

Review

Modified Half-Titanocenes as Polymerization Catalysts: Basic Concept, Displayed Promising Characteristics and Some Mechanistic Insights

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Abstract

Development of new polymers that cannot be achieved by using conventional catalysts has been the central research objective, and copolymerization is an effective strategy to modify the materials' (thermal, physical, mechanical and electronic) properties. Modified half-titanocenes, $\text{Cp}'\text{TiX}_2(\text{Y})$ (Cp' = cyclopentadienyl, X = Cl, Me, etc, Y = anionic donor such as phenoxide, ketimide, amidinate, etc.), are known to be effective catalysts. This review introduces several selected efforts for efficient synthesis of ethylene copolymers containing cyclic olefins, biobased conjugated dienes, and disubstituted α -olefins, including the effect of cocatalysts. Moreover, here we introduce an analysis using XAS (X-ray absorption spectroscopy), which has been recognized as a powerful method providing direct information on the catalytically active species, such as coordination numbers and the distances of the coordinated atoms as well as oxidation state and the geometry of the metal centre in catalyst solution.

Keywords: titanium catalysts; polymerization; polyolefin; copolymerization; half-titanocene; homogeneous catalysts; XANES; EXAFS; ethylene

1. Introduction

Polyolefins [linear high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), low-density polyethylene (LDPE), and isotactic polypropylene (PP)] are the dominant commodity thermoplastics, accounting for over 50% of global plastic production in the world; the growth of the world production has still been observed especially in Asia [1]. Transition-metal-catalyzed olefin coordination insertion polymerization is the key technology for the industrial production [2–8]. The development of new polymers that cannot be achieved by using conventional catalysts (such as Ziegler–Natta, metallocene catalysts) has been considered as the central research objective [2–6,9–23]. Copolymerization has been taken into consideration as an effective strategy, because the thermal, physical, mechanical and electronic properties of the resulting copolymers can be modified by the individual components, incorporating two (or three) monomer units [4,6,14–17]. Design and development of the molecular catalysts that display high activity with better comonomer incorporation has thus been the pivotal challenge [2–23].

Discovery of metallocene catalysts (called single-site catalysts), bearing two cyclopentadienyl (Cp') ligands of type $\text{Cp}'_2\text{MX}_2$ (M = Ti, Zr, Hf; X = halogen, etc.), marked an importance point in catalyst design, since the resultant copolymer possesses uniform composition with controlled molecular weight due to the formation of single active species in



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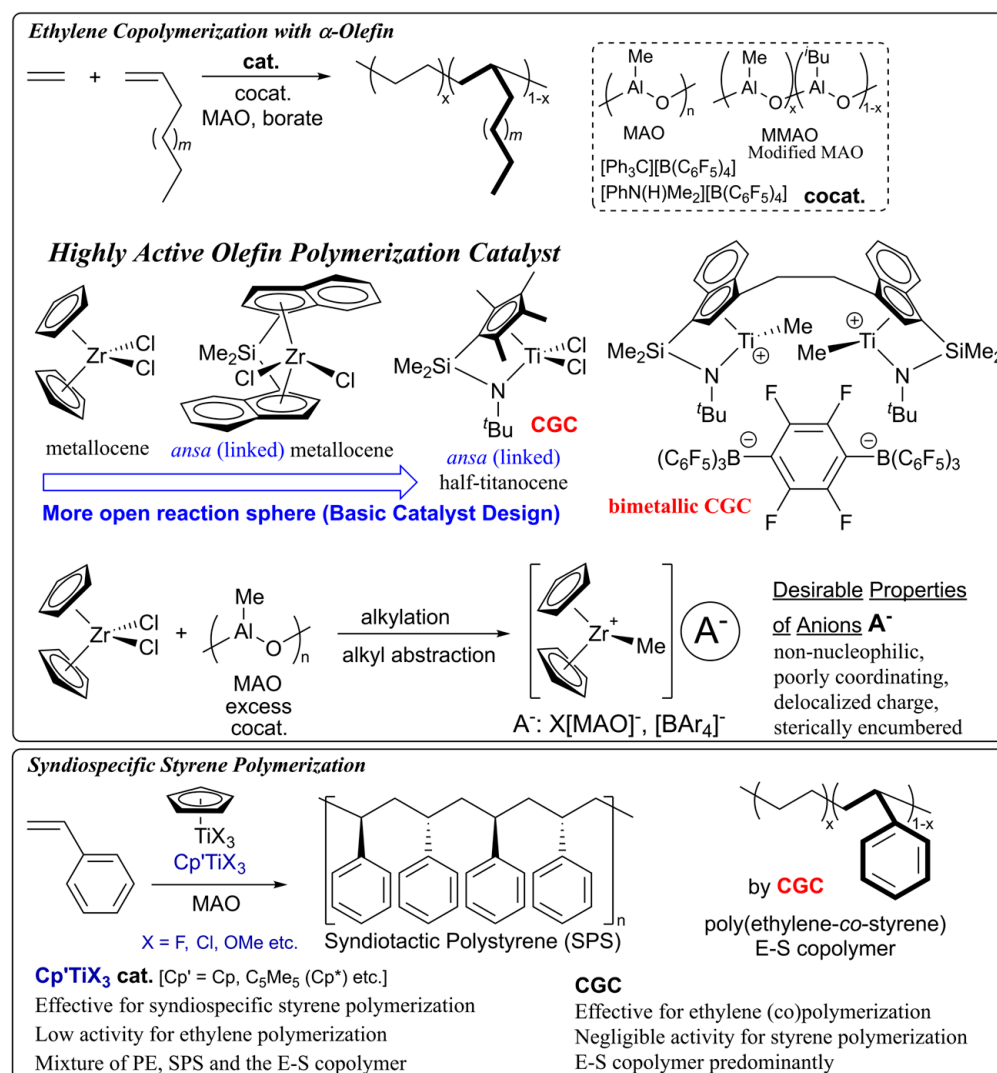
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the catalytic polymerization [5,9–12]. The fact displayed a different feature in the copolymerization using the Ziegler–Natta catalysts (called multi-site catalysts), which generate several catalytically active species in situ; as a result, Ziegler–Natta catalysts afford the copolymer with multiple compositions [5,9–12]. The high oxidation state cationic alkyl species, $\text{Cp}'_2\text{M}^+\text{R}$ (R = alkyl), formed by treating with borate or methylaluminoxane (MAO) through alkyl abstraction, has been proposed as the active species in this catalysis (Scheme 1) [5,9–17,24–27]. In this catalysis, the nature of the active species, such as basic geometry and electronic and steric bulk of the ligand sets, directly affects the catalytic activity, stereo specificity, and the comonomer incorporation in the copolymerization.



Scheme 1. Group 4 transition metal complex catalysts for olefin polymerization and syndiospecific styrene polymerization (SSP).

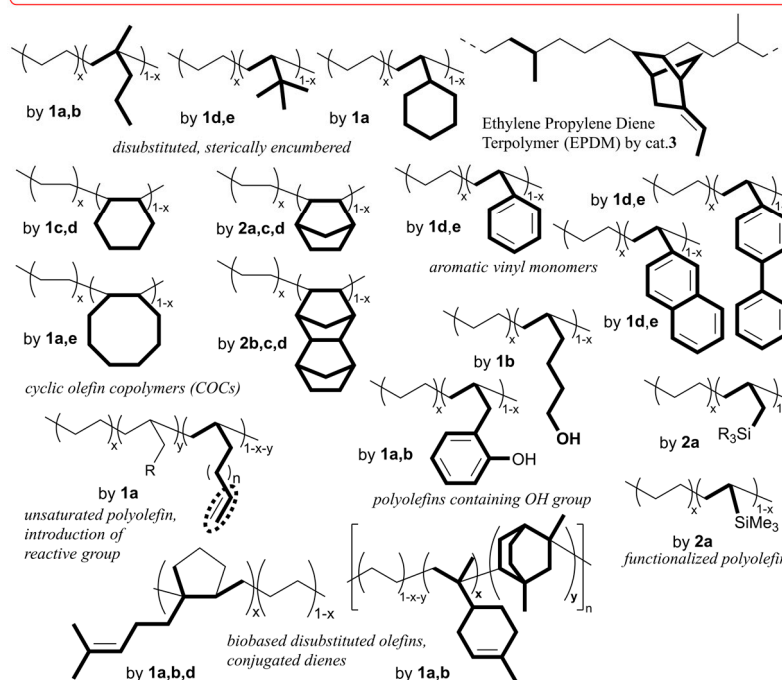
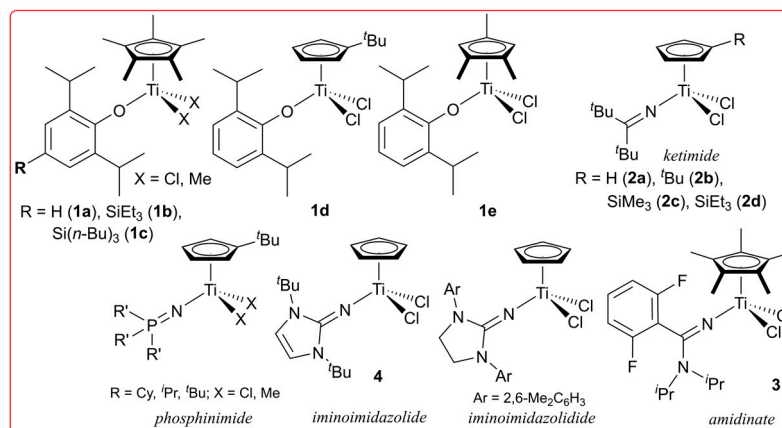
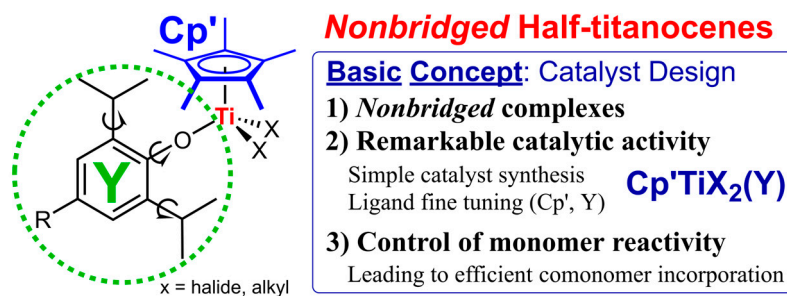
It is widely recognized in ethylene copolymerization with α -olefin that bridged (*ansa*, linked) metallocene catalysts generally showed better α -olefin incorporation than the unbridged analogues; the fact was explained as due to the different coordination environment imposed by the bridging framework (Scheme 1) [5,9–17,28,29]. Accordingly, linked (*ansa*, bridged) half-titanocenes exemplified as constrained geometry catalyst (CGC), $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}^t\text{Bu})]\text{TiCl}_2$ [12,13,28–33], exhibit enhanced ability in α -olefin incorporation in the copolymerization. Interestingly, CGC exhibited styrene incorporation in the ethylene copolymerization, although the incorporation level typically remained below 50 mol% [33–35]. This limitation was later overcome by the bimetallic system (**bimetallic**

CGC, Scheme 1), which enabled synthesis of the copolymer with high styrene content (76 mol%) [21,22,36,37].

In contrast, it has been widely known that ordinary half-titanocenes containing one Cp' of type $\text{Cp}'\text{TiX}_3$ are effective catalysts for the synthesis of syndiotactic polystyrene (SPS, Scheme 1) that is inaccessible by conventional radical or ionic (anionic, cationic) polymerization [38–40]. However, these $\text{Cp}'\text{TiX}_3$ catalysts generally display low catalytic activity for olefin polymerization, and the (attempted) ethylene/styrene copolymerization yielded a mixture of polyethylene, SPS, and the copolymer in small amounts [34,41]. The behaviour displays the sharp contrast from the facts that **CGC** and ordinary metallocene catalysts showed the negligible catalytic activities [34,36,37]. Moreover, as described above, **CGC** predominantly produces the ethylene/styrene copolymers [33–37]; these facts led to an assumption that the active species in olefin polymerization differ from those in the syndiospecific styrene polymerization, as described in detail below.

It is well known that modified half-titanocenes featuring anionic donor ligands, $\text{Cp}'\text{TiX}_2(\text{Y})$ (Scheme 2, Y = phenoxide, ketimide, amidinate, phosphinimide, iminoimidazolidide, iminoimidazolidide, etc.) [6,14–17], first introduced by our team [42,43], display remarkably distinctive catalytic properties, particularly in the copolymerization of ethylene (or propylene, α -olefin) with sterically encumbered olefins, cyclic olefins, and with aromatic vinyl monomers (Scheme 2) [14–17]. The phenoxide (**1**) [42–45] and the ketimide (**2**) [46–52] catalysts have proven distinctively effective for synthesis of new (co)polymers [6,14–17]; it has become clear that effective catalyst for the targeted (co)polymerization can be finely tuned through modification of cyclopentadienyl (Cp') and the anionic donor (Y) ligands. Later, the η^1 -amidinate analogue (**3**) [4,53–55] enabled industrial-scale production of ethylene propylene diene terpolymer (EPDM) [4], such as chlorine-free synthetic rubber, without deep cooling, characteristic of conventional (Ziegler type) vanadium-based catalyst systems, therefore highlighting the practical significance of this catalyst platform [37]. Moreover, interestingly, the phenoxide catalysts exhibit remarkable activities for SSP [56,57] and exclusively afford ethylene/styrene copolymers in copolymerization [56,58]. Moreover, these catalysts enabled the synthesis of a series of ethylene copolymers with other aromatic vinyl monomers (Scheme 2) [59]. The observed characteristics are quite different from those observed by metallocene and linked half-titanocene catalysts.

This review thus introduces several selected recent efforts for synthesis of ethylene copolymers containing cyclic olefins [60–68], biobased conjugated dienes [69,70], disubstituted α -olefins [44,71–74], including the effect of cocatalysts [75]. Moreover, here we also introduce analysis results by synchrotron XAS (X-ray absorption spectroscopy) [27,76,77], which has been recognized as useful to obtain information not only of valence (oxidation state) and the basic structure (geometry) through XANES (X-ray Absorption Near Edge Structure), but also number of coordination atoms and the distance to the centered metal through EXAFS (Extended X-ray Absorption Fine Structure) analysis.



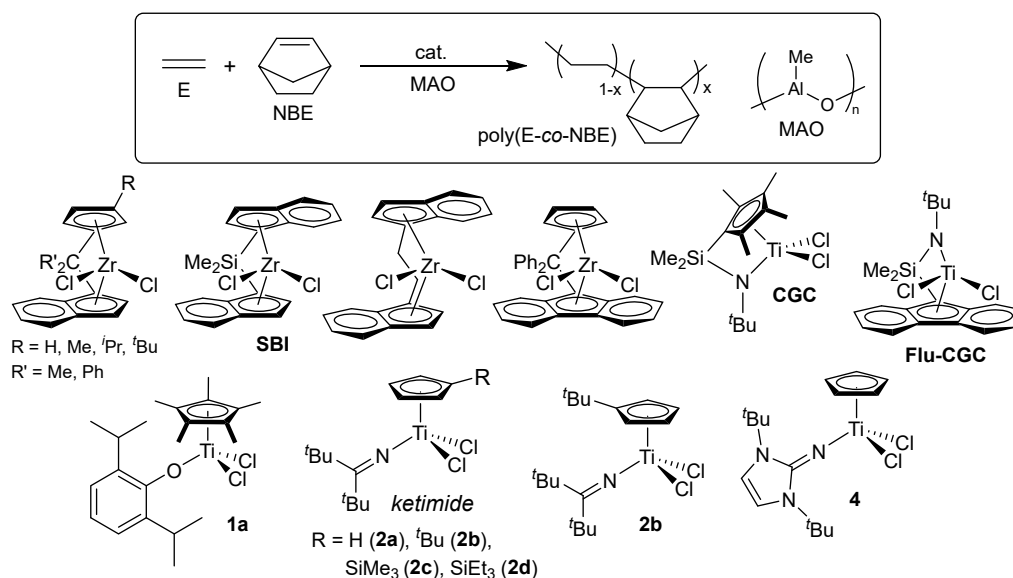
Scheme 2. Nonbridged half-titanocenes: Basic catalyst design and selected examples of catalysts and copolymers.

2. Efficient Synthesis of Cyclic Olefin Copolymers (COCs)

Certain amorphous cyclic olefin copolymers (COCs) are polymeric materials with high transparency in the UV-vis region, thermal resistance (possessing high glass transition temperature, T_g), humidity resistance (negligible water absorption), low dielectric constants, and dimensional stability [78–86], such as commercialized as TOPAS[®] [87] and APEL[®] [88], ethylene-based copolymers with norbornene (NBE) and tetracyclododecene (TCD, a mixture of isomers, mostly *endo-exo* form), respectively, for optical lenses and films for medical applications. There have been an extensive number of reports for ethylene/NBE copolymerization using group 4 transition metal complexes, including met-

allocenes [89–95], bridged half-metallocenes (so-called constrained geometry type) [96–99], modified non-bridged half-metallocenes [60–63], and the others called post-metallocene catalysts [100–105]. However, reports for the efficient synthesis of high molar mass, the ethylene/NBE copolymers possessing high T_g values (high NBE contents), with efficient and random NBE incorporation remain scarce [61,63]. Moreover, vanadium-based catalyst systems, such as VOCl_3 or $\text{VO}(\text{OEt})\text{Cl}_2$, together with $\text{EtAlCl}_2 \cdot \text{Et}_2\text{AlCl}$ cocatalyst, which have been employed in the commercial production of ethylene/TCD copolymers, require deep-cooling conditions because of the limited thermal stability of these catalyst systems [106]. The efficient synthesis of high molar mass ethylene/TCD copolymers have still been limited by the ketimide analogue [63,64], whereas copolymerization employing conventional metallocene catalysts [107–110] and the known linked half-titanocene catalyst (CGC) [64] generally suffers from low catalytic activity and/or inefficient TCD incorporation. The catalyst development for synthesis of high molecular weight COCs possessing high glass transition temperature maintaining promising optical properties (birefringence, with low water absorption, dielectric constants, and dimensional stability) has been an attractive subject [78–86].

As described above, ethylene/NBE copolymers are known to be commercialized as COC, such as TOPAS® [87], using metallocene–MAO catalysts (Scheme 3). In general, the copolymerization by ordinary metallocenes (**SBI-Zr**) and linked half-titanocene catalysts (**CGC**) afforded amorphous poly(ethylene-*co*-NBE)s with uniform compositions possessing a sole glass transition temperature (T_g) by DSC thermograms [79–85]. However, both the activity and the M_n values in the resultant copolymers decreased upon increase in the NBE/ethylene feed molar ratios (increasing the NBE concentration charged and/or lowering ethylene pressure) [89–99], as exemplified in Table 1 [61,82]. The fluorenyl-substituted CGC (**Flu-CGC**) enables living NBE polymerization in the presence of dried MAO or MMAO (obtained as white solid by removal of AlMe_3 and Al^iBu_3 from the commercially available samples) with much improved NBE incorporation [99]; the resultant copolymers with α -olefins (1-octene, 1-decene, and 1-dodecene) possessed gradient NBE incorporation (monomer sequences in the copolymers) due to different reactivity between two monomers [6,84].



Scheme 3. Ethylene copolymerization with norbornene (NBE).

Table 1. Ethylene (E) copolymerization with norbornene (NBE) by [Me₂Si(indenyl)₂]ZrCl₂ (**SBI**), [Me₂Si(C₅Me₄)(N^tBu)]TiCl₂ (**CGC**), Cp⁺TiCl₂(N = C^tBu₂) [Cp⁺ = Cp (**2a**), ^tBuC₅H₄ (**2b**), Me₃SiC₅H₄ (**2c**), Et₃SiC₅H₄ (**2d**)], and CpTiCl₂[1,3-^tBu₂(CHN)₂C = N] (**4**)–MAO catalysts (in toluene, ethylene 2 or 4 atm, 10 min) [61–63] ^a.

Cat. (μmol)	Temp. /°C	E /atm	NBE ^b /M	Activity ^c	M _n ^d ×10 ^{−4}	M _w / M _n ^d	T _g ^e /°C	NBE ^f /mol%
SBI (0.10)	25	4	0.2	28,900	23.1	2.02		10.8
SBI (0.10)	25	4	1.0	4860	22.9	2.37		29.5
CGC (0.50)	25	4	0.2	2460	21.1	1.88		9.6
CGC (0.50)	25	4	1.0	2000	12.8	2.15		26.5
2a (0.02)	80	4	1.0	133,000	33.8	2.34		61.7
2a (0.02)	60	4	1.0	194,000	47.5	2.20		51.2
2a (0.02)	40	4	1.0	48,900	62.0	2.37		45.9
2a (0.02)	25	4	1.0	40,200	71.9	2.9		40.7
2a (0.02) ^g	25	4	1.0	59,700	61.3	2.18		41.0
2a (0.01) ^h	25	2	2.5	90,000	32.3	2.09		58.8
2a (0.01) ^h	25	2	5.0	85,800	34.0	2.00		65.8
2a (0.01) ^h	25	2	10.0	31,500	44.4	2.01		73.5
2b (0.01) ⁱ	25	4	1.0	68,400	62.4	2.8		38.2
2b (0.10) ⁱ	25	4	5.0	15,000	17.5	2.05		52.7
2c (0.02) ⁱ	25	4	1.0	28,300	79.5	1.82	99.6	36.2
2c (0.05) ⁱ	50	2	6.0	32,700	55.2	2.04	238	72.7 ^j
2d (0.01) ⁱ	25	4	1.0	49,800	82.9	2.06	94.1	37.5 ^j
2d (0.01) ⁱ	50	4	1.0	91,400	110	1.94	113	42.1 ^j
4 (0.20)	25	4	1.0	6180	108	2.5		31.4
4 (0.20)	80	4	1.0	5780	80.0	2.35		36.9

^a Conditions: Toluene + NBE total 50 mL, d-MAO 0.5–3.0 mmol. ^b Initial NBE feed conc. (mmol/mL). ^c Activity in kg-polymer/mol-M·h (M = Ti, Zr). ^d GPC data in *o*-dichlorobenzene vs. PS stds. ^e By DSC thermograms. ^f NBE content (mol%) estimated by ¹³C NMR spectra. ^g Time 30 min. ^h Toluene + NBE total 10 mL. ⁱ Toluene + NBE total 30 mL. ^j Estimated on the basis of the plots of T_g and NBE content.

The ketimide-modified half-titanocene, CpTiCl₂(N=C^tBu₂) (**2a**, Scheme 3) first demonstrated efficient synthesis of ethylene random copolymers with high NBE contents possessing high M_n values (Table 1) [61]. The activities (productivities) did not change significantly even over 30 min and increased at elevated temperature (60 °C); the copolymerization conducted at 80 °C did not show a significant decrease in the activity [61]. In contrast to the observation in the copolymerization using the metallocene, **CGCs**, the activity by **2a**–MAO catalyst increased upon increase in the initial NBE feed concentration, the catalyst afforded the high molar mass copolymers [61]; Al cocatalyst (MAO, MMAOs) does not significantly affect the activity and the NBE incorporation. Therefore, this catalysis method using **2a** gave the high molar mass copolymers with high NBE contents (58.8–73.5 mol%, Table 1) with uniform compositions [61]. Previous computational studies revealed that monomer coordination to a cationic titanium species [Cp⁺Ti(2-alkyl-norbornyl)(Y)]⁺ is the rate-determining step in the copolymerization, since a linear correlation between the coordination energy of ethylene and the catalytic activity was seen [15,61]. Moreover, a good correlation between coordination energy after NBE insertion and the NBE contents under the same conditions was also observed [61], suggesting that the NBE incorporation is governed by the coordination preference of NBE and ethylene to the cationic alkyl species [15,61].

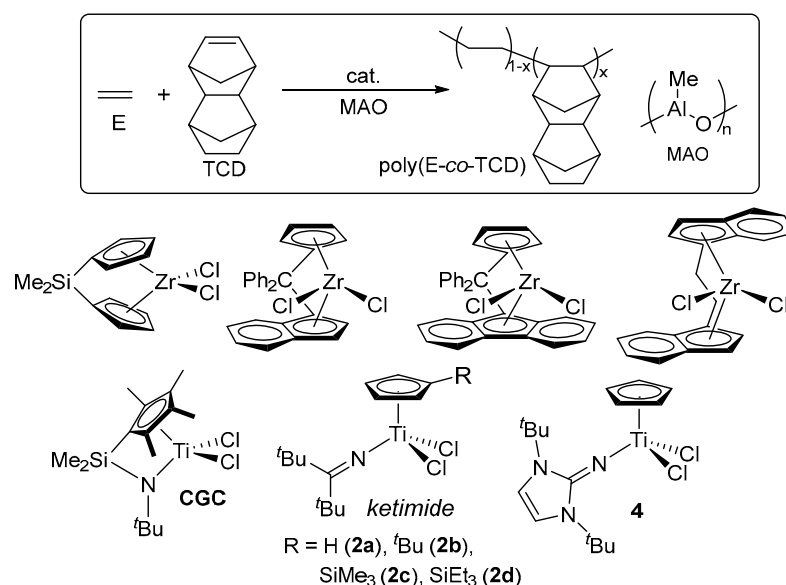
A linear correlation between the T_g values and the NBE content in the copolymers was demonstrated even at high NBE contents, strongly suggesting the NBE random incorporation. The random NBE incorporation was also demonstrated by their microstructural analyses of the copolymers (by ¹³C NMR spectra), consisting of NBE isolated, alternating, repeat incorporation without stereoregularity [6,61,63,80,82].

The imidazolin-2-iminato modified half-titanocene, CpTiCl₂[1,3-^tBu₂(CHN)₂C=N] (**4**), also exhibited promising capabilities in the copolymerization, probably due to the strong σ-donating nature. The catalyst (**4**) showed high catalytic activity affording high molar mass copolymers with efficient NBE incorporation as well as uniform composition [65].

The activities by **4** were rather low compared to the ketimide analogue (**2a**) and further ligand modification might be required, suggesting that the anionic donor ligand plays an important role in both the catalytic activity and the NBE incorporation.

More recently, as summarized in Table 1, improved catalytic activities and NBE incorporation from the above ketimide catalyst (**2a**) could be achieved by the introduction of trialkylsilyl group on the cyclopentadienyl fragment, $(\text{RC}_5\text{H}_4)\text{TiCl}_2(\text{N}=\text{C}^t\text{Bu}_2)$ [$\text{R} = \text{SiMe}_3$ (**2c**) SiEt_3 (**2d**)]. These catalysts displayed remarkable activities (25700–91400 kg-polymer/mol-Ti·h) in the copolymerization at 50 °C to afford high molar mass copolymers with high NBE contents (NBE 36.2–72.7 mol%) possessing high T_g value (238 °C) [63]. The observed results show unique contrast to those in copolymerization using the *tert*- BuC_5H_4 analogue (**2b**, Table 1).

As described above, ethylene/TCD copolymers are known to be commercialized COC, as APEL[®] [88], which have been produced using vanadium-based catalyst systems ($\text{VOCl}_3\text{--EtAlCl}_2\text{·Et}_2\text{AlCl}$, etc.) under deep-cooling conditions [106]. It seemed that the conventional (metallocene, linked half-titanocene) catalysts face difficulty for synthesis of the high molar mass ethylene/TCD copolymers at moderate temperature (>50 °C, Scheme 4) [107–110].



Scheme 4. Catalysts reported for ethylene copolymerization with tetracyclododecene (TCD).

The ketimide-modified half-titanocene, $(^t\text{BuC}_5\text{H}_4)\text{TiCl}_2(\text{N}=\text{C}^t\text{Bu}_2)$ (**2b**), demonstrated synthesis of the copolymers with remarkable activities (43700 kg-polymer/mol-Ti·h) to afford the copolymers possessing high T_g values (108–203 °C) with uniform compositions (Scheme 4, Table 2) [64]. The Cp analogue (**2a**) showed lower catalytic activity than **2b**, and the M_n value in the resultant copolymer was low compared to that prepared by **2b** under the same conditions; modification of cyclopentadienyl fragment thus plays a key role [64]. The imidazolin-2-iminato analogue (**4**) also displayed a rather low capability for the copolymerization [64]. Thus, the ketimide analogues seem to be promising for synthesis for COCs.

More recently, as seen in the ethylene/NBE copolymerization, the catalyst capability could be improved by the introduction of trialkylsilyl group on the cyclopentadienyl fragment, $(\text{RC}_5\text{H}_4)\text{TiCl}_2(\text{N}=\text{C}^t\text{Bu}_2)$ [$\text{R} = \text{SiMe}_3$ (**2c**) SiEt_3 (**2d**), Table 2] [63]. In particular, the SiEt_3 analogue (**2d**) showed higher catalytic activities at 50 °C, affording the high molecular weight copolymers with uniform composition possessing sole T_g values. The TCD contents in the copolymer increased with increase in the TCD concentration charged (as well as lowering the ethylene pressure), and these catalysts (**2c,d**) demonstrated synthesis of the

copolymers with TCD content higher than 50 mol% ($T_g = 255\text{ }^\circ\text{C}$, TCD 52.3 mol%) [63]. The results clearly indicate that further improvement in the catalyst capability can be achieved by the ligand modification.

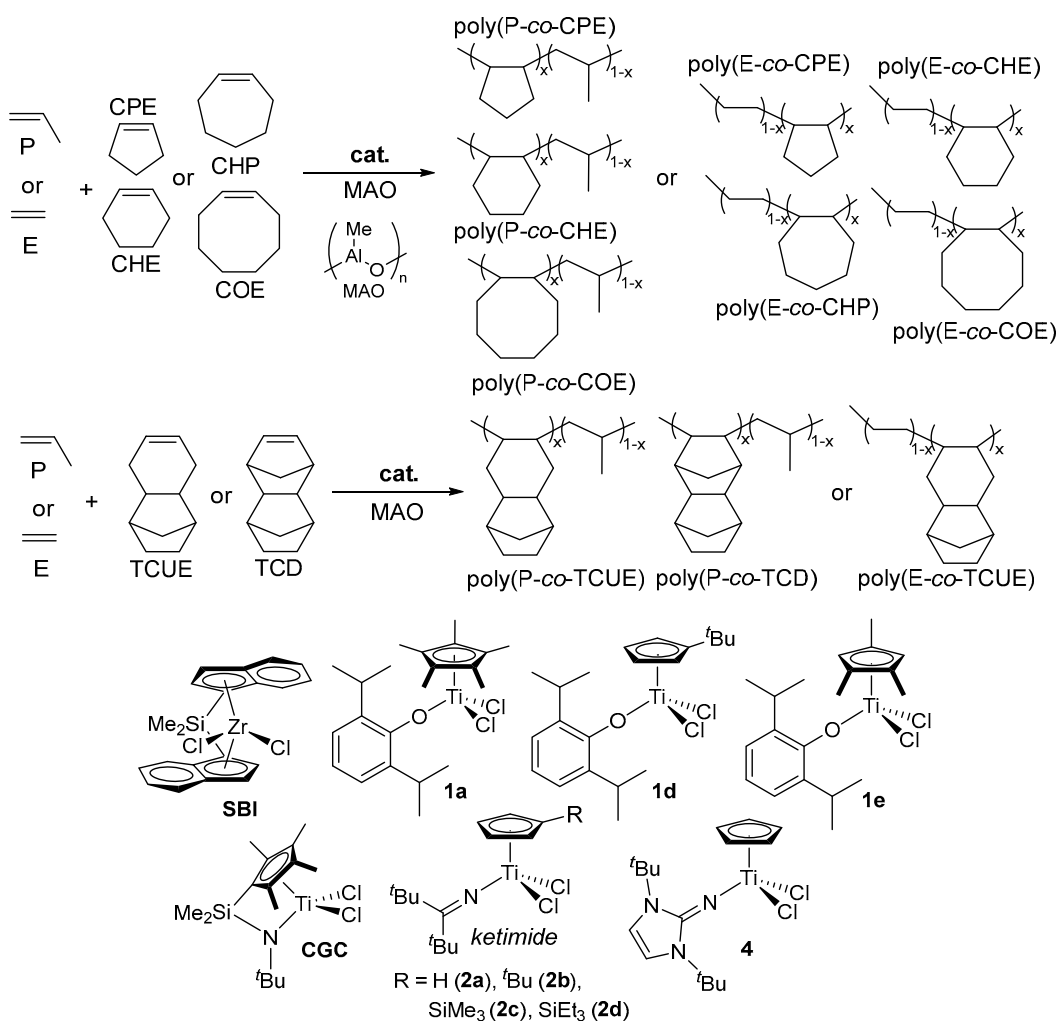
Table 2. Ethylene copolymerization with tetracyclododecene (TCD) by $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}^t\text{Bu})\text{TiCl}_2$ (CGC), $\text{Cp}'\text{TiCl}_2(\text{N}=\text{C}^t\text{Bu}_2)$ [$\text{Cp}' = \text{Cp}$ (**2a**), $^t\text{BuC}_5\text{H}_4$ (**2b**), $\text{Me}_3\text{SiC}_5\text{H}_4$ (**2c**), $\text{Et}_3\text{SiC}_5\text{H}_4$ (**2d**)]–MAO catalysts (in toluene, ethylene 4 or 6 atm, 10 min) [63,64] ^a.

Cat. (μmol)	E /atm	TCD ^b /M	Temp. / $^\circ\text{C}$	Activity ^c	$M_n^d \times 10^{-5}$	M_w/M_n^d	T_g^e / $^\circ\text{C}$	TCD ^f /mol%
CGC (0.05)	6	1.0	25	13,900	14.3	1.58	56	
2a (0.80)	6	2.0	25	1650	1.92	1.41	150	
2b (0.02)	6	1.0	25	43,700	5.88	1.60	108	25.6
2b (0.02)	6	2.0	25	23,900	6.38	1.50	153	32.8
2b (0.02)	6	2.0	40	27,800	6.43	1.67	170	33.5 ^g
2b (0.02)	6	2.0	60	33,300	6.53	1.72	177	35.3
2b (0.02)	6	3.0	25	16,800	6.43	1.61	171	33.6 ^g
2b (0.02)	6	4.0	60	22,400	6.08	1.61	203	36.7
2c (0.02)	6	1.0	25	33,400	17.3	2.03	102	23.7 ^g
2c (0.05)	6	4.0	25	7710	6.41	2.03	202	42.5 ^g
2c (0.10)	4	4.0	50	2560	3.90	1.95	255	52.3 ^g
2d (0.02)	6	1.0	25	55,900	7.29	1.88	119	26.9 ^g
2d (0.04)	6	4.0	25	15,700	5.40	2.41	203	41.9
2d (0.10)	4	2.0	50	9550	5.76	1.53	186	38.3
2d (0.20)	4	3.0	50	7790	3.98	1.72	234	48.3 ^g
2d (0.10)	4	4.0	50	3790	2.79	1.79	244	50.3 ^g

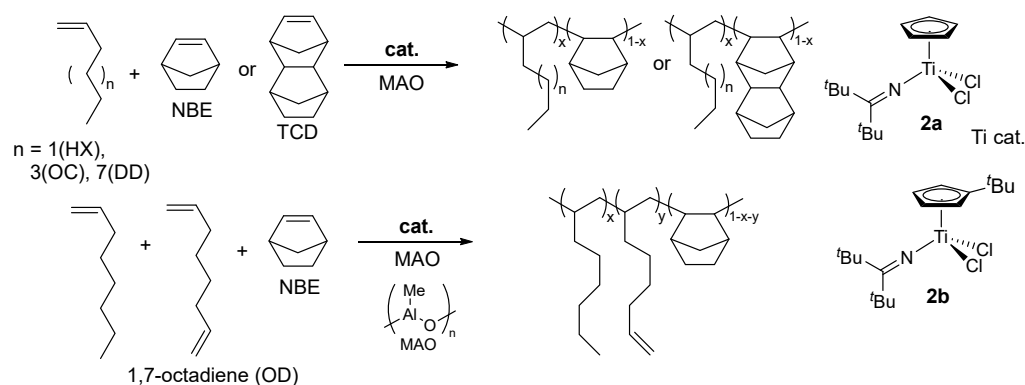
^a Polymerization conditions: Toluene and TCD total 30 mL, d-MAO 3.0 mmol. ^b Initial TCD concentration in mmol/mL. ^c Activity = kg-polymer/mol-Ti·h. ^d GPC data in *o*-dichlorobenzene vs. PS standards. ^e By DSC thermograms. ^f TCD content (mol%) estimated by ^{13}C NMR spectra. ^g Estimated based on the plots of T_g and TCD content.

Basic structure (size, strain, etc.) in cyclic olefin directly affects not only the efficiency of cyclic olefin incorporation in the (ethylene) copolymerization, but also the properties in the resultant COCs (thermal and tensile properties, dielectric constant, etc.) [6,84]. As described in the introduction, limited number of reports were known for successful synthesis of (rather high molar mass) amorphous ethylene copolymers with so-called low-strained cyclic olefins such as cyclohexene (CHE) [66,68], cycloheptene (CHP) [66,67], and *cis*-cyclooctene (COE) [66,67]. Recently, as shown in Scheme 5, synthesis of a series of amorphous ethylene and propylene copolymers with CPE, CHE, CHP, COE, tricyclo[6.2.1.0(2,7)]undeca-4-ene (TCUE), and with TCD, was demonstrated [66,67]. Linear relationships between the T_g values and the cyclic olefin contents were demonstrated in all cases. These results thus strongly suggest that T_g values were affected by the cyclic structure in COCs (except the copolymers with CPE, COE). The T_g values in the propylene copolymers in the region of low cyclic olefin contents (up to 25 mol%) seemed rather high compared to those in the ethylene copolymers [66]. This is due to rather high T_g value in the atactic polypropylene.

The cyclic olefin copolymers of norbornene (NBE) or tetracyclododecene (TCD) with various linear α -olefins, such as 1-hexane (HX), 1-octane (OC), and 1-dodecene (DD), using ketimide half-titanocene catalysts $\text{Cp}'\text{TiCl}_2(\text{N}=\text{C}^t\text{Bu}_2)$ [$\text{Cp}' = \text{Cp}$ (**2a**), $^t\text{BuC}_5\text{H}_4$ (**2b**)] (Scheme 6) [65]. The Cp analogue (**2a**) exhibited superior activity to the $^t\text{BuC}_5\text{H}_4$ derivative (**2b**), exhibiting over 10 times higher activity and more efficient comonomer incorporation under the same conditions. While these half-titanocene catalysts successfully produced high molecular weight TCD/ α -olefins copolymers [65], the conventional metallocene and Flu-CGC failed to synthesize the high molecular weight copolymers, yielding only low molecular weight oligomers [111–114].



Scheme 5. Propylene or ethylene copolymerization with (low-strained) cyclic olefins [66–68].



Scheme 6. Copolymerization of norbornene (NBE), tetracyclododecene (TCD), with α -olefin (1-hexene, 1-octene, 1-dodecene, 1,7-octadiene) [65].

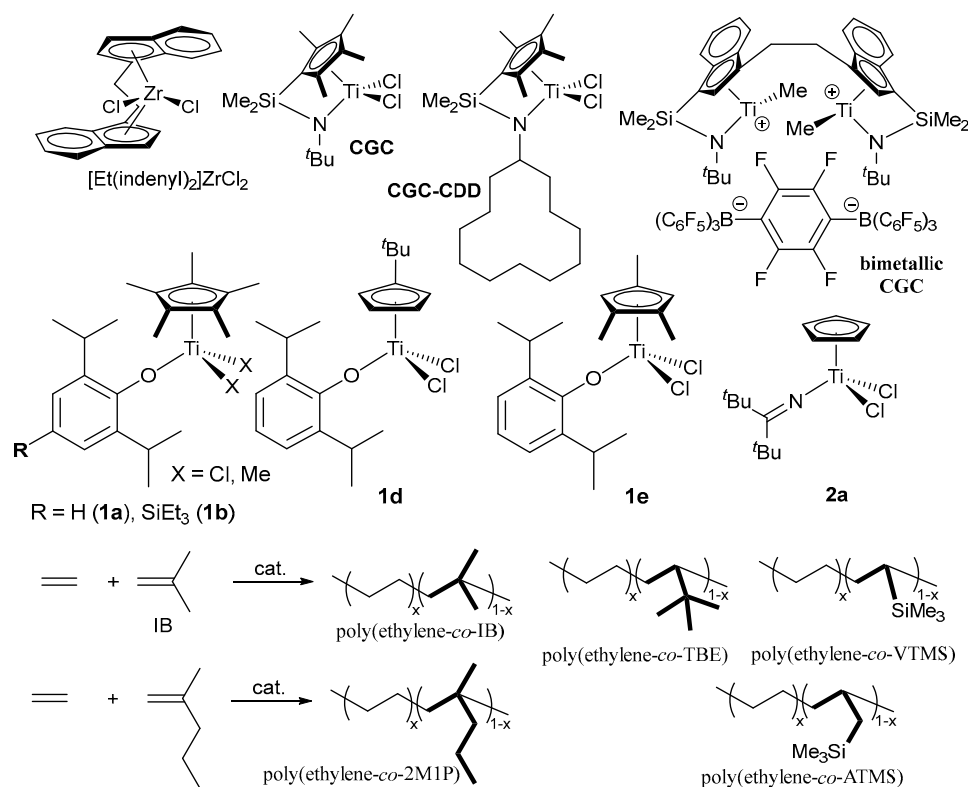
A critical finding in this copolymer system is the linear relationship observed between the cyclic olefin content and glass transition temperature across all synthesized polymers. Copolymers with TCD exhibited higher T_g values than their NBE counterparts at equivalent cyclic olefin concentrations (exceeding 200 °C). The T_g values are further influenced by the α -olefins chain length, decreasing in the order of 1-hexene > 1-octene > 1-dodecene. Additionally, the reactive functionality was demonstrated by introducing the incorporation of 1,7-octadiene (OD), which adds terminal olefinic double bonds to the side chains. In this

term, the $t\text{BuC}_5\text{H}_4$ analogue (**2b**) proved more suitable than Cp analogue (**2a**) because the latter caused unwanted isomerization of the terminal double bonds into internal olefins [65].

3. Ethylene Copolymerization with Sterically Encumbered Olefins

Ethylene copolymerization with 1,1-disubstituted α -olefins such as isobutene (IB), 2-methyl-1-pentene (2M1P) has rarely been reported in metal-catalyzed olefin coordination insertion polymerization [115]; these monomers have long been regarded as “traditionally unreactive” in this field. However, these ethylene copolymers are expected to show enhanced weather resistance compared with conventional ethylene/ α -olefin copolymers, because of the absence of reactive tertiary C–H bonds in the polymer backbone, which are removed by oxidative or UV-induced degradation. For instance, the ethylene/IB copolymerization using $[\text{Et}(\text{indenyl})_2]\text{ZrCl}_2$ gave the copolymer with low (<2.8 mol%) IB content even under large excess IB concentration conditions (charge molar ratio of ethylene/IB = 1/4000) [116].

Ordinary CGC showed negligible IB incorporation in the ethylene copolymerization; the IB incorporation was much improved by using cyclododecylamide analogue (CGC-CDD, Scheme 7) [117]; the fluorenyl analogue (Flu-CGC-CDD, Scheme 7) later showed IB incorporation [118]. However, the copolymerization with 2M1P by CGC-CDD afforded the polymer possessing large PDI (polydispersity index, $M_w/M_n = 5.90$) [117]. The bimetallic CGC consisting of dinuclear catalyst and dianionic borate catalyst system (Scheme 7) showed improved IB incorporation from the mononuclear CGC (IB 3.1 mol% vs. 15.2 mol%: ethylene 1 atm, IB 1.3 M, 24 °C), but showed low activity and the obtained polymer possessed rather large PDI ($M_w/M_n = 3.67$) [119,120]. The catalyst system incorporated methylenecyclopentene and methylenecyclohexene in the ethylene copolymerization. The attempted copolymerization with 2-methyl-2-butene gave the copolymer by incorporation as 2-methyl-1-butene formed by olefin isomerization [120]. Reports for synthesis of high molar mass ethylene copolymers with 1,1-disubstituted α -olefins (except IB) have still remained scarce.



Scheme 7. Ethylene copolymerization with α -olefins containing steric bulk [71–75,116–121].

Synthesis of ethylene/2M1P copolymers was achieved by the phenoxide-modified half-titanocene catalyst with rather efficient 2M1P incorporation (**1a**, $M_n = 3.30\text{--}13.0 \times 10^4$, $M_w/M_n = 1.70\text{--}1.90$) [71,73]. As summarized in the selected data in Table 3, 2M1P content in the resultant copolymer increased upon increasing upon increase in the 2M1P concentration and charged or lowering ethylene pressure (6 $\rightarrow$ 4 atm) with decrease in the activity [71,73]. The resultant copolymers possessed uniform compositions confirmed by DSC thermograms and their microstructural analysis by ^{13}C NMR spectra revealed that 2M1P was incorporated in an isolated and/or alternating manner (without repeat insertions). Use of the *tert*-BuC₅H₄ analogue (**1c**) led to decrease in both the activity and the 2M1P incorporation explained as due to the steric bulk [71,73]. Later, the activity by the SiEt₃ analogue (**1b**) increased at elevated temperature (up to 80 °C) [75]. In contrast, the Cp–ketimide analogue (**2a**) showed poor 2M1P incorporation, suggesting that the nature of anionic donor ligand (as well as steric bulk on Cp') affects the comonomer incorporation. Moreover, as described above, CGC also showed poor 2M1P incorporation under the same conditions.

Table 3. Ethylene (E) copolymerization with 2-methyl-1-pentene (2M1P), *tert*-butylethylene (TBE), and with vinyltrimethylsilane (VTMS) by Cp'TiCl₂(OAr) [OAr = O-2,6-*i*Pr₂C₆H₃, Cp' = Cp* (**1a**), ^{*t*}BuC₅H₄ (**1d**), CpTiCl₂(N=C^{*t*}Bu₂) (**2a**), [Me₂Si(C₅Me₄)(N^{*t*}Bu)]TiCl₂ (CGC)–MAO catalysts (in toluene at 25 °C, 10 min) ^a.

Cat. (μmol)	E/atm	Comonomer/M ^b	Activity ^c	$M_n^d \times 10^{-4}$	M_w/M_n^d	Cont. ^e /mol%
1a (0.10)	4	---	12100	40.0	3.70	
1a (0.50)	6	2M1P	6980	13.0	1.70	
1a (0.50) ^f	6	2M1P	8460	12.0	2.10	3.3
1a (0.50) ^f	6	2M1P	5760	10.0	1.80	5.7
1a (0.50) ^f	4	2M1P	4240	6.50	2.00	5.0
1a (0.50) ^f	4	2M1P	2680	4.90	1.60	9.4
1d (2.0)	6	2M1P	573	5.80	2.00	
2a (0.20)	6	2M1P	19100	53.0	2.10	
2a (0.20)	6	2M1P	10100	43.0	2.00	
2a (0.20)	6	2M1P	6960	34.0	1.80	0.3
CGC (1.0) ^g	6	2M1P	1840	12.0	2.40	0.3
CGC (1.0) ^g	4	2M1P	1420	9.70	2.50	
CGC (1.0) ^g	4	2M1P	1320	7.40	2.40	0.4
1a (0.20)	6	TBE	14100	15.5	2.00	trace
1a (0.50)	6	VTMS	1870	30.5	1.90	5.1
1d (1.0)	6	TBE	3310	11.7	2.50	1.3
1d (1.0) ^h	4	TBE	2020	8.17	2.40	3.3
1d (2.0) ^h	2	TBE	918	7.27	2.10	4.4
1d (2.0) ^h	2	TBE	756	4.04	2.00	6.8
1d (0.20)	6	VTMS	92	1.41	2.80	13.6
2a (0.20)	6	TBE	7830	71.1	1.90	trace
2a (0.20)	6	TBE	6000	68.7	1.90	trace
2a (1.0)	6	VTMS	3730	57.3	2.30	11.9
2a (1.0)	4	VTMS	1560	42.2	2.30	18.7
CGC (0.25)	6	TBE	3020	32.0	2.00	none
CGC (0.25)	6	VTMS	2280	36.7	2.50	10.4

^a Conditions: Comonomer + toluene total 30 mL, d-MAO 3.0 mmol. ^b Initial comonomer feed conc. (mmol/mL).

^c Activity in kg-polymer/mol-Ti·h. ^d GPC data in *o*-dichlorobenzene vs. polystyrene standards. ^e Comonomer content (mol%) estimated by ^{13}C NMR spectra. ^f MAO 4.5 mmol. ^g Polymerization 6 min. ^h TBE + toluene total 10 mL.

The Cp*–phenoxide analogue (**1a**) also showed efficient VCH incorporation in the ethylene copolymerization [72], whereas incorporation of branched (γ-disubstituted) α-olefins in the copolymerization using the conventional catalysts seemed difficult [72]. However, as summarized in Table 3, **1a** showed negligible *tert*-butyl ethylene incorporation, and showed rather poor VTMS incorporation compared to the Cp–ketimide analogue (**2a**), CGC; the VTMS incorporation was improved by using the *tert*-BuC₅H₄ analogue (**1c**) but the resultant copolymer possessed rather low M_n values compared with those prepared by **2a** [121]. Synthesis of ethylene copolymers with *tert*-butyl ethylene (TBE) was achieved by

the *tert*-BuC₅H₄ analogue (**1d**) and the 1,2,4-Me₃C₅H₂ analogue (**1e**); the observed effect on Cp' was the same as that in the ethylene copolymerization with cyclohexane [68].

Effect of Borate Cocatalysts Toward Activity, Comonomer Incorporation in Alkane Solvent

Recently, it has been recognized that solvent coordination (toluene vs. alkane) in addition to catalyst–cocatalyst interaction (nuclearity effect) affect both the catalytic activity and comonomer incorporation in olefin polymerization [75,122,123]. For instance, as summarized in Table 4, [Me₂Si(C₅Me₄)(N^tBu)]TiCl₂ (**CGC**), Cp*TiMe₂(O-2,6-*i*Pr₂-4-RC₆H₂) [R = H (**1a'**), SiEt₃ (**1b'**)]–borate, [A(H)]⁺[BAR₄][−] (Ar = C₆F₅ or C₁₀F₇, **B1**–**B6** in Scheme 8) catalyst systems conducted in methylcyclohexane (MCH) exhibited better comonomer incorporation than those conducted in toluene (in the presence of MAO, borate cocatalysts) in the ethylene copolymerization with 2M1P, 1-dodecene, VCH [75].

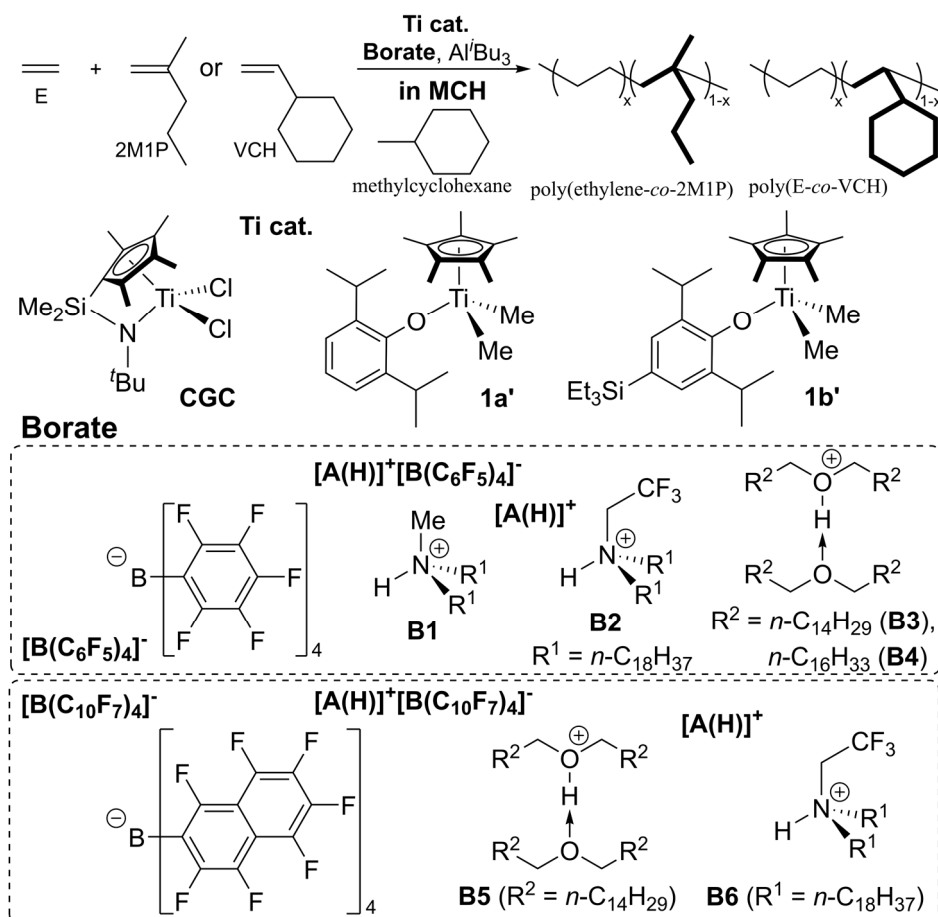
Table 4. Ethylene copolymerization with 2-methyl-1-pentene (2M1P) or vinylcyclohexane (VCH) by [Me₂Si(C₅Me₄)(N^tBu)]TiCl₂ (**CGC**), Cp*TiMe₂(O-2,6-*i*Pr₂-4-R'-C₆H₂) [R = H (**1a'**), SiEt₃ (**1b'**)]–borate cocatalyst systems [at 25 °C, ethylene 4 atm, 10 min (2M1P); ethylene 6 atm 6 min (VCH)]^a.

Cat. (μmol)	Solvent	Al Cocat.	Borate	Comonomer	Activity ^b	M _n ^c ×10 ^{−4}	M _w / M _n ^c	T _m ^d /°C	cont. ^e /mol%
CGC (1.0)	MCH	Al ⁱ Bu ₃ ^f	B1	2M1P	149	6.88	3.09	131	
CGC (1.0)	MCH	Al ⁱ Bu ₃ ^f	B2	2M1P	3770	38.9	5.88	122	
CGC (1.0)	MCH	Al ⁱ Bu ₃ ^f	B3	2M1P	6810	44.9	6.42	120	0.4
CGC (1.0)	MCH	Al ⁱ Bu ₃ ^f	B5	2M1P	2660	32.0	5.66	122	
CGC (1.0)	MCH	Al ⁱ Bu ₃ ^f	B6	2M1P	768	26.1	5.23	126	
CGC (0.1)	toluene	MAO	---	2M1P	5090	32.4	3.66	129	trace
1a' (1.0)	MCH	Al ⁱ Bu ₃	B3	2M1P	4210	6.28	1.93	99.0	5.5
1a' (1.0)	MCH	Al ⁱ Bu ₃	B4	2M1P	1280	7.87	1.84	96.9, 122	
1a' (1.0)	MCH	Al ⁱ Bu ₃	B5	2M1P	4260	5.76	1.76	93.6	6.8
1a' (1.0)	MCH	Al ⁱ Bu ₃	B6	2M1P	1870	4.93	1.89	94.5	
1a' (0.05)	toluene	MAO	---	2M1P	11,200	8.41	2.25	111	2.6
1b' (1.0)	MCH	Al ⁱ Bu ₃	B1	2M1P	547	7.04	2.47	99.5, 121	
1b' (1.0)	MCH	Al ⁱ Bu ₃	B2	2M1P	2680	3.82	1.96	98.7	
1b' (1.0)	MCH	Al ⁱ Bu ₃	B3	2M1P	4040	4.11	1.90	101	5.0
1b' (1.0)	MCH	Al ⁱ Bu ₃	B4	2M1P	3980	3.21	2.41	98.4	
1b' (1.0)	MCH	Al ⁱ Bu ₃	B5	2M1P	5060	5.41	1.84	97.9	6.0
1b' (0.05)	toluene	MAO	---	2M1P	18,600	8.34	2.05	109	3.1
CGC (0.05)	MCH	Al ⁱ Bu ₃	B2	VCH	16,800	7.70	1.70	87.5	8.8
CGC (0.05)	MCH	Al ⁱ Bu ₃	B3	VCH	44,000	6.31	1.65	86.0	9.0
CGC (0.05)	MCH	Al ⁱ Bu ₃	B4	VCH	10,600	5.93	1.75	87.0	8.7
CGC (0.05)	MCH	Al ⁱ Bu ₃	B5	VCH	69,000	8.65	1.98	81.4	9.7
CGC (0.05)	toluene	MAO	---	VCH	39,400	21.4	3.38	92.5	6.0
CGC (0.05)	toluene	Al ⁱ Bu ₃	B1	VCH	1090	10.8	2.28	98.6	
CGC (0.05)	toluene	Al ⁱ Bu ₃	B2	VCH	16,500	13.0	2.30	96.3	5.6
CGC (0.05)	toluene	Al ⁱ Bu ₃	B3	VCH	14,100	13.1	2.59	96.9	5.6
CGC (0.05)	toluene	Al ⁱ Bu ₃	B4	VCH	21,100	8.55	2.21	97.0	5.4
CGC (0.05)	toluene	Al ⁱ Bu ₃	B5	VCH	31,000	13.8	3.07	94.2	5.8
1b' (0.01)	toluene	MAO	---	VCH	224,000	17.5	2.43	(−15.1)	24.1

^a Conditions: 2-Methyl-1-pentene (2M1P) 5.0 mL (1.35 M) or vinylcyclohexane (VCH) 5.0 mL (1.22 M), 2M1P (or VCH) + methylcyclohexane (MCH) or toluene total 30.0 mL, AlⁱBu₃ [0.55 mmol/L hexane, Al/Ti = 1000 (molar ratio)] or MAO 3.0 mmol, borate (borate/Ti molar ratio = 1.0). ^b Activity = kg-polymer/mol-Ti·h. ^c GPC data in *o*-dichlorobenzene vs. polystyrene standards (M_n in g/mol). ^d By DSC thermograms. ^e 2M1P or VCH content (mol%) estimated by ¹³C NMR spectra. ^f Al/Ti = 500, molar ratio.

The activity by **CGC** in the E/2M1P (co)polymerization (ethylene 4 atm, 25 °C) in MCH was affected by the borate cocatalyst employed and increased in the order: activity = 149 kg-polymer/mol-Ti·h (**B1**) < 768 (**B6**) < 2660 (**B5**) < 3770 (**B2**) < 6810 (**B3**). Interestingly, **CGC**–**B3** catalyst system in MCH afforded the copolymer (2M1P 0.4 mol%, by DSC thermogram and ¹³C NMR spectrum), whereas **CGC**–MAO catalyst system in toluene showed negligible 2M1P incorporation under the same conditions [75]. It seems that the 2M1P incorporations (estimated by the T_m values) were also affected by the borate cocatalyst employed. Similarly, the activities by **1a'** and **1b'** were affected by the borate cocatalyst employed, and **1b'**–**B5**

catalyst system showed the highest activity (5060 kg-polymer/mol-Ti·h) and the resultant copolymer possessed higher 2M1P content than that conducted in toluene by **1b'**—MAO catalyst system (6.0 mol% vs. 3.1 mol%) [75]. In contrast, **1b'**—**B1** catalyst system showed low activity affording the polymer with two compositions estimated by DSC thermograms. It should be noted that the 2M1P incorporation was affected by the borate cocatalyst employed: **B5** showed better 2M1P incorporation than **B3**. It was shown that conducting these copolymerizations in MCH in the presence of borate cocatalysts (**B2**–**B6**) showed better 2M1P incorporation than that conducting in toluene in the presence of MAO [75].

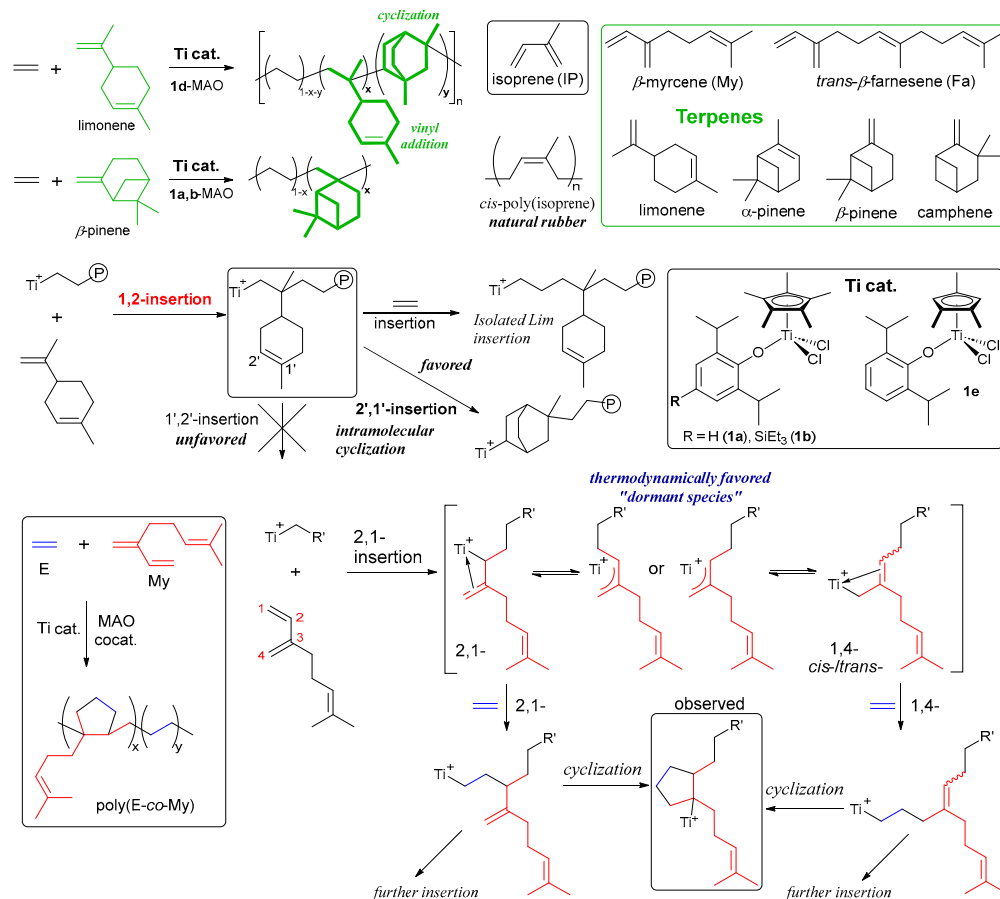


Scheme 8. Effect of borate cocatalysts (**B1**–**B6**) in Ethylene copolymerization with 2-methyl-1-pentene (2M1P), vinylcyclohexane (VCH) by [Me₂Si(C₅Me₄)(N^{*t*}Bu)]TiCl₂ (**CGC**), Cp^{*}TiMe₂(O-2,6-*i*Pr₂-4-R'^{*}C₆H₂) [R' = H (**1a'**), SiEt₃ (**1b'**)] in methylcyclohexane (MCH) [75].

Moreover, the activity by **CGC** conducted in MCH was affected by the borate cocatalyst employed. **CGC**—**B5** catalyst system in MCH exhibited higher catalytic activity and better VCH incorporation than **CGC**—MAO catalyst system in toluene [75]. Note that no significant differences in the VCH contents in the copolymers were observed when these polymerizations using **CGC**—borate catalyst systems were conducted in toluene; the VCH incorporation was thus affected by the solvent (toluene vs. MCH). The results thus suggest that the observed difference in MCH would be due to a weak cation—anion interaction *without* coordination of toluene (and amine or ether, exhibited **A** formed after treatment of **CGC** with borate) to the assumed cationic alkyl species [122–124]. Non-coordinating oxonium ion, especially HO⁺(*n*-C₁₄H₂₉)₂·O(*n*-C₁₄H₂₉)₂ (**B5**) containing long alkyl chains, was preferred over the ammonium salts (probably due to poor coordination ability of O(*n*-C₁₄H₂₉)₂ to the assumed cationic species) [75]. As expected for better anion delocalization (BAr₄⁻), perfluorinated naphthyl borate, B(C₁₀F₇)₄⁻, showed higher activity than B(C₆F₅)₄⁻.

4. Synthesis of Biobased Polyolefins: Copolymerization of Biobased Conjugated Dienes

Development of functional polymers from renewable feedstocks has been an important subject in circular economy [125–132]. Cyclic monoterpenes consisting of two isoprene units as formula of $C_{10}H_{16}$ shown in Scheme 9 can be considered as promising monomers obtained from the abundant plant oil [133,134]. However, the successful synthesis by coordination insertion polymerization has been scarce until recently [69,135], whereas there are the reports by ionic (cationic, radical) polymerization.



Scheme 9. Synthesis of biobased ethylene copolymers with limonene, β -pinene, and myrcene [69].

(1,2,4- $Me_3C_5H_2$)TiCl₂(O-2,6-*i*-Pr₂C₆H₃) (**1e**) enabled synthesis of ethylene/limonene copolymers possessing rather high molecular weights ($M_n = 4.00\text{--}12.6 \times 10^4$) with unimodal molecular weight distributions [135]. As observed in the ethylene/2M1P copolymerization (Table 3), increase in the limonene concentration led to decrease in the activity and the M_n value in the copolymer, while simultaneously increasing the limonene content in the copolymer. In contrast, the Cp* analogues (**1a,b**) showed less efficient limonene incorporation and CGC showed the negligible incorporation. Microstructural analysis revealed resonances consistent with 1,2-limonene insertion followed by cyclization, favouring a 2',1'-insertion (than 1',2'-insertion) pathway (Scheme 9) [135].

The Cp* analogues (**1a,b**)-MAO catalyst gave high molar mass poly(ethylene-*co*- β -pinene)s ($M_n = 2.10\text{--}22.4 \times 10^4$) possessing unimodal molecular weight distributions ($M_w/M_n = 1.53\text{--}2.32$). The activity was influenced by the β -pinene concentration charged, ethylene pressure, Al/Ti molar ratio and the temperature. The 1,2,4- $Me_3C_5H_2$ analogue (**1e**) showed low activities compared with **1a,b**, affording the copolymers possessing rather low M_n values [135]. The attempted copolymerization by CGC gave polymers with negligible β -pinene incorporation.

β -Myrcene (myrcene, My), a promising biobased linear terpene, has been polymerized by radical or anionic polymerization and reports concerning the metal-catalyzed ethylene copolymerization have been limited by scandium catalysts [136] or half-titanocene catalysts [69], whereas there are reports for the styrene/My copolymerization [137–143]. The scandium catalysts, however, afforded copolymers possessing multi-block microstructures, expressed as poly(E-*bl*-My), possessing melting temperature of polyethylene segment (133 °C, My 9 mol%) [136]. Phenoxide-modified Cp* analogues (**1a,b**) demonstrated synthesis of high molar mass (semicrystalline or amorphous) random ethylene/My copolymers with efficient My incorporation [69]. The microstructural analysis using ^{13}C NMR spectra of the resultant (unsaturated) copolymers and the saturated copolymers prepared by olefin hydrogenation. The analysis data revealed that the copolymers possessed cyclopentane units containing My pendant arm ($-\text{CH}_2\text{CH}=\text{CMe}_2$), which are presumably formed by 2,1- or 1,4-My insertion and subsequent cyclization after ethylene insertion (Scheme 9) [69]. In general, formation of η^3 -allyl intermediate, considered as dormant, disturbs proceeding further olefin insertion. In this catalysis, the subsequent cyclization enabled to proceed the copolymerization with random My incorporation. The elongation (tensile strain) at break increased with increasing the My contents accompanied with decrease in the tensile stress (strength); the copolymer showed promising elastic behaviours as biobased elastomers [69]. The catalysts also enabled synthesis of ethylene/isoprene copolymers possessing cyclopentane and cyclohexane units [70].

5. Analysis of Catalytically Active Species Through XAS (X-Ray Absorption Spectra)

5.1. Introduction: XAS for Analysis of Catalytically Active Species

Identification of catalytically active species and the reaction chemistry are prerequisite not only for clear understanding of the catalysis mechanism, but also for catalyst design through the structural and electronic insight. Single crystal X-ray diffraction analysis provides structural information of the proposed intermediate(s) in solid state, although such species are often (sometimes) required by certain stabilization for isolation and the information is limited to be in solid state. Mechanistic studies are also supported by reaction chemistry, stoichiometric and/or catalytic reactions, using model complexes (and the isolated species in the catalytic reaction) and computational studies. However, we often observed that the isolated species exhibit apparently low catalytic activities or are inactive due to required stabilization for the isolation and/or isolated species which are indeed dormant in the catalysis cycle.

Nuclear magnetic resonance (NMR) spectroscopy is the principal technique for characterization of diamagnetic inorganic and organometallic compounds in (partially) deuterated solvent. Electron spin resonance (ESR) spectroscopy has been a powerful method for analysis of the paramagnetic species that exhibit negligible or broadened NMR signals [144,145]. However, these methods still provide limited access for the obtainment of real/clear structural information (image) in catalysis solutions. Moreover, ESR often lacks quantitative analysis/reliability [144–146], and a possibility of co-presence of “ESR silent” species cannot be excluded. For example, vanadium(III) species with $3d^2$ electron configuration ($S = 1$, triplet, $S =$ spin quantum number) are ESR silent due to an interaction between the two unpaired electrons, while vanadium(IV) dimers coupled antiferromagnetically also become ESR-silent through spin–orbit coupling (SOC) [146,147].

Analysis by XAS (X-ray absorption spectroscopy), XANES (XANES = X-ray Absorption Near Edge Structure) and EXAFS (EXAFS = Extended X-ray Absorption Fine Structure), performed at synchrotron facilities provides information of not only oxidation state and the basic geometry around the metal centre (by XANES), but also kind of atoms and

the distances connected (coordinated) to the metal centre (by EXAFS). More recently, we see growth in the number of reports identifying homogeneous, molecular catalysis through XAS analysis [27,76,148–159], whereas the methods are common in heterogeneous catalysis [160–164]. The methods are recognized as a useful analysis method especially of catalysis research with early transition metals, as exemplified in analysis of paramagnetic vanadium(III) species and titanium(III) species that cannot be observed, especially by NMR spectroscopy [27,76,148,149,153,154,158].

Although we need to use the appropriate synchrotron facility (e.g., SPring-8, BL01B1 beamline), we do not need any specified apparatus, and the sample preparations are possible on site in the drybox. Moreover, we demonstrated good reproducibility (in the independent runs even conducted during the different beam times) and no severe X-ray radiation damages during data acquisition were observed [27,76]. Herein, we first describe basics in XAS analysis for uninitiated researchers and introduce selected results in analysis of catalytically active species in olefin polymerization and syndiospecific styrene polymerization using half-titanocene catalysts.

5.2. Basics in XANES Spectra

It has been known that pre-edge peak intensity and edge absorption (exemplified in Figure 1) in XANES spectra are influenced by the oxidation state and the basic geometry around the centred metal [27,148,149,160–173]. For basic introduction, V-K edge XANES spectra of vanadium oxides with various oxidation states are shown in Figure 1a [174]. The basic geometries [octahedral (O_h), square pyramidal (C_{4v}), tetrahedral (T_d)] and their selected irreducible and relating functions and point groups are also placed in the figure. Pre-edge absorption is known to provide information about basic (local) geometry around the metal centre reflected by $s \rightarrow d$ transitions (quadrupole transition); dipole transition ($s \rightarrow p$) is also considered depending on degree of p–d orbital hybridization [166,169,175,176]. For instance, complexes with T_d and C_{4v} symmetries display higher pre-edge peak intensity than those in O_h symmetry. The observed difference can be explained as due to a difference in the possibility of a p–d orbital hybridization, realized from a table in irreducible representations and the relating functions in the complexes with these symmetries (Figure 1b).

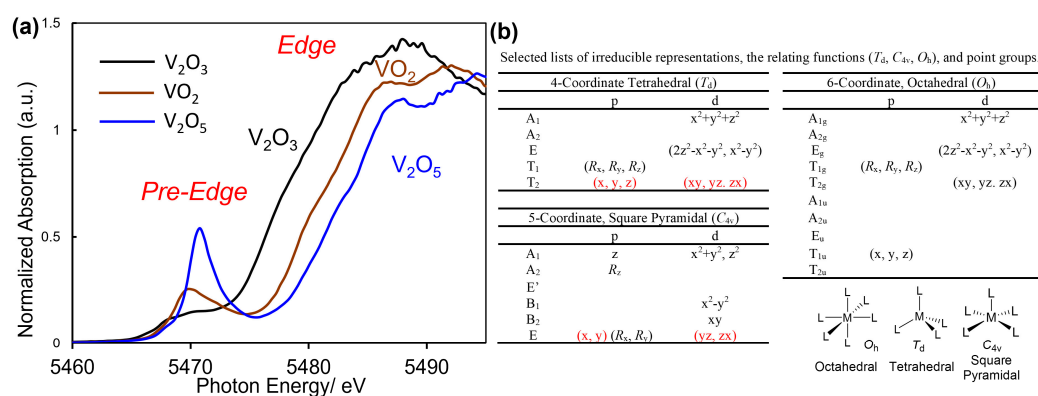


Figure 1. (a) V K-edge spectra (5.46 keV, by using synchrotron radiation at SPring-8, BL01B1 beamline) for vanadium oxides with various oxidation states, (b) selected irreducible and relating functions and point groups in octahedral, square pyramidal and tetrahedral complexes [27,148].

The complex with tetrahedral geometry (T_d) leads to an increase in the degree of electric dipole transition of a 1s electron to the p–d hybridized orbital [166,169,175,176]. This is because p_x , p_y , p_z orbitals and d_{xy} , d_{yz} , d_{zx} orbitals in T_d symmetry (or p_x , p_y orbitals and d_{yz} , d_{zx} orbitals in C_{4v} symmetry) belong to the irreducible representation, leading to formation of a p–d hybridized orbital with increased electric dipole transition

of a 1s electron occurring with the hybridized orbital [169,176]. However, no irreducible representations containing d and p orbitals are present for the complexes with octahedral geometry (O_h point group). Therefore, the intensity of the pre-edge peak is generally weak because only the relatively weak quadrupole transition ($s \rightarrow d$ transition) is allowed, while the dipole transition ($s \rightarrow p$) is forbidden; distortion of the symmetry (symmetry breaking), however, enables p–d hybridization that allows the dipole transition. Therefore, simple prediction of the pre-edge peak intensity could be possible without theoretical calculations by using the character tables of group theory. V_2O_3 and V_2O_4 also fold a distorted octahedral geometry around vanadium, whereas V^{5+} ions in V_2O_5 fold distorted tetragonal pyramid [27,148,149,174]. Observed pre-edge peaks [at 5468.4 and 5469.8 eV (V_2O_3), 5470.0 eV (VO_2), 5470.8 eV in V_2O_5] are, as described above, generally assigned as due to a transition from 1s to 3d + 4p [166,169,175,176].

Figure 2a shows Ti K-edge XANES spectra in toluene for $CpTiCl_3$, Cp^*TiX_3 ($X = OCH_3$, Cl) measured at 25 °C (Ti K-edge 4.97 keV, through use of synchrotron radiation at SPring-8, BL01B1 beamline). These spectra show rather strong pre-edge absorption at 4965–4967 eV due to tetrahedral geometry around titanium, as described above. Rather strong absorption bands called shoulder-edge at 4977.0 eV in Cp^*TiCl_3 and $CpTiCl_3$, whereas no such absorption was seen in $Cp^*Ti(OCH_3)_3$; the absorption was due to presence of Ti–Cl bond, known as a shakedown peak assigned to the metal 1s to 4p coupled with the ligand to metal charge transfer (LMCT) [170–173]. No significant differences in the spectra were seen between $CpTiCl_3$ and Cp^*TiCl_3 because of the similar geometry and number of chloride ligands around titanium.

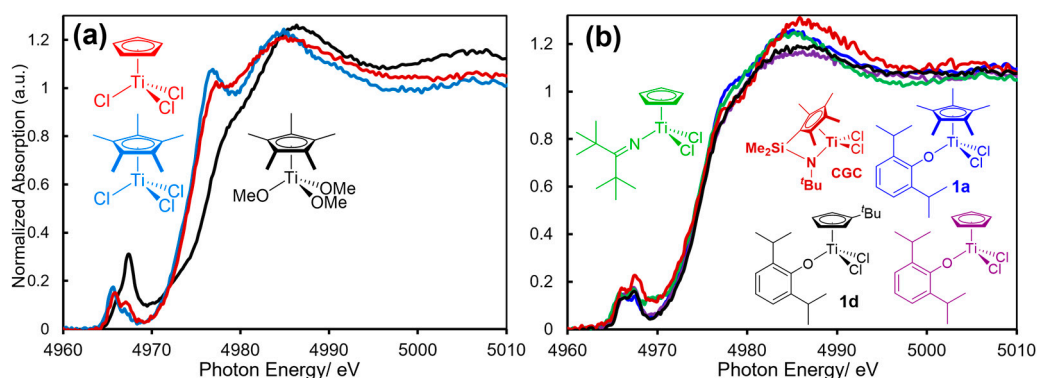


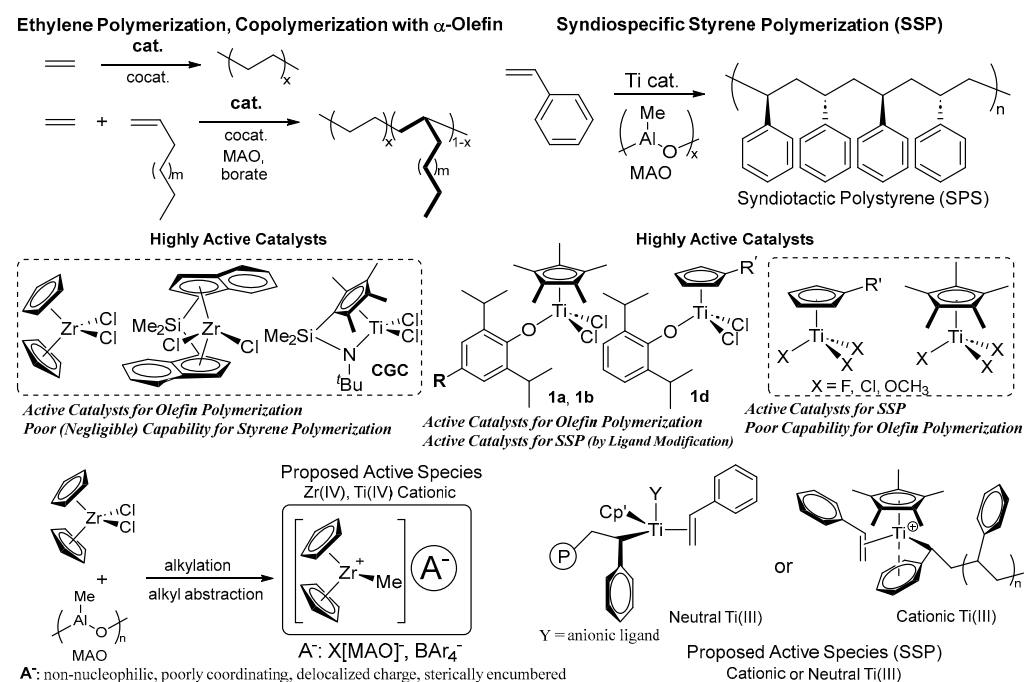
Figure 2. The solution-phase Ti K-edge XANES spectra (in toluene at 25 °C, Ti K-edge 4.97 keV, through the use of synchrotron radiation at SPring-8, BL01B1 beamline) for (a) $CpTiCl_3$, Cp^*TiX_3 ($X = OCH_3$, Cl), and (b) $Cp^*TiCl_2(O-2,6-iPr_2C_6H_3)$ [$Cp' = Cp$, $tBuC_5H_4$ (**1d**), Cp^* (**1a**)], $CpTiCl_2(N=C^tBu_2)$ (**2a**), and $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**CGC**) [27,76].

Figure 2b shows Ti K-edge XANES spectra in toluene solution (at 25 °C, conc. 50 $\mu\text{mol-Ti/mL}$) for $Cp^*TiCl_2(O-2,6-iPr_2C_6H_3)$ [$Cp' = Cp$, $tBuC_5H_4$ (**1d**), Cp^* (**1a**)], $CpTiCl_2(N=C^tBu_2)$ (**2a**), and $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**CGC**) [27]. The XANES spectrum of **1a** shows strong pre-edge absorptions at 4966.2 and 4967.6 eV and these are similar to those in the dimethyl complex, $Cp^*TiMe_2(O-2,6-iPr_2C_6H_3)$ (**1a'**), which showed at 4966.1 and 4967.7 eV. As described above, these are generally considered as due to a transition from 1s to 3d + 4p [166,169,175,176]. Moreover, as described above, **1a** shows an absorption maximum at 4978.0 eV (called as shoulder-edge) ascribed to the presence of a Ti–Cl bond [76,170–173]. Interestingly, as described above, positions of the edge peak (absorption) and the intensities in the half-titanocenes chosen in Figure 2b are close, whereas **CGC** shows rather high intensity at the pre-edge absorption at 4967.6 eV. Moreover, the spectra in toluene solution were highly analogous to those measured in solid (tablets with boron nitride) [76], strongly

suggesting that these are Ti(IV) complexes with (a distorted) tetrahedral geometry in solid and solution [76].

5.3. XAS Analysis for Exploring Active Species in Olefin Polymerization and Syndiospecific Styrene Polymerization (SSP) by Half-Titanocene Catalysts

The high oxidation state group 4 cationic metal-alkyl species, $\text{Cp}'_2\text{M}^+\text{R}$ (R = alkyl) or $\text{Cp}'\text{M}^+(\text{Y})\text{R}$ (Y = anionic ancillary donor), formed from the dialkyl analogues by reaction with borate or MAO through alkyl abstraction, play an essential role as the catalytically active species in this catalysis cycle (Scheme 10) [5,9–17,24–27]. However, effective catalysts for olefin polymerization (especially metallocene, linked half-titanocene) display poor (negligible) capability for synthesis of syndiotactic polystyrene (SPS) [34,36–39]. In contrast, half-titanocene catalysts, $\text{Cp}'\text{TiX}_3$ (X = F, Cl, OMe, etc.), enable high catalytic activities for syndiospecific styrene polymerization (SSP) [38–40], whereas these catalysts exhibited low catalytic activities for ethylene polymerization and afforded a mixture of polyethylene, SPS and the copolymer, poly(ethylene-*co*-styrene) [34,41]. It has thus been recognized that the active species between olefin polymerization and SSP are different. The oxidation state of the active species in the SSP had thus been proposed as cationic Ti(III) species [177–179] or neutral Ti(III) species [56,57,180,181]. However, these mechanistic studies lacked “direct evidence” until recently, especially from the catalyst solution in the presence of styrene and MAO.



Scheme 10. Proposed catalytically active species in olefin polymerization and syndiospecific styrene polymerisation (SSP).

As described above, XANES (XANES = X-ray Absorption Near Edge Structure) and EXAFS (EXAFS = Extended X-ray Absorption Fine Structure) analyses provide direct information on not only oxidation state and the basic geometry around the metal centre (by XANES), but also kind of atoms and the distances connected (coordinated) to the metal centre (by EXAFS). Therefore, here we introduce a summary of the mechanistic studies reported recently [27,76].

Figure 3a shows the XANES spectra for the phenoxide-modified half-titanocene dichloride (**1a**) and dimethyl complexes (**1a'**), and the catalyst solution in the presence of MAO and 1-hexene, exhibiting catalytic activities for 1-hexene polymerisation

in situ [27,76]. These complexes (**1a**, **1a'**) exhibit high catalytic activities for ethylene polymerization [14–17,42–44], α -olefin polymerization [182], and ethylene copolymerization with various monomers (as described above) [14–17,42–44].

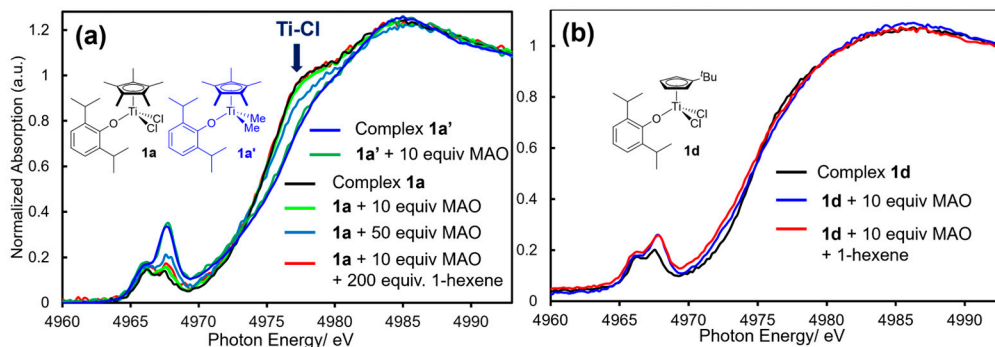


Figure 3. Ti K-edge XANES spectra (in toluene at 25 °C) for (a) $\text{Cp}^*\text{TiX}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$ [$\text{X} = \text{Cl}$ (**1a**), Me (**1a'**)] or (b) $(t\text{BuC}_5\text{H}_4)\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$ (**1d**), and the spectra upon addition of MAO, and 1-hexene [76].

As shown in Figure 3a, the pre-edge peak positions and edge absorption of **1a** [4966.2 and 4967.6 eV (pre-edge), 4978.0 eV (shoulder-edge)] did not change upon addition of MAO, whereas intensity in the shoulder edge absorption in **1a**, ascribed to Ti–Cl bond, decreased upon addition of MAO (especially 50 equiv) [76]. No apparent changes in the spectra were observed even upon addition of excess 1-hexene (200 equiv). Moreover, the spectra did not change when the dimethyl complex (**1a'**) was added with MAO (10 equiv). These results strongly suggest that the oxidation state as well as basic geometry around titanium is preserved under these conditions, even in the addition of MAO and 1-hexene (excess amounts). Similarly, as shown in Figure 3b, no significant differences in the XANES spectra were seen when the **1d** was treated with d-MAO and 1-hexene [76]. These results also suggest the same possibility that major species formed as Ti(IV) species upon addition of MAO.

Although no significant changes in the XANES spectra were observed, the corresponding EXAFS spectra, shown in Figure 4 [oscillations (left) and the FT-EXAFS spectra (right)], provide a clearer image of the information in the reactions. The XANES spectra for $\text{Cp}^*\text{TiCl}_2(\text{OAr})$ (**1a**) and the catalyst solution in the presence of MAO (10 and 50 equiv) showed no distinct spectral changes in toluene solution and in solid state (in solid, disc with boron nitride) measured at 25 °C (Figure 4a,b). The summary of coordination number (C.N., number of prescribed atom, such as O, C and Cl, coordinated to metal) and the distance (Å) in the atoms connected to titanium analyzed through the curve fitting are summarized in Table 5 [76].

The Ti–C (on Cp' coordinated) and Ti–O (phenoxide) bonds were preserved even after treating **1a** with MAO (10 and 50 equiv). In contrast, C.N. of Ti–Cl decreased by treating with MAO (Figure 4d, Table 5), clearly indicating that the Ti–Cl bonds were reacted (dissociated) with MAO (alkylation). Since separation of Ti–C and Ti–O bonds seemed difficult (distances are close) in the analysis, the observed increase in the C.N. of Ti–O bond upon addition of MAO could be explained as due to a subsequent formation of Ti–C bond [76]. These data also suggest that the Ti–Cl bonds in **1a** were reacted with MAO without dissociation of the Ti–O bond to form dimethyl complexes; the data support that the Ti(IV)-alkyl species play a role in this catalysis [14–17,76].

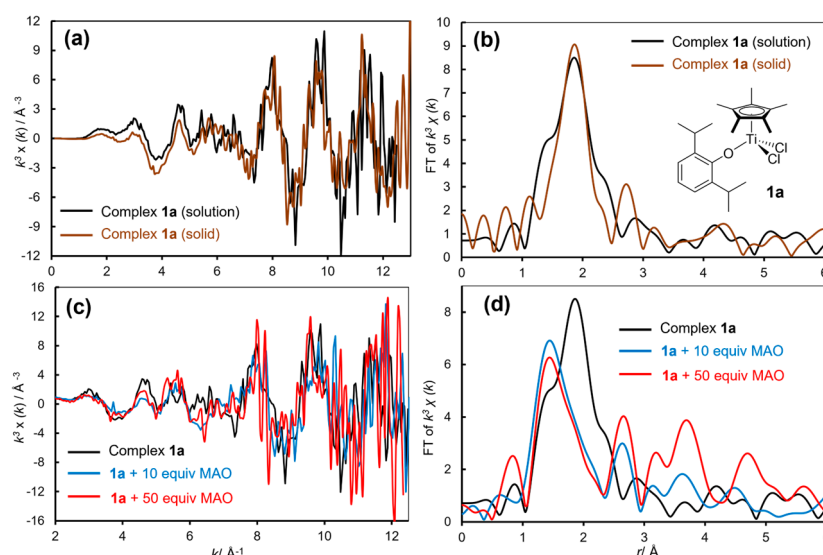


Figure 4. Ti K-edge (a) EXAFS oscillations and (b) FT-EXAFS spectra for $\text{Cp}^*\text{TiCl}_2(\text{OAr})$ (**1a**, in toluene or solid), and (c) EXAFS oscillations and (d) FT-EXAFS spectra by treating **1a** with MAO (10 or 50 equiv, in toluene at 25 °C) [76].

Table 5. Summary of analysis data (by curve fitting) for toluene solution of $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$ (**1a**), and **1a** treated with MAO (10 and 50 equiv) [76].

Atom ^a	$\text{Cp}^*\text{TiCl}_2(\text{OAr})$ (1a)			1a + 10 Equiv MAO ^e			1a + 50 equiv MAO ^e		
	C.N. ^b	<i>r</i> (Å) ^c	D.W. ^d	C.N. ^b	<i>r</i> (Å) ^c	D.W. ^d	C.N. ^b	<i>r</i> (Å) ^c	D.W. ^d
O	1.3(1)	1.803(6)	0.0013(10)	2.3(2)	1.81(1)	0.0035 (12)	3.4(6)	1.87(1)	0.0059(25)
C	4.7(9)	2.42(1)	0.0030(19)	5.5(9)	2.13(2)	0.0047(22)	4.5(9)	2.14(1)	0.0040(30)
Cl	2.4(3)	2.269(7)	0.0047(13)	0.9(3)	2.18(3)	0.0062(49)			

^a Atom: Neighbour atom. ^b C.N.: coordination number. ^c *r*: bond length. ^d D.W.: Debye-Waller factor. ^e For analysis, fixed ΔE values were used. *R* factors = 11.4%, 14.8%, and 12.9%, respectively, for complex **1a**, **1a** treated with MAO (10 equiv, 50 equiv).

As described above, the oxidation state of the active species in the SSP has been proposed as cationic or neutral Ti(III) species, $\text{Cp}^*\text{Ti}^+(\text{R})(\text{styrene})$ [177–179] or $\text{Cp}^*\text{Ti}(\text{R})(\text{Y})(\text{styrene})$ [56,57,180,181] (Scheme 10). The cationic Ti(III) species were proposed based on the results in ESR measurement [177], reaction chemistry (formation of SPS) [179], and theoretical support [178]. The neutral Ti(III) species were proposed based on the results of (i) polymerization data (ligand effect, anionic donor) [56,57], (ii) step (co)polymerization [181], and (iii) theoretical support [180]. However, until recently, there was no “direct evidence” from the catalyst solution containing MAO and styrene [27,76,183].

Figure 5 shows Ti K-edge XANES spectra (in toluene at 25 °C) for $\text{Cp}^*\text{TiCl}_2(\text{OAr})$ [$\text{Cp}^* = t\text{BuC}_5\text{H}_4$ (**1d**, left), Cp (**1e**, right)], and the spectra of solutions containing **1d** or **1e** and MAO (50 equiv), styrene (200 equiv), which produce SPS in situ. The XANES spectrum of **1d** shows pre-edge absorptions (4966.5, 4967.5 eV) and a shoulder-edge absorption (4977.9 eV, presence of Ti–Cl bond) [27,170–173]. Addition of MAO (50 equiv) did not lead to significant spectral changes, except a decrease in the intensity of the shoulder-edge absorption in **1d** which was observed, suggesting dissociation of Ti–Cl bond by alkylation [76].

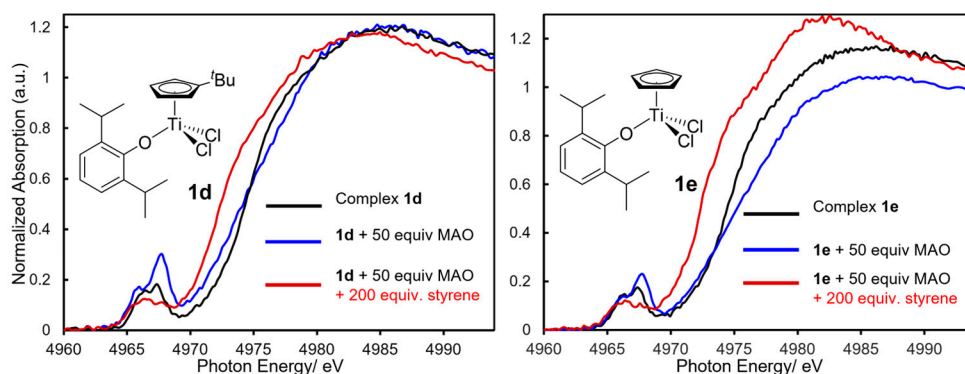


Figure 5. Ti K-edge XANES spectra (in toluene at 25 °C) for $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$ [$\text{Cp}^* = t\text{BuC}_5\text{H}_4$ (**1d**), Cp (**1e**)], and the spectra for the catalyst solutions with addition of MAO, styrene [76].

In contrast, noteworthy, styrene addition (200 equiv) into the solution (**1d** and MAO 50 equiv) led to the clear low energy shift (2.2 eV on the basis of the inflection point) in the edge absorption accompanied with decrease in intensities of two pre-edge peaks. The results thus strongly suggest that complex **1d** was reduced by addition of styrene (not by MAO). Moreover, the low energy shift in the edge absorption was observed upon increase in the amount of styrene charged (100→200 equiv) [76]. Moreover, as shown in Figure 5 (right), the solution containing **1e** showed the similar change when 200 equiv of styrene and 50 equiv of MAO were added into a toluene solution, which also produced SPS in situ [57]. These analysis data strongly suggest a formation of Ti(III) species from Ti(IV), derived from **1d**, accompanied with the structural changes upon addition of styrene.

Figure 6 shows EXAFS oscillations and the FT-EXAFS spectra (in toluene at 25 °C) for $(t\text{BuC}_5\text{H}_4)\text{TiCl}_2(\text{OAr})$ (**1d**), and the solution with addition of 50 equiv of MAO and excess (200 equiv) styrene; as shown in Figure 5 (XANES spectra), the solution showed a significant changes in the oxidation state upon addition of styrene. The analysis data by curve fitting are summarized in Table 6 [76].

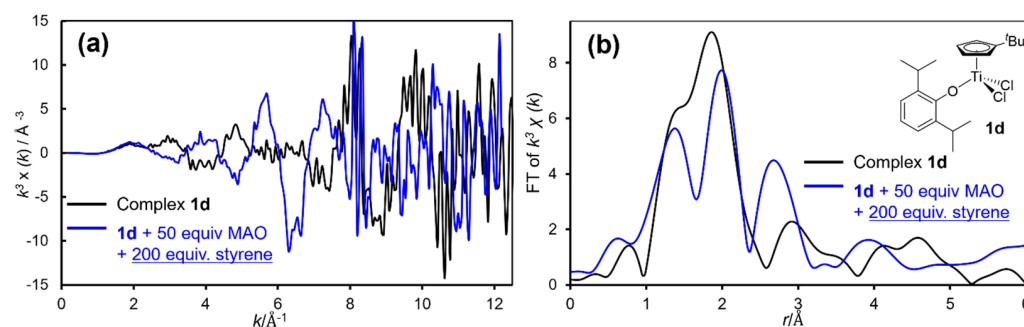


Figure 6. Ti K-edge (in toluene at 25 °C) (a) EXAFS oscillations and (b) FT-EXAFS spectra for $(t\text{BuC}_5\text{H}_4)\text{TiCl}_2(\text{OAr})$ (**1d**) upon addition of MAO (50 equiv) and styrene (200 equiv) [76].

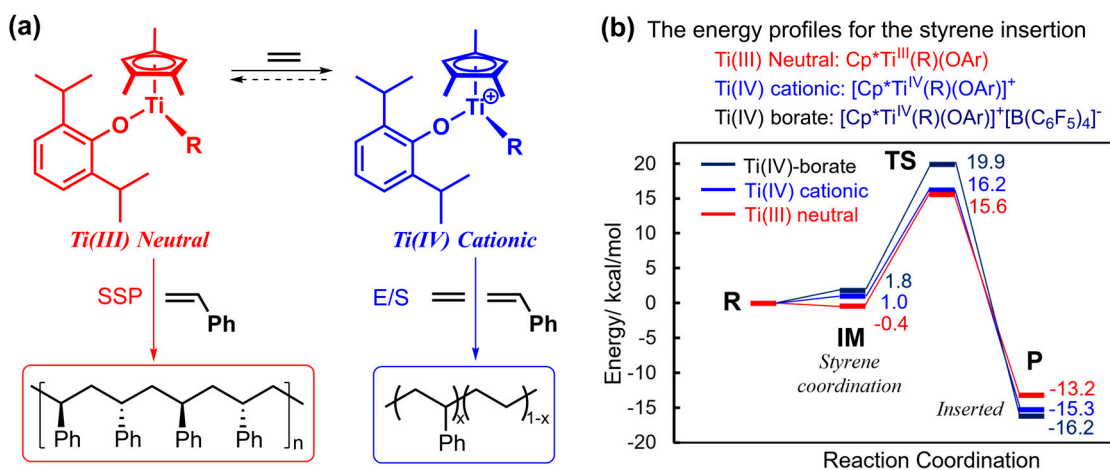
Apparent change in the EXAFS oscillations from a toluene solution of **1d** to the solution with addition of MAO and styrene strongly suggest certain structural change (accompanied with change in the oxidation state). As observed by **1a**, C.N. of Ti–Cl diminished along with observation of new Ti–C bond which is formed by methylation with MAO, whereas C.N. and bond lengths in Ti–C bonds corresponding to Cp^* were unchanged before/after the reaction. Importantly, the Ti–O bond (corresponding to phenoxide ligand) remained even after reaction of **1d** with MAO and styrene (200 equiv). The analysis data clearly demonstrate formation of the catalytically active species for SSP bearing Ti–O bond accompanied with reduction, strongly suggesting generating the phenoxide species $(t\text{BuC}_5\text{H}_4)\text{Ti}(\text{R})(\text{OAr})$ [or $\text{CpTi}(\text{R})(\text{OAr})$] in the solution [27,76]. The result is a

good agreement with our previous assumption on the basis of two-step ethylene/styrene (co)polymerization (Scheme 11) [181] as well as the effect of anionic donor ligand in SSP [57] that the neutral Ti(III) species containing phenoxide ligand thus plays a role for the SSP [181].

Table 6. Summary of analysis data (by curve fitting) for toluene solution of (*t*BuC₅H₄)TiCl₂(O-2,6-*i*Pr₂C₆H₃) (**1d**), and **1d** with addition of MAO (50 equiv) and styrene (200 equiv) at 25 °C [76].

Atom ^a	(<i>t</i> BuC ₅ H ₄)TiCl ₂ (OAr) ^e (1d)			1d + 50 Equiv MAO + 200 Equiv Styrene ^e		
	C.N. ^b	<i>r</i> (Å) ^c	D.W. ^d	C.N. ^b	<i>r</i> (Å) ^c	D.W. ^d
O	1.3 (1)	1.76 (1)	0.0010 (5)	0.7 (4)	1.80 (2)	0.0064 (54)
Cl	1.7 (1)	2.25 (1)	0.0012 (4)	---	---	---
C1	5.2 (9)	2.41 (2)	0.0055 (45)	5.2 (3)	2.40 (1)	0.0040 (15)
C2	---	---	---	1.3 (6)	1.95 (3)	0.0034 (28)

^a Atom: neighbour atom. ^b C.N.: coordination number. ^c *r*: bond length. ^d D.W.: Debye-Waller factor. ^e For analysis, fixed Δ*E* values were used. *R* factors = 10.7%, 7.5%, respectively, for complex **1d**, **1d** treated with MAO and styrene.



Scheme 11. (a) Proposed active species for syndiospecific styrene polymerization (SSP) confirmed by two-step copolymerization, XAS analysis [76,181]. (b) The energy profiles for styrene insertion to assumed three species containing phenoxide ligand [76].

Moreover, the proposed catalytically active species based on XAS analysis as well as step ethylene/styrene (co)polymerization (Scheme 11a) was further supported by theoretical calculation [27,76,183]. DFT calculation was conducted for syndiospecific styrene insertion step of the three possible models of the active species containing the phenoxide ligand, neutral Ti(III), cationic Ti(IV), and Ti(IV)–B(C₆F₅)₄ catalysts (shown in Scheme 11b). The calculation was conducted from the Ti catalysts containing the phenylpropyl group, as a model of polystyrene in chain-propagation step (**R**; styrene + Ti, zero), and the styrene coordinated models (**IM**), and inserted model (**P**) in which styrene was inserted to the phenylpropyl moiety [76]. As shown in Scheme 11b, the results clearly indicate that the neutral Ti(III) catalyst exhibits the lower activation energy than the others, thus strongly supporting the above mechanism. The computational analysis also led to a conclusion that the neutral Ti(III) species containing the phenoxide ligand is a more efficient and plausible catalyst model; formation of the Ti(III) species, proposed in Scheme 11, is a key to promoting the SSP in an efficient manner [76]. Further DFT calculation results revealed that the neutral Ti(III) active species has high selectivity in SSP; the orientation of styrene (*si*-/*h*-/*re*-) insertions is related to the stereoselectivity of polystyrene. The spin density analysis indicated the neutral Ti(III) centre promotes an electron transfer from the polymeric chain to the incoming styrene [183].

6. Concluding Remarks and Outlook

Olefin polymerization by group 4 transition metal catalysts has been the key technology for production of polyolefins, commodity plastics in our daily life. Development of new polymers that cannot be achieved by using conventional catalysts has been the central research objective and copolymerization is an effective strategy. In this reviewing article, modified half-titanocenes, $\text{Cp}^*\text{TiX}_2(\text{Y})$ (Y = anionic donor such as phenoxide, ketimide, amidinate, etc.) [6,14–17], contributed a significant effort for efficient, exclusive synthesis of ethylene copolymers containing cyclic olefins (COCs) [60–68], biobased conjugated dienes [69,70], disubstituted α -olefins [44,71–74], aromatic vinyl monomers [34,41,56,58,59], ethylene/ α -olefin copolymers containing hydroxy group [44], etc. More recently, we realized that the catalysts containing unsymmetric iminoimidazolid ligands exhibited promising capabilities for synthesis of COCs [184]. Moreover, modification of phenoxide *para*-position enhanced the activity in ethylene polymerization and the copolymerization with α -olefin [45]. It is thus clear that, as introduced herein, the catalysts of this type are highly suited to synthesis of new copolymers with monomers that cannot be incorporated by the conventional catalysts such as metallocene, linked half-titanocenes (called constrained geometry type). These results thus strongly suggest that the catalysts of this type will continue to contribute to the development of new polyolefins.

Moreover, this manuscript introduces an analysis of catalytically active species through XAS (X-ray absorption spectroscopy). The XAS analysis provides information on the oxidation state, basic geometry around the centered metal, ligand coordinated and their distances (electronic natures) in solution. However, as described previously [27], combined results on spectroscopic analysis (solution XAS, NMR, ESR, and crystallographic), reaction chemistry, and computational analysis should provide a clear image of the catalysis mechanism including the nature of the catalytically active species. We highly hope that the analysis method can be used for more research in the near future for better understanding of the catalysis cycle.

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Data Availability Statement: Data on studies by authors are available from the corresponding author upon reasonable requests.

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