkalis (up to 1680 h at 80°C in 1 M NaOH) and had high hydroxide and bicarbonate conductivities.

According to UV spectroscopy and cyclic voltammetry, ethylene copolymers with polar monomer **C062** containing $C_6H_4NPh_2$ groups had HOMO and LUMO with relative energies of –5.45 and –1.97 eV, respectively, which made them promising for the fabrication of the hole-conducting layer for organic light-emitting diodes using aluminum tris(8-hydroxyquinoline) (λ_{em} = 524 nm).[97] Ethylene copolymers with **C063** or **C064**, containing *o*-tolyl and 1-naphthyl groups, which possessed a higher oxidation stability than ethylene copolymer with **C062**, were synthesized in a more recent study.[93]

Another promising trend is the development of composite materials in which a polar copolymer acts as a compatibilizer between an inorganic filler and a polyethylene matrix. The product of reaction of MCM-41 (mesoporous silica with cylindrical oriented pores, pore diameter of 1.8–3.3 nm) with **C014**-$AlBu^i_2$ was subjected to **Zr01**/MAO-catalyzed copolymerization with ethylene in order to change the pore diameter and gas permeability of the material as a result of partial filling of the pores with the resulting copolymer.[86,87] The obtained materials (7.9–10.3 mass% MCM-41) were used to fabricate gas permeable membranes by melt compression.[86] In a later study using the same monomer and catalyst, nano-sized MCM-41 particles were employed, and the rheological behavior and mechanical characteristics of the resulting composites were studied in detail; the strength of the composite melt was found to increase with increasing content of the polar comonomer.[85] Montmorillonite-based composites were obtained by introducing polar comonomer **C065**, containing ammonium ions and acetyl moieties, between the layers of inorganic filler followed by treatment with MAO and **Zr25**; copolymerization was carried out at 60°C and 1 atm.[98] The resulting composites were characterized by high stability because of chemical binding of PE to the surface of montmorillonite.

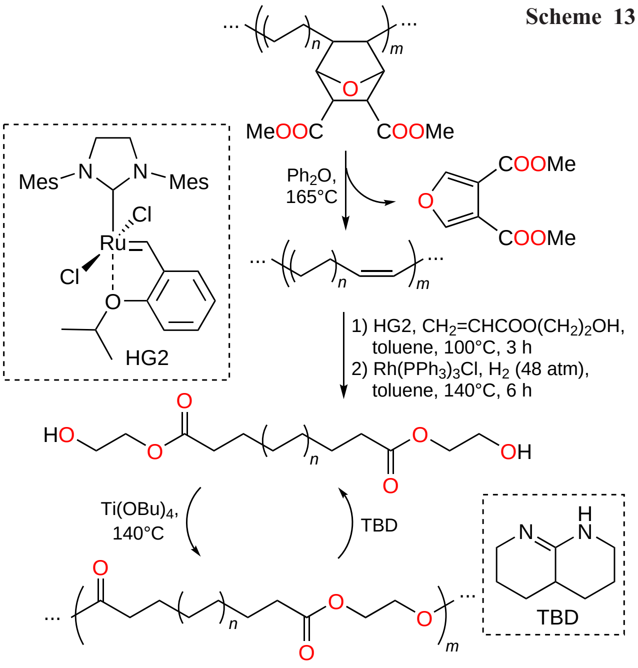
The products of thermolysis of ethylene copolymer with **C142** were subjected to cross-metathesis with 2-hydroxyethyl acrylate (in the presence of Hoveyda–Grubbs catalyst, 2nd generation, HG2) and to hydrogenation to give macromonomers, which were then transesterified to give polyesters with extended PE sequences (Scheme 13).[159] The obtained copolymers had $T_m = 127.4–133.9$°C and $\Delta H_m = 26.3–35.9$ cal g^{-1} (for HDPE, $T_m = 136.7$°C and $\Delta H_m = 47.8$ cal g^{-1}) and higher elasticity compared to HDPE. Ethenolysis of polymers with higher contents of C=C groups (HG2 catalyst) afforded mixtures of α,ω-dienes.[157]

3. Copolymers of propylene with polar vinyl monomers

3.1. Copolymerization of propylene catalyzed by Group 4 metal complexes

Many Group 4 metal complexes effectively catalyze polymerization of propylene; in particular, catalysts of this type are widely used to produce isotactic polypropylene [173] and

Scheme 13



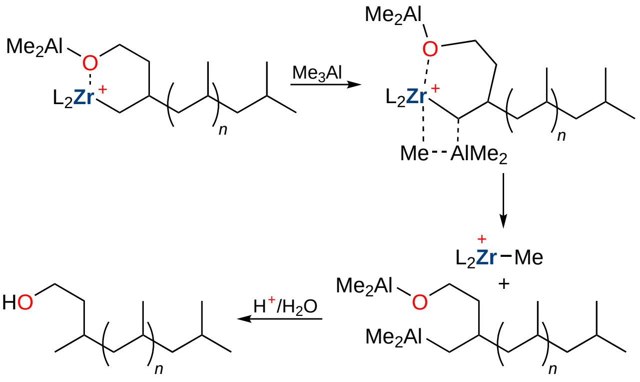
polypropylene-based elastomers.[174] As in the case of copolymerization involving ethylene, copolymerization of carboxylic acid derivatives, alcohols, and amines requires the use of OAC as masking reagents. Meanwhile, particularly in the copolymerization with propylene, monomers with latent reactivity (haloalkenes, alkenylboranes) have been widely used without organoaluminum masking reagents. Quite a few catalysts and comonomers mentioned in Section 2 were also studied in the copolymerization with propylene. The structural formulas of comonomers and precatalysts presented below supplement the list of structures considered in the previous Sections; the results of investigation of propylene copolymerization with polar monomers reported in numerous publications [10,31,32,37,39,70,76,78,81,91,101,175–207] are summarized in Table 10.

Analysis of the scientific periodicals devoted to the copolymerization of propylene with polar comonomers [10,31,32,37,39,70,76,78,81,91,101,175–207] distinguishes three periods: (1) evaluation of the prospects of using polar comonomers with existing catalytic systems (Ziegler–Natta catalysts and simple metallocenes; late 1980s–1990s), (2) use of conventional single-site catalysts (*rac*-forms of *ansa*-zirconocenes, 1990s–2000s), (3) search for effective single-site catalysts, monomers, new approaches, and applications for new materials (currently).

Early experiments on the copolymerization of polar vinyl monomers using single-site catalysts revealed a number of trends. Classic Ziegler–Natta catalysts (exemplified by $TiCl_3$ and $AlTi_3Cl_{12}$, as late-generation donor-containing titanium magnesium catalysts are hardly applicable) showed poor performance.[31,32,175–178]

When single-site catalysts are used, MAO shows low efficiency as a masking reagent for ω-alkenols and ω-alkenylcarboxylic acids compared to Me_3Al (Ref. 37) or Bu^i_3Al.[39] The use of equivalent amounts of Bu^i_3Al for binding reactive monomers resulted in the formation of copolymers with higher M_n;[189] In all probability, this is due to the suppression of chain transfer to Al. Hagihara *et al.*[76] found that in the copolymerization with **C002**, chain transfer to Al is promoted by using Me_3Al and results in the formation of characteristic terminal groups (Scheme 14).[76] This type of chain termination is more pronounced in the copolymerization of lower unsaturated alcohols (*e.g.*, **C002**) that are able to form intramolecular complexes with the unstrained metallacycle. Consequently, the use of Bu^i_3Al as a masking reagent results in the formation of random copolymers, while in the presence of a tenfold excess of Me_3Al, low-molecular-weight polymers containing characteristic >$CHMeCH_2CH_2OH$ terminal groups are formed.[76] Similar terminal groups were also detected in the copolymerization with $CH_2{=}CHCH_2X$ (X = OH, NH_2, SH); NH- and SH-acids reacted with R_3Al similarly to unsaturated alcohols.[191]

Scheme 14



Among early studies, the paper by Paavola *et al.*[190] deserves particular attention. A broad range of copolymers characterized by M_n = 6.6–55.5 kDa, $Đ_M$ = 1.9–2.0, and X_M of up to 2 mol.% were obtained by **Zr10**/MAO-catalyzed copolymerization of **C006**. For **Zr23**/MAO, it was shown that the rate constant for **C006**-$AlBu^i_2$ consumption differs from the rate constant for chain propagation during propylene homopolymerization by less than an order of magnitude.[208] When **Zr10**/MMAO was used together with 2,6-di-*tert*-butyl-4-methylphenol (butylated hydroxytoluene, BHT) to bind Me_3Al, catalyst activities of up to 10 000 and 18500 kg mol^{-1} h^{-1}, respectively, were achieved in the copolymerization of propylene with **C004** and **C006**.[193] The copolymerization constants for propylene (r_P) and comonomers (r_C) were 9.01 and 0.72, respectively (**C004**-$AlBu^i_2$) and 7.32 and 0.33, respectively (**C006**-Al^iBu_2). The $r_P \times r_{C004}$ and $r_P \times r_{C006}$ values equal to 6.49 and 2.42, respectively, reflect the tendency towards the formation of polypropylene blocks, which is more pronounced for the copolymer with shorter comonomer **C004**.[193]

Most of studies of propylene copolymerization with polar monomers included experiments at low (1–2 atm) monomer pressures and a temperature of 25°C. In 2022, Duchateau and co-workers [197] investigated copolymerization of propylene an **C006**-$AlBu^i_2$ at elevated pressure (5 atm) and temperature that are used in the polyolefin industry; complex **Zr10** demonstrated the most promising characteristics.[197] However, attempts to use a **Zr10**-based copolymerization catalyst supported on silica were unsuccessful. In a later study,[10] the same research group investigated **Hf05**/MAO-catalyzed copolymerization of propylene and Et_3Al- or Bu^i_3Al-treated **C004**. The oligomeric (trimeric at 20°C and dimeric at elevated temperature) nature of $ROAlR'_2$ was responsible for decreasing comonomer conversion and X_M (since after incorporation of one alkenyl moiety of an oligomeric complex, the other moieties remained idle), and the copolymerization efficiency was increased by introduction of $BuOAlR_2$.[77] Another substantial factor that restricts the use of Bu^i_3Al as a masking reagent is the possibility of hydroalumination

Structures C150 – C186, Ti60 – Ti62, Zr39 – Zr42, Hf02 – Hf05

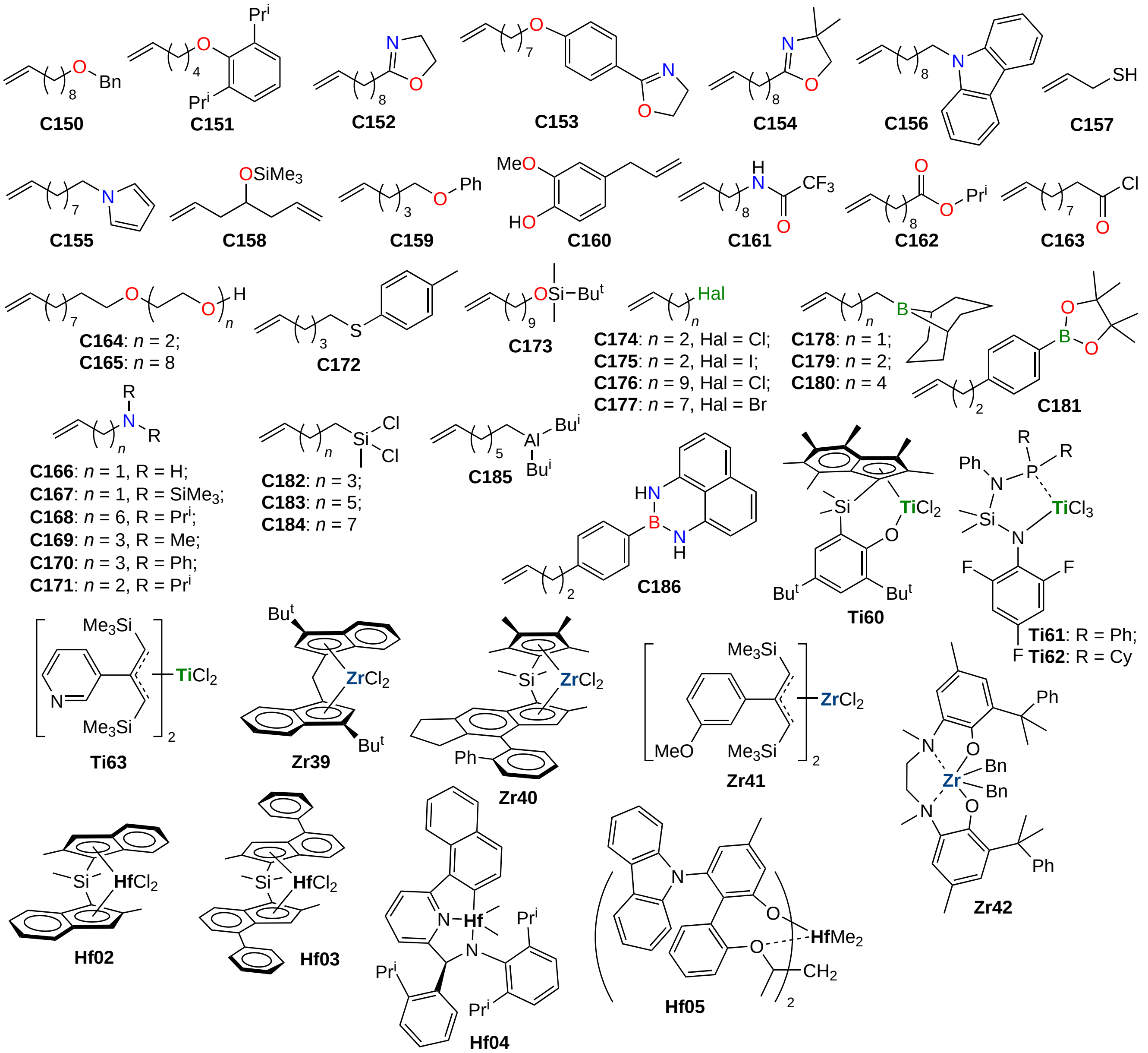


Table 10. Main characteristics of the copolymerization of propylene with polar monomers catalyzed by Group 4 metal complexes.

Catalyst/activator	Al/M	Comonomer	OAC	P_{P}, atm	T, °C	Activity, kg mol^{-1} h^{-1}	X_{M} (mol.%)	Comments	Ref.
Ti complexes *Polar vinyl comonomers*									
$AlTi_3Cl_{12}/Et_2AlCl$	3.7	**C020**	Et_2AlCl	1[a]	20	2.3	6	The copolymer was hydrolyzed to the carboxylic acid	32
$TiCl_3/Et_2AlCl$	20	**C014**	Et_2AlCl	2	90	38 – 92	<4	K salts were prepared and studied	175
$AlTi_3Cl_{12}/Et_2AlCl$	4	**C020**	Et_2AlCl	1	25	1 – 4	<5		31
$TiCl_3/Et_2AlCl$	4	**C014**	Et_2AlCl	0.3	50	<0.4	<3	Terpolymer containing 1-hexene	176
$AlTi_3Cl_{12}/Et_2AlCl$	6	**C167**	Et_2AlCl	4	60	8.6	0	M_v = 311 kDa, T_m = 160.9°C	177
$AlTi_3Cl_{12}/Et_2AlCl$	6	**C148**	Et_2AlCl	4	60	4.3	0.1	M_v = 245 kDa, T_m = 156.9°C	177
Comonomers with latent reactivity									
$AlTi_3Cl_{12}/Et_2AlCl$	2.3	**C112**	none	3.5	70	8.0	2.5		178
$AlTi_3Cl_{12}/Et_2AlCl$	3	**C176**	none	3.5	70	8.6	2.9		178

Table 10 (continued).

Catalyst/activator	Al/M	Comonomer	OAC	P_P, atm	T, °C	Activity, kg mol^{-1} h^{-1}	X_M (mol.%)	Comments	Ref.
Ti complexes									
Comonomers with latent reactivity									
$AlTi_3Cl_{12}/Et_2AlCl$	10	**C180**	none	n.d.	20	n.d.	0.3–62		179
Ti56/MAO	600	**C079**	none	2/2	50	500	1.23	M_n = 123.3 kDa, $Đ_\mathrm{M}$ = 2.23	180
Ti61/MAO	600	**C079**	none	2/2	50	470	1.08	M_n = 110.5 kDa, $Đ_\mathrm{M}$ = 2.20	180
Ti62/MAO	600	**C079**	none	2/2	50	420	0.97	M_n = 120.2 kDa, $Đ_\mathrm{M}$ = 1.98	180
Ti56/MAO	600	**C177**	none	2/2	50	550	2.23	M_n = 90.1 kDa, $Đ_\mathrm{M}$ = 2.23	180
Ti56/MAO	600	**C084**	none	2/2	50	590	2.49	M_n = 91.6 kDa, $Đ_\mathrm{M}$ = 2.49	180
$AlTi_3Cl_{12}/Et_2AlCl$	2	**C084**	none	1.4	70	6.5 g $g_{TiCl_3}^{-1}$	20.8	M_n = 22.4 kDa, $Đ_\mathrm{M}$ = 6.6	181
Ti60/MAO	1000	**C084**	Bu^i_3Al	2	50	940	15.5	M_n = 211.9 kDa, $Đ_\mathrm{M}$ = 2.4	10
Zr complexes									
Polar vinyl comonomers									
Zr23/MAO	1900	**C004**	Me_3Al	n.d.	25	70	1.4		37
		C006				370	3		
		C014				770	2.4		
Zr07/MAO	2000	**C066**–**C070**	MAO	1.5	50	80–1500	0.04–0.96		91
Zr15/MAO	640	**C004**	Bu^i_3Al	0.4	20	36	<50	M_n = 36.8 kDa, $Đ_\mathrm{M}$ = 2.52	39
Zr23/MAO	1000	**C021**, **C027**, **C032**,**C033**, **C150**	MAO	1	60	230–440	0.3–2.0	M_n = 0.95–6.3 kDa	70
Zr23/MAO	4300	**C006**	MAO	2	60	270	0.94	M_n = 10 kDa, $Đ_\mathrm{M}$ = 2.1	182
Zr07/MAO	4300	**C006**	MAO	2	60	260	0.91	M_n = 24 kDa, $Đ_\mathrm{M}$ = 2.0	182
Zr08/MAO	4300	**C006**	MAO	2	60	560	0.69	M_n = 99.0 kDa, $Đ_\mathrm{M}$ = 2.1	182
Zr17/MAO	4300	**C006**	MAO	2	60	430	0.67	M_n = 123.8 kDa, $Đ_\mathrm{M}$ = 2.1	182
Zr23/MAO	4000	**C004**, **C006**, **C008**, **C009**, **C014**, **C018**, **C022**	MAO	3	30	110–8600	<0.7	In toluene, the concentration of comonomers was 3.3–19 mM. **C008** was not incorporated; the best incorporation ratio was found for **C006**	183
Zr09/MAO	3000	**C089**	MAO	2	20	640–5370	<0.6		184
Zr23/MAO	10 000	**C152**	MAO	3	30	157	0.49	*mmmm* = 89.0%	185
		C153				153	0.38		
Zr17/MAO	10 000	**C152**	MAO	3	30	107 <1860	0.2–0.53	*mmmm* (iPP) = 97.5%; *mmmm* (**C152**/PP) = 82.5–89.6% *mmmm* = 95.5 for 0.32 mol.%	185
		C153							
Zr23/MAO	10 000	**C152**, **C153**, **C154**	MAO	3	30	115–170	0.49–0.61	M_n = 8.4–12.3 kDa, $Đ_\mathrm{M}$ = 1.5–1.9	186
	5000		Bu^i_3Al	3	30	247–482	0.39–0.40	M_n = 11.0–14.9 kDa, $Đ_\mathrm{M}$ = 1.9–2.5	186
Zr07/MAO	300	**C001**	Bu^i_3Al	1	20	570	0.08	M_n = 15.8 kDa, $Đ_\mathrm{M}$ = 1.71, *mmmm* = 83.9%	187
		C166	Me_3Al	1	20	38	0.65	M_n = 7.4 kDa, $Đ_\mathrm{M}$ = 1.67, *mmmm* = 83.3%	187
Zr23/MAO	10 000	**C006**	MAO	3	30	3900	0.20	M_n = 16.8 kDa, $Đ_\mathrm{M}$ = 2.1	188
		C014				3100	0.18	M_n = 15.5 kDa, $Đ_\mathrm{M}$ = 2.1	
		C152, **C153**, **C154**				115–170	0.49–0.61	M_n = 8.4–12.3 kDa, $Đ_\mathrm{M}$ = 1.5–1.9	
		C163				n.d.	n.d.		
Zr10/MAO	>2000	**C006**	Bu^i_3Al	3	80	11 000–39 000	0.1–0.9	M_n = 48.4–56.3 kDa, $Đ_\mathrm{M}$ = 1.9–2.0	189
Zr07/MAO	~200	**C002**	Bu^i_3Al	1	20	900	1	M_n = 10.5 kDa, $Đ_\mathrm{M}$ = 1.7	76
Zr07/MAO	~200	**C002**	Me_3Al	1	20	<215	0.6–3.7	M_n = 2.0–12.2 kDa, $Đ_\mathrm{M}$ = 1.46–2.3	76
Zr10/MAO	7500	**C006**	Bu^i_3Al	2	70	34500	1.5	M_n = 45 kDa, $Đ_\mathrm{M}$ = 2.0, T_m = 136.5°C	190
Zr07/MAO	300	**C157**	Bu^i_3Al	1	25	11	0.11	M_n = 11.6 kDa, $Đ_\mathrm{M}$ = 1.73, *mmmm* = 94.7%, no reaction in the case of Me_3Al	191

Table 10 (continued).

Catalyst/activator	Al/M	Comonomer	OAC	P_P, atm	T, °C	Activity, kg mol^{-1} h^{-1}	X_M (mol.%)	Comments	Ref.
Zr complexes *Polar vinyl comonomers*									
Zr08/MAO	300	**C157**	$\mathrm{Bu^i_3Al}$	1	25	13	0.17	M_n = 22.8 kDa, $Đ_\mathrm{M}$ = 2.0, *mmmm* = 96.7%	191
Zr10/MAO	300	**C157**	$\mathrm{Bu^i_3Al}$	1	25	9	0.53	M_n = 17.1 kDa, $Đ_\mathrm{M}$ = 2.22, *mmmm* = 96.4% no reaction in the case of $\mathrm{Me_3Al}$	191
Zr23/MAO	8000	**C006**	$\mathrm{Bu^i_3Al}$	1.5	30	936–3086	0.15–9.2	T_m = 76–138 °C	78
Zr17/MAO	>4000	**C164**	$\mathrm{Bu^i_3Al}$	1.2	50	25–960	0.51–1.6	M_n = 16.7–36.9 kDa, $Đ_\mathrm{M}$ = 1.3–1.8	78
Zr17/MAO	>4000	**C165**	$\mathrm{Bu^i_3Al}$	1.2	50	44–73	0.1–0.31	M_n = 16.9–22.5 kDa, $Đ_\mathrm{M}$ = 1.5–1.6	78
Zr23/MAO	200	**C006**	$\mathrm{Bu^i_3Al}$	n.d.	n.d.	n.d.	4–17	M_n = 5.0–22.3 kDa, $Đ_\mathrm{M}$ = 1.3–1.8	192
Zr23/MAO	200	**C173**	MAO	n.d.	n.d.	n.d.	15–29	M_n = 0.75–0.9 kDa, $Đ_\mathrm{M}$ = 2.4–2.8	192
Zr23/MAO	200	**C161**	MAO	0.09 M	n.d.	n.d.	2–15	M_n = 4.4–12.9 kDa, $Đ_\mathrm{M}$ = 1.9–2.1	192
Zr23/dMAO	12 000	**C148**	dMAO	8	40	3100	0.5	M_v = 38 kDa, T_m = 125.2 °C	177
Zr39/dMAO	12 000	**C148**	dMAO	8	40	1850	0.4	M_v = 96 kDa, T_m = 146.8 °C	177
Zr10/dMAO	12 000	**C148**	dMAO	8	40	3200	<3.0	M_v = 269 kDa, T_m = 131.7 °C	177
Zr23, **Zr39**, **Zr10**/dMAO	12 000	**C167**	dMAO	8	40	1600–2500	0	M_v = 58–388 kDa, T_m = 138.3–157°C	177
Zr10/MMAO/BHT	2000	**C004**	$\mathrm{Bu^i_3Al}$	1	25	5100–10 000	2.7–5.7	M_n = 8.5–18 kDa, $Đ_\mathrm{M}$ = 2.0–2.3	193
	2000	**C006**	$\mathrm{Bu^i_3Al}$	1	25	9500–18 500	2.1–2.3	M_n = 9.7–18.5 kDa, $Đ_\mathrm{M}$ = 2.1–2.3	193
Zr23/MAO	650	**C018**	$\mathrm{Bu^i_2AlH}$	1	50	5900	0.46	M_n = 12.3 kDa, $Đ_\mathrm{M}$ = 1.86, T_m = 121.5°C	81
Zr10/MAO	1000	**C006**	MAO	8.3	40	<4300	1.5–6		194
Zr23/$\mathrm{Bu^i_3Al}$/TB$^\mathrm{F}$	100	**C046**, **C101**, **C169**,	none	1	25	0	–		195
Zr23/$\mathrm{Bu^i_3Al}$/TB$^\mathrm{F}$	100	**C170**	none	1	25	4750–6480	1.5–3.4	M_n = 13.9–18.9 kDa, $Đ_\mathrm{M}$ = 1.8–2.1, T_m = 116.6–123.9°C	195
Zr23/$\mathrm{Bu^i_3Al}$/TB$^\mathrm{F}$	100	**C062**	none	1	25	5280–6360	1.4–3.1	M_n = 9.2–21.7 kDa, $Đ_\mathrm{M}$ = 1.8–2.4, T_m = 92–139°C	195
Zr07′/TB$^\mathrm{F}$	–	**C048**	none	1	25	431–4208	0.4–4.0	M_n = 29–41 kDa, *mmmm* = 82.3–83.7%	196
Zr07′/TB$^\mathrm{F}$	–	**C168**	none	1	25	4468	1.5	M_n = 57 kDa, *mmmm* = 81.5%	196
Zr22′/TB$^\mathrm{F}$	–	**C048**	none	1	25	15–465	0.5–1.5	M_n = 52–70 kDa, *rrrr* = 76.6–78.9%	196
Zr22′/TB$^\mathrm{F}$	–	**C168**	none	1	25	940	0.7	M_n = 46 kDa, *rrrr* = 72.1%	196
Zr08/MMAO	8090	**C006**	$\mathrm{Bu^i_3Al}$	5	80	$1.1–2 \times 10^5$	0.1–0.5	M_n = 12.1–15.8 kDa, $Đ_\mathrm{M}$ = 2.3	197
Zr10/MMAO	8300	**C006**	$\mathrm{Bu^i_3Al}$	5	80	$2.5–13.2 \times 10^5$	0.2–0.8	M_n = 80.5–162.6 kDa, $Đ_\mathrm{M}$ = 2.4–3.0	197
Zr07/MMAO-12	3077	**C155**	MMAO	1.5	25	419–1239	0.6–2.6	M_n = 34.4–47.4 kDa	198
Zr07/MMAO	500	**C156**	MMAO	1.5	25	662–1948	0.2–1.8	M_n = 30.4–43.3 kDa	199
Comonomers with latent reactivity									
Zr07/MAO	2000	**C176**	none	3.5/1.5	20	5500	2	M_n = 66 kDa, $Đ_\mathrm{M}$ = 1.7	200
Zr23/MAO	2000	**C084**	none	1	40	624–1851	1.5–10.3	Decrease in the activity and M_n with increasing content of **C084**	201
Zr23/MAO	200	**C176**	none	0.09 M	n.d.	n.d.	5–22	M_n = 1.0–1.1 kDa, $Đ_\mathrm{M}$ = 2.9–6.2	192
Zr23/$\mathrm{Bu^i_3Al}$/TB$^\mathrm{F}$	100	**C175**	none	1	25	72–312	0.2	M_n = 7.6 kDa, $Đ_\mathrm{M}$ = 2.2	202
		C111, **C174**					0		
Zr23/$\mathrm{Bu^i_3Al}$/TB$^\mathrm{F}$	100	**C176**	none	1	25	1850	1.25	M_n = 11.4 kDa, $Đ_\mathrm{M}$ = 1.9, T_m = 119°C	202
Zr23/$\mathrm{Bu^i_3Al}$/TB$^\mathrm{F}$	100	**C084**	none	1	25	2590	1.4	M_n = 11.1 kDa, $Đ_\mathrm{M}$ = 2.0, T_m = 120°C	202
Zr23/$\mathrm{Bu^i_3Al}$/TB$^\mathrm{F}$	100	**C083**	none	1	25	2640–3050	1.9–5.5	M_n = 13.2–13.9 kDa, $Đ_\mathrm{M}$ = 1.76–1.9, T_m = 85–118°C	202
Zr42/MAO/BHT	200	**C181**	none	1	25	20	3.5	M_n = 16 kDa, $Đ_\mathrm{M}$ = 1.9, *mmmm* = 85%	203
	200	**C186**	none	1	25	8–23	1.2–3.8	M_n = 16–30 kDa, $Đ_\mathrm{M}$ = 1.8–2.4	203

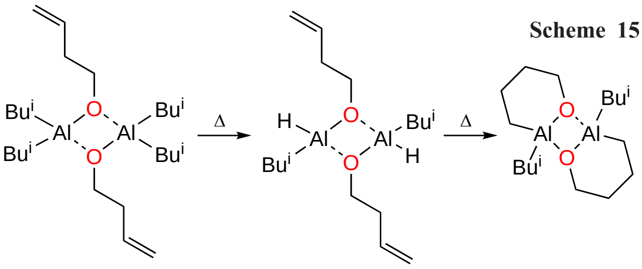
Table 10 (continued).

Catalyst/activator	Al/M	Comonomer	OAC	P_P, atm	T, °C	Activity, kg mol^{-1} h^{-1}	X_M (mol.%)	Comments	Ref.
Zr complexes *Comonomers with latent reactivity*									
Zr08/TB$^\mathrm{F}$	n.d.	**C185**	none	1	40	n.d.	0.8–9.6	M_n = 24–94 kDa, Đ$_\mathrm{M}$ = 2.6–3.1	204
Zr18 /TB$^\mathrm{F}$	n.d.	**C185**	none	1	40	n.d.	1.3–7.1	M_n = 64–70 kDa, Đ$_\mathrm{M}$ = 2.1–2.8	204
Zr40@SiO$_2$/$\mathrm{Bu^i_3Al}$	100	**C185**	none	1	70	$2-2.5\times10^5$	0.01–0.09	M_n = 68.3–170.3 kDa, Đ$_\mathrm{M}$ = 2.9–3.6, T_m = 159–159°C	205
Zr10/MAO	1500	**C182**, **C183**, **C184**	none	4	50	1200–5900	n.d.	M_w = 264–347 kDa	206
Zr23/MAO	1000	**C078**	$\mathrm{Bu^i_3Al}$	2	70	0			10
Zr23/MAO	1000	**C079**	$\mathrm{Bu^i_3Al}$	2	70	282	5.1	M_n = 3.6 kDa, Đ$_\mathrm{M}$ = 1.6	10
Zr23/MAO	1000	**C084**	$\mathrm{Bu^i_3Al}$	2	70	843	4.0	M_n = 4.9 kDa, Đ$_\mathrm{M}$ = 1.9	10
Zr23/MAO	1000	**C084**	$\mathrm{Bu^i_3Al}$	2	50	1790	2.0	M_n = 13.0 kDa, Đ$_\mathrm{M}$ = 2.2, *mmmm* = 86.8%	10
Zr10/MAO	1000	**C084**	$\mathrm{Bu^i_3Al}$	2	50	3630	1.64	M_n = 42.3 kDa, Đ$_\mathrm{M}$ = 3.6, *mmmm* = 98.4%	10
Zr18/MAO	1000	**C084**	$\mathrm{Bu^i_3Al}$	2	50	1100	3.95	M_n = 118.1 kDa, Đ$_\mathrm{M}$ = 2.3, *rrrr* = 71.7%	10
Hf complexes *Polar vinyl comonomers*									
Hf04/$\mathrm{Bu^i_3Al}$/TB$^\mathrm{F}$	100	**C169**, **C101**	none	1	25	0	–		195
Hf04/$\mathrm{Bu^i_3Al}$/TB$^\mathrm{F}$	100	**C046**	none	1	25	110–1080	2.7-7.8	M_n = 35.2–74.3 kDa, Đ$_\mathrm{M}$ = 2.1–2.7, T_m = 74.4–129.7°C	195
Hf04/$\mathrm{Bu^i_3Al}$/TB$^\mathrm{F}$	100	**C170**	none	1	25	4940–6580	1.6–4.6	M_n = 60.0–77.1 kDa, Đ$_\mathrm{M}$ = 2.4–3.1, T_m = 133.5–147.1°C	195
Hf04/$\mathrm{Bu^i_3Al}$/TB$^\mathrm{F}$	100	**C062**	none	1	25	4920–7440	1.1–11.6	M_n = 189.0–324.1 kDa, Đ$_\mathrm{M}$ = 1.7–3.6, T_m = 85–152°C	195
Hf02/MMAO	4280	**C006**	$\mathrm{Bu^i_3Al}$	5	80	$7.4-14.3\times10^5$	0.1–0.6	M_n = 44.9–69.7 kDa, Đ$_\mathrm{M}$ = 2.6–4.9	197
Hf03/MMAO	4280	**C006**	$\mathrm{Bu^i_3Al}$	5	80	$6.9-9.6\times10^5$	0.2–0.8	M_n = 40.6–45.8 kDa, Đ$_\mathrm{M}$ = 3.1–3.3	197
Hf04/TB$^\mathrm{F}$	–	**C159**	none	1	25	86–729	0.08–1.43	M_n = 375.8–962.0 kDa, Đ$_\mathrm{M}$ = 1.48–2.47	207
Hf04/TB$^\mathrm{F}$	–	**C172**	none	1	25	1119	0.54	M_n = 623.5 kDa, Đ$_\mathrm{M}$ = 1.79	207
Comonomers with latent reactivity									
Hf04/$\mathrm{Bu^i_3Al}$/TB$^\mathrm{F}$	110	**C083**	none	1	25	7200	29.7	M_n = 131.3 kDa, Đ$_\mathrm{M}$ = 2.30	101
Hf04/$\mathrm{Bu^i_3Al}$/TB$^\mathrm{F}$	50	**C175**	none	1	25	140	1.8	M_n = 39.6 kDa, Đ$_\mathrm{M}$ = 2.02	202
		C111, **C174**					0		
Hf04/$\mathrm{Bu^i_3Al}$/TB$^\mathrm{F}$	50	**C176**	none	1	25	72	3	M_n = 36.4 kDa, Đ$_\mathrm{M}$ = 2.97, T_m = 123°C	202
Hf04/$\mathrm{Bu^i_3Al}$/TB$^\mathrm{F}$	50	**C084**	none	1	25	140	3.4	M_n = 57.6 kDa, Đ$_\mathrm{M}$ = 2.1, T_m = 119°C	202
Hf04/$\mathrm{Bu^i_3Al}$/TB$^\mathrm{F}$	50	**C083**	none	1	25	460–1200	2.8–11.7	M_n = 69.0–71.3 kDa, Đ$_\mathrm{M}$ = 1.85–2.03, T_m = 82–130°C	202
Hf04/$\mathrm{Bu^i_3Al}$/TB$^\mathrm{F}$	100	**C083**	none	1	25	380	11.7	M_n = 68.0 kDa, Đ$_\mathrm{M}$ = 1.97, T_m = 82°C	32

Note. *mmmm* is the content of isotactic pentads, iPP is isotactic polypropylene, rrrr is the content of syndiotactic pentads. [a] 9 : 1 (v/v) mixture of propylene and ethylene.

at elevated temperatures (>100°C) found in the same study (Scheme 15).

Scheme 15



Like in the copolymerization of ethylene, the best results were achieved by using comonomers that directly react with OAC such as unsaturated alcohols.[188] Alkenyl-substituted oxazolines[188] and sterically unhindered ethers proved to be poorly reactive comonomers.[78] A comparative study of the reactions of ethers $CH_2{=}CH(CH_2)_8OR$, **C021**, **C150**, **C027**, **C032**, and **C033**, with the complex $Cp_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$ demonstrated that the presence of sterically hindered substituents R (CPh_3, $SiPh_3$) prevents the coordination of oxygen to the Zr atom.[70] Meanwhile, the results of copolymerization experiments using **Zr23**/MAO catalysts indicated relatively low reactivity of these comonomers. The **Hf04**/TB$^\mathrm{F}$ catalytic system proved to be much more effective; upon the introduction of **C159**, the activity substantially decreased (by an order of magnitude for 150 equiv. of the comonomer added), while M_n of the polymer increased by a large factor (up to 0.9×10^6 Da).[207] According to DFT modelling of the copolymerization mechanism, the increase in M_n was attributed to the reversible intramolecular Hf···O coordination, which prevents chain termination by the β-hydride elimination mechanism (intermediate P_{xx} is 5.8 kcal mol^{-1} more stable than $P_{x\beta\text{-}H}$, Fig. 6). The decrease in the activity was explained by the difference between the $\Delta G^{\neq}$ values for propylene insertion in intermediates $P5_{re}$ and P_{xx} (14.6 and 18.4 kcal mol^{-1}, respectively).[207]

Tertiary ω-alkenamines are a promising type of comonomers. Apart from steric factors, the reactivity of these comonomers is influenced by the nature of substituents at the N atom: when the **Hf04**/Bu^i_3Al/TB^F catalyst was used, comonomers **C169** and **C101** with NMe_2 and NEt_2 terminal groups proved to be inactive; comonomer **C046** with the NPr^i_2 group did react, with copolymer M_n decreasing with increasing comonomer concentration; and when comonomer **C170** with the NPh_2 terminal group was used, M_n virtually did not change (60–77.1 kDa) even after a threefold increase of the molar content of **C170** in the reaction product.[195] In 2020, Marks and co-workers[196] described propylene copolymerization with $CH_2{=}CH(CH_2)_nNPr^n_2$ [$n = 2$ (**C044**), 3 (**C045**), 6 (**C048**)] and $CH_2{=}CH(CH_2)_6NPr^i_2$ (**C168**) catalyzed by **Zr07′**/TB^F and **Zr22′**/TB^F. Comonomers **C044** and **C045** in concentrations of 0.012 M virtually deactivated both catalysts. As the concentration of comonomer **C048** increased from 0.012 to 0.1 mol L^{-1}, the activity of **Zr07′**/TB^F decreased by an order of magnitude (4208 *vs* 431 kg mol^{-1} h^{-1}); an even more pronounced dependence of the activity on the comonomer concentration was observed for **Zr22′**/TB^F (465 and 15 kg mol^{-1} h^{-1} for [**C048**] = 0.012 and 0.05 mol L^{-1}, respectively). The stereoregularity of the obtained isotactic (**Zr07′**/TB^F) and syndiotactic (**Zr22′**/TB^F) copolymers proved to be higher than the stereoregularity of the parent polypropylene (PP): *mmmm* = 82.3–83.7% *vs* 59.5% and *rrrr* = 76.6–78.9% *vs* 66.3%.[196] The copolymerization experiments with 1-octene in the presence of R_3N also revealed an increase in the stereoregularity: most likely, reversible Zr···N coordination increases the stereoselectivity of coordination and monomer incorporation in some way. A slight increase in the stereoselectivity was also observed for the **Zr07**/MMAO-12-catalyzed propylene copolymerization with ω-alkenylpyrrole **C155**.[198] In the copolymerization of **C155** in the presence of the same catalyst, the introduction of 1 mol.% comonomer induced an increase in the activity, which is generally not typical of reactions involving polar monomers.[199,209]

A number of studies report unexpected and somewhat discouraging results. Eisen and co-workers[192] described copolymerization of propylene with $CH_2{=}CH(CH_2)_8NHC(O)CF_3$ (**C161**) catalyzed by **Zr23**/MAO ([Al]/[Zr] = 200 : 1) to give random copolymers without the use of masking reagents. In the cited study, the choice of amides was substantiated by the fact that they cause lower deactivation of the catalytic site, which casts some doubts, in view of high donor properties of amides in comparison with other carboxylic acid derivatives (fundamental study by Gutmann[210]). Eisen and co-workers[192] also reported data on the propylene copolymerization with **C006** catalyzed by complexes **Zr41** and **Ti63**; the reactions gave an atactic polymer with a low comonomer incorporation ratio.

The possibility of using ω-halogenated α-olefins in the coordination (co)polymerization was demonstrated back in 1965.[211] Study of the reactions of various types of R–Hal with OAC showed than only primary halogen derivatives can be applied as comonomers. The $TiCl_3/R_3Al$ catalyst was found to benefit from addition of an extra donor (pyridine).[178] More recently, Zhang *et al.*[181] prepared the propylene copolymer with **C084** and propylene terpolymer with **C084** and 4-butenylstyrene using the $TiCl_3/Et_2AlCl$ catalyst, which exhibited a very low activity (~10 g $g_{TiCl_3}^{-1}$). In 2024, O'Hare and co-workers[10] published the results of a comparative study of the catalytic behaviours of **Zr23**, **Zr10**, **Zr18**, and **Ti02** in the propylene copolymerization with ω-bromo-1-alkenes to give isotactic, syndiotactic, and atactic copolymers, with the highest reactivity found for comonomer **C084**.[10]

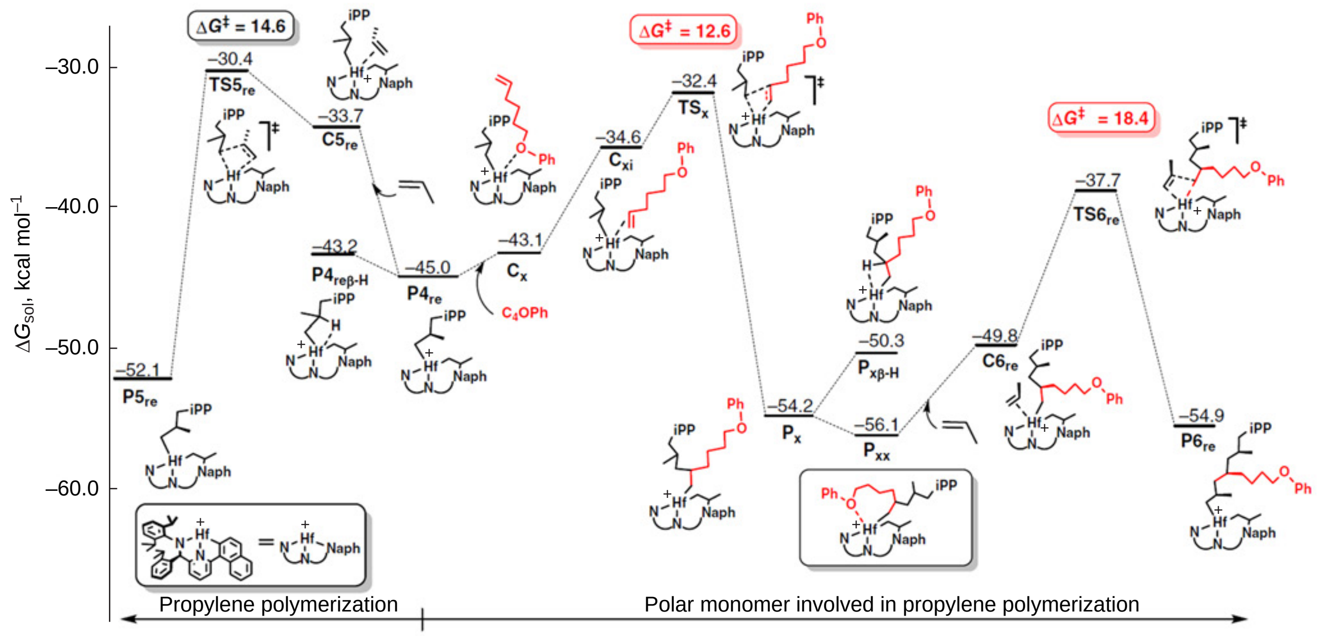


Figure 6. Results of DFT modelling of the copolymerization of propylene and **C159** catalyzed by **Hf04**/TB^F.[207] Reproduced under Creative Commons License CC-BY.

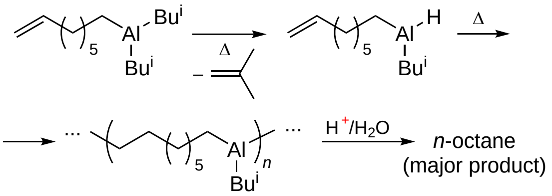
A comparative study of the catalytic activity of **Zr23**/$Bu^{i}_{3}Al$/TB^{F} and **Hf04**/$Bu^{i}_{3}Al$/TB^{F} in the propylene copolymerization with ω-halogen-substituted 1-butene and 1-undecene indicated a higher activity for zirconocene compared to the post-metallocene Hf complex. The reactivity of comonomers increased with increasing length of the $(CH_2)_n$ fragment between the C=C bond and the halogen atom and decreased in the series I > Br > Cl.[202] A ^{1}H NMR spectroscopy study of the mixtures of **Hf04**/B^F with $CH_2{=}CH(CH_2)_2Hal$ [Hal = Cl (**C174**), Br (**C111**), I (**C175**)] indicated the formation of complexes with the Hf···Hal bond for **C174** and **C111** and no iodine coordination to the Hf atom, which correlates with experimental results: among 4-halo-1-butenes, only iodo derivative **C175** proved to be capable of being incorporated into the growing polymer chain.[212]

ω-Alkenylboranes (borates) are another type of comonomers with latent reactivity. There are few examples of copolymerization of propylene with these comonomers. Propylene copolymers with alkenylborane **C180** were obtained using $TiCl_3/Et_2AlCl$.[179] In the presence of **Zr42**/MAO/BHT catalyst, diester **C181** and diamide **C186** formed copolymers (X_M of up to 3.8 mol.%) with *mmmm* = 85–90%.[203]

The compound $CH_2{=}CH(CH_2)_6Al^{i}Bu_2$ (**C185**) can also be classified as having latent reactivity. Back in 2002, Shiono and co-workers[204] proposed to use **C185** as a comonomer; **Zr08**- and **Zr18**-catalyzed copolymerization of propylene and **C185** in the presence of TB^F followed by oxidation and hydrolysis resulted in a product containing side-chain $(CH_2)_6OH$ groups.[204] In 2024, O'Hare and co-workers[10] showed experimentally that the use of **C185** in industry (at elevated temperatures) may be complicated by hydroalumination (Scheme 16).[10]

Wang *et al.*[206] used **Zr10**/MAO-catalyzed copolymerization of propylene with $CH_2{=}CH(CH_2)_nSiMeCl_2$ (n = 2, 4, 6) followed by hydrolysis to obtain polypropylene with long-chain branches. The formation of copolymers was complicated by the reaction of MAO with Si–Cl groups during the copolymerization, and by gelation during the hydrolysis; the prospects for practical application of the proposed approach are questionable.

Scheme 16



Scandium and vanadium complexes have been barely studied in the propylene copolymerization with non-conjugated polar vinyl monomers. Et_2AlCl-aactivated $VOCl_3$ showed a very low activity in the copolymerization of propylene, ethylene, and **C020**.[32]

3.2. Copolymerization of propylene catalyzed by Group 10 metal complexes

Catalysts based on Group 10 metals generally exhibit low stereoselectivity in propylene polymerization;[19] that is why propylene copolymerization with non-conjugated polar vinyl monomers has been addressed in much fewer publications compared to ethylene copolymerization. The latest achievements in this field were summarized in 2021.[23] The present Section considers the results of studies published in 2020–2025.

Single-component catalysts based on Ni complexes were not used in the copolymerization of propylene with non-conjugated polar vinyl monomers in the 2020s. In 2025, Chen *et al.*[213] reported the development of a complex catalytic system for the synthesis of polar high-impact polypropylene using [N,N]-complexes **Ni13** or **Ni14** and Ziegler–Natta catalysts. The deposition of both types of catalysts (1 and 10 μmol, respectively) on a polar support (Table 11) afforded a 'mixed' catalyst, which was then used in the polymerization of ethylene to give branched PE (the major contribution to PE formation was made by the Ni catalyst) and then in the isotactic polymerization of propylene in the presence of $Bu^{i}_{3}Al$, which deactivated Ni catalyst and activated the Ziegler–Natta catalyst. This two-step copolymerization resulted in the formation of a material with enhanced σ_t and impact resistance (see Section 3.5).

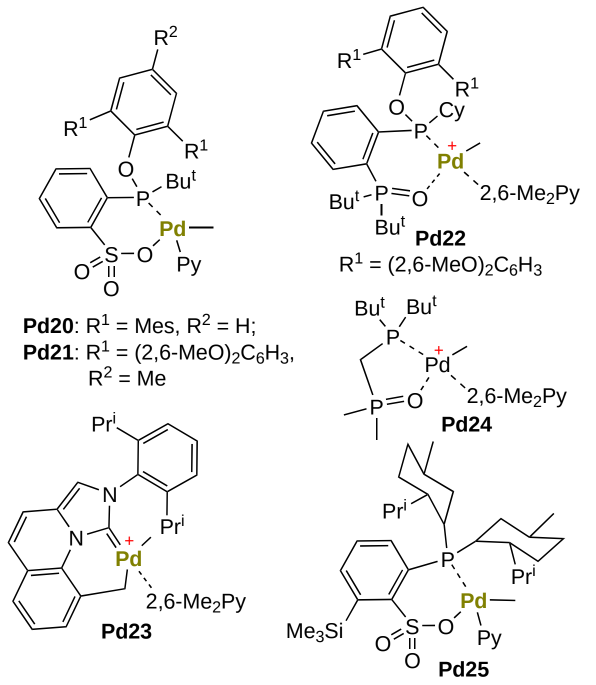
[P,O]-complexes **Pd20**–**Pd22** were of low activity in the copolymerization of propylene with allyl acetate **C125** (0.19–0.49 kg mol^{-1}_{cat} h^{-1}); for copolymers with X_M = 0.85, 1.82, and 0.05 mol.%, the contents of isotactic triads *mm* were 0.51, 0.65, and 0.74%, respectively; in the copolymerization with

Table 11. Main characteristics of two-step copolymerization of ethylene and propylene using two-component catalysts under general conditions: Ni catalyst (1 μmol) and ZNC (10 μmol) (the support was prepared by polymerization of 0.38 mmol of $[CH_2{=}CH(CH_2)_8CO_2]_2AlCl$ with Et_2AlCl, Al/Ni = 250/1), 3.0 mmol of $Bu^{i}_{3}Al$, 90 mL of n-heptane (ethylene polymerization: 25°C, 0.8 MPa, 2 min; propylene polymerization: 60°C, 0.1 MPa, 45 min, if not otherwise indicated in a footnote).[213]

No.	Cat.	Yield, g	Ethylene 10^4/propylene 10^3 activity (kg mol^{-1}_{cat} h^{-1})	Ratio of E/P units in the product mol.%/mol.%	M_n, kDa	$Đ_M$
1	ZNC	9.5	–/1.3	0/100	185.4	4.1
2	**Ni13**/ZNC	10.8	4.9/1.2	15/85	312.8	3.9
3[a]	**Ni13**/ZNC	10.2	4.0/1.2	13/87	348.5	3.3
4[b]	**Ni13**/ZNC	10.0	3.6/1.2	12/88	248.6	3.5
5[c]	**Ni13**/ZNC	8.5	3.6/0.97	14/86	335.5	3.1
6[d]	**Ni13**/ZNC	11.5	3.3/1.2	24/76	275.0	4.0
7[e]	**Ni13**/ZNC	12.0	1.9/0.96	40/60	448.2	5.6
8[f]	**Ni13**/ZNC	12.7	1.5/0.6	29/71	289.7	5.8
9	**Ni14**/ZNC	12.5	3.8/1.5	10/90	250.0	3.4
10[d]	**Ni14**/ZNC	12.1	2.6/1.3	18/82	441.7	2.4

[a] 0.6 MPa for ethylene polymerization. [b] 0.4 MPa for ethylene polymerization. [c] 50°C for ethylene polymerization. [d] 5 min for ethylene polymerization. [e] 15 min for ethylene polymerization. [f] 15 min for ethylene polymerization, 90 min for propylene polymerization.

Structures Pd20–Pd25



Pd20: R^1 = Mes, R^2 = H;
Pd21: R^1 = (2,6-MeO)$_2$C$_6$H$_3$, R^2 = Me

R^1 = (2,6-MeO)$_2$C$_6$H$_3$

allyl chloride, **Pd20** and **Pd22** were even less active (0.08 and 0.25 kg mol$_{cat}^{-1}$ h^{-1}, respectively).[214] The very fact of isotacticity is certainly of interest, but practical application of these catalysts is out of the question. Low activities (0.21 – 1.8 kg mol$_{cat}^{-1}$ h^{-1}) in the copolymerization of propylene with 5-norbornene-2-carboxylic acid esters **C118** and **C133** were also found for catalysts **Pd23** – **Pd25**.[215]

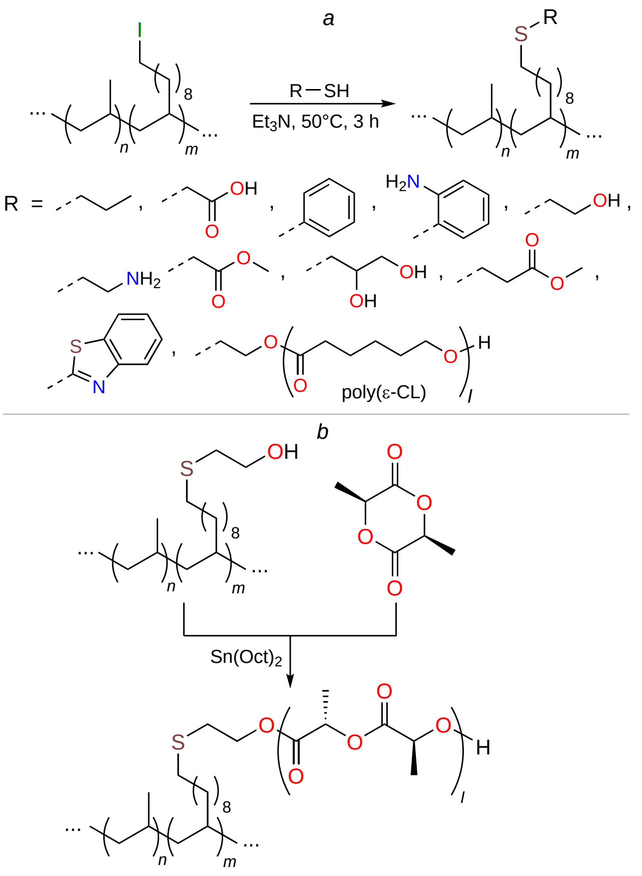
3.3. Post-modification of propylene copolymers and polypropylene ionomers

In a review published in 2014,[216] non-conjugated dienes and ω-alkylstyrenes were mainly considered as comonomers with latent reactivity. The presence of CH=CH$_2$ groups in the side chain is an obvious and commercialized advantage of rubbers, which are not the subject of this review. Meanwhile, a number of examples of successful post-modification of propylene copolymers with monomers containing reactive functional groups with heteroatoms can be found in scientific periodicals.

In early stages of research, copolymers of propylene with alkenylborane **C180** prepared using AlTi$_3$Cl$_{12}$/Et$_2$AlCl were converted to polyols and polyiodo derivatives in high yields;[179,216] however, the same copolymers can also be synthesized by copolymerization of propylene with OAC-protected alkenols and ω-iodo-1-alkenes (see Table 4). In a later study, of copolymers involving arylboronic acid diester **C181** and diamide **C186**, deprotection to give terminal phenolic moieties was performed by treating the copolymer with HCl/MeOH.[203]

Propylene copolymers with ω-halogen-substituted α-olefins are promising starting compounds for post-modification. Scheme 17*a* shows examples of replacement of halogen atoms in copolymers of this type using S-nucleophiles (including the synthesis of graft copolymer with ε-caprolactone).[32,217] The polymerization of *L*-lactide initiated by SCH$_2$CH$_2$OH-functionalized polypropylene (PP) afforded graft copolymers containing up to 70 mass% poly(*L*-lactide) (Scheme 17*b*).[217]

Scheme 17

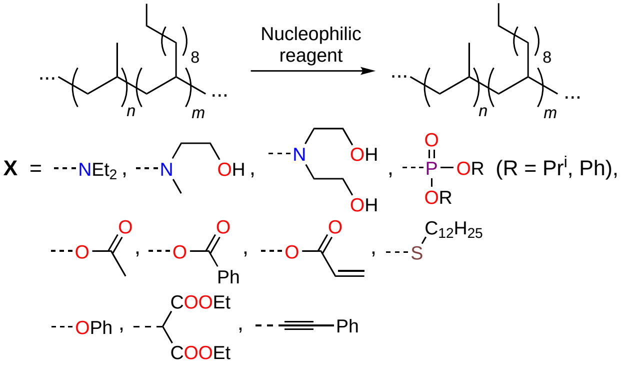


In 2024, O'Hare and co-workers[10] reported the results of a study devoted to post-modification of propylene copolymers with **C084** using various N-, O-, S-, and P-nucleophiles (Scheme 18).[10]

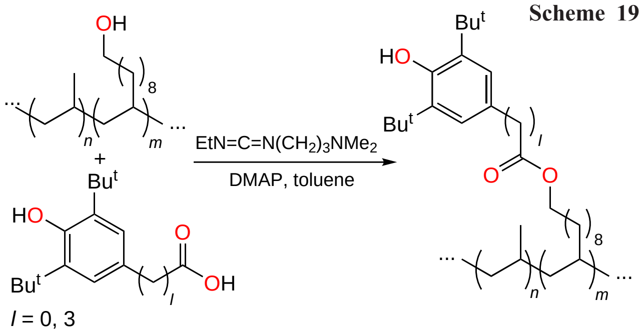
Post-modification is also possible for polyols. Polypropylene copolymer with **C006** was treated with 2,6-di-*tert*-butylphenol derivatives (Scheme 19) to increase the antioxidant properties of PP.[194]

Polypropylene ionomers are copolymers containing side-chain charged groups such as carboxylate anion (CO_2^-, early study[32]) or ammonium ions (more recent studies). A general approach to ionomers containing ammonium ions is based on reactions of propylene — ω-halo-1-alkene copolymers with amines, *e.g.*, the reaction of the propylene — **C083** copolymer with Et$_3$N and *N*-methylimidazole (Scheme 20)[218] or the reaction of the propylene — **C084** copolymer with NMe$_3$ and NMe$_2$(n-C$_{16}$H$_{33}$).[181]

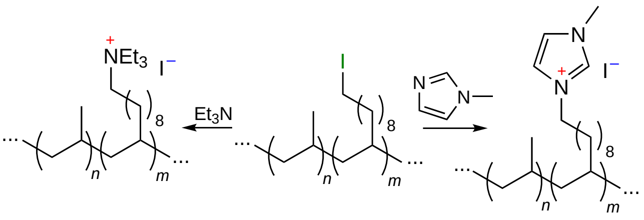
Scheme 18



Scheme 19



Scheme 20

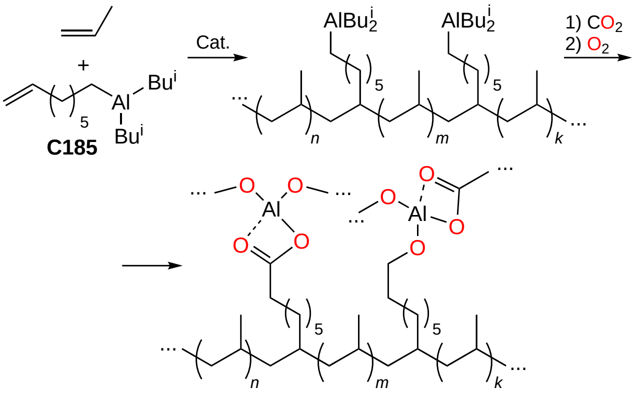


The reactions of the copolymer of propylene and **C083** with $Me_2N(CH_2)_6NMe_2$ and Me_3N gave cross-linked quaternized materials with anion exchange properties.[101] An alternative approach to polypropylene ionomers containing ammonium ions is based on the acid hydrolysis of a propylene copolymer with **C148**.[177]

In 2022, Lin and co-workers[205] proposed using $CH_2{=}CH(CH_2)_6Al^iBu_2$ (**C185**) for the synthesis of anionic polypropylene ionomers containing Al carboxylates.[205] In the presence of a supported catalyst based on new complex **Zr040**, activities of up to 2.5×10^5 kg mol^{-1} h were achieved. The resulting copolymer was treated with CO_2 and then with O_2 to give ionomers containing 0.01–0.09 mol.% Al carboxy/alkoxy derivatives (Scheme 21) with promising mechanical characteristics (see Section 3.5).

In 2024, Wang *et al.*[219] described anionic ionomers synthesized using the ionic cluster strategy. Ionic clusters were formed during the copolymerization of propylene with $[CH_2{=}CH(CH_2)COO]_2AlCl$ catalyzed by commercial titanium-magnesium Ziegler–Natta catalyst. The comonomer was obtained by the reaction of 10-undecenoic acid **C014** with Et_2AlCl. The highest activity of 10 600 kg mol^{-1} h^{-1} was attained at 60°C (8 atm), $X_M = 0.12$ mol.%.

Scheme 21



3.4. Properties of propylene copolymers and prospects of their practical application

The properties of propylene copolymers with polar vinyl monomers depend on the comonomer nature, copolymer composition, and chain microstructure, including distribution of the units and stereoregularity. Stereoregularity is determined, first of all, by the nature of the catalyst. It is commonly known that C_1-symmetric *rac*-forms of *ansa*-zirconocenes can catalyze isotactic polymerization, and in the early stages of research, particularly these complexes were used in the synthesis of functional PP.

For example, copolymerization of propylene with 10-undecenoic acid amides **C066**–**C070** furnished isotactic copolymers with $M_n = 6.8–20.5$ kDa and $Đ_M = 2.0–2.3$.[91] The comonomer incorporation into PP macromolecule resulted in a regular decrease in T_m of the copolymer (148°C for isotactic PP; 136–146°C for copolymer with the comonomer content of 0.96–0.04 mol.%).[91] Even early studies noted the importance of removing traces of inorganic impurities from copolymers synthesized using a substantial excess of OAC, which markedly decreases the melting enthalpy of the polymer.[189] The tendency towards decreasing T_m was also observed for PP ionomers.[218]

When the comonomer content is low (<5%), phase transitions in functional PP are usually determined by the melting and crystallization processes of polypropylene segments. In the case of block copolymers and graft copolymers, the second melting point may appear at high comonomer contents: for example, graft copolymer of PP and *L*-lactide (70 mol.%) has two T_m amounting to 124 and 141°C, which are characteristic of PP and poly(*L*-lactide), respectively.[217]

As a rule, copolymers of propylene with polar vinyl monomers have lower σ_t, E_t, and greater elasticity (relative elongation at break ε) than isotactic polypropylene (iPP). These values depend on the chemical structure and content of the comonomer. Table 12 presents the results of tensile tests for iPP and copolymers with **C062** containing $(CH_2)_6$-*p*-$C_6H_4NPh_2$ moieties.[195] As can be seen, the introduction of ~1 and ~12 mol.% comonomer induced a considerable decrease in σ_t (from 39 to 22 MPa), a critical drop of E_t (from 773 to 40 MPa), and a more than 40-fold increase in ε.

Molding and processing of PP products require increasing the thermo-oxidative stability of the polymer. In the production of polyolefins, this is attained by adding antioxidants, derivatives of sterically hindered phenols, to the melt. However, low-molecular-weight antioxidants are washed out from the polymer on exposure to solvents, heat, and strong electromagnetic fields. The first experiments on the synthesis of copolymers of propylene and **C089**, containing a phenolic moiety, were carried out back in 1994; the resulting materials were stable at 110°C for 400–700 h (in the case of iPP, the first signs of oxidation appear as soon as after 6 h).[184] In 2015, Chung and co-workers[194] proposed using PP containing sterically hindered phenolic

Table 12. Results of tensile tests of iPP samples and copolymers of propylene with **C062** (ISO 527-1).195

Mol.% **C062**	M_n, kDa	σ_t, MPa	E_t, MPa	ε (%)
0 (iPP)	61.4	38±1	733±23	14±1
1.1	163.9	39±1	773±17	18±8
5.6	139.0	21±2	177±9	452±44
11.6	137.0	22±1	40±1	774±33

moieties for the manufacture of films in metalllized polymer capacitors.[194] A pronounced increase in the thermal stability of iPP was also achieved by introducing Ph_2N groups into the side chain: for iPP, the temperature of the onset of weight loss in air T_p was 280°C, whereas the copolymer containing 1.1 mol.% comonomer **C062** had $T_p = 350°C$.[195] A substantial increase in the thermo-oxidative stability was also observed for the copolymer of propylene with ω-alkenylpyrrole **C155**.[198]

The first study dealing with the adhesive properties of functional iPP was published in 2004;[189] the copolymer with **C006** (0.4 mol.%) exhibited fairly high (up to 420 N m^{-1}) peel strength from an aluminum surface (although it was inferior in this characteristic to graft copolymers of iPP and maleic anhydride and acrylic acid). In a recent study by Duchateau’s research group,[220] the terpolymer of propylene with 1-hexene and hexen-1-ol (**C004**), synthesized in the presence of the **Hf05**/MAO catalyst, containing < 0.5 mol.% hydroxyl groups was proposed as a hot-melt adhesive for iPP/Al and iPP/steel pairs. In a number of experiments, the adhesive strength using these copolymers exceeded 16 MPa (steel) and reached almost 8 MPa (Al).[220] A fairly high adhesive efficiency was also found for the reaction products of the copolymer of propylene and **C084** with *N*-ethylethanolamine and *N*,*N*-diethanolamine (Fig. 7).[10]

The use of copolymerization of propylene with polar monomers is also of obvious interest for the manufacture of composites. The **Zr23**/MAO-catalyzed *in situ* copolymerization of propylene with **C006** in the presence of glass fiber provided a stronger binding between iPP and the filler.[221,222] The use of **C004** copolymers as bitumen modifiers was recently studied by Duchateau and co-workers.[223,224] The copolymers showed high efficiency in the manufacture of road surfacing materials using recycled rubber crumbs.

Historically, copolymers of propylene with polar vinyl monomers have been assigned to a specific group of copolymers, so-called ionomers, polymer materials with a hydrocarbon backbone and slight contents of charged side groups (carboxylates, ammonium ions). The introduction of even minor amounts of comonomers with charged groups leads to significant changes in the characteristics of copolymers. Back in 1989, Landoll and Breslow[175] showed that copolymers of propylene and 10-undecenoic acid (as the anion) have the activation energy for viscous flow E_a of ~48 kcal mol^{-1} (for iPP, it is ~10 kcal mol^{-1}), which may markedly facilitate thermoforming.

The effect of charged substituents $[(CH_2)_4NH_3^+]Cl^-$ in the iPP backbone on the mechanical properties of polymers obtained by copolymerization of propylene and **C148** followed by acid hydrolysis ($M_n = 181-195$ kDa, $Đ_M = 2.15-2.33$) is depicted in Table 13; the introduction of ammonium groups into the macromolecule resulted in a considerable increase in the strength of the material.[177]

Powder X-ray diffraction study of polypropylene ionomers obtained using $CH_2{=}CH(CH_2)_6AlBu^i_2$ (**C185**) in the solid state and in the melt indicated the presence of ionic clusters.[205] At low concentration (< 0.1 mol.%), these clusters had little effect on the crystallinity and T_m, but they crucially improved the rheological behaviour important for thermoforming such as melt strength, shear thinning, and extensional strain hardening.[205,225]

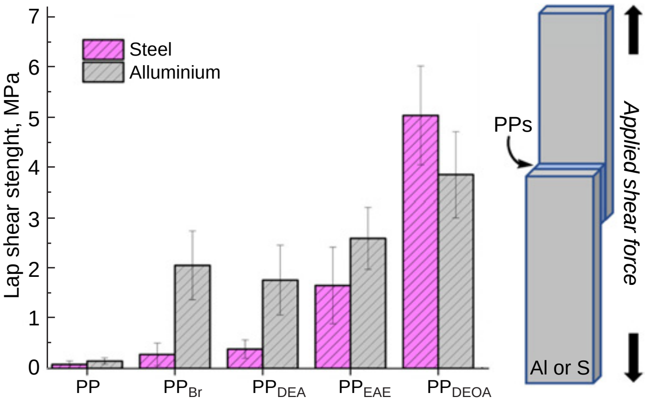


Figure 7. Adhesive strength achieved using products of post-modification of propylene copolymer with **C084** (PP_{Br}) on treatment with $NHEt_2$ (PP_{DEA}), $NH(Et)CH_2CH_2OH$ (PP_{EAE}), and $NH(CH_2CH_2OH)_2$ (PP_{DEOA}).[10] Reproduced under Creative Commons License CC-BY.

The PP foam samples manufactured from polypropylene ionomers were not inferior in their characteristics to iPP-based samples with long-chain branches.[226]

Propylene copolymers synthesized using ionic cluster strategy by copolymerization of propylene and **C014**-AlEtCl are also promising materials for the manufacture of polymer composites.[219] After treatment with HCl, these copolymers acted as effective compatibilizers markedly improving the mechanical characteristics of recycled plastics (PETP/HDPE) and the quality of 3D-printed products based on iPP and talc.

Films based on ionomers with $[(CH_2)_9NMe_2R]^+$ terminal groups (R = Me, n-$C_{16}H_{33}$) obtained by hot pressing of copolymers with **C084** followed by quaternization showed a low tendency towards swelling in aqueous solutions and a linear temperature dependence of the hydroxide conductivity, but an insufficient chemical stability in an NaOH solution.[181] Further enhancement of characteristics of conducting membranes for fuel cells was achieved through cross-linking by the $(CH_2)_9NMe_2^+(CH_2)_6NMe_2^+(CH_2)_9$ moieties. The resulting materials demonstrated the hydroxide and bicarbonate conductivities of up to 140 and 35 mS cm^{-1}, respectively, and high stability to the action of alkalis (up to 70 days without swelling or conductivity loss).[101]

Apart from changing the mechanical properties, adhesion characteristics, and hydrophilicity, copolymerization with polar vinyl monomers endows iPP with conceptually new properties. For example, copolymers with **C062** possessed blue luminescence, with the absorption (excitation, λ_{ex}) and

Table 13. Results of tensile tests of iPP samples and copolymers of propylene with $[(CH_2)_4NH_3^+]Cl^-$ substituents in the backbone.[177]

Mol.% $[NH_3^+]Cl^-$	25°C			85°C			145°C		
	σ_t, MPa	E_t, MPa	ε (%)	σ_t, MPa	E_t, MPa	ε (%)	σ_t, MPa	E_t, MPa	ε (%)
0	35 ± 5	1285 ± 125	458 ± 82	17 ± 3	340 ± 55	858 ± 120	3 ± 1	60 ± 5	1150 ± 150
1	62 ± 5	1360 ± 88	542 ± 56	38 ± 5	648 ± 54	980 ± 120	12 ± 3	122 ± 14	1540 ± 120
2	70 ± 5	1420 ± 108	588 ± 52	46 ± 5	726 ± 54	1088 ± 128	14 ± 3	148 ± 14	1640 ± 128
3	77 ± 4	1540 ± 125	612 ± 62	52 ± 5	806 ± 77	1052 ± 130	16 ± 3	158 ± 14	1750 ± 144

Table 14. Mechanical characteristics of copolymers prepared by two-step copolymerization of ethylene and propylene (see Table 11).[213]

No.	M_n, kDa	$Đ_M$	T_m, °C	σ_t, MPa	Yield strength, MPa	Izod impact strength, kJ m^{-2}	Flexural modulus E_f (MPa)
1	185.4	4.1	158	42±2	29±1	5.0±0.3	1026±8
2	312.8	3.9	125/159	42±2	30±1	42±2	1319±52
3	348.5	3.3	120/159	43±2	30±1	41±1	1243±21
4	248.6	3.5	120/160	36±2	27±1	31±2	1124±49
5	335.5	3.1	119/159	39±2	24±1	51±3	1090±74
6	275.0	4.0	121/159	43±2	26±1	50±2	1046±32
7	448.2	5.6	119/159	44±2	21±1	90±2	868±18
8	289.7	5.8	124/158	46±1	18±1	63±3	986±70
9	250.0	3.4	129/160	49±1	31±1	14±1	1575±20
10	441.7	2.4	129/155	29±1	28±1	36±1	1161±47
iPP/POE[a]	n.d.	n.d.	n.d.	30±1	30±1	16±1	929±23

[a] A 85 : 15 mixture of commercial iPP (PPH–T03 brand) and PP-based polyolefin elastomer (POE) (8450 brand) was used.

fluorescence (λ_{em}) maxima being at 340 nm and 468–494 nm, respectively, while an increase in the **C062** content in the copolymer induced a red shift of λ_{em}.[195] Luminescence properties were also inherent in the copolymer with **C156** containing a carbazole moiety, which proved the formation of carbazole associates and created conditions for UV-initiated oxidative cross-linking.[199]

In conclusion of the Section, mention should be made of polymer materials with mechanical characteristics superior to those of polyolefins (Table 14) that are prepared using two-component catalysts and the comonomer $[CH_2{=}CH(CH_2)_8CO_2]_2AlCl$.[213] The higher impact strength of these materials, as well as the presence of polar comonomers in the macromolecules, allows these copolymers to be considered as a promising base for composites with inorganic fillers and glass fiber.

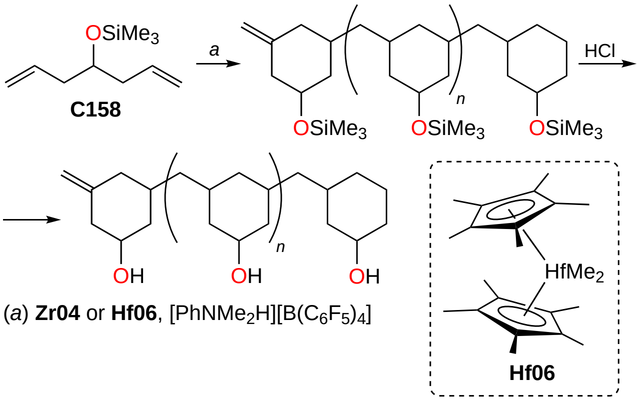
4. Copolymers of 1-butene and higher α-olefins with polar vinyl monomers

4.1. Synthesis and properties of homopolymers of polar vinyl monomers

The synthesis of homopolymers of functional α-olefins is addressed in a relatively small number of papers. The first isotactic homopolymers of $CH_2{=}CH(CH_2)_nNR_2$ ($n = 2, 3, 5, 9$; R = Me, Et, Pr^i) and $CH_2{=}CH(CH_2)_nOSiMe_3$ ($n = 3, 9$) were synthesized using $TiCl_3/R_3Al$ catalyst back in 1967.[227] Poly(penten-4-ol) and poly(10-undecenol) obtained by hydrolysis of silyl ethers had $T_m = 300$°C (dec.) and 134°C, respectively. The homopolymer of **C020**-Al^{i}BuCl was obtained in the late 1980s using $TiCl_3/Bu^i_2AlCl$.[228,229] In early studies, monomers with latent reactivity resulting from the reaction of non-conjugated dienes with 1 equiv. of 9-borabicyclononane (9-BBN), **C178**–**C180**, were also used ($TiCl_3/Et_2AlCl$ catalyst).[230] The oxidation of homopolymer **C180** afforded poly(octen-1-ol) characterized by high thermal stability ($T_m = 110$°C, 3% mass loss at 300°C). The homopolymer of **C020** prepared using the $TiCl_3/R_2AlCl$ catalyst was hydrolyzed to polycarboxylic acid, which was treated with *N*,*N*′-carbonyl-bis-imidazole to give reactive imidaziolides,[231] which were allowed to react with phenols and aromatic amines.[232]

The homopolymerization of **C046**, **C029**, and diene polar monomer **C158** (Scheme 21) catalyzed by **Zr03**/NB^F and **Zr25′**/NB^F was studied in 1992.[233] In the last-mentioned case, cyclopolymerization took place to give low-molecular-weight products; a polymer with $M_n = 46$ kDa and $Đ_M = 3.1$ was obtained using **Hf06**/NB^F (Scheme 22). The TON values for **Zr03**/NB^F were from 80 (**C046**) to 280 (**C158**).[233]

Scheme 22



(*a*) **Zr04** or **Hf06**, $[PhNMe_2H][B(C_6F_5)_4]$

The **Zr03**/NB^F catalyst was also studied in the homopolymerization of ω-alkenamines **C169**, **C101**, **C046**, and **C170**; The highest polymerization rate was observed for sterically hindered monomer **C046**.[234] Homopolymerization of **C046** was performed using catalysts based on complexes **Zr04′**, **Zr21′**, **Zr25′**, **Zr22**, and **Zr23′**; the last-mentioned catalyst provided isotacticity *mmmm* = 99.1%. The resulting homopolymers of **C046** had $T_m = 85–115$°C.[234] In a recent theoretical study,[235] the high activity of monomer **C046** was attributed to the absence of Zr···NPr$^i_2$ coordination at the catalytic site, whereas the Zr···NMe$_2$ coordination is preferred over the Zr coordination to the C=C bond ($\Delta G = 3.8$ kcal mol^{-1}). It was shown in the same study that polymerization of $CH_2{=}CHCH_2X$ (X = OR, NR$_2$, *etc.*) is, in principle, possible for half-sandwich Ti(III) and Zr(III) complexes; however, this hypothesis has not yet been experimentally confirmed.

In 2010, Schulze *et al.*[80] synthesized the homopolymer of 10-undecenol **C006**-AlBu$^i_2$ using **Ti02**, **Zr01**, and **Zr17**/MAO. Catalysis by chiral **Zr17**/MAO resulted in the formation of homopolymers with *mmmm* of up to 83%, M_n of up to 28 kDa, and $T_m = 119–126$°C.[236] An alternative approach to the 10-undecenol homopolymer is based on the polymerization of **C035** catalyzed by post-metallocene complex **Zr35**/dMAO (the product had M_n = 8.3 – 20.9 kDa, *mmmm* > 95%) followed by treatment with $[\text{Bu}_4\text{N}]\text{F}$.[237]

In a study of homopolymerization of **C091**, **C098**, and their structural analogues with longer $(\text{CH}_2)_n$ sequences between the $\text{CH}_2\text{=CH}$ group and the donor heteroatom catalyzed by **Sc12** – **Sc15**/TB$^\text{F}$, syndiotactic homopolymers were obtained.[112] The formation of syndiotactic polymers was due to intramolecular coordination of the heteroatom; the stereocontrol mechanism was investigated in detail using DFT modelling.

In 2022, Liu and Xu[238] reported the results of their study of homopolymerization of S-containing polar monomers **C187** – **C200** catalyzed by complexes **Sc16** and **Sc17**. The TB$^\text{F}$-activated complex **Sc16** showed a higher performance and catalyzed the formation of syndiotactic homopolymers (for **C192**, *rrrr* = 86%).

4.2. Coordination copolymerization of 1-butene and higher α-olefins

The coordination copolymerization of 1-butene and higher α-olefins with polar vinyl monomers is addressed in a relatively small number of papers.

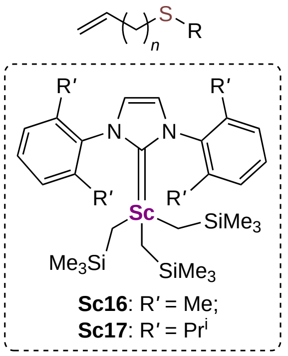
4-Methyl-1-pentene (4M1P) was studied in 1999 by Waymouth's research group;[239] the authors conducted copolymerization of 4M1P with **C046** catalyzed by NB$^\text{F}$-activated **Zr23′** and **Zr03**; the copolymerization constants $r1$ and $r2$ were 1 and 3, respectively (**Zr23′**) and 0.5 and 5, respectively (**Zr03**). The **Zr23′**/NB$^\text{F}$-catalyzed copolymerization of 1-hexene with **C046** was characterized by $r1 = 0.9$ and $r2 = 1.1$, *i.e.*, a highly random copolymer was formed.[239] Complex **Zr23′** catalyzed the formation of the isotactic copolymer. It is of certain interest to compare the properties of homopolymers of 4M1P and **C046** with the properties of copolymers. The introduction of N$^\text{i}$Pr$_2$ polar groups into the side chain substantially increased the thermal stability of the polymer. The methanol solubility of the copolymer containing 4M1P (2.5%) as the hydrochloride is of certain interest.

In 2009, Lohse and co-workers[79] studied **Hf07**/NB$^\text{F}$-catalyzed copolymerization of 1-tetradecene and 1-octene with 10-undecen-1-ol **C006**-AlOct$_2^\text{n}$ and silyl ether **C173** containing the bulky SiMe$_2{}^t$Bu substituent. The authors were unable to obtain copolymers with **C006**-AlOct$_2^\text{n}$. In the case of **C173**, random copolymers with a polar comonomer content of up to 23 mol.% were formed; the reaction products contained both OSiMe$_2$Bu$^\text{t}$ and OH groups. The **Zr01**/MAO-catalyzed (10^4 equiv.) copolymerization of 1-hexene with **C004**-AlEt$_2$ afforded a product containing 3.1 mol.% comonomer.[240]

To increase the thermo- and photo-oxidative stability of isotactic poly(1-butene), a study of the copolymerization of 1-butene with eugenol **C160**-AlBu$_2^\text{i}$ catalyzed by a Bu$_3^\text{i}$Al-activated titanium-magnesium catalysts was undertaken in 2020.[241] The resulting copolymers contained 0.19 – 0.62 mol.% comonomer and had an isotactic index of 91.8 – 94.3%. The 1-butene copolymerization with pentafluorophenyl 10-undecenoate **C160**-AlEt$_2$ resulted in the formation of copolymers with 0.03 – 0.59 mol.% comonomer and isotactic index of 77.6 – 92%.[242] These copolymers were converted to polymers containing methoxylated poly(ethylene glycol) moieties mPEG350, mPEG500, mPEG750, and mPEG2000.

Post-metallocene complexes **Hf04**, **Hf08** – **Hf10** activated by TB$^\text{F}$ effectively catalyzed copolymerization of 4-methyl-1-pentene, 1-hexene, or 1-octene with sterically hindered ether **C151** in the absence of masking reagents (Table 15).[243] The copolymerization products had higher M_n values compared to the corresponding homopolymers of α-olefins. Jian and co-workers[243] attributed this fact to suppression of β-hydride transfer by interaction of the catalytic sites with the oxygen atom of **C151**.

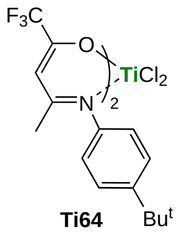
Structures of Sc16, Sc17 and comonomers C187 – C200



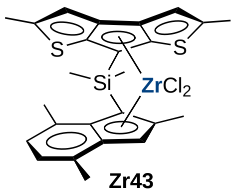
Sc16: R′ = Me;
Sc17: R′ = Pr$^\text{i}$

C187: n = 2, R = 4-MeC$_6$H$_4$;
C188: n = 3, R = 4-MeC$_6$H$_4$;
C189: n = 3, R = 3-MeC$_6$H$_4$;
C190: n = 3, R = 2-MeC$_6$H$_4$
C191: n = 3, R = 2,4-Me$_2$C$_6$H$_3$;
C192: n = 3, R = 2,6-Me$_2$C$_6$H$_4$;
C193: n = 3, R = 4-ClC$_6$H$_4$;
C194: n = 3, R = 4-FC$_6$H$_4$;
C195: n = 3, R = Bn;
C196: n = 3, R = Cy;
C197: n = 3, R = Pr;
C198: n = 3, R = n-C$_6$H$_{13}$;
C188: n = 3, R = 4-MeOC$_6$H$_4$;
C200: n = 4, R = 4-MeC$_6$H$_4$

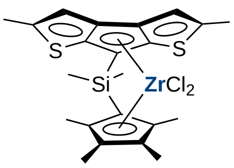
Structures Ti64, Zr43–Zr45, Hf06 – Hf10, Sc18, Ni60 – Ni64



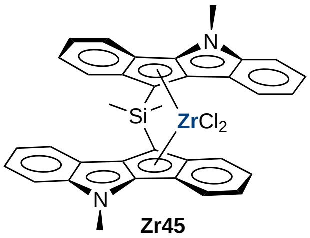
Ti64



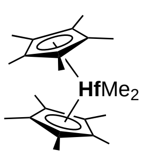
Zr43



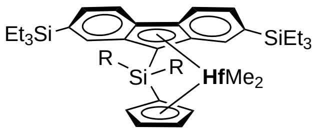
Zr44



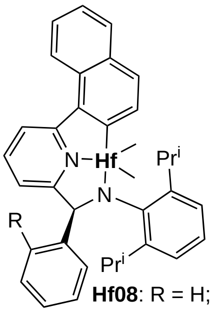
Zr45



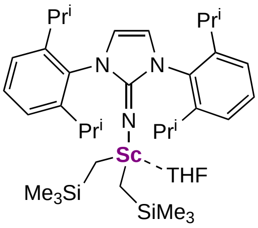
Hf06



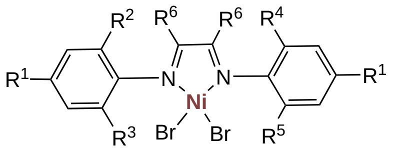
Hf07
R = p-C$_4$H$_6$SiEt$_3$



Hf08: R = H;
Hf09: R = CF$_3$;
Hf10: R = OMe



Sc18



Ni60: R^1 = R^2 = R^3 = R^4 = R^5 = R^6 = Me;
Ni61: R^1 = R^2 = R^4 = R^5 = R^6 = Me, R^3 = 4-MeC$_6$H$_4$;
Ni62: R^1 = R^4 = R^5 = R^6 = Me, R^2 = R^3 = 4-MeC$_6$H$_4$;
Ni63: R^1 = R^5 = R^6 = Me, R^2 = R^3 = R^4 = 4-MeC$_6$H$_4$;
Ni64: R^1 = R^3 = R^5 = R^6 = Me, R^2 = R^4 = 4-MeC$_6$H$_4$

Table 15. Main characteristics of the copolymerization of α-olefins with polar comonomer **C151** (10 μmol of the precatalyst; 10.5 μmol of TBF, 6.5 mmol of α-olefin, and 0.5 mmol of **C151** in 5 mL of toluene, 25°C, 5 h).[243]

Precatalyst	α-olefin	Yield, g	Conversion (%)	M_n, kDa	$Đ_M$	*mmmm* (%)	Mol.% comonomer	T_m (T_g)
Hf08	4M1P	0.03	3.2	326.8	1.90	99	1.32	206.2
Hf04	4M1P	0.76	81.7	779.5	1.76	99	3.09	205.0
Hf09	4M1P	0.51	54.7	242.9	1.84	n.d.	n.d.	209.9
Hf10	4M1P	0.18	19.0	412.0	2.08	99	1.76	207.4
Hf08	1-hexene	0.76	81.6	527.0	2.44	99	2.98	(–38.0)
Hf04	1-hexene	0.78	83.7	868.2	1.92	99	4.52	(–36.6)
Hf09	1-hexene	0.64	68.7	1348	1.66	99	1.85	n.d.
Hf10	1-hexene	0.76	81.5	436.1	2.82	84	3.80	(–37.5)
Hf08	1-octene	0.03	2.5	1447	1.83	99	0.84	n.d.
Hf04	1-octene	1.11	92.4	564.8	2.10	99	3.33	(–58.4)
Hf09	1-octene	0.83	69.2	263.8	2.35	n.d.	n.d.	(–60.0)
Hf10	1-octene	0.25	21.0	1670.4	1.79	99	0.32	(–59.1)

Relatively recent publications address **Hf04**/TB^F-catalyzed copolymerization of 1-butene with 11-iodo-1-undecene **C083** (Ref. 244) and 6-iodo-1-hexene **C113**.[245] The copolymer of 1-butene with **C083** (1.24 mol.%) was treated with *N*-methylimidazole to give the corresponding ionomers with the BF_4^-, Tf_2N^-, or PF_6^- counter-ions.[244] Copolymers with **C113** (0.38 and 1.31 mol.%) were converted to polymers containing side-chain $SCH_2CH(OH)CH_2OH$ groups.[245]

Ansa-zirconocenes **Zr07’** and **Zr22′** activated by TB^F catalyzed the copolymerization of 1-hexene and ether **C159** in the absence of masking reagents, while **Zr1′**/TB^F and **Zr35**/TB^F proved to be inactive.[207] In the case of **Hf04**/TBF, M_n increased from 179.1 kDa [poly(1-hexene)] to 1119.2 kDa (copolymer containing 10 mol.% **C159**), while the activity decreased twofold.[207]

In 2023, Zhang *et al.*[168] used **Ti64**/MAO to synthesize the terpolymer of ethylene, 1-hexene (14.7–21.2 mol.%), and 5-iodomethyl-2-norbornene **C149** (3.6–7.4 mol.%), which was converted to ionomers with MsO$^-$, TfO$^-$, and Tf_2N^- counter-ions by treatment with *N*-methylimidazole followed by ion exchange.[168]

In 2024, Nifant’ev and co-workers[246] carried out copolymerization of 1-hexene with polar olefins in the presence of *ansa*-complexes **Zr43**–**Zr45**, representatives of so-called ‘heterocenes’,[247] sandwich complexes with η^5-ligands containing a fused electron-donating heterocyclic moiety (thiophene, pyrrole, indole). 10-Undecenoic acid derivatives **C006** and **C162** (pretreated with Bu^i_3Al) and **C034** and **C066** were used in the copolymerization without masking reagents. The precatalysts were activated in two steps (successive treatment with 20 equiv. of Bu^i_3Al and 20 equiv. of modified methylaluminoxane MMAO-12. The best results were obtained for **C006**-$AlBu^i_2$ and precatalyst **Zr43**; the highly random isotactic copolymers with comonomer content of up to 32.2 mol.% were obtained.

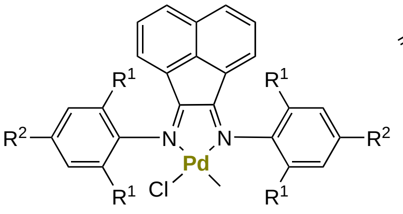
The copolymer of 8-bromo-1-octene (**C081**) and 4-methylpentene was obtained back in 1965 using the $TiCl_3$/OAC catalyst.[178] Copolymers of **C084** and 4-methylpentene with comonomer content of 4.2–41.4 mol.% and M_n = 15.9–39.8 kDa were prepared in 2016 ($TiCl_3/Et_2AlCl$ catalyst).[248] Hot-pressed films were then treated with Me_3N in order to modify the surface with ammonium groups (see Section 4.3.2).

In 2020, copolymers of 1-hexene with haloalkenes **C078**, **C081**, and **C111**–**C113** were obtained using the **Sc18**/TB^F catalyst, the TOF of which did not exceed 100 h^{-1}, and X_M depended on the length of the $(CH_2)_n$ sequence, being in the range from 0.04 mol.% (**C111**) to 1.22 mol.% (**C114**).[249]

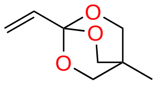
Complexes **Ni02** and **Ni60**–**Ni64** activated by 500 equiv. of Et_2AlCl were studied in 2024 in the copolymerization of 1-octene with **C018**.[250] At 25°C, complex **Ni02** showed very low performance, while **Ni60**–**Ni64** had a moderate performance (TOF = 105–273 h^{-1}, X_M = 2.0–3.0 mol.%). In 2021, Osakada and co-workers[251] investigated copolymerization of 1-decene and comonomers derived from acrylic acid (**C205**) and acrolein (**C206**) containing no conjugated C=C bonds. Complexes **Pd26** and **Pd27** in the presence of $Na[B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ were used as catalysts. The copolymerization proceeded at a very low rate (TOF ~1 h^{-1}) and was accompanied by isomerization of the carbon skeleton to give macromolecules containing up to 50% units resulting from 1,10-insertion of 1-decene.

In recent years, homopolymerization of polar vinyl monomers has found use in the synthesis of PE and PE-based composites. In 2023, Chen and co-workers[137] proposed using the ionic cluster strategy mentioned above for the preparation of PE composites, namely, **Ni13**- or **Ni14**-catalyzed homopolymerization of the product of the reaction of **C014** with Et_2AlCl, $(CH_2{=}CH(CH_2)_8COO)_2AlCl$, in the presence of a filler to give heterogeneous active species and the subsequent ethylene polymerization. Depending on the type of filler (fly ash, wood flour, nanoclay, carbon nanotubes, Al_2O_3, TiO_2), the composites formed *in situ* had enhanced mechanical characteristics and specific properties (microwave absorption, gas impermeability, electrical conductivity, fire resistance, *etc.*) compared to composites produced by extrusion. When catalyst mixtures **Ni13**–**Ni15** were used, the ionic cluster strategy made it possible to control the structure of the supported catalyst particles and

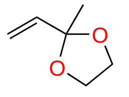
Structures of Pd26, Pd27 and comonomers C201, C202



Pd26: $R^1 = R^2 = Me$;
Pd27: $R^1 = Pr^i$, $R^2 = H$



C201



C202

obtain in-reactor PE mixtures with improved mechanical properties.[138]

4.3. Cationic co-oligomerization

Oligomers of higher α-olefins are used as bases of polyolefin motor oils and lubricants and in the production of fuel additives.[252] The large-scale oligomerization processes are based on the use of electrophilic (acid) catalysis;[253,254] However, a high degree of structural homogeneity of oligomers is achieved only when metallocene catalysts are used.[255–257] Coordination (co)oligomerization of polar vinyl monomers has not yet been studied. In recent years, only two studies dealing with the preparation of co-oligomers of α-olefins with ω-alkenols catalyzed by $AlCl_3$ have been reported by N.Bahri-Laleh's research group.[258,259] Co-oligomerization of 1-decene and decen-1-ol (**C005**) carried out for 1.5 h at 50°C gave a product with $M_n = 1.85$ kDa and $Đ_M = 1.5$ (2.55 molar ratio of 1-decene and **C005**) and the kinematic viscosity at 40°C of 206 cSt.[258] The reaction of 1-decene, 1-octene, and 1-hexene with the corresponding ω-alkenols **C005**, 7-octen-1-ol (**C207**), and **C004** in the presence of $AlCl_3$ resulted in the formation of co-oligomers containing 4 to 5 OH groups per molecule and characterized by $M_n = 1.5-2.1$ kDa, $Đ_M = 1.3-1.4$, and kinematic viscosity at 40°C of 145–205 cSt.[259]

4.4. Properties of copolymers of higher α-olefins and prospects of their practical application

Isotactic poly(1-butene) has a unique set of mechanical properties and is widely used to manufacture high-pressure tanks, pipes, and food packaging.[260] Copolymerization of 1-butene with polar monomers could probably expand the range of characteristics of this material; however, the results of studies along this this line are reported only in few publications. It was shown[241] that copolymers of 1-butene and eugenol have higher thermo-oxidative stability; however, the introduction of a polar comonomer even in minor amounts markedly decreases the crystallinity of the polymer and hampers the phase transition of the tetragonal form II to hexagonal form I, which may considerably complicate the extrusion and die casting of the products.[261] The opposite effect was observed for poly(1-butenes) containing methylated poly(ethylene glycol) (mPEG) moieties: for these copolymers, the II → I phase transition was facilitated compared to that in the homopolymer,[242] which may enable the future use of these copolymers as components accelerating the phase transition during molding.

The positively charged *N*-methylimidazolium moieties with the BF_4^-, Tf_2N^-, or PF_6^- counter-ions in poly(1-butene) ionomers also had a beneficial effect on the dynamics of the II → I phase transition.[244] The presence of hydroxyl groups in the copolymer prepared from 1-butene with **C113** facilitated the II → I phase transition, but this was observed when the comonomer content reached ~1.3 mol.%.[245] As regards the practical use of 1-butene copolymers with polar monomers, it is fundamentally important that in the presence of polar groups, this phase transition can be accomplished at elevated temperature. However, the **Hf04**/TB^F catalytic system did not provide a high isotactic index of the (co)polymers, and a relevant area of further studies of functional polybutenes is to look for catalysts that give rise to copolymers with isotactic index of 98% and more.

Li and co-workers[248] reported the results of studying films based on Me_3N-quaternized copolymers of 11-bromo-1-undecene (**C084**) and 4-methylpentene as anion conductive membranes. In comparison with membranes based on polypropylene ionomers,[181] the reported materials had a higher hydroxide conductivity, but were markedly inferior to iPP-based products in the mechanical characteristics; however, these studies were not further developed.

The mechanical properties of copolymers of higher linear α-olefins with polar vinyl monomers have been little studied due to the amorphous nature of these copolymers. Karimi and co-workers[240] assumed that copolymers of 1-hexene with **C004** could find use for modification of the polyolefin surface and as adhesives; however, no further studies along this line were undertaken. The results of studies of α-olefin copolymerization with sterically hindered unsaturated ethers **C151** (Ref. 243) and **C159**,[207] resulting in the formation of ultrahigh- molecular-weight copolymers, may be of certain practical interest. Copolymers of this type may be used as polyolefin drug reducing agents and viscosity reducing additives for the pipeline transportation of hydrocarbons.

Nifant'ev and co-workers[246] studied the dependence of T_g of the copolymers of 1-hexene and **C006** on the percentage of comonomers and the adhesive properties of the resulting materials. The T_g value was found to follow a linear dependence on the weight content of **C006** according to the Fox equation, which allowed T_g of the homopolymer of **C006** to be estimated as –3.5°C. Meanwhile, previously, it was shown that homopolymer **C006** does not have a T_g.[236] Examination of the adhesive properties of the copolymers of 1-hexene and **C006** revealed high copolymer adhesion to a steel surface, but insufficiently high toughness.[246]

Co-oligomers of 1-decene and **C005** (~6 OH groups per molecule) were post-modified by treatment with $CH_2=CHCOCl$ and cross-linked on exposure to visible light.[258] The resulting films demonstrated high biocompatibility with L929 fibroblast cells.

The functional co-oligomers of α-olefins and ω-alkenols with various chain lengths prepared in a similar way also exhibited high biocompatibility. The functional co-oligomer of 1-hexene and hexen-1-ol was used to fabricate a composite with halloysite characterized by higher surface hydrophilicity and biocompatibility and a lower tendency for swelling compared to the poly(1-hexene)-based material.[259]

5. Conclusion

Figure 8 shows a diagram that reflects the number of publications devoted to the top 7 polar monomers.

Lead comonomers are polar α-olefins of natural origin, that is, 10-undecen-1-ol **C006**, 10-undecenoic acid **C014**, and methyl 10-undecenoate **C018**; the fourth most advanced compound is 9-decen-1-ol **C005**. This fact can be attributed not only to the advantage of presence of a long hydrocarbon chain between the C=C bond and the polar group, but also to the ready availability of 10-undecenoic acid, which is obtained from renewable raw materials, namely castor oil.[262] The number of publications devoted to the copolymerization of 9-decen-1-ol **C005** is much lower, but in view of the progress in the development of effective catalysts for the cross-metathesis of methyl oleate,[263–265] 9-decenoic acid derivatives may find wide application in the synthesis of functional polyolefins even in the near future. 10-Hexen-1-ol **C004** is in the fifth place in the list shown in Fig. 8. The use of ω-halogen-substituted α-olefins (sixth and seventh places) as comonomers seems promising at the first glance, as the post-functionalization of the corresponding copolymers may give materials with advantageous

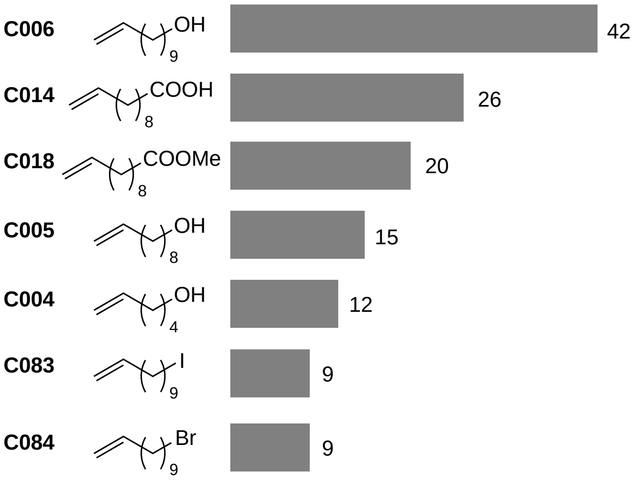


Figure 8. Number of publications devoted to (co)polymerization of top 7 non-conjugated polar α-olefins.

characteristics. However, the very idea of using these copolymers does not comply with the green chemistry principles, post-modification of polymers in solution is hardly applicable in the industrial production of polyolefins, and, hence, this research area is rather of theoretical interest.

A structural feature of lead polar comonomers **C004**–**C006**, **C014**, and **C018** is the presence of the acidic OH group, which can react with cationic catalytic sites formed by Group 4 metal complexes. In order to avoid these reactions, polar comonomers are treated with OAC (see Scheme 3). Scandium complexes have been barely studied in the copolymerization of ethylene with **C004**–**C006**, **C014**, and **C018**. Vanadium complexes are inferior in activity to catalysts based on Group 4 metal complexes, but they do not require the use of expensive cocatalysts, MAO and perfluoroalkylborates, with Et_2AlCl being a universal masking and activating reagent for these complexes.[121,125] Ni and Pd complexes proved to have low activity in the copolymerization of ethylene and **C004**–**C006**, **C014**, and **C018**. Only Group 4 metal complexes can provide a

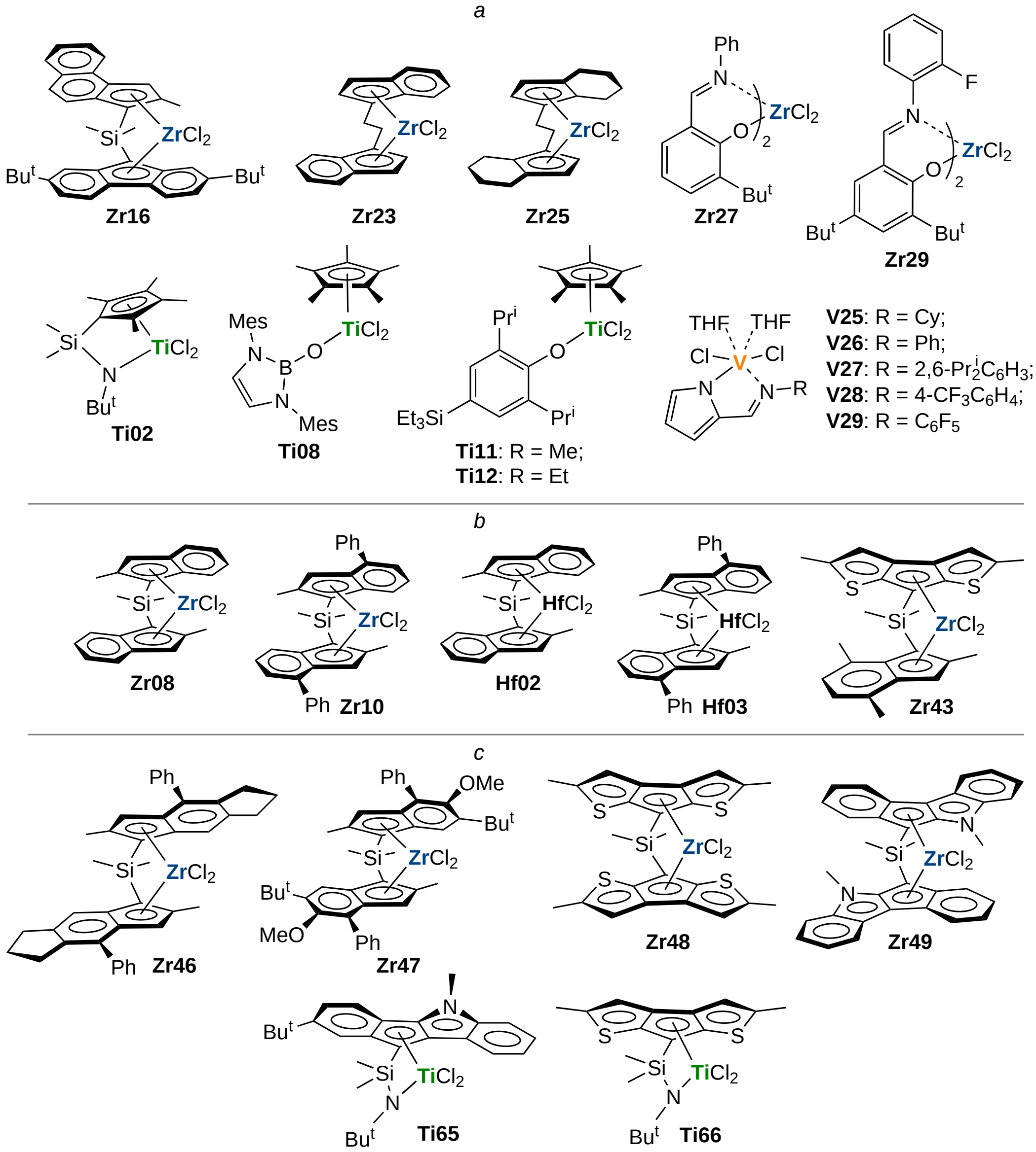


Figure 9. Structural formulas of the complexes that showed high activity in the copolymerization of ethylene (*a*) and α-olefins (*b*) with polar vinyl monomers. Promising precatalysts that have not been investigated in the synthesis of functional polyolefins (*c*).

high degree of isotacticity in the copolymerization of propylene and higher α-olefins with polar monomers.

Figure 9 presents the structural formulas of some precatalysts that demonstrated high activity ($>10^4$ kg mol^{-1} h^{-1}) in the copolymerization of ethylene (Fig. 9*a*), propylene, and higher α-olefins (Fig. 9*b*) with comonomers **C004**–**C006**, **C014**, and **C018**. Except for synthetically available complexes **V25**–**V29**, the complexes depicted in Fig. 9 are metallocene and post-metallocene precatalysts for (co)polymerization of ethylene, propylene, and 1-butene developed in the 1990s. According to our estimate, precatalysts **Ti01**–**Ti64**, **Zr01**–**Zr45**, and **Hf01**–**Hf10** tested in the copolymerization of polar monomers that we mentioned in this review represent only a minor portion (at best, a few percent) of the total number of Group 4 metal complexes studied in the (co)polymerization of ethylene, propylene, and higher olefins. The elaboration of these catalysts remains relevant, and, in our opinion, the key trends in the development of metallocene catalysts can be extrapolated to the copolymerization of olefins with polar comonomers.

Presumably, to provide high performance of catalysts towards OAC-treated comonomers **C004**–**C006**, **C014**, **C018**, and their analogues, it is important that precatalysts be capable of forming active species upon activation with small amounts of MAO. This implies enhanced stability of catalytic sites and their ability to coordinate and incorporate ethylene, propylene, and higher α-olefins at comparable rates. One way to address this problem is the introduction of electron-donating groups into the corresponding η^5-ligand molecules: this approach was implemented in relation to complexes **Zr46** and **Zr47** for the synthesis of polypropylene elastomers,[266,267] heterocenes for the synthesis of ethylene and 1-octene copolymers[268] and poly(1-octene),[269] complex **Zr43** for the synthesis of copolymers of α-olefins with non-conjugated dienes,[270] and complexes **Ti65**–**Ti67** for the (co)polymerization of ethylene.[271] This assumption is also confirmed by heterocene **Zr43** used in the copolymerization of 1-hexene[246] and 1-butene[272] with **C006**-AlBu^{i}_{2}. In our opinion, further study of metallocenes with donor η^5-ligands is a promising trend for the design of effective catalysts for the copolymerization of ethylene and α-olefins with readily available polar vinyl monomers.

Functional polyolefins can find use as compatibilizers of polymer composites. In some cases, the introduction of small amounts of polar comonomers provided a qualitative improvement of the mechanical characteristics of polyolefins, an increase in the thermo-oxidative stability, and an increase in surface hydrophilicity. The use of polar polyolefins as adhesives also appears promising. Meanwhile, large-scale implementation of functional polyolefins requires further development of supported single-site catalysts for copolymerization that could be implemented at existing PE and PP production plants.

In our opinion, an attractive arrangement for the production and application of functional polyolefins, first of all, from the practical standpoint, is to use relatively small amounts (0.2–1%) of available polar monomers (including those obtained from renewable raw materials) in the copolymerization of ethylene, propylene, and 1-butene catalyzed by single-site catalysts, Group 4 metal derivatives (including prospective ones that have not been previously studied in the copolymerization of polar monomers, see Fig. 9*c*, and their analogues). Ziegler–Natta catalysts can also be effective in the production of polyolefins for construction purposes, which was confirmed by recent research.[213]

Funding

This study was supported by the Russian Science Foundation, No 21-73-30010P.

Conflict of interest

The authors declare that there are no conflicts of interest to declare in this paper.

6. List of abbreviations and symbols

$Đ_{\mathrm{M}}$ — polydisperity, M_{w} and M_{n} ratio,
ΔH_{m} — melting enthaply,
ε — relative elongation at break,
M_{n} — number-average molecular weight,
M_{w} — weight-average molecular weight,
mmmm — isotactic index of polyolefin, content of isotactic pentads,
rrrr — syndiotactic index of polyolefin, content of syndiotactic pentads,
T_{g} — glass transition temperature,
T_{m} — melting point,
X_{C} — degree of crystallinity,
X_{M} — comonomer incorporation ratio,
σ_{t} — tensile strength,
$\mathrm{B^F}$ — $\mathrm{B(C_6F_5)_3}$,
BHT — 2,5-di-*tert*-butyl-4-methylphenol,
DFT — density functional theory,
DIBP — diisobutyl phthalate,
ETA — ethyl trichloroacetate $\mathrm{CCl_3COOEt}$,
Hal — halogen,
iPP — isotactic polypropylene,
LLDPE — linear low-density polyethylene;
MAO — methylaluminoxane,
MMAO — modified methylaluminoxane,
MCM-41 — mesoporous silica gel with cylindrical oriented pores,
4M1P — 4-methylpent-1-ene,
mPEG — methoxylated poly(ethylene glycol),
$\mathrm{NB^F}$ — $\mathrm{[PhNMe_2H][B(C_6F_5)_4]}$,
OAC — organoaluminum compound,
PE — polyethylene,
PP — polypropylene,
SSA — successive self-nucleation and annealing,
$\mathrm{TB^F}$ — $\mathrm{[Ph_3C][B(C_6F_5)_4]}$,
UHMWPE — ultra-high molecular weight polyethylene,
ZNC — Zigler–Natta catalyst.

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